USE OF DYNAMIC MECHANICAL TESTING, WAXD AND SEM IMAGE ANALYSIS TO STUDY THE PROPERTIES OF POLYPROPYLENE/CALCIUM CARBONATE NANOCOMPOSITES

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ABSTRACT

Polypropylene (PP) is the most widely used thermoplastic. It has a good combination of physical and chemical properties, reduced cost per volume, great recyclability and good processability. PP nanocomposites have received a lot of attention in the past years because the addition of calcium carbonate nanoparticles to PP is expected to increase its stiffness and impact strength. The low concentration of nanofillers could be a cost effective alternate solution to engineering thermoplastics as long as good dispersion is achieved.

Numerous studies have been made to understand the influence of calcium carbonate (CaCO₃) nanoparticles and their properties on the morphology and mechanical properties of the PP/CaCO₃ nanocomposites. Some of those studies focused on median particle size and surface treatment of calcium carbonate. Particle size distribution is one of the most important characteristic of fillers. However, not much attention has been paid to studying the particle size distribution of nanoparticles after mixing.

In this work, polypropylene homopolymer composites were prepared using a Brabender internal mixer with CAM rotors (a medium shear-rate blade combining milling, mixing, and shearing forces against the test sample) at 190°C and 60rpm. Different compositions of calcium carbonate with different median particles sizes, including 0.07µm nanoparticles, with and without surface treatment were added to the polypropylene matrix.
SEM image analysis was used to obtain the particle size distribution of calcium carbonate in the polypropylene matrix. The Gamma Variate function was found to fit the particle size distribution of nanoparticles after mixing with a correlation coefficient above 0.99.

In addition to SEM image analysis, DSC and X-ray diffraction were used to investigate the morphology of the PP nanocomposites and its effect on their tensile and impact properties. Dynamic mechanical testing was also used to study the polymer melt behavior at low frequencies.

The X-Ray diffraction showed three strong α crystalline form peaks and one β crystalline form peak. The intensities of these peaks were used to calculate the k parameter to quantify the β-iPP in the PP composites. Based on this parameter, calcium carbonate nanoparticles seem to be more effective in promoting the formation of β-iPP than microparticles.

The results of the tensile tests showed that the elastic modulus increased up to 30% in comparison with that of neat PP with the addition of 20% of calcium carbonate nanoparticles. Tensile strength was also highest with the addition of 2wt% and 5wt% nanoparticles but the improvement was of only of 5% compared with neat PP. The highest tensile strength and elastic modulus were found with approximately 40% crystallinity.

Impact strength was higher with the addition of calcium carbonate microparticles. However, surface treated nanoparticles at 2wt% and 5wt% compositions and high k proved to increase the impact strength of PP above 40% compared with neat PP.
The best combination of mechanical properties was found for PP nanocomposites filled with 2wt% of 0.07µm treated particles and k=0.22.
DEDICATION

I would like to dedicate this work to my family and especially my parents, Edgar and Dina, for their love, guidance and unconditional support throughout my life.
I would like to thank my advisor Dr. Kyonsuku Min for her help and supervision while writing this thesis, the University of Akron and The Polymer Engineering Department for giving me the opportunity and funding to be part of this graduate program. I gained invaluable knowledge and most importantly, I had the chance to meet wonderful people who filled my time in Akron with great memories.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF TABLES</th>
<th>xv</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>xvii</td>
</tr>
</tbody>
</table>

## CHAPTER

### I. INTRODUCTION

1

### II. BACKGROUND AND LITERATURE SURVEY

5

#### 2.1 Polypropylene

5

1. Polymorphic forms of isotactic polypropylene (iPP)

6

1.1 α-iPP

6

1.2 β-iPP

10

1.3 γ-iPP

13

1.2 Relationship of molecular weight and tacticity with melting behavior and mechanical properties.

16

#### 2.2 Fillers

20

1. Filler characteristics

20

2. Calcium carbonate

21

2.1 Production of calcium carbonate

22

2.2 Surface treatment of calcium carbonate

22

2.3 Composites of polypropylene with calcium carbonate

24

3. Talc

24
2.2.3.1 Composites of polypropylene with talc ............................................. 25

2.2.4 Glass fiber ............................................................................................... 27

2.2.4.1 Composites of polypropylene filled with glass fiber ......................... 28

2.3 Polypropylene/CaCO₃ composites .............................................................. 29

2.3.1 Effect of calcium carbonate on the structural development of PP/CaCO₃ composites .................................................................................. 29

2.3.1.1 Effect of particle size, size distribution and crystal shape of calcium carbonate .................................................................................. 31

2.3.1.2 Effect of surface treatment of calcium carbonate ................................. 31

2.3.1.3 Effect of composition ......................................................................... 32

2.3.2 Effect of calcium carbonate on the tensile and impact properties of PP/CaCO₃ composites .................................................................................. 34

2.3.2.1 Effect of particle size, size distribution and crystal shape of calcium carbonate .................................................................................. 37

2.3.2.2 Effect of surface treatment of calcium carbonate ................................. 39

2.3.2.3 Effect of composition ......................................................................... 41

2.4 Nanocomposites .......................................................................................... 44

2.5 PP/CaCO₃ Nanocomposites ....................................................................... 46

2.5.1 Effect on nano calcium carbonate on the structural development of PP/CaCO₃ nanocomposites ................................................................. 46

2.5.1.1 Effect of particle size, size distribution and crystal shape of calcium carbonate .................................................................................. 47

2.5.1.2 Effect of surface treatment of calcium carbonate .................................. 48

2.5.1.3 Effect of composition ......................................................................... 49

2.5.2 Effect of nano calcium carbonate on the tensile and impact properties of PP/CaCO₃ nanocomposites ................................................................. 49
2.5.2.1 Effect of particle size, size distribution and crystal shape of calcium carbonate ..........................................................50
2.5.2.2 Effect of surface treatment of calcium carbonate..............................52
2.5.2.3 Effect of composition ....................................................................53
2.5.3 Effect of nano calcium carbonate on the dynamic rheological behavior of PP/CaCO₃ nanocomposites .................................................................55
2.5.3.1 Effect of particle size of calcium carbonate and composition ..........55
2.5.3.2 Effect of surface treatment of calcium carbonate .........................58

III. MATERIALS AND EXPERIMENTAL PROCEDURE .............................................60
3.1 Materials .................................................................................................60
3.2 Experimental procedures ........................................................................62
  3.2.1 Sample preparation ............................................................................62
    3.2.1.1 Mixing .......................................................................................63
    3.2.1.2 Compression molding .................................................................63
    3.2.1.3 Grinding ....................................................................................64
    3.2.1.4 Injection molding ......................................................................64
  3.2.2 Characterization ..................................................................................66
    3.2.2.1 Dynamic Mechanical Testing (ARES) ........................................66
    3.2.2.2 Thermal Analysis (DSC) .............................................................66
    3.2.2.3 X-Ray Diffraction ....................................................................67
  3.2.3 Particle dispersion and particle size distribution .................................68
    3.2.3.1 Scanning Electron Microscopy ..................................................68
    3.2.3.2 Image Analysis ........................................................................69
  3.2.4 Tensile test .........................................................................................72
3.2.5 Impact test.................................................................74

IV. RESULTS AND DISCUSSION .........................................................76

4.1 Dynamic rheological properties of polypropylene (PP) and PP/CaCO₃ composites...76

4.1.1 Polypropylene ........................................................................76

4.1.2 Polypropylene/3.2µm CaCO₃ composites ..................................77

  4.1.2.1 Non treated 3.2µm particles of ground marble .....................77

  4.1.2.2 Surface treated 3.2µm particles of ground marble ...............80

  4.1.2.3 Non treated 3.2µm particles of ground limestone ...............82

  4.1.2.4 Surface treated 3.2µm particles of ground limestone ..........84

4.1.3 Polypropylene/1.1µm CaCO₃ composites ..................................86

  4.1.3.1 Non treated 1.1µm particles of ground limestone ...............86

  4.1.3.2 Surface treated 1.1µm particles of ground limestone ..........86

  4.1.3.3 Surface treated 0.7µm particles of precipitated limestone ......89

4.1.4 Polypropylene/0.07µm CaCO₃ composites ................................91

  4.1.4.1 Non treated 0.07µm particles of precipitated limestone .........91

  4.1.4.2 Surface treated 0.07µm particles of precipitated limestone ....93

4.1.5 Effect of particle size, composition and surface treatment of calcium carbonate on the elastic modulus $G'$ and dynamic viscosity $|\eta^*|$ of PP/CaCO₃ composites ...............................................................95

4.2 Thermal Characterization Studies .............................................105

4.2.1 Polypropylene ......................................................................105

4.2.2 Polypropylene/3.2µm CaCO₃ composites ...............................106

  4.2.2.1 Non treated 3.2µm particles of ground marble .....................106

  4.2.2.2 Surface treated 3.2µm particles of ground marble .............108
4.2.2.3 Non treated 3.2µm particles of ground limestone ........................................ 109
4.2.2.4 Surface treated 3.2µm particles of ground limestone ................................... 111
4.2.3 Polypropylene/1.1µm CaCO₃ and Polypropylene/0.7µm CaCO₃ composites .113
  4.2.3.1 Non treated 1.1µm particles of ground limestone .................................... 113
  4.2.3.2 Surface treated 1.1µm particles of ground limestone ............................... 115
  4.2.3.3 Surface treated 0.7µm particles of precipitated limestone ...................... 116
4.2.4 Polypropylene/0.07µm CaCO₃ composites ................................................... 119
  4.2.4.1 Non treated 0.07µm particles of precipitated limestone ......................... 119
  4.2.4.2 Surface treated 0.07µm particles from precipitated limestone ................. 120
4.2.5 Effect of calcium carbonate on the % crystallinity of PP/CaCO₃ composites.. 123
  4.2.5.1 Effect of particle size and shape of calcium carbonate ............................ 127
  4.2.5.2 Effect of surface treatment of calcium carbonate .................................. 128
  4.2.5.3 Effect of composition ............................................................................. 129
4.2.6 % Crystallinity for tensile and impact tests................................................. 130
4.3 Wide Angle X-ray diffraction ............................................................................. 132
  4.3.1 Polypropylene ............................................................................................... 133
  4.3.2 Polypropylene/3.2µm CaCO₃ composites ..................................................... 134
    4.3.2.1 Surface treated 3.2µm particles of ground marble ................................. 134
    4.3.2.2 Non treated 3.2µm particles of ground limestone ................................ 136
    4.3.2.3 Surface treated 3.2µm particles of ground limestone ............................ 137
  4.3.3 Polypropylene/1.1µm CaCO₃ composites ..................................................... 137
    4.3.3.1 Non treated 1.1µm particles of ground limestone ................................ 138
    4.3.3.2 Surface treated 1.1µm particles of ground limestone ............................ 139
4.3.4 Polypropylene/0.07µm CaCO₃ composites .......................................................... 139
  4.3.4.1 Non treated 0.07µm particles of precipitated limestone......................... 139
  4.3.4.2 Surface treated 0.07µm particles of precipitated limestone................... 139

4.3.5 The k parameter for impact test samples ....................................................... 143

4.4 Particle dispersion and particle size distribution of calcium carbonate in PP/CaCO₃ composites ................................................................. 144
  4.4.1 Polypropylene .................................................................................................. 144
  4.4.2 Polypropylene/3.2µm CaCO₃ composites .......................................................... 145
    4.4.2.1 Non treated 3.2µm particles of ground limestone ..................................... 145
    4.4.2.2 Surface treated 3.2µm particles of ground limestone ............................... 147
  4.4.3 Polypropylene/1.1µm CaCO₃ composites .......................................................... 149
    4.4.3.1 Non treated 1.1µm particles of ground limestone ..................................... 149
    4.4.3.2 Surface treated 1.1µm particles of ground limestone .................................. 151
  4.4.4 Polypropylene/0.07µm CaCO₃ composites .......................................................... 153
    4.4.4.1 Non treated 0.07µm particles of precipitated limestone ........................... 153
    4.4.4.2 Surface treated 0.07µm particles of precipitated limestone .................. 155

4.5 Tensile properties of PP/CaCO₃ composites ....................................................... 164
  4.5.1 Polypropylene .................................................................................................. 164
  4.5.2 Polypropylene/3.2µm CaCO₃ composites .......................................................... 164
    4.5.2.1 Non treated and surface treated 3.2µm particles of ground marble ......... 165
    4.5.2.2 Non treated and surface treated 3.2µm particles of ground limestone ....... 167
  4.5.3 Polypropylene/1.1µm and Polypropylene/0.7µm CaCO₃ composites ............... 168
    4.5.3.1 Non treated and treated 1.1µm particles of ground limestone .................. 168
4.5.3.2 Surface treated 0.7µm particles of precipitated limestone...................... 170

4.5.4 Polypropylene/0.07µm CaCO\textsubscript{3} composites ............................................................ 172

4.5.4.1 Non treated and treated 0.07µm particles of precipitated limestone......172

4.5.5 Effect of calcium carbonate on the tensile properties of PP/CaCO\textsubscript{3} composites ........................................................................................................ 174

4.5.5.1 Effect of the particle size of calcium carbonate.................................178

4.5.5.2 Effect of the surface treatment of calcium carbonate..........................178

4.5.5.3 Effect of composition .......................................................................179

4.5.5.4 Effect of the %crystallinity ..............................................................180

4.5.6 Comparison of the elastic modulus results with semi empirical models ......185

4.6 Impact properties of PP/CaCO\textsubscript{3} composites................................................................. 186

4.6.1 Polypropylene .................................................................................. 186

4.6.2 Polypropylene/3.2µm CaCO\textsubscript{3} composites .................................................. 186

4.6.3 Polypropylene/1.1µm CaCO\textsubscript{3} composites .................................................. 187

4.6.4 Polypropylene/0.07µm CaCO\textsubscript{3} composites .................................................. 188

4.6.5 Effect of calcium carbonate on the impact properties of PP/CaCO\textsubscript{3} composites ........................................................................................................ 189

4.6.5.1 Effect of the particle size of calcium carbonate.................................190

4.6.5.2 Effect of the surface treatment of calcium carbonate..........................190

4.6.5.3 Effect of composition .......................................................................192

4.6.5.4 Effect of % crystallinity....................................................................192

4.6.5.5 Effect of β-iPP .................................................................................. 194

V. CONCLUSIONS ....................................................................................... 196

REFERENCES ............................................................................................. 200

xiv
LIST OF TABLES

Table                                  Page

2.1 Characteristics of spherulite types (Reproduced with permission from Elsevier)........7

2.2 Relationship of molecular structure with mechanical properties of different types of Polypropylene (Reproduced with permission from Elsevier).................................10

2.3 Static Tensile Characteristics of α-iPP and β-iPP (Testing speed 1mm/min) (Reproduced with permission from Taylor & Francis) .................................................................10

2.4 Effect of various additives on the number of heterogeneous nuclei on the composite PP + 10% CaCO₃ (Reproduced with permission from John Wiley & Sons) ...33

2.5 Mechanical properties of composites with PP-g-MA and PP-g-AA (Reproduced with permission from Springer) ........................................................................................................40

2.6 Optimum amount of PP-g-MA for tensile strength of composites (Reproduced with permission from Springer) ........................................................................................................40

2.7 Summary of Physical Testing Results of PP Moldings with 40 wt % CaCO₃ (Reproduced with permission from John Wiley & Sons)...............................................................41

2.8 Mechanical properties of PP nanocomposites (Reproduced with permission from Elsevier) ............................................................................................................................54

3.1 Properties of polypropylene resin Sunoco D080T (Sunoco Chemicals datasheet).....61

3.2 Calcium carbonate characteristics .............................................................................61

3.3 Percentage of surface treatment .............................................................................62

3.4 Mass of material used for each type of injection molded samples .......................65

4.1 Thermal properties of neat PP pellets and neat PP mixed in Brabender internal mixer at 180°C ..................................................................................................................106

4.2 DSC results for PP mixed with non treated 3.2µm particles of ground marble ......107
4.3 DSC results for PP mixed with treated 3.2µm particles of ground marble ..........109
4.4 DSC results for PP mixed with non treated 3.2µm particles of ground limestone ....110
4.5 DSC results for PP mixed with treated 3.2µm particles of ground limestone ........112
4.6 DSC results for PP mixed with non treated 1.1µm particles of ground limestone ....114
4.7 DSC results for PP mixed with treated 1.1µm particles of ground limestone ..........116
4.8 DSC results for PP mixed with treated 0.7µm particles of precipitated limestone ...117
4.9 DSC results for PP mixed with non treated 0.07µm particles from precipitated limestone ...............................................................................................................................................120
4.10 DSC results for PP mixed with treated 0.07µm particles from precipitated limestone ...............................................................................................................................................121
4.11 % Crystallinity for tensile and impact samples from injection molding ............131
4.12 k values and variation of k in comparison with neat PP for all PP composites ......142
4.13 Particle size average, median and mode and $R^2$ and Standard deviation from the Gamma Variate fit ..................................................................................................................................................157
4.14 PP tensile properties from pellets and after mixed in the Brabender ...............164
4.15 Polypropylene’s impact resistance ....................................................................186
4.16 Impact strength as a function of % crystallinity, k mixing (after mixing) and k imp (from impact specimens) ..................................................................................................................................................195
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Different spherulite types viewed in polarized light (a) Type I Tc=128°C, (b) Type II Tc=138°C, (c) Type III Tc=125°C, (d) Type IV Tc=130°C (Scale bar 200 microns) (Reproduced with permission from Elsevier)</td>
<td>7</td>
</tr>
<tr>
<td>2.2 Various shapes and their growth in β-nucleated iPP samples (a) Tc = 135°C, t_c = 50min; (b) Tc = 135°C, t_c = 62min (1) β-hexagonite, (2) β-needle crystal, (3) β-ovalite, (4) β-spherulite, (5) α-spherulite (Reproduced with permission from Springer)</td>
<td>11</td>
</tr>
<tr>
<td>2.3 γ spherulites produced at 200 MPa and different isothermal crystallization temperatures (a) Negative birefringence 190°C (b) Positive birefringence at 205°C (c) Mixed birefringence at 198°C (Reproduced with permission from Elsevier)</td>
<td>15</td>
</tr>
<tr>
<td>2.4 Viscosity Average Molecular Weights M_v and Molecular weight polydispersity index PI (Reproduced with permission from John Wiley &amp; Sons)</td>
<td>17</td>
</tr>
<tr>
<td>2.5 Total degree of crystallinity Φ_tot and Relative content of the β Form Φ_β in the iPP samples, isothermally crystallized at 90°C (Reproduced with permission from John Wiley &amp; Sons)</td>
<td>17</td>
</tr>
<tr>
<td>2.6 Wide angle X-Ray 20 scans for α-phase and γ-phase from X-ray diffractometer (Reproduced with permission from the American Institute of Physics)</td>
<td>18</td>
</tr>
<tr>
<td>2.7 Wide angle X-ray diffraction 20 scans taken at 25°C and after 5 min at 154°C (Reproduced with permission from the American Institute of Physics)</td>
<td>19</td>
</tr>
<tr>
<td>2.8 Variations in the Ci of samples; (O) prior to melt crystallization and after melt crystallization at Tc values of (x) 110°C and (Δ) 115°C (Reproduced with permission from Springer)</td>
<td>33</td>
</tr>
<tr>
<td>2.9 Tensile modulus vs. calcium carbonate content (○)α-PP (●)β-PP (Reproduced with permission from John Wiley &amp; Sons)</td>
<td>36</td>
</tr>
<tr>
<td>2.10 Critical strain energy release rate vs. calcium carbonate content (○)α-PP (●)β-PP (Reproduced with permission from John Wiley &amp; Sons)</td>
<td>36</td>
</tr>
</tbody>
</table>
2.11 Particle size distributions of two types of calcium carbonate (Reproduced with permission from Taylor & Francis)........................................................................................................38

2.12 Effect of silane treatment on the tensile strength of PP/CaCO\textsubscript{3} composites
(○) Stearic acid (△) Silane treatment (Reproduced with permission from John Wiley & Sons)........................................................................................................................................40

2.13 Dependence of relative modulus on filler concentration: (A) the original Kerner,
(B) the modified Kerner equation; (C) the Mooney equation. Circles correspond to experimental results (Reproduced with permission from John Wiley & Sons)..................43

2.14 The notched Izod impact strength of PP filled with (left) excellently and (right)
poorly adhering chalk particles as a function of the volume (●) 3.5μm (○) 130μm
(Reproduced with permission from Springer)..................................................................................44

2.15 Types of polymer/layer structures: (a) Microcomposites (b) Intercalated
nanocomposites (c) Exfoliated nanocomposites (Reproduced with permission from Elsevier).......................................................................................................................................45

2.16 Histograms of size distribution of the three different types of particles. Fraction of agglomerates are amplified by a factor given in each chart (Reproduced with permission from Elsevier).........................................................................................................................51

2.17 Relative toughness vs. filler content (▲) Untreated CaCO\textsubscript{3} (■)CaCO\textsubscript{3}-Titanate coupling agent (●)CaCO\textsubscript{3}-Stearic acid (Reproduced with permission from John Wiley & Sons)..................................................................................53

2.18 Linear moduli of suspensions containing various volume fractions of 1.4μm particles: (a) loss modulus (b) storage modulus (Reproduced with permission from ACS Publications)...............................................................................................................................56

2.19 Storage modulus and complex viscosity as a function of the angular frequency at small strain amplitude γ\textsubscript{o}= 6% for treated CaCO\textsubscript{3}-filled PP melts at 200°C
(Reproduced with permission from John Wiley & Sons)........................................................................................................................................57

2.20 Comparison of storage modulus for pure PP, NC1-25 (2% surface treatment-25 wt% particles), NC1-30 (2% surface treatment-30 wt% particles), and NC2-25 (6% surface treatment-25 wt% particles) at 200°C (Reproduced with permission from Taylor & Francis)........................................................................................................................................59

3.1 Precipitated calcium carbonate (PCC) vs. Ground calcium carbonate (GCC)
(Specialty Minerals) ........................................................................................................................................62

3.2 DSC samples for impact and tensile strength.........................................................................................67
3.3 Image and Analyze menus for the ImageJ software ..........................................................70

3.4 Image analysis: (a) Original SEM photograph (b) Image obtained after software analysis ..........................................................71

3.5 Particle size distribution analysis: (a) Histogram obtained from the image analysis (b) Curve fit obtained using the Gamma Variate function ..........................................................72

4.1 Dynamic viscosity for different mixing conditions ..........................................................77

4.2 Dynamic rheological properties for PP composites filled with non treated 3.2µm CaCO₃ particles from ground marble: (a) Elastic modulus G’ (b) Loss modulus G” (c) Dynamic viscosity \( \eta^* \). (x) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt% ..................79

4.3 Dynamic rheological properties for PP composites filled with treated 3.2µm CaCO₃ particles of ground marble: (a) Elastic modulus G’ (b) Loss modulus G” (c) Dynamic viscosity \( \eta^* \). (x) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt% ..................81

4.4 Dynamic rheological properties for PP composites filled with non treated 3.2µm CaCO₃ particles of ground limestone: (a) Elastic modulus G’ (b) Loss modulus G” (c) Dynamic viscosity \( \eta^* \). (x) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt% ..................83

4.5 Dynamic rheological properties at 210°C for PP composites filled with treated 3.2µm CaCO₃ particles of ground limestone: (a) Elastic modulus G’ (b) Loss modulus G” (c) Dynamic viscosity \( \eta^* \). (x) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt% ..................85

4.6 Dynamic rheological properties for PP composites filled with non treated 1.1µm CaCO₃ particles of ground limestone: (a) Elastic modulus G’ (b) Loss modulus G” (c) Dynamic viscosity \( \eta^* \). (x) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt% ..................87

4.7 Dynamic rheological properties for PP composites filled with treated 1.1µm CaCO₃ particles of ground limestone: (a) Elastic modulus G’ (b) Loss modulus G” (c) Dynamic viscosity \( \eta^* \). (x) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt% ..................88

4.8 Dynamic rheological properties for PP composites filled with treated 0.7µm CaCO₃ particles of precipitated limestone: (a) Elastic modulus G’ (b) Loss modulus G” (c) Dynamic viscosity \( \eta^* \). (x) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt% ..................90

4.9 Dynamic rheological properties for PP composites filled with non treated 0.07µm CaCO₃ particles of precipitated limestone: (a) Elastic modulus G’ (b) Loss modulus G” (c) Dynamic viscosity \( \eta^* \). (x) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt% ..................92

4.10 Dynamic rheological properties for PP composites filled with treated 0.07µm CaCO₃ particles from precipitated limestone: (a) Elastic modulus G’ (b) Loss modulus G” (c) Dynamic viscosity \( \eta^* \). (x) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt% ..................94
4.11 Elastic modulus G’ vs. CaCO₃ median particle size at 0.1 rad/s for (a) non treated and (b) treated particles..............................................................96

4.12 Dynamic viscosity vs. CaCO₃ median particle size at 0.1 rad/s for (a) non treated and (b) treated particles..............................................................97

4.13 Elastic modulus G’ vs. CaCO₃ median particle size at 1 rad/s for (a) non treated and (b) treated particles..............................................................99

4.14 Dynamic viscosity vs. CaCO₃ median particle size at 1 rad/s for (a) non treated and (b) treated particles..............................................................100

4.15 (a) Elastic modulus and (b) Dynamic viscosity vs. CaCO₃ (wt %) at 0.1 rad/s for non treated and treated particles.............................................................104

4.16 DSC plot for PP from pellets and after mixing in brabender ..................106

4.17 DSC plot for PP mixed with non treated 3.2µm particles of ground marble ....107

4.18 DSC plot for PP mixed with treated 3.2µm particles of ground marble ........108

4.19 DSC plot for PP mixed with non treated 3.2µm particles of ground limestone.....110

4.20 DSC plot for PP mixed with treated 3.2µm particles of ground limestone..........111

4.21 % Crystallinity as a function of composition (wt %) for 3.2µm calcium carbonate particles..............................................................................113

4.22 DSC plot for PP mixed with non treated 1.1µm particles of ground limestone.....114

4.23 DSC plot for PP mixed with treated 1.1µm particles of ground limestone........115

4.24 DSC plot for PP mixed with non treated 0.7µm particles of precipitated limestone ..............................................................117

4.25 Crystallinity as a function of composition (wt %) for 1.1µm and 0.7µm calcium carbonate particles..............................................................................118

4.26 DSC plot for PP mixed with non treated 0.07µm particles from precipitated limestone ..............................................................................119

4.27 DSC plot for PP mixed with treated 0.07µm particles from precipitated limestone ................................................................................121
4.28 Crystallinity as a function of composition (wt %) for 0.07µm calcium carbonate particles.................................................................................................................................................. 122

4.29 % Crystallinity vs. median particle size of CaCO₃ for the first DSC scan:
(a) Non treated particles (b) Treated particles.................................................................................................................. 124

4.30 % Crystallinity vs. median particle size of CaCO₃ for the second DSC scan for:
(a) Non treated particles (b) Treated particles................................................................................................................. 125

4.31 Average torque for the Brabender mixing for PP composites filled with different types of calcium carbonate................................................................................................................................................................................................. 131

4.32 WAXD diagram for α, β and γ forms of iPP (Reproduced with permission from John Wiley & Sons)................................................................................................................................................................................................. 133

4.33 WAXS θ scan for iPP with a mixture of α and β forms (Reproduced with permission from John Wiley & Sons) ................................................................................................................................................................................................. 133

4.34 20 scan of neat PP after mixing in Brabender internal mixer ................................. 134

4.35 20 scan for PP filled with treated 3.2µm particles of ground marble ................. 135

4.36 20 scan for PP filled with non treated 3.2µm particles of ground limestone ...... 136

4.37 20 scan for PP filled with treated 3.2µm particles of ground limestone.............. 137

4.38 20 scan for PP filled with non treated 1.1µm particles of ground limestone ....... 138

4.39 20 scan for PP filled with non treated 0.07µm particles from precipitated limestone ................................................................................................................................................................................................. 140

4.40 WAXS for PP mixed with treated 0.07µm particles from precipitated limestone ..141

4.41 SEM photograph of the fractured surface of neat PP after mixed in the Brabender internal mixer ................................................................................................................................................................................................. 144

4.42 SEM image and particle distribution for PP filled with 5wt% of non treated 3.2µm calcium carbonate for two different sections (a) and (b) .......................................................... 145

4.43 SEM image and particle distribution for PP filled with 20wt% of non treated 3.2µm calcium carbonate for two different sections (a) and (b) .......................................................... 146

4.44 SEM image and particle distribution for PP filled with 5wt% of treated 3.2µm calcium carbonate for two different sections (a) and (b) .......................................................... 147
4.45 SEM image and particle distribution for PP filled with 20wt% of treated 3.2µm calcium carbonate for two different sections (a) and (b) ......................................................... 148

4.46 SEM image and particle distribution for PP filled with 5wt% of non treated 1.1µm calcium carbonate for two different sections (a) and (b) ......................................................... 149

4.47 SEM image and particle distribution for PP filled with 20wt% of non treated 1.1µm calcium carbonate for two different sections (a) and (b) ......................................................... 150

4.48 SEM image and particle distribution for PP filled with 5wt% of treated 1.1µm calcium carbonate for two different sections (a) and (b) ......................................................... 151

4.49 SEM image and particle distribution for PP filled with 20wt% of treated 1.1µm calcium carbonate for two different sections (a) and (b) ......................................................... 152

4.50 SEM image and particle distribution for PP filled with 2wt% of non treated 0.07µm calcium carbonate for two different sections (a) and (b) ......................................................... 153

4.51 SEM image and particle distribution for PP filled with 5wt% of non treated 0.07µm calcium carbonate for two different sections (a) and (b) ......................................................... 154

4.52 SEM image and particle distribution for PP filled with 2wt% of treated 0.07µm calcium carbonate for two different sections (a) and (b) ......................................................... 155

4.53 SEM image and particle distribution for PP filled with 5wt% of treated 0.07µm calcium carbonate for two different sections (a) and (b) ......................................................... 156

4.54 Comparison between the amount of CaCO$_3$ added to PP and the value found using SEM image analysis ................................................................. 158

4.55 Median particle size from image analysis vs. the median particle size from the datasheet ........................................................................................................ 159

4.56 R$^2$ calculated from the Gamma Variate .................................................... 162

4.57 Tensile properties vs. CaCO$_3$ (wt %) for PP composites filled with 3.2µm particles of ground marble: (a) Tensile strength, (b) Elastic modulus ......................... 165

4.58 % Elongation at break vs. CaCO$_3$ (wt %) of 3.2µm particles from ground marble .............................................................................................................. 166

4.59 Tensile properties vs. CaCO$_3$ (wt %) for PP composites filled with 3.2µm particles of ground marble: (a) Tensile strength, (b) Elastic modulus ......................... 167
4.60 % Elongation at break vs. CaCO$_3$ (wt %) for 3.2µm particles from ground limestone ................................................. 168

4.61 Tensile properties vs. CaCO$_3$ (wt %) for PP composites filled with 1.1µm particles of ground marble: (a) Tensile strength, (b) Elastic modulus ......................... 169

4.62 %Elongation at break vs. CaCO$_3$ (wt %) for 1.1µm particles from ground limestone .................................................................................................................. 170

4.63 Tensile properties vs. CaCO$_3$ (wt %) for PP composites filled with 0.7µm particles of ground marble: (a) Tensile strength, (b) Elastic modulus ......................... 171

4.64 %Elongation at break vs. CaCO$_3$ (wt %) for 0.7µm particles from precipitated limestone .................................................................................................................. 171

4.65 Tensile properties vs. CaCO$_3$ (wt %) for PP composites filled with 0.07µm particles of ground marble: (a) Tensile strength, (b) Elastic modulus ......................... 173

4.66 %Elongation at break vs. CaCO$_3$ (wt %) for 0.07µm particles ................................................. 173

4.67 Tensile properties vs. CaCO$_3$ median particle size (a) Tensile Strength, (b) Elastic modulus......................................................... 176

4.68 %Elongation at break vs. CaCO$_3$ median particle size ................................................. 177

4.69 Tensile strength vs. % crystallinity .................................................................................................................. 182

4.70 Elastic modulus vs. % crystallinity .................................................................................................................. 183

4.71 %Elongation at break vs. % crystallinity .................................................................................................................. 184

4.72 Comparison of elastic modulus results with the Chantler and Halpin Tsai models .................................................................................................................. 185

4.73 Impact strength for PP composites filled with 3.2µm particles of ground limestone .................................................................................................................. 187

4.74 Impact strength for PP composites filled with 1.1µm particles ................................................. 188

4.75 Impact strength for PP composites filled with 0.07µm particles ................................................. 189

4.76 Impact resistance vs. median particle size of calcium carbonate for PP composites filled with (a) non treated and (b) treated particles .................................................................................................................. 191

4.77 Impact Strength of PP composites vs. % crystallinity .................................................................................................................. 193
CHAPTER I

INTRODUCTION

Polypropylene (PP) is the most widely used thermoplastic. It was first produced forty five years ago after the development of a suitable stereo-specific catalyst\(^1\). In 1996 it ranked third in consumption, close behind to low density polyethylene and polyvinyl chloride (PVC)\(^2\). With its worldwide growth rate of 7% it overtook PVC a few years later and its consumption is expected to keep growing because of the expanding number of end use products for the automotive (especially under the hood applications) and film industries\(^1\).

The reason for the popularity of polypropylene lies on its versatility. It has a good combination of physical and chemical properties, reduced cost per volume (low density 0.9 g/cm\(^3\)), great recyclability and good processability. Besides automotive and film, other polypropylene applications include appliances, textiles and nonwovens, packaging, consumer products, building and construction\(^2\).

Polypropylene homopolymer is a hard tough material and shows relatively high yield strength and high elongation at break. However, its tensile strength is inferior compared with other thermoplastics. Polypropylene homopolymer performs reasonably well in impact but it is outranked by low density polyethylene (LDPE), high density polyethylene (HDPE), acrylonitrile butadiene styrene (ABS), polyamide 6 and other engineering thermoplastics like polycarbonate or poly(p-phenylene oxide)(PPO)\(^2\).
Polypropylene has been modified to improve its properties, especially its elastic modulus and impact strength. Polypropylene has an important ability to accept fillers and reinforcements (much superior to that of polyethylene) together with clarifiers, nucleating agents, lubricants, release agents and antistatic agents.\(^2\)

As a result, polypropylene has penetrated in the market of polyethylene, polystyrene, PVC, thermoplastic polyesters, nylon 6 or 66 and sometimes competes directly with metals or thermoset polymers. Polypropylene’s advantage over polyethylene is its temperature resistance and density of material (especially for cost unit basis). For the PVC rigid and flexible applications, polypropylene has proved to be a reasonable alternative but so far had moderate success. Recycling of PVC is an important environmental issue that could favor polypropylene in the future.\(^1\)

Calcium carbonate is one the most commonly used inorganic fillers for PP due to its low cost and availability. Calcium carbonate nanoparticles have received much industrial and research interest in the last years. As with other nanofillers, their large interfacial area can improve the properties of composites in great extent even at low loadings.

Addition of calcium carbonate nanoparticles to PP is expected to increase its stiffness and impact strength. The low concentration of nanofillers could be a cost effective alternate solution to engineering thermoplastics as long as good dispersion is achieved. However, homogeneous dispersion of nanoparticles is very difficult because they agglomerate easily due to their high surface energy.

Complex methods with high cost have been used to disperse nanoparticles uniformly but they are limited to laboratory scale. Blending nanoparticles with polymers...
at large scales and low cost production seems to be the route for the existing plastics industry. In order to overcome the agglomeration of nanoparticles using this process, surface treatment, compatibilizers and coupling agents have been used.

Various studies have been made to understand the influence of the characteristics of calcium carbonate nanoparticles on the morphology and mechanical properties of the PP/CaCO$_3$ nanocomposites. Particle size and surface treatment of calcium carbonate were studied previously. However, the effect of the particle size distribution is not well understood.

Particle size distribution is one of the most important characteristic of fillers. The datasheets of calcium carbonate show the particle size distribution obtained usually from the sedigraph method or image analysis. Not much attention has been paid to the particle size distribution after mixing and the information that could be obtained from it. Finding a mathematical model that predicts the particle size distribution can be a helpful to further understand the formation and size of agglomerates. The results might be associated with the characteristics of calcium carbonate and polypropylene, perhaps even mixing conditions.

The first objective of the work presented in this thesis was to find the particle size distribution of calcium carbonate nanoparticles in the polypropylene matrix after mixing using SEM image analysis. Also, to find a mathematical function that fit with the results obtained.

The second objective was to combine the results of the thermal, image and X-Ray analysis to study the effect of the particle size, surface treatment and composition of calcium carbonate on the mechanical properties of the PP/CaCO$_3$. X-Ray diffraction was
used to verify the formation of β-iPP with addition of calcium carbonate to PP during mixing and injection molding. The k parameter was used to quantify the amount of β-iPP in the composites. An attempt was made to find a relation between the k parameter and the impact properties of the PP composites.
CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Polypropylene

Polypropylene has different crystalline forms, depending on tacticity and crystallization conditions. Isotactic polypropylene presents three main different forms: α, β and γ. In some cases these forms can coexist and change into another.

Highly stereospecific syndiotactic polypropylene was made possible with the development of metallocene catalysts. Metallocene catalysts allow the synthesis of polypropylenes with much broader physical properties than previously possible and have enriched the field of olefin polymerization.

Mesomorphic or smectic polypropylene has high clarity and is useful in film applications. Amorphous polypropylene is used for hot melts and pressure sensitive adhesives, sound insulation and as a modifier for rubber, polyethylene and asphalt.

Commercial forms of polypropylene include homopolymers, random copolymers, impact copolymers, random block copolymers, thermoplastic olefins and thermoplastic vulcanizates. Homopolymer provides stiffness and toughness but exhibits low impact strength at low temperatures and low clarity for certain applications. Random copolymers are used when high impact resistance at low temperatures is required. Thermoplastic olefins (TPO) and thermoplastic vulcanizates (TPV) provide elastomeric properties for
automotive and other applications\textsuperscript{2}. Isotactic homopolymer is the subject of the investigation in this thesis.

2.1.1 Polymorphic forms of isotactic polypropylene (iPP)

The crystalline architecture of isotactic polypropylene is complex and multifaceted. Several spherulite types of iPP have been reported\textsuperscript{4}. The most widely known crystal structure was determined first by Natta and Corradini\textsuperscript{5}, a monoclinic lattice referred as α structure. Later, a hexagonal lattice was recognized and was called β structure\textsuperscript{6}. The β structure occurs occasionally as a minority constituent. A triclinic lattice called γ was identified later\textsuperscript{7,8}.

Padden and Keith\textsuperscript{9} observed a variety of spherulitic types in iPP. Types I and II differ in temperature range and birefringence values and crystallize with the monoclinic α structure. Type III and IV occur sporadically within certain isothermal crystallization temperatures and they crystallize with hexagonal β structure. Most bulk samples have a mixed spherulite type with random distributions of positively and negatively birefringent regions. Examples of these spherulite types are presented on Figure 2.1\textsuperscript{4}. Natta and Corradini\textsuperscript{5} reported the main characteristics of the spherulite types including crystal structure and birefringence as demonstrated in Table 2.1\textsuperscript{4}.

2.1.1.1 α-iPP

The α phase of isotactic PP has important characteristics that need to be understood including structure, melting behavior and mechanical properties.

2.1.1.1.1 Structural architecture

Isotactic PP in the α-form exhibits a unique tendency for lamellae to organize into a crosshatched pattern. The previous studies of Binsenberg and Lange\textsuperscript{10} indicate the
coexistence of radial lathlike lamellae and a crosshatched tangential lamellae oriented nearly orthogonal to the radial direction. The lamellar morphology of iPP has been used to explain the optical classification of α-form on different spherulites types. This indicates the strong link between lamellar and spherulitic morphologies.

Figure 2.1 Different spherulite types viewed in polarized light (a) Type I Tc=128°C, (b) Type II Tc=138°C, (c) Type III Tc=125°C, (d) Type IV Tc=130°C (Scale bar 200 microns) (Reproduced with permission from D.R. Norton and A. Keller, Polymer, 26, 704. Copyright 1985, Elsevier)

Table 2.1 Characteristics of spherulite types (Reproduced with permission from D.R. Norton and A. Keller, Polymer, 26, 704. Copyright 1985, Elsevier)

<table>
<thead>
<tr>
<th>Spherulite Type</th>
<th>I</th>
<th>Mixed</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>α</td>
<td>α</td>
<td>α</td>
<td>β</td>
<td>β</td>
</tr>
<tr>
<td>Birefringence (Δn)</td>
<td>−0.003</td>
<td>± 0.002</td>
<td>0.002</td>
<td>0.007</td>
<td>0.007</td>
</tr>
<tr>
<td>Sign of birefringence</td>
<td>+</td>
<td>±</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>Isothermal Tc</td>
<td>&lt; 134 °C</td>
<td>134 °C-138 °C</td>
<td>&gt; 138 °C</td>
<td>&lt; 122 °C</td>
<td>122 °C-132 °C</td>
</tr>
</tbody>
</table>
Spherulites of Type I, II and mixed forms are often collectively referred as α spherulites. Table 2.1 suggests that Type I spherulites form at lower crystallization temperature \((T_c < 134^\circ C)\) and Type II form at elevated crystallization temperature \((T_c > 138^\circ C)\). The temperatures for which the different types of spherulites grow in practice depend on the melt history and specific grade of iPP.

2.1.1.1.2 Melting behavior of α-iPP

The melting point of α-iPP is strongly dependent on tacticity\(^{11,12}\) and thermal history\(^{12,13}\). The thermal behavior of α-iPP is complicated to explain due to the multiple melting endotherms and isothermal thickening during crystallization\(^{14}\). The dominant mechanisms for multiple melting endotherms are dependent on the molecular weight and tacticity\(^{15}\). Multiple melting endotherms are reduced with higher molecular weight or higher tacticity\(^{16}\).

In the absence of other polymorphic forms (β, γ and mesomorphic forms), the multiple endotherm behavior of α form can be explained by a number of mechanisms common to other semicrystalline polymers including:

1) Tendency for melting recrystallization remelting (MRM) during scanning in DSC which diminishes as the molecular weight increases and as the crystallization temperature approaches the equilibrium melting point\(^{17}\), and

2) Self annealing of crystallites during heating and presence of crystallites of varying stability\(^{18}\).

α-iPP also shows strong tendency for cocrystallization of components with different tacticity and composition provided that the melting point disparity of the components is not too large\(^{3}\).
2.1.1.1.3 Mechanical properties of α-iPP

The α form of iPP is stable and the most commonly observed. Most of the early studies for iPP addressed the effect of α crystalline morphology on mechanical properties.

Spherulite size affects strength and ductility. In fracture, smaller spherulites exhibit more ductile behavior and crazing in the surrounding crack tip. Larger spherulites resulted in more brittle behavior due to increased segregation of impurities to the boundaries and the formation of voids during contraction on cooling\(^{19,20,21}\). Other studies suggested that it is not spherulite size, but structural variations, that are responsible for the adverse effects on iPP. Also, the effect of processing conditions showed that high undercooling improves yield stress due to increasingly crosshatched structure\(^{22}\).

Finer spherulites tend to form finely dispersed crazes which improves the fracture toughness. Friedrich\(^{20}\) studied the effect of morphology on strength and fracture of iPP and suggested that specific resistances to crack propagation can be attributed to regions with different molecular structure. The sensitivity of crack propagation can be lowered by the right molecular composition (atactic content and molecular weight) and by controlled production of certain morphology\(^{21}\). Friedrich\(^{21}\) summarized the results of impact strength with increasing molecular weight or reduction of the melt flow index (MFI) as shown in Table 2.2. For the same MFI, impact strength increases with increasing atactic content.

Many investigators have compared the mechanical properties of α and β forms. Aboulfaraj et. al.\(^{23}\) reported that α spherulites exhibit elastic behavior under tensile stress followed by brittle fracture which starts at the spherulite center and propagates to produce a crack. Table 2.3 shows a comparison on tensile properties for α-iPP and β-iPP given by Varga\(^{24}\).
Table 2.2 Relationship of molecular structure with mechanical properties of different types of Polypropylene (Reproduced with permission from K. Friedrich, Progress in Colloid and Polymer Science, 66, 299. Copyright 1979, Elsevier)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Melting Flow Index</th>
<th>Atactic Content</th>
<th>Density</th>
<th>Melting Temperature $T_m$ [°C]</th>
<th>Shear Modulus $G'(25°C)$ [MPa]</th>
<th>Impact Strength $\sigma_1(35°C) [kJ/m^2]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP 1120 LX</td>
<td>4.5–6</td>
<td>5</td>
<td>0.908</td>
<td>160–165</td>
<td></td>
<td>630</td>
</tr>
<tr>
<td>PP 1120 HX</td>
<td>1.5–2.2</td>
<td>5</td>
<td>0.907</td>
<td>160–165</td>
<td></td>
<td>600</td>
</tr>
<tr>
<td>PP 1320 L</td>
<td>4.5–6</td>
<td>20</td>
<td>0.896</td>
<td>157–162</td>
<td></td>
<td>300</td>
</tr>
</tbody>
</table>

Table 2.3 Static Tensile Characteristics of $\alpha$-iPP and $\beta$-iPP (Testing speed 1mm/min) (Reproduced with permission from J. Varga, Journal of Macromolecular Science, 41, 1121. Copyright 2002, Taylor & Francis)

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>$\alpha$-iPP</th>
<th>$\beta$-iPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$-modulus ($E$)</td>
<td>GPa</td>
<td>2.0</td>
<td>1.8</td>
</tr>
<tr>
<td>Yield stress ($\sigma_y$)</td>
<td>MPa</td>
<td>36.5</td>
<td>29.5</td>
</tr>
<tr>
<td>Elongation at yield ($\varepsilon_y$)</td>
<td>%</td>
<td>$\sim 12$</td>
<td>$\sim 7$</td>
</tr>
<tr>
<td>Necking stress ($\sigma_n$)</td>
<td>MPa</td>
<td>27.5</td>
<td>28</td>
</tr>
<tr>
<td>Elongation at necking ($\varepsilon_n$)</td>
<td>%</td>
<td>$\sim 22$</td>
<td>—</td>
</tr>
<tr>
<td>Tensile strength ($\sigma_t$)</td>
<td>MPa</td>
<td>39.5</td>
<td>44.0</td>
</tr>
<tr>
<td>Elongation at break ($\varepsilon_t$)</td>
<td>%</td>
<td>$\sim 420$</td>
<td>$\sim 480$</td>
</tr>
</tbody>
</table>

2.1.1.2 $\beta$-iPP

Previous studies have described the different characteristics of the $\beta$ phase of isotactic PP. Those characteristics are presented in this section.

2.1.1.2.1 Structural architecture

The $\beta$-iPP spherulites show a radial lamellar morphology similar to polyethylene and other polymers$^{10}$. $\beta$-iPP is characterized by extensive disorder. The simplest satisfactory model is trigonal unit cell as reported by Lovingen et. al.$^{25}$.

Formation of pure $\beta$-iPP has two melting points, an upper temperature $T(\beta\alpha)\sim 141°C$ and a lower temperature $T(\alpha\beta)\sim 105°C$, as shown by optical microscopy.
studies by Varga and Ehrenstein\textsuperscript{26}. In between 105°C and 141°C, different structural features can be formed depending on thermal conditions of crystallization, melt history, mechanical stresses and presence of fillers or other particles\textsuperscript{24}. Figure 2.2\textsuperscript{26} shows these features for crystallization temperature of 135°C.

![Figure 2.2 Various shapes and their growth in β-nucleated iPP samples](image)

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
</tbody>
</table>

Figure 2.2 Various shapes and their growth in β-nucleated iPP samples (a) Tc = 135°C, t\textsubscript{c} = 50min; (b) Tc = 135°C, t\textsubscript{c} = 62min (1) β-hexagonite, (2) β-needle crystal, (3) β-ovalite, (4) β-spherulite, (5) α-spherulite (Reproduced with permission from J. Varga and G. W. Ehrenstein, Colloid and Polymer Science, 275, 511. Copyright 1997, Springer)

2.1.1.2 Melting behavior of β-iPP

Estimates of the equilibrium melting point of the β crystalline form vary from 170°C to 184°C\textsuperscript{28,36}. It was suggested that the β form has a slightly reduced equilibrium melting point relative to the α form. It is said that a definitive value is difficult to determine due to the transformation of the β phase into α phase during partial melting of β phase\textsuperscript{24}. Under typical polypropylene processing conditions, the presence of β phase is associated with a low melting point and has important commercial consequences for temperature dependent forming processes\textsuperscript{3}.

The β to α modification results from an interplay of α and β phase crystal growth rates and melting-recrystallization processes. β phase growth rates are higher than α
phase only for a crystallization temperature between 100°C to 141°C. A second nucleation mechanism takes above 140°C where α overgrowths on β lamellae\(^{27}\).

Padden and Keith\(^6\) demonstrated that β spherulites recrystallize into α modification (βα recrystallization) when heated. Once formed, the β-iPP samples are susceptible to βα recrystallization only if they were cooled below the critical temperature of ~100-105°C as shown by Varga\(^{28}\). Postcrystallization or secondary crystallization below that critical temperature yields highly dispersed α phase overgrowths in β spherulites. When melting the β spherulites, growth on these overgrowths produces a thermally stable, high melting α phase in the conventional α melting range.

Fujiwara\(^{29}\) showed that the melting curves of iPP with mixed polymorphic content have a complicated melting profile. The melting of α and β phases coexists with the βα recrystallization phenomenon.

There is also a βα phase transition induced by deformation such as linear and biaxial drawing, cold and hot rolling\(^{30}\). In the orientation range, during necking, a marked β to α phase transition takes place and the transformation finishes at the break. The β-α recrystallization observed during stretching cannot be interpreted by a one-phase model where the structural changes take place in the solid crystalline phase\(^{31}\) or a two-phase model where there is melting due to stretching the crystallites followed by recrystallization\(^{32}\). Several intermediate models were published based on local melting or formation of transient amorphous phases\(^{33,34,35}\).

2.1.1.2.3 Mechanical properties of β-iPP

The β-iPP has a lower elastic modulus and yield stress that of α-iPP\(^{24,37}\) but the impact strength and toughness exceeds those of α-iPP. The latter can be attributed to the
combined effect of the peculiar lamellar morphology, mechanical damping and phase transformation (β to α transition during mechanical tests) of β-iPP\textsuperscript{36}. Tjong et. al.\textsuperscript{37} suggested that the radial morphology of the β spherulite promotes extensive crazing.

The products with high level of β form in iPP require the use of β nucleating agents and proper processing conditions: crystallization temperature range between 105°C and 140°C and flow relaxation conditions\textsuperscript{24}. Fillers can be effective to promote β phase formation. However, it is important to avoid fillers such as talc that will act as strong α nucleating agents\textsuperscript{38}. Rybnikar\textsuperscript{39} and Pukanszky\textsuperscript{40} found that talc is a strong α nucleating agent and inhibits the formation of β phase and that calcium carbonate benefits the manufacturing of products with high amount of β-iPP because it is a very weak α nucleant. Tjong et. al.\textsuperscript{41} showed that talc suppresses the formation of β-PP dramatically. At 20% loading of talc the PP composites were mainly α-PP.

Applications of products with high amounts of β-iPP are based on its high impact resistance and toughness. Therefore, it is used in industrial pipeline construction, dielectric capacitors with roughened surface, etc\textsuperscript{24}.

2.1.1.3 γ-iPP

The presence of γ-iPP form is uncommon in iPP homopolymer commercially available produced under typical processing conditions\textsuperscript{3}. The γ phase is a minor constituent in bulk crystallization of iPP at atmospheric pressure. The appearance of γ phase is favored by presence of short polymer chains\textsuperscript{42} and it was demonstrated that for commercial iPP with long polymer chains, γ phase can be generated at high pressure\textsuperscript{43}.  

13
2.1.1.3.1 Structural architecture

Initially the $\gamma$ structure formed a triclinic unit cell similar to the one for $\alpha$ form. Later Bruckner and Meille\textsuperscript{44} proposed a structure of $\gamma$-iPP with nonparallel chains within the unit cell. They also found that the lattice parameters of the modified triclinic structure permit the transformation to a face-centered orthorhombic unit cell. The development of morphological details of the $\gamma$ phase such as lamellae organization and chain orientation has not been fully understood\textsuperscript{3}. Mezghani\textsuperscript{45} showed that the $\gamma$-form, crystallized at elevated pressures, exhibited three distinct classes of spherulites, categorized according to the sign of the different types of birefringence as shown in Figure 2.3.

2.1.1.3.2 Melting behavior of $\gamma$-iPP

Several studies reported the stability of $\gamma$ formed during heating treatments. Morrow\textsuperscript{46} showed that $\gamma$-phase could be produced at high-pressure from commercial polypropylene. Moreover, it did not convert to $\alpha$-phase either by thermal treatment or mechanical stress. He suggested that the equilibrium crystal form is the $\gamma$ rather than the $\alpha$ ordinarily observed. Other later studies showed the $\gamma$-$\alpha$ transformation on heating or annealing. Pae et. al.\textsuperscript{47} found $\gamma$-$\alpha$ transformation at elevated temperatures. They also showed that slow heating rates favor the $\gamma$-$\alpha$ transformation. Mezghani et. al\textsuperscript{48} developed a map for equilibrium melting point for iPP as a function of pressure. It was demonstrated that the equilibrium melting point of $\gamma$ phase is similar to the one for $\alpha$ phase when extrapolated to atmospheric pressure. A comparison of the equilibrium melting point of the $\gamma$ phase and $\alpha$ phase requires more experimental studies\textsuperscript{3}. 
2.1.1.3.3 Mechanical behavior of $\gamma$-iPP

Most manufacturing processes in the plastics industry are conducted at high pressures in the range of 1 to 2 kbar (100 to 200 MPa) in which iPP tends to form $\gamma$ structure. Therefore, the experimental determination of the mechanical properties of $\gamma$ structure is crucial to achieve the desired properties of final products.

Figure 2.3 $\gamma$ spherulites produced at 200 MPa and different isothermal crystallization temperatures:
(a) Negative birefringence 190°C (b) Positive birefringence at 205°C (c) Mixed birefringence at 198°C (Reproduced with permission from K. Mezghani and P. J. Phillips, Polymer, 38, 5725. Copyright 1997, Elsevier)
Kalay et. al. explored the effects of different grades of iPP on the structural development of γ-phase by injection molding. They showed that the γ-phase can occur in commercially processed iPP in moldings with pronounced molecular orientation. The specimens containing the γ-phase exhibit an increase in Young’s modulus and tensile strength when there was no excessive shear during melt processing. This was attributed not only to the presence of the γ-phase but also the molecular orientation, presence of shishkebab morphology and the increase of crystallinity. In addition, the γ-phase developed in injection molding is stable and does not transform to another phase during the deformation process.

Mezghani et. al. also investigated the tensile properties of iPP with the γ-phase compared with one with the α phase. The iPP with γ-phase was much tougher than the α-phase and both showed similar yield strength. The main difference between the two forms is the high ductility of the γ-phase, considerably higher elongation at break and small reduction in stiffness.

2.1.2 Relationship of molecular weight and tacticity with melting behavior and mechanical properties

The melting and crystallization behavior of iPP were studied intensively based on molecular weight and isotacticity.

Janimak et. al. found that the crystal unit-cell parameters, crystallinity, crystal size and lamellar crystal thickness depended on crystallization temperature and isotacticity. Paukkeri also found that isotacticity was the main parameter determining crystallization, melting temperature, crystallinity and crystallization rate for isothermal crystallization. Molecular weight has little effect on crystallization rate and almost no
influence on crystallinity $^{54,55}$ but it influences the melting temperature which increases with increasing molecular weight.

Marigo et. al.$^{56}$ studied the influence of molecular weight and molecular weight distribution on the crystallization of $\beta$-iPP and found that the highest amount of $\beta$ phase was obtained with high average molecular weights and wide molecular weight distributions as shown in Figure 2.5. The highest $\beta$-iPP content was obtained with the highest average molecular weight and the highest polydispersity index. The different characteristics of PP used in their experiments are shown in Figure 2.4.

![Table 2.4 Viscosity Average Molecular Weights $M_v$ and Molecular weight polydispersity index $PI$](image1)

![Table 2.5 Total degree of crystallinity $\Phi_{tot}$ and Relative content of the $\beta$ Form $\Phi_\beta$ in the iPP samples, isothermally crystallized at 90°C](image2)

As mentioned before $\gamma$-iPP formation is influenced by molecular weight. At atmospheric pressure only iPP with really low average molecular weight can form $\gamma$ phase. At normal molecular weights around 200 000, high pressure (100-200MPa) is necessary for formation of $\gamma$ phase. Morrow et. al.$^{42}$ used very low number average
molecular weights Mn between 740 and 3880 and obtained the wide angle X-ray 2θ scans showed in Figure 2.6.

Sauer et. al.\textsuperscript{43} used high pressure 3.86 kbar (386 MPa) with an average molecular weight of 325 000 and obtained the 2θ scan showed in Figure 2.7. Both 2θ scans are the expected from the triclinic or γ-phase of PP. The most significant difference between α-phase and γ-phase is the third 2θ peak. For the γ-phase, this strong reflection is located at 20.1 deg. and for the α-phase it is present at about 18.6 deg.

![Figure 2.6 Wide angle X-Ray 2θ scans for α-phase and γ-phase from X-ray diffractometer (Reproduced with permission from D. R. Morrow and B. A. Newman, Journal of Applied Physics, 39, 4944. Copyright 1968, American Institute of Physics)]
Figure 2.7 Wide angle X-ray diffraction 20 scans taken at 25°C and after 5 min at 154°C (Reproduced with permission from J. A. Sauer and K. D. Pae, Journal of Applied Physics, 39, 4959. Copyright 1968, American Institute of Physics)

The stress-strain properties of polypropylene are dependent on molecular weight as reported in many previous studies. The tensile strength and elongation increase with molecular weight\textsuperscript{57,58,59,60,61}. The failure mechanism of iPP under tension was explained as following. At the beginning, crystallites serve as filler particles or cross links holding the material together, but with increasing strain these crystallites begin to deform and fail.

In general, a decrease on degree of crystallinity is observed with increasing molecular weight which improves toughness. On the other hand, low molecular weight reduces the number of ‘tie molecules’ and material tends to be brittle and have low strength\textsuperscript{62}. Van Shooten et. al.\textsuperscript{63} studied the influence of molecular weight and molecular weight distribution on the mechanical properties of PP. They found that yield stress, mechanical damping and hardness depend only on the degree of crystallinity, whereas impact strength and elongation at break also depend on molecular weight and molecular
weight distribution. They suggested that high impact strength required a high molecular weight and a narrow molecular weight distribution.

2.2 Fillers

Fillers were initially added to materials in the quest for cost reduction and increase of volume. However, nowadays cost reduction is not the only or even most important consideration for using fillers in composite materials. Cost reduction depends on the relative cost of the polymer and the filler. The price of the filler per unit volume must be compared. It depends greatly in the particle size\textsuperscript{64}. Besides cost reduction, composite systems afford a means of extending the available volume of resins while improving many properties including faster molding cycles due to increased thermal conductivity and fewer rejects due to minimizing warpage\textsuperscript{65}.

Many other attributes can be influenced by fillers. Fillers are used either to increase or to decrease the density of a product, to obtain smooth surfaces or decrease the coefficient of friction of materials. Fillers influence optical, electrical, mechanical and rheological properties and they affect material durability and morphology of materials\textsuperscript{64}.

2.2.1 Filler characteristics

The effect of fillers on resin properties depends primarily on the particle size distribution, particle shape (aspect ratio), surface area and chemical composition (reactivity). Particle size and shape affect both the properties of the final product and also the processing conditions. Size, shape and distribution are associated with other physical properties like surface area and they cannot be considered separately. Other secondary properties of fillers are optical: color, refractive index; thermal: conductivity, heat capacity, thermal expansion coefficient; and physical: density and hardness\textsuperscript{65}. 20
2.2.2 Calcium carbonate

Calcium carbonate is the most widely used filler for the plastic industries. It is inexpensive and can be added up to high loadings of 60 % weight. It is generally used as an extender but it can improve stiffness and impact strength, especially with fine micron particles and nowadays even nano particles (~0.1 microns)\(^2\).

There are three crystalline forms which are mostly used in production of calcium carbonate filler: Two types of calcite, with trigonal rhombohedral or trigonal scalenohedral form and Aragonite, which has orthorhombic crystals. Aragonite is a less stable form and it can be converted by heating to calcite\(^64\).

Both minerals can be easily distinguished by their physical properties such: density (aragonite 2.9 and calcite 2.7), refractive index (aragonite 1.7, calcite with two refractive indices of 1.49 and 1.66 which causes a double refraction effect) and hardness (aragonite 3.5 - 4 and calcite 3)\(^65\).

There are several minerals and rocks from which calcium carbonate is produced. The most used are chalk, limestone and marble. Chalk is a soft texture sedimentary rock from nanofossils; limestone is a consolidated sedimentary rock; and marble is a metamorphic rock originally composed of either calcite, aragonite or dolomite\(^64\).

Depending upon the conditions of heat, pressure, movement, time, and the presence or lack of water and other types of nearby materials, deposits can be formed from high purity white marble to highly contaminated off color limestone.

Different types of calcium carbonate are commercially available. The different purity and crystalline structures will give rise to different properties. Thus it is important
to be aware that all carbonates are not equal. Most plastic applications require basic purity standards and basic color properties.

The compounds with calcium carbonate are widely used in various fields: in building, for manufacture of cement, glass, and ceramics; in pharmacology, to manufacture toothpastes; in cosmetics, to produce creams; in paper industry, to manufacture cigarette, chalk-overlay, and tracing paper; in production of plastics and artificial leather. In all these fields, commercial characteristics are imposed on calcium carbonate’s chemical composition, size and shape of particles.

2.2.2.1 Production of calcium carbonate

Two major processes are used in the production of calcium carbonate filler: milling/grounding and precipitation. More than 90% of calcium carbonate is produced by milling using wet and dry methods and with technology developed for reproducibility and to obtain the required particle size distribution. Commercial finely ground calcium carbonate can range down in particle size to 1 to 3 microns, with the top size controlled to 5 to 10 microns for high performance applications.

Precipitated calcium carbonate is also termed synthetic calcium carbonate since several chemical operations are performed. Depending on the process parameters, different grades are produced. These grades can be distinguished by particle size distribution or crystalline form and can be used in different applications. Precipitated calcium carbonate can have an average particle size of 40nm.

2.2.2.2 Surface treatment of calcium carbonate

Surface treatment is an additional modification to enhance performance of the matrix-calcium carbonate interactions. In order to obtain the desired results, the type and
mechanism of treatment must be chosen according to the chemical and physical properties of the components. The incompatibility of the high energetic hydrophilic surface of calcium carbonate with the low-energy surface of hydrophobic polymers, as polyethylene and polypropylene, is a particular problem that requires surface treatment of fillers\textsuperscript{68}.

Surface treatments can be reactive and non reactive. Non reactive surface treatment, the oldest and most used modification, covers the filler with a small molecular weight organic compound (surfactant). A typical example is calcium carbonate with stearic acid. The surface of calcite is also modified with silanes and titanates but stearic acid is the most common surface modifier because of its low cost\textsuperscript{66}. Rhombohedral calcite is the most likely to be coated with stearic acid\textsuperscript{64}.

Calcium carbonate surface adsorbs the polar group of stearic acid by the formation of ionic bonds between stearic acid and the surface of calcium carbonate. In non reactive treatment, it is really important to know the right amount of surfactant to use in order to obtain the desired properties\textsuperscript{69}.

As a result of treatment, surface energy of the fillers decreases dramatically\textsuperscript{70}. The surface energy of the filler particles determines the matrix-filler and the particle-particle interactions. The reduction of surface energy decreases the particle-particle and matrix-particle interactions. Weaker particle-particle interaction reduces aggregation and improves dispersion, homogeneity, processing, mechanical properties and appearance\textsuperscript{71,69}.

Reactive treatments assume a chemical reaction of the coupling agent with both of the components filler and matrix and create covalent bonds between the reactive groups
of the polymer matrix and those of the filler. Silane coupling agents were proved successful with fillers that have reactive OH groups on their surface like glass fiber, mica and in recent years with CaCO₃.

It is difficult to bind fillers to the matrix polymer by covalent bonds, especially polyolefins, because these do not possess reactive chemical groups. Non-reactive surface treatment modifies only the secondary (van der Waals) forces between the surface of the filler and the matrix.

Compatibilizers are another option to improve adhesion between polymer and filler. PP modified with maleic anhydride or acrylic acid are frequently used because they adsorb to the surface of most fillers and proved to improve filler-matrix adhesion and mechanical properties.

The majority of treated calcium carbonates are post-treated on a separate production line at the end of the other processes. Surface treatment levels are usually determined by the mineral’s surface area. Typically there will be a slight excess of treatment to insure complete encapsulation/reaction.

2.2.2.3 Composites of polypropylene with calcium carbonate

Details of the use of calcium carbonate with polypropylene and the effects of calcium carbonate on polypropylene’s properties will be discussed in the next sections.

2.2.3 Talc

The mineral talc is hydrated magnesium silicate and its composition varies depending on where it is mined. Talc is the major constituent of rocks known as soapstone or steatite. It might be accompanied by tremolite (a fibrous type of tremolite was used as asbestos) which might be of concern for many potential applications.
The talc of major interest to plastics is a finely ground product with thin platelets and preferable white. Talc can be classified as both, an extender and reinforcement. Low cost makes talc an extender while its high aspect ratio (15-20) qualifies it as a reinforcing filler.

Composites with talc exhibit higher stiffness and creep resistance compared with composites with particulate fillers such as calcium carbonate. High stiffness is usually accompanied by reduction of impact strength but that effect can be minimized with the right selection of particle size and size distribution, surface treatments and formulations.

Talc are also soft solid particles (it has the lowest Mohs hardness 1.0) with low abrasion texture. Its specific gravity ranges from 2.7-2.8. Talc is unaffected by high temperature processing conditions and exhibits low thermal and electric conductivity.

Talc processing is relatively simple with emphasis placed on avoiding contamination and sorting it according to mineralogy and color using manual and optical methods. After mining, there are two ways to process talc: dry and wet. The dry process starts with selective mining and sorting of heterogeneous deposits followed by grinding and fine milling. The wet process starts with crushing followed by the separation of contamination through flotation and finally fine milling. Some talc grades also have surface treatments.

2.2.3.1 Composites of polypropylene with talc

Talc is the most widely used inorganic filler in PP. The improved particle properties of talc could be loaded up to 50% weight into PP. The addition of talc in PP provides a wide variety of properties for different applications and surface coupling agents are available to further improve mechanical properties of PP filled with talc.
Depending on its surface, talc can be hydrophobic or hydrophilic. Water absorption of PP filled with talc can be considerable and can create improper surface appearance of final products and poor adhesion to the polymer matrix\textsuperscript{80}.

The addition of talc in PP improves stiffness, dimensional stability, heat distortion and creep, and reduces impact strength, resistance to degradation and weldability of PP\textsuperscript{2}. Platy morphology of talc tends to orient along flow directions in the polypropylene matrix\textsuperscript{81} during molding which results in increased stiffness of the compounds. Higher aspect ratio of the talc particles will give greater stiffness. As the particle size of talc decreases, tensile strength increases slightly\textsuperscript{82,88}.

The poor dispersion of talc causes large agglomerations and poor impact strength\textsuperscript{82}. The selection of talc fineness is very important to obtain ductile fracture. A fine talc particle is required for high impact performance\textsuperscript{88}.

It is important to mention that talc is a very strong nucleating agent for PP. Increased talc concentration will increase the crystallinity of polypropylene\textsuperscript{40}. Rybnikar\textsuperscript{83} and Varga\textsuperscript{84} added up to 10\% of talc to PP and reported increased concentration of nuclei using optical microscopy. They also showed increased crystallization temperature as evidence of the nucleating effect of talc.

Fujiyama and Wakino\textsuperscript{85} studied injection molded samples of PP and talc. They found an increase of 1-2\% on crystallinity with addition of 0.5 weight \% of talc. Pukanszky et. al.\textsuperscript{40} reported an increase of crystallinity of \textasciitilde10\% at 0.3 volume fraction of talc. They also showed that with increasing talc concentration the young modulus improved but yield stress, yield strength and elongation at break decreased. They
suggested that the orientation of talc particles has a more pronounced effect on mechanical properties than nucleation.

Nucleation activity of talc at the proper shear conditions was reported as epitaxial crystallization. Rybnikar\textsuperscript{86} found a clear epitaxial polymer growth on the talc surface (transcrystallinity) in polyethylene and talc compounds and a less developed epitaxial growth for iPP\textsuperscript{87}.

Talc filled polypropylene is used in the automotive-under the hood applications, domestic appliances, power tool housings and furniture\textsuperscript{2}. Talc also is used to provide barrier properties, especially in film applications. The future of talc is related to the development of new submicron talc products, improved surface treatments and compacted talc to enhance mechanical and optical properties\textsuperscript{88}.

2.2.4 Glass fiber

Glass fibers are the most widely used reinforcement in thermoplastics and the third most important filler for polypropylene\textsuperscript{2}. Glass fibers are manufactured in a direct process. First, the metered ingredients are melted in a furnace. The liquid glass is conveyed into a bushing and flows through individual tips by gravity. The glass is then quenched by air or water and finally a mechanical gathering device and a winder collect the fiber\textsuperscript{89}. The rotation speed of the winder is the key parameter to the determination of fiber diameter and final form. Many different forms of fiber glass products are available after different processes\textsuperscript{90}. Chu’s monograph\textsuperscript{89} provided a review of the manufacturing glass fiber process and the different resulting products together with a list of the standard fiber’s diameter designations.
The physical and chemical properties of glass fiber depend on its composition. For example, E-glass is known for its excellent electrical resistance. C-glass is more chemically resistant and D-glass has lower dielectric strength\textsuperscript{89}.

2.2.4.1 Composites of polypropylene filled with glass fiber

Glass fibers are used to enhance mechanical properties of polypropylene. E-glass and R-glass are commonly used reinforcing fillers for plastics. Glass fibers are usually coated to avoid fiber breakage and to provide better fiber-polymer adhesion. Coupling agents such as maleic anhydride or acrylic acid have been used to further increase the adhesion between the filler and polymer\textsuperscript{80}.

Glass fiber also induces heterogeneous nucleation. Folkes\textsuperscript{91} described how isolated spherulites start to grow along the fiber but when nucleation density is high they impinge each other and only grow in one direction, normal to the surface. This phenomenon is known as transcryallinity. He also suggested that PP polymorphism makes possible to have different crystal forms on the fiber surface and on the rest of the matrix.

Polypropylene is the most common polymer used in glass mat reinforced thermoplastics (GMT). Thomason et. al. studied the influence of glass fiber on the properties of GMT and found improved tensile strength\textsuperscript{92}, modulus\textsuperscript{93}, heat deflection temperature\textsuperscript{94} and impact strength\textsuperscript{95} with increasing glass fiber concentration.

The addition of glass fibers into polypropylene injection molded parts increases the tensile strength, flexural modulus, dimensional stability and heat distortion temperature of polypropylene, but reduces its elongation at break\textsuperscript{96}. Anisotropic
properties caused by non uniform fiber glass orientation during processing also create a
tendency for distortion in injection molding parts\textsuperscript{97,89,98,99}.

The stress-strain behavior of fiber filled composites is very complex and factors
including interfacial adhesion, fiber alignment and overlapping have great importance\textsuperscript{100}. Compounding and processing tend to reduce the fiber length by fracture\textsuperscript{101}. The stress in composites with short fiber is transferred from the matrix to the fiber by shear. The fibers’ ends carry lower load than the middle section, therefore, there is a critical length below which fibers are ineffective carrying load\textsuperscript{62}. As a result, greater improvements can be produced by reinforcing polypropylene with long fibers\textsuperscript{102,103} because it increases the section capable of carrying load. Long fibers together with reduced fiber diameter can challenge engineering plastics with comparable properties but substantial reduced cost\textsuperscript{104}.

2.3 Polypropylene/CaCO\textsubscript{3} composites

As mentioned before, other than cost, the primary effect of fillers and
reinforcements is to modify mechanical properties of polypropylene. In order to utilize all the advantages of calcium carbonate, it is important to understand its effect on the structure and properties of polypropylene.

2.3.1 Effect of calcium carbonate on the structural development of PP/CaCO\textsubscript{3} composites

The introduction of a filler or reinforcement can change the crystalline structure of polypropylene which results in property differences\textsuperscript{105}. The main effect of particulate fillers is their ability to act as nucleating agents providing a facile site for heterogeneous nucleation\textsuperscript{69}. The nucleation effect of fillers on iPP can be seen as increased crystallization temperature (Tc), crystallization/nucleation rate and crystallization half time as well as reduction in spherulite size.
Numerous studies revealed heterogeneous nucleation in isotactic polypropylene\textsuperscript{106,107,108}. Rybnikar\textsuperscript{83} studied the nature of nuclei in iPP and found two kinds of heterogeneous nuclei depending on melting conditions: Solid heterogeneities, probably catalyst residues and, at low melting temperatures, nuclei that seemed remnants of polymer crystalline phase.

Numerous fillers and reinforcements are added to iPP. Calcium carbonate occupies the second place behind talc as the most widely used filler for polypropylene\textsuperscript{69}. Studies of crystallization behavior and morphology of PP filled by calcium carbonate have shown its weak nucleation activity in PP in comparison with other fillers like talc.

Rybnikar\textsuperscript{39} reported that the polypropylene filled with calcium carbonate crystallizes faster and has a greater number of spherulites than PP alone. Nevertheless, he observed that only a small fraction of filler particles act as nuclei after comparing the concentration of calcium carbonate particles (10\textsuperscript{11} particles per cm\textsuperscript{3}) and the increase in number of heterogeneous nuclei (10\textsuperscript{5} to 10\textsuperscript{6} per cm\textsuperscript{3}) with addition of calcium carbonate in the composite. Pukanszky et. al\textsuperscript{40} also found that spherulite size reduced its size significantly with talc but much less with CaCO\textsubscript{3}.

The flow effects of extension and shear during the melt processing are also crucial for the nucleating effect of fillers and the resulting morphology. PP is processed in different ways especially through injection molding and extrusion for packaging films and fiber\textsuperscript{2}. Fujiyama and Wakino\textsuperscript{85} studied the structure and properties of injection molded polypropylene filled with calcium carbonate and talc and found increased crystallinity only in the case of talc. They also suggested that increased crystallization
temperature, as a result of the addition of nucleators, produces a higher degree of crystalline orientation and better mechanical properties.

2.3.1.1 Effect of particle size, size distribution and crystal shape of calcium carbonate

Kowalewski and Galeski\textsuperscript{109} studied the crystallization of polypropylene filled with calcium carbonate (chalk). They examined a large number of spherulite centers under transmission electron microscope and found that the primary nucleation ability of calcium carbonate depends on its crystal structure, surface topography and on its agglomeration. They found that single small calcite particles acted as single nucleation centers and that aragonite acted as nucleation centers only when it agglomerated. They also suggested that epitaxial crystallization planes are easily found in calcite and that without remarkable concentration of defects, calcite is not capable of spherulite nucleation.

Decreasing the specific surface area of calcium carbonate from 2.2 m\textsuperscript{2}/g to 16.5 m\textsuperscript{2}/g leads to the appearance of a second crystallization peak and a shift of the crystallization exotherm to higher temperatures showing a stronger nucleation effect as reported by Pukanszky\textsuperscript{69}.

2.3.1.2 Effect of surface treatment of calcium carbonate

There are not many studies of the effect of surface treatments of calcium carbonate on the nucleation effect on PP/CaCO\textsubscript{3} composites.

Rybnikar\textsuperscript{39} studied the effect of different surface treatments in the nucleation effect of polypropylene and polypropylene filled with calcium carbonate. Table 2.4 shows that the nucleation activity could be increased or reduced by surface modification. The addition of 0.5\% of stearic acid was shown to destroy or block heterogeneous nuclei
in polypropylene and reduce the nucleation effect of calcium carbonate in the PP/CaCO$_3$ composites.

Kowalewski and Galeski $^{109}$ used oligomer of ethylene oxide (OEO) as a liquid modifier for calcium carbonate and showed that it reduces nucleating ability and decreases the nuclei number with increasing crystallization temperature.

Mc Genity et. al.$^{110}$ also studied the influence of stearic acid on nucleation effect and crystallinity. The number of nucleating sites per surface area of filler decreased with stearic acid treatment. The % crystallinity for PP filled with 40% weight of calcium carbonate was not affected.

2.3.1.3 Effect of composition

Pukanszky et. al.$^{40}$ showed that the crystallization temperature increased slightly with higher amount of CaCO$_3$. The % crystallinity increased up to 0.1 volume fraction and remained the same or decreased at higher loadings of calcium carbonate.

Khare et. al.$^{111}$ found that higher concentration of CaCO$_3$ containing mainly aragonite increased spherulitic growth and reduced the size of the spherulites. They used wide angle X-ray to plot the crystallinity index versus the concentration of calcium carbonate. Figure 2.8 shows that the crystallinity index has a maximum at 10% CaCO$_3$ weight concentration. They compared compression molded samples prior and after melt crystallization.

High concentration of CaCO$_3$ did not restrict growth of spherulites as it would be expected. It was suggested that there are clusters of aragonite particles acting as nuclei that allow more space for spherulitic growth. This was previously observed by Kowalewski and Galeski$^{109}$. 

32
Table 2.4 Effect of various additives on the number of heterogeneous nuclei on the composite PP + 10% CaCO₃ (Reproduced with permission from F. Rybnikar, Journal of Applied Polymer Science, 42, 2727. Copyright 1991, John Wiley & Sons)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Additive, 0.5%</th>
<th>N × 10⁻⁷/cm²</th>
<th>Type of Action</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>O</td>
<td>1.38</td>
<td>Primary nucleation agent</td>
</tr>
<tr>
<td>PP</td>
<td>Phthalic acid</td>
<td>134</td>
<td>Secondary nucleation agent</td>
</tr>
<tr>
<td>PP</td>
<td>Benzoic acid</td>
<td>20.4</td>
<td>Secondary nucleation agent</td>
</tr>
<tr>
<td>PP</td>
<td>Slovason O</td>
<td>3.27</td>
<td>Inert</td>
</tr>
<tr>
<td>PP</td>
<td>Ca–stearate</td>
<td>1.37</td>
<td>Destroys or blocks heterogeneous nuclei in polymer</td>
</tr>
<tr>
<td>PP</td>
<td>Stearic acid</td>
<td>0.48</td>
<td>Destroys or blocks heterogeneous nuclei in polymer</td>
</tr>
<tr>
<td>PP</td>
<td>KOH</td>
<td>0.49</td>
<td>Destroys or blocks heterogeneous nuclei in polymer</td>
</tr>
<tr>
<td>PP</td>
<td>Mg–stearate</td>
<td>0.006</td>
<td>Destroys or blocks heterogeneous nuclei in polymer</td>
</tr>
<tr>
<td>PP</td>
<td>CaCO₃</td>
<td>11.95</td>
<td>Weak primary nucleation agent</td>
</tr>
<tr>
<td>PP + 10% CaCO₃</td>
<td>O</td>
<td>10.58</td>
<td>Weak primary nucleation agent</td>
</tr>
<tr>
<td>PP + 10% CaCO₃</td>
<td>Phthalic acid</td>
<td>707</td>
<td>Increases nucleation of CaCO₃</td>
</tr>
<tr>
<td>PP + 10% CaCO₃</td>
<td>Benzoic acid</td>
<td>67</td>
<td>Increases nucleation of CaCO₃</td>
</tr>
<tr>
<td>PP + 10% CaCO₃</td>
<td>Slovason O</td>
<td>2.15</td>
<td>Decreases nucleation of CaCO₃</td>
</tr>
<tr>
<td>PP + 10% CaCO₃</td>
<td>Ca–stearate</td>
<td>1.04</td>
<td>Decreases nucleation of CaCO₃</td>
</tr>
<tr>
<td>PP + 10% CaCO₃</td>
<td>Stearic acid</td>
<td>0.707</td>
<td>Decreases nucleation of CaCO₃</td>
</tr>
</tbody>
</table>

*C* Crystallization temperature 138°C.

Figure 2.8 Variations in the Ci of samples; (O) prior to melt crystallization and after melt crystallization at Tc values of (x) 110°C and (Δ) 115°C (Reproduced with permission from A. Khare, A. Mitra and S. Radhakrishnan, Journal of Materials Science, 31, 5691. Copyright 1996, Springer)
2.3.2 Effect of calcium carbonate on the tensile and impact properties of PP/CaCO$_3$ composites

Heterogeneous polymer systems, composed by a polymer matrix and fillers, show a distribution of stress around the filler particles under external load. This determines the micromechanical deformations and as a result, the macroscopic properties and performance of the material$^{113}$. Modulus is the most frequently measured and modeled property because it is determined at very low deformations and the analysis based on linear viscoelasticity. It can be used to develop the relationship of property and structure$^{69}$. The addition of rigid particle fillers like calcium carbonate increases the modulus of polypropylene when there is good adhesion or even with poor adhesion since thermal coefficients impose a squeezing force on the filler by the matrix preventing relative motion$^{112}$. Yield stress and tensile strength is reduced because calcium carbonate modifies the shape of the PP matrix and often induces yield points. Calcium carbonate reduces the effective cross section of the matrix and leads to increased internal stress facilitating failure at lower external load in comparison with unfilled PP$^{71}$. The drastic decrease in elongation at break of polypropylene filled with a rigid filler like calcium carbonate results from the fact that all the deformation comes from the polymer especially when adhesion is good. If there is poor adhesion, elongation to break could decrease more gradually$^{62}$. Voros and Pukanszky$^{113}$ revealed that the prevailing deformation mechanism of a polymer is determined by the properties of the polymer matrix and the local stress distribution. The magnitude and distribution of local stresses are determined by three
factors: stress concentration, thermal stresses and interaction of the components. The basic deformation mechanisms for unmodified polymers are shear yielding and crazing.

Pukansky$^{114}$ suggested that those basic deformation mechanisms can be replaced or accompanied by debonding in particulate filled composites. Debonding is especially important for PP because of its low polarity and surface free energy which makes interfacial adhesion with calcium carbonate weak. Although crazing has been detected, debonding proved to be the dominant process in particulate filled PP composites. The competitive character of the micromechanical deformation processes leads to large variations of properties with particle and matrix characteristics$^{69,115}$.

McGenity et. al.$^{116}$ studied samples of polypropylene filled with calcium carbonate and talc and their impact strength. They found that the main factors that contribute to impact properties are: (1) good filler dispersion, (2) the ability of the filler to pin or block cracks, (3) particle pull out or debonding which occurs when there is no strong filler-matrix bonding, and (4) low stress concentration in the vicinity of the filler particles which could produce weak point for initiation of cracks. Stress concentration is higher for high aspect ratio particles like talc.

In addition to those factors, formation of small quantities of $\beta$-PP can be promoted adding calcium carbonate. $\beta$ spherulites are a sheaf-like structure with branching and twisting of lamellae. This structure exhibits higher impact but lower yield and elastic modulus than those of $\alpha$-PP$^{24}$. Microfibrils and microcrazes are found extensively in $\beta$-PP which contributed to higher impact strength$^{117}$.
Figure 2.9\textsuperscript{117} and Figure 2.10\textsuperscript{117} show the tensile modulus and critical strain energy versus calcium carbonate content respectively. It is important to notice that without fillers, the impact properties of β-PP are extremely better than for α-PP.

Figure 2.9 Tensile modulus vs. calcium carbonate content (○)α-PP (●)β-PP (Reproduced with permission from S.C. Tjong, R. K. Y. Li and T. Cheung, Polymer Engineering and Science, 37, 1, 166. Copyright 1997, John Wiley & Sons)

Figure 2.10 Critical strain energy release rate vs. calcium carbonate content (○)α-PP (●)β-PP (Reproduced with permission from S.C. Tjong, R. K. Y. Li and T. Cheung, Polymer Engineering and Science, 37, 1, 166. Copyright 1997, John Wiley & Sons)

Ouederni and Phillips\textsuperscript{118} took other approach and suggested that the important factor of fracture mechanism is the increase in crystallization temperature by adding nucleating agents. The lamellar thickness increases with crystallization temperature and
lowers the tie molecule population. Tie molecules represent a mechanical continuity from one crystal to the other. With higher tie molecule population, the amorphous phase would be less susceptible to crack propagation and originated cracks would grow slower.

2.3.2.1 Effect of particle size, size distribution and crystal shape of calcium carbonate

The large particle size of fillers influences the abrasion and appearance of products and have an adverse effect on deformation and failure characteristics of composites\textsuperscript{69}. It is well known that reducing the particle size of fillers in PP increases the tensile strength and modulus, but reduces deformability and impact strength\textsuperscript{119,69}. The main concern is that small particles also facilitate agglomeration of fillers. Extensive agglomeration leads to insufficient homogeneity and lower impact strength. Aggregates act as crack initiation sites in impact\textsuperscript{120,71}.

Experiments conducted by Kawasaki et. al.\textsuperscript{121} showed an increase of modulus with decreasing particle size. Nielsen\textsuperscript{62} suggested the following phenomena with reduction of particle size: (1) the surface area of particles increases and (2) the surface energy increases causing increased particle-particle interaction and agglomeration. The resultant agglomerates may be strong enough to increase the modulus.

Mitsuishi et. al.\textsuperscript{121} found that particle size has little effect on the modulus if there is no agglomeration of filler particles. He also found that increasing the particle size of the filler strongly decreases the tensile strength. The latter can be explained because increasing particle size increases the volume in which the stress concentration is effective. With more volume there is a bigger chance of finding a flaw. Also, if debonding occurs, a larger filler particle creates a larger void becoming more detrimental for the tensile strength\textsuperscript{62}. 
As mentioned before, reinforcement effect of fillers is better with higher aspect ratio (anisotropy). Plate fillers like talc\textsuperscript{74,75} or mica reinforce PP better than aragonite or calcite and even better reinforcement are obtained with glass fibers because of the high aspect ratio of glass fibers\textsuperscript{102,103}.

The particle size distribution is very important to characterize fillers and it is usually determined by sedimentation techniques\textsuperscript{65}. The results obtained from this method compared with microscopy techniques can differ significantly as shown in Figure 2.11.

Milewski\textsuperscript{122} showed that mixtures of different particle sizes can pack more densely because small particles can find passages between large particles resulting in a very efficient packing. Bimodal mixtures have been used in order to reduce the melt viscosity of highly filled polypropylene composites. Zhang et. al.\textsuperscript{123} showed that melt viscosity decreased when polypropylene was mixed with two types of calcium carbonate of 12 µm and 2.8 µm. Both fillers were blended and added to the polypropylene matrix at 30% weight.

![Figure 2.11 Particle size distributions of two types of calcium carbonate (Reproduced with permission from B. Pukanszky, Particulate filled polypropylene: structure and properties, In: J. Karger-Kocsis editor, Polypropylene Structure, blends and composites, Vol. 3, Copyright 1995, Taylor & Francis)]
2.3.2.2 Effect of surface treatment of calcium carbonate

Surface treatment has a pronounced effect on the matrix-filler and particle-particle interactions. As we mentioned before, the most common non reactive treatment surface for calcium carbonate due to low cost is stearic acid. Silane coupling agents are also used as well as compatibilizers like PP modified with maleic anhydride or acrylic acid.

The non reactive type of chemical treatment generally improves dispersion but decreases matrix-polymer interaction\textsuperscript{69}. Pegoraro et.al.\textsuperscript{124} suggested that surface treatment reduces the work of adhesion. Lower work of adhesion results in reduced debonding stress and the composite endures lower external load. The consequences are decreased yield stress and strength and improved deformability\textsuperscript{71}.

Demjem and Pukanszky\textsuperscript{75} studied the influence of calcium carbonate treated with commercial coupling agents on the mechanical properties of PP/CaCO\textsubscript{3} composites. The yield stress, modulus and tensile strength increased with increasing amounts of coupling agent and reached a maximum at around 1.0 % weight concentration. They suggested that adhesion between the filler and the polymer can be so strong that debonding does not take place and brittle failure occurs. Figure 2.12 shows the effect of coupling agents on tensile strength in comparison with stearic acid.

Tucker et. al.\textsuperscript{78} showed that composites treated with compatibilizers increase their tensile strength by 33% with 10% PP-g-MA (maleic anhydride) and 16% with 10% PP-g-AA (acrylic acid). Higher effect of compatibilizing is obtained with maleic anhydride. A PP-g-MA compatibilized composite also shows increases of 20% in flexural modulus and 30% in elongation at break due to improved adhesion.
Figure 2.12 Effect of silane treatment on the tensile strength of PP/CaCO$_3$ composites (○) Stearic acid (△) Silane treatment (Reproduced with permission from Z. Demjen and B. Pukanszky, Polymer Composites, 18, 741. Copyright 1997, John Wiley & Sons)

Table 2.5 Mechanical properties of composites with PP-g-MA and PP-g-AA (Reproduced with permission from J. D. Tucker, P. L. Lear, G. S. Atkinson, S. Lee and S. J. Lee, Korean Journal of Chemical Engineering, 17, 506. Copyright 2000, Springer)

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa)</th>
<th>Bending modulus (Gpa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncompatibilized</td>
<td>12.28</td>
<td>6.20</td>
<td>6.70</td>
</tr>
<tr>
<td>10% PP-g-MA</td>
<td>16.33</td>
<td>7.46</td>
<td>8.69</td>
</tr>
<tr>
<td>10% PP-g-AA</td>
<td>14.26</td>
<td>7.67</td>
<td>6.64</td>
</tr>
</tbody>
</table>

Table 2.6 Optimum amount of PP-g-MA for tensile strength of composites  (Reproduced with permission from J. D. Tucker, P. L. Lear, G. S. Atkinson, S. Lee and S. J. Lee, Korean Journal of Chemical Engineering, 17, 506. Copyright 2000, Springer)

<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5% PP-g-MA</td>
<td>14.17</td>
</tr>
<tr>
<td>5% PP-g-MA</td>
<td>14.91</td>
</tr>
<tr>
<td>7.5% PP-g-MA</td>
<td>15.01</td>
</tr>
<tr>
<td>10% PP-g-MA</td>
<td>14.88</td>
</tr>
</tbody>
</table>
Table 2.5 shows the mechanical properties of the composites with and without coupling agents. A value of around 5% in the addition of PP-g-MA was found beyond which a further increase in the tensile strength is not obtained as shown in Table 2.6.

Ansari and Price\textsuperscript{125} prepared PP/CaCO\textsubscript{3} composites with 40% weight content of 1µm CaCO\textsubscript{3} modified with stearic acid or a compound of stearic acid and sodium polyacrylate. Using inverse gas chromatography for characterizing the compatibility of polymer–filler combinations, they found that optimum impact properties were obtained when the filler was completely coated and when the surface free energy of the filler was slightly lower than that of the polymer matrix as shown in Table 2.7.

\textbf{Table 2.7 Summary of Physical Testing Results of PP Moldings with 40 wt % CaCO\textsubscript{3} (Reproduced with permission from D. M. Ansari and G. J. Price, Journal of Applied Polymer Science, 88, 1951. Copyright 2003, John Wiley & Sons)}

<table>
<thead>
<tr>
<th>System</th>
<th>Relative properties of moldings (PP = 1)</th>
<th>Surface free energy (mJ m\textsuperscript{-2})\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>Notched Izod strength</td>
<td>Impact strength (fail energy)</td>
</tr>
<tr>
<td>PP + PCC-SA</td>
<td>2.4</td>
<td>3.5</td>
</tr>
<tr>
<td>PP + PCC-SA</td>
<td>3.3</td>
<td>7.0</td>
</tr>
<tr>
<td>PP + PCC-SA</td>
<td>1.9</td>
<td>2.8</td>
</tr>
<tr>
<td>PP</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Values measured at 80–110°C.  
\textsuperscript{b} Surface energy of PP homopolymer.

2.3.2.3 Effect of composition

The properties of polypropylene filled with particulates depend strongly on the compositions. The desired properties can be achieved with a particular filler content. They are also accompanied with deterioration of other properties such as elongation to break.

Often linear dependence of modulus of composition is observed although models predict non linear dependence\textsuperscript{121}. The Mooney equation which characterizes the dependence of relative viscosity on volume fraction for a suspension of dispersed spheres
is not appropriate when the matrix is a rigid material. For rigid matrices, the Kerner equation was used as the best approximation to the experimental values.

$$\frac{G_c}{G_1'} = \frac{1 + AB\phi_2}{1 - B\phi_2} \quad \text{Equation 2.1}$$

Where \( A = \frac{7 - 5\nu_1}{8 - 10\nu_1} \) and \( B = \frac{(G_2'/G_1') - 1}{(G_2'/G_1') + A} \)

\( \frac{G_c'}{G_1'} \) is the relative shear modulus between matrix and filler, \( \nu_1 \) is Poisson constant of the matrix and \( \phi_2 \) is the volume fraction of the filler.

Nielsen and Lewis \(^{126}\) modified the Kerner equation using the maximum packing fraction \( \phi_m \) by introducing the function \( \psi \)

$$\frac{G_c'}{G_1'} = \frac{1 + AB\phi_2}{1 - B\psi\phi_2}$$

which is solved to give \( \psi\phi_2 = 1 - \exp\left(\frac{-\phi_2}{1 - (\phi_2 / \phi_m)}\right) \)

Figure 2.13 compares the experimental data on the epoxy resin filled with glass beads with the original Kerner equation, the generalized Kerner equation using \( \phi_m = 0.64 \) and the Mooney equation. The introduction \( \phi_m \) brings the predicted values much closer to the experimental values.

Previous studies found that with increasing filler volume fraction up to 40%, the young modulus increases, yield stress and strength decrease and elongation to break decreases drastically. There are not many studies with higher volume fraction of calcium carbonate than 40% \(^{127,121,40}\).
Figure 2.13 Dependence of relative modulus on filler concentration: (A) the original Kerner, (B) the modified Kerner equation; (C) the Mooney equation. Circles correspond to experimental results (Reproduced with permission from T. B. Lewis and L. E. Nielsen, Journal of Applied Polymer Science, 14, 1449. Copyright 1970, John Wiley & Sons)

The young modulus for CaCO$_3$ increases according to the theoretical prediction of the modified Kerner equation. The reduction of yield stress and tensile strength is due to the increase of local microdeformation around the particles$^{127}$. Drastic decrease in elongation at break and increase of brittleness result from the increased deformation of the polypropylene matrix with filler content$^{62}$.

Impact properties normally show a maximum as a function of composition. Interfacial adhesion of calcium carbonate to the matrix is crucial. Poor adhesion results in particle debonding and produces extensive crazing, especially at low concentrations and small particle size of the fillers$^{127}$. Figure 2.14 shows the notched impact strength as a function of concentration, particle size and filler-matrix adhesion.
Figure 2.14 The notched Izod impact strength of PP filled with (left) excellently and (right) poorly adhering chalk particles as a function of the volume (●) 3.5µm (○) 130µm (Reproduced with permission from P. H. TH. Vollenberg and D. Heikens, Journal of Materials Science, 25, 3089. Copyright 1990, Springer)

2.4 Nanocomposites

The first studies of nanocomposite materials were dated back to 1963. Union Oil company filed a patent describing nanocomposites of organoclay and polyolefins\textsuperscript{128}. Two decades later, in 1985 nanocomposites (PCN) of nylon with nanoclay were invented at Toyota Central R&D Lab\textsuperscript{129}.

Takayanagi first proposed the concept of a molecular composite with a filler of molecular size. Akada and Usuki thought about platelets to increase the contact surface and montmorillonite appeared as the potential candidate since it is composed of several layers of silicates and it is a really common clay mineral. If the silicates were dispersed randomly and homogeneously, the interface area would be increased greatly and a large interaction would be achieved. It was then demonstrated that the molecular level of composites was possible with a low concentration of clay\textsuperscript{133}.
Depending on the nature of the components used and the method of preparation, three main types of composites may be obtained when a layered clay is associated with a polymer. (1) Microcomposite, when several platelets are stacked together and surrounded by the matrix. (2) Intercalated, occurs when the gallery spacing is expanded but does not eliminate the initial layered structure. (3) Exfoliated, occurs when individual clay platelets with high aspect ratios are created. Figure 2.15 shows the different types of nanofiller dispersion.

In practice, however, the above classification for intercalation and exfoliation seems too simplified. Vaia expanded this classification scheme and both intercalated and exfoliated structures were further divided into ordered and disordered, depending on the change in layer spacing and orientation.

![Diagram of polymer/layer structures](image)

**Figure 2.15** Types of polymer/layer structures: (a) Microcomposites (b) Intercalated nanocomposites (c) Exfoliated nanocomposites (Reproduced with permission from M. Alexandre and P. Dubois, Materials Science and Engineering, 28, 1. Copyright 2000, Elsevier)
Several strategies have been considered to prepare polymer-layered silicate nanocomposites. They include four main processes: (1) exfoliation-adsorption, (2) in situ intercalative polymerization, (3) melt intercalation, and (4) template synthesis\textsuperscript{132}.

Nowadays besides nylon-clay nanocomposites, many others clay based nanocomposites have been developed including polyimides, polyolefins, rubber and thermosetting resins, hydrogels and liquid crystals\textsuperscript{133}.

2.5 PP/CaCO\textsubscript{3} Nanocomposites

After nylon nanocomposites were successfully developed, many efforts were made worldwide to reinforce polypropylene using clay with little successful results at the beginning. Okada and Usuki revealed that there was enormous difficulty to prepare PP-Clay nanocomposites because polypropylene is hydrophobic and clay is hydrophilic. Later, a compatibilizer was used and the preparation of exfoliated samples was achieved but the properties were not as good as expected\textsuperscript{133}.

Addition of nanofillers to PP is expected to increase stiffness and enhance dimensional stability, impact strength and barrier properties at low loading levels. The low concentration of nanofillers could be a cost effective alternative solution to engineering thermoplastics as long as good dispersion, exfoliation or intercalation is achieved. In addition, because of their nano-size dimensions, nanoparticles do not change the optical properties and appearance of polypropylene\textsuperscript{80}.

2.5.1 Effect on nano calcium carbonate on the structural development of PP/CaCO\textsubscript{3} nanocomposites

Chang et. al.\textsuperscript{134} revealed that the addition of nano calcium carbonate particles does not affect crystallinity in polypropylene but demonstrated a very effective nucleation
effect as seen by the reduction of spherulite size. This did not happen with micro particles of CaCO$_3$.

Yang et. al.$^{135}$ studied samples prepared through injection molding and found that, with introduction of 30% weight of 0.07 µm calcium carbonate nanoparticles, the spherulitic structure of pure polypropylene could not be formed. They suggested that the large number of nuclei centers produced by nano CaCO$_3$ cause crystalline defects and distort the shape of the spherulites.

Wan et. al.$^{139}$ studied the morphology of PP/CaCO$_3$ nanocomposites using DSC and observed the presence of two melting peaks which evidenced that nano calcium carbonate induces the formation of the β form of PP crystallization. The β phase was also found by Chan et. al.$^{134}$ and Weon et. al.$^{136}$.

2.5.1.1 Effect of particle size, size distribution and crystal shape of calcium carbonate

The tendency for the agglomeration is more pronounced with decreasing particle diameter$^{137}$. However, if good dispersion is achieved, the number of nano-particles for the same content of calcium carbonate is very large in comparison with micro-particles. If only part of them become nucleating sites, the number of spherulites will increase dramatically and the size of the spherulites will reduce significantly$^{134}$.

Avella et. al.$^{140}$ studied the role of nanoparticle shape (elongated and spherical) on crystallization of iPP using calorimetry and optical analysis. They found a very weak influence of particle shape on the nucleation effect of nano calcium carbonate. The particle shape effect was overwhelmed by the effect of the surface treatment on crystallization.
2.5.1.2 Effect of surface treatment of calcium carbonate

There are not many papers that focus on the nucleating effect of the surface treatment of calcium carbonate nanoparticles in PP. The main purpose of surface treatment in calcium carbonate nanoparticles is to improve its dispersion and adhesion to the polymer matrix. Nanoparticles were coated previously with different substances like stearic acid, PP modified with maleic anhydride (PPMA) and acrylic acid (PPAA), and fatty acids.

Lin et. al.\textsuperscript{138} studied the effect of stearic acid, PP grafted with acrylic acid (PPAA) and acrylic acid (AA) in PP/NanoCaCO\textsubscript{3} composites. They found that at low loadings, nano calcium carbonate did not act as a nucleating agent because of the presence of stearic acid. They also found that the addition of low content of acrylic acid weakened the heterogeneous nucleation effect of nano CaCO\textsubscript{3} and that excessive acrylic acid reacted with nano-CaCO\textsubscript{3} and improved heterogeneous nucleation.

Wan et. al.\textsuperscript{139} used an aluminum coupling agent and an aluminum coupling agent/stearic acid (AC/SA) compound as surface treatments. These surface treatments facilitated the nucleation process. Polarized optical microscopy showed that spherulites become smaller and distorted with addition of nanoparticles. AC/SC treatment showed more nucleation sites due to enhanced dispersion.

Avella et. al.\textsuperscript{140} used maleated polypropylene (PPMA) and fatty acid as surface treatments. They showed that the coating agent influences the nucleating ability of calcium carbonate but has limited influence on crystal growth rate. PPMA favors crystallization whereas fatty acids delay the crystallization rate. PPMA bonds onto
CaCO₃ and facilitates crystal growth. Fatty acids complicate or inactivate the role of calcium carbonate nanoparticles as substrates for heterogeneous nucleation.

2.5.1.3 Effect of composition

It was reported that nanoparticles may act as effective nucleating agents. Usually only small quantities of nanoparticles are added to the polymer matrix. Avella et. al. added 1% and 3% weight of nano calcium carbonate to polypropylene and showed that nanoparticles induced higher crystallization temperatures when at least 3% weight was added. This indicates that there is a minimum amount of nanosized CaCO₃ to effectively nucleate iPP.

Lin et. al. also studied the effect of composition for nano calcium carbonate treated with stearic acid and found a higher crystallization temperature and an increased heterogeneous nucleation effect only when the nano CaCO₃ content is higher than 10% weight. The nucleating effect becomes more significant with increasing nano CaCO₃ content up to 40% weight. They suggested that high nano CaCO₃ contents can increase the melt viscosity and friction can remove the stearic acid treatment from the particles increasing the interfacial interaction between nano CaCO₃ and PP.

2.5.2 Effect of nano calcium carbonate on the tensile and impact properties of PP/CaCO₃ nanocomposites

Sumita et. al. showed that the yield stress and modulus of composites with micron size particles are inferior to those with nanoparticles for the same filler. The use of nano CaCO₃ can bring new insights in the study of polymer filler interaction because of the dramatic increase in the interfacial area between the polymer and filler.
Toughening of the polymers with inorganic fillers has been explained to work because the rigid particles resist the propagation of cracks\textsuperscript{62}. However, a particle size of 50nm or less may not be able to resist propagation of cracks and a new mechanism of toughness may be needed to explain the toughening effect of nanoparticles.

Chang et. al.\textsuperscript{134} used Izod and J-Integral tests and showed a dramatic increase of fracture toughness and modulus. They suggested that the nanoparticles act as stress concentration sites and promote debonding at the polymer-filler boundary. Debonding triggers plastic deformation of the matrix and consumes tremendous fracture energy.

Weon et. al.\textsuperscript{136} also studied the fracture mechanism of PP with 9.2% volume of 40nm calcium carbonate particles treated with stearic acid and suggested that debonding and massive crazing followed by shear banding of the matrix are responsible for the impressive improvements on impact strength and modulus. They also consider possible to increase modulus, even with no adhesion to PP matrix, because thermally induced contraction produces strong interfacial adhesion to prevent premature debonding.

All advantages offered by the use of nanofillers can be exploited only if the particles are distributed homogeneously in the polymer matrix. Small particles with high surface energy have a strong tendency to aggregate. Aggregation and agglomeration create weak points and result in poor mechanical properties. The extent of aggregation is determined by the relative magnitude of adhesive and shear forces during compounding and it can be hindered with surface treatment of the particles\textsuperscript{144}.

2.5.2.1 Effect of particle size, size distribution and crystal shape of calcium carbonate

Thio et. al.\textsuperscript{145} studied the toughening effect of nano and micro calcium carbonate 70nm, 0.7μm, 3.5μm at a filler volume fraction of 0.05 and 0.30. In slow tension,
modulus increased and yield stress decreased for all particles. Strain at break increased with initial incorporation of fillers but decreased at higher loading. 0.7\(\mu\)m particles were the only that increased impact strength. Failure of the 70nm particles was attributed to agglomeration. On the other hand, the presence of individual particles larger than critical flaw size for composites with 3.5\(\mu\)m particles initiated brittle behavior.

Zuiderduin et. al.\(^{146}\) compared 70nm and 0.7\(\mu\)m calcium carbonate particles at 30% weight and found that 0.7\(\mu\)m gave the best combination of properties. They showed aggregates of 70nm particles using SEM images and proved that dispersion of non treated particles is very difficult and has a detrimental effect on impact properties. Yield stress and modulus were not affected by the particle size.

Particle distribution has not been studied in depth for polypropylene/calcium carbonate nanocomposites. Thio et. al.\(^{145}\) used SEM at lower magnifications to

![Histograms of size distribution of the three different types of particles. Fraction of agglomerates are amplified by a factor given in each chart (Reproduced with permission from Y. S. Thio, A. S. Argon, R. E. Cohen and M. Weinberg, Polymer, 43, 3661. Copyright 2002, Elsevier)](image)
characterize agglomerate size distribution and higher magnifications to obtain individual particle distribution. Figure 2.16 shows the histograms for the three different particles used. Dispersion was good below 20% volume fraction after which agglomerates are observed. All the histograms presented show bimodal distribution size except for 3.5µm at low loading. A large number of agglomerates were observed for 70nm particles even at low loadings. The average agglomerate size also increased with increasing volume fraction.

2.5.2.2 Effect of surface treatment of calcium carbonate

Coating of CaCO₃ can change the behavior of the filler particles and form looser aggregates. However, it does not eliminate aggregation completely. Zuiderduin et. al. found that surface treatment has little effect for modulus and yield stress. Furthermore, surface treatment does not seem crucial for debonding of particles to occur in the matrix.

Levita et. al. studied the strength and fracture properties of polypropylene filled with nano calcium carbonate (0.07µm) from of 0 to 40% volume. Untreated and surface treated particles with stearic acid and a titanate coupling agent were used. The untreated filler caused a decrease of toughness whereas a maximum around 10 % volume was observed for the treated filler as shown in Figure 2.17.

Zhang et. al. prepared PP/CaCO₃ (85/15) nanocomposites by melt compounding in a twin screw extruder. The dispersion quality of CaCO₃ particles in PP was greatly improved by the addition of 1.5% weight of the nonionic modifier polyoxyethylene nonyphenol (PN). The nanocomposites did not change the strength and modulus very much but increased the impact strength significantly.
Wang et al.\textsuperscript{150} showed that nano CaCO\textsubscript{3} could be uniformly modified with stearic acid in an ultra high speed mixer (6000 rpm) in comparison with the common high speed mixer (2000 rpm). As a result, improved dispersion of nanoparticles was achieved and yield strength, modulus and impact strength of the PP/CaCO\textsubscript{3} composites improved.

2.5.2.3 Effect of composition

Dispersion of nanoparticles and particle-matrix bonding are the key for improved properties. As the concentration of CaCO\textsubscript{3} increases, agglomerates and debonding or breaking of aggregates becomes more evident\textsuperscript{62}.

Chang et al.\textsuperscript{134} found that dispersion of nano calcium carbonate (44nm) was good below 9.2% volume content. The composites showed increased modulus by 85% and unaffected yield stress and strain. The Izod impact test revealed that impact strength significantly increased by 300%.
Thio et. al.\textsuperscript{145} studied the effect 70nm calcium carbonate up to 30\% volume fraction in polypropylene. They found that modulus increased and yield stress decreased with increasing particle volume fraction.

Yang et. al.\textsuperscript{135} studied the effect of calcium carbonate nanoparticles (70nm) up to 40\% weight loading in PP homopolymer, PP copolymer and a blend of those two. The CaCO\textsubscript{3} nanoparticles were treated with a liquid silane coupling agent. The results for PP homopolymer are shown in Table 2.8. Flexural modulus and impact strength increased with increasing filler content. Yield strength increased with low contents (2\%-10\%) but decreased at higher content. Yang explained that at the highest loads, CaCO\textsubscript{3} nanoparticles agglomerate, debond easily from the matrix and do not bear any fraction of the external load.

Table 2.8 Mechanical properties of PP nanocomposites (Reproduced with permission from K. Yang, Q. Yang, G. Li, Y. Sun and D. Feng, Material Letters, 60, 805. Copyright 2006, Elsevier)
2.5.3 Effect of nano calcium carbonate on the dynamic rheological behavior of PP/CaCO\textsubscript{3} nanocomposites

Dynamic rheology testing is an effective method to characterize the structure of multicomponent polymer systems because the structure formed is not destroyed at small strain amplitudes\textsuperscript{151}. The storage modulus G’ and the loss modulus G” show important information concerning the viscoelastic behavior of materials especially at very low frequencies (terminal region)\textsuperscript{152}.

The rheological property changes induced by the incorporation of fillers in a polymer matrix are thought to be caused by two factors: the mechanical coupling between filler and polymer matrix and the interface morphological structure due to interfacial adhesion or adsorption between the phases\textsuperscript{151}.

According to the linear viscoelasticity theory G’ and G” for homogeneous polymer systems are proportional to $\omega^2$ and $\omega$ at low frequencies respectively. These relationships are not maintained in heterogeneous polymer systems. The deviation from linear viscoelasticity is significant especially in particulate-filled polymer systems\textsuperscript{153}.

2.5.3.1 Effect of particle size of calcium carbonate and composition

Le Meins et. al.\textsuperscript{154} studied the effect of particle size and composition on the flow behavior of particle-filled polymer melts. They found that there is a critical particle volume fraction below which hydrodynamic effects dominate the rheology of the melt. The critical volume fraction decreases with particle size. With increasing volume fraction of filler, a progressive increase of the moduli G” and G’ is observed as shown in Figure 2.18.
Above the critical volume concentration, $G'$ and $G''$ become almost frequency independent in the low frequency region. Appearance of a plateau in the terminal region is typical of the solid-like behavior and indicates that relaxation is quite slow and the molecular chain motion is strongly restrained\textsuperscript{155}. The plateau is considered to be induced by the formation of a higher order structure of particles: agglomerated structure, skeleton or network structure\textsuperscript{151}.

Osman et. al.\textsuperscript{155} showed that using polyethylene with melt flow index of 0.5 (2.16 kg at 190 °C) filled with calcium carbonate, the terminal plateau was observed at 30% volume fraction for micro-composites and 10% for nanocomposites.

Figure 2.18 Linear moduli of suspensions containing various volume fractions of 1.4µm particles: (a) loss modulus (b) storage modulus (Reproduced with permission from J. F. Le Meins, P. Moldenaers and J. Mewis, Industrial and Engineering Chemistry Research, 41, 6297. Copyright 2002, ACS Publications)
The fact that G' curves reach a plateau at low frequency regions for high volume fraction compounds can be considered as the evidence of yield behavior as mentioned by Wang et. al. They found that the rheological properties and hence the yield behavior of polymer melts containing 25-30wt% of 0.8μm CaCO₃ is dominated by the formation of a network structure as a result of particle-particle interaction and the large surface area of small particles. Another evidence of yield behavior is suggested to be the unbound intrinsic viscosity at low frequencies. Figure 2.19 shows the terminal plateau and the unbound complex viscosity (45° slope) as evidence for the yield behavior.

Figure 2.19 Storage modulus and complex viscosity as a function of the angular frequency at small strain amplitude γ₀ = 6% for treated CaCO₃-filled PP melts at 200°C (Reproduced with permission from Y. Wang and J. J. Wang, Polymer Engineering and Science, 39, 190. Copyright 1999, John Wiley & Sons)

Wang and Yu studied polypropylene filled with calcium carbonate and also suggested that the yield regime occurs above a critical filler loading of approximately 25vol%. The increasing presence of aggregates leads to the appearance of thixotropy.
Thixotropic structures are difficult to process because they break down in shearing and slowly rebuild at rest. The material response of thixotropic materials depends on the duration of shear as well as the rate of shear.

2.5.3.2 Effect of surface treatment of calcium carbonate

The filler volume fraction for which the composites show the terminal plateau at low frequencies increases with filler surface treatment. Osman et. al.\textsuperscript{155} found that stearic acid treatment of nanoparticles increased the critical volume fraction from 10\% to 20\%.

Wang et. al.\textsuperscript{157} found that previous treatment of calcium carbonate with a titanium coupling agent substantially reduced the filler-filler interaction and decreased the dynamic properties of the PP/CaCO\textsubscript{3} composites due to improved dispersion.

Gong et. al.\textsuperscript{158} studied the dynamic behavior of PP filled with nano CaCO\textsubscript{3} treated with 2\% and 6\% of stearic acid. They found that the critical volume fraction characteristic of solid-like behavior was lower for 6\% surface treatment. Also, at the same filler content, 6\% surface treatment showed higher moduli and complex viscosity at low frequencies. They suggested that properly coated and well dispersed nanoparticles have a more significant effect on restricting the macromolecular chain motion than the largely observed aggregates due to insufficient surface treatment. Figure 2.20 compares the dynamic storage modulus for 2\% and 6\% surface treatments. The terminal G’ plateau became prominent at 25wt\% for 6\% surface treatment and for 30wt\% for 2\% surface treatment.
Figure 2.20 Comparison of storage modulus for pure PP, NC1-25 (2% surface treatment-25 wt% particles), NC1-30 (2% surface treatment-30 wt% particles), and NC2-25 (6% surface treatment-25 wt% particles) at 200°C (Reproduced with permission from G. Gong, J. Wu, Y. Lin, C. Chan and M. Yang, Journal of Macromolecular Science, Part B: Physics, 48, 329. Copyright 2009, Taylor & Francis)
CHAPTER III

MATERIALS AND EXPERIMENTAL PROCEDURE

3.1 Materials

The materials used in this study were polypropylene, Sunoco D080T, and six calcium carbonates types: Hubercarb G3, G3T, Q1, Q1T and Specialty Minerals Super-Pflex, Multifex-MM and Ultra-Pflex.

The polypropylene used was produced by Sunoco Corporation. It is a high melt flow polypropylene homopolymer resin provided in pellet form. The typical properties of the resin provided by the manufacturer are listed in Table 3.1^159.

The six types of calcium carbonate and their characteristics are listed in Table 3.2^160. For these experiments, the 3.2µm and 1.1µm were considered as microparticles and the 0.07µm as nanoparticles.

It can be observed that there are two production processes of calcium carbonate: ground and precipitated and two deposit types: marble and limestone. The main difference between ground and precipitated calcium carbonate is the particle size distribution curve. Precipitated calcium carbonate has a narrower particle size distribution as it can be seen in Figure 3.1. The aspect ratios of these six particles are close to unity and their specific gravity values are between 2.6 and 2.72.

Table 3.3 shows the percentage of stearic acid surface treatment for Ultra-Pflex, Super-Pflex, Q1T and G3T calcium carbonates.
Table 3.1 Properties of polypropylene resin Sunoco D080T (Sunoco Chemicals datasheet)

<table>
<thead>
<tr>
<th>Property</th>
<th>Units</th>
<th>Typical value</th>
<th>Test Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Melt Flow rate (230 °C/2.16kg)</td>
<td>g/10 min</td>
<td>8</td>
<td>ASTM D1238</td>
</tr>
<tr>
<td>Tensile Strength at Yield (2 in/min, 50 mm/min)</td>
<td>MPa</td>
<td>37</td>
<td>ASTM D638</td>
</tr>
<tr>
<td>Elongation at yield (2 in/min, 50 mm/min)</td>
<td>%</td>
<td>9</td>
<td>ASTM D638</td>
</tr>
<tr>
<td>Flexural Modulus (0.05 in/min, 1.3 mm/min, 1% secant)</td>
<td>MPa</td>
<td>1586</td>
<td>ASTM D790A</td>
</tr>
<tr>
<td>Notched Izod Impact Strength at 23 °C</td>
<td>J/m</td>
<td>32</td>
<td>ASTM D256A</td>
</tr>
<tr>
<td>Rockwell Hardness</td>
<td>R</td>
<td>106</td>
<td>ASTM D785</td>
</tr>
</tbody>
</table>

Table 3.2 Calcium carbonate characteristics

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Product name</th>
<th>Median particle size</th>
<th>Surface treatment</th>
<th>Crystal habit</th>
<th>Particle shape</th>
<th>Deposit type</th>
<th>Production Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Huber</td>
<td>G3</td>
<td>3.2 µm</td>
<td>None</td>
<td>Calcite</td>
<td>Rhombic</td>
<td>Marble</td>
<td>Ground</td>
</tr>
<tr>
<td>Huber</td>
<td>G3T</td>
<td>3.2 µm</td>
<td>Stearic acid</td>
<td>Calcite</td>
<td>Rhombic</td>
<td>Marble</td>
<td>Ground</td>
</tr>
<tr>
<td>Huber</td>
<td>Q1</td>
<td>1.1 µm</td>
<td>None</td>
<td>Calcite</td>
<td>Rhombic</td>
<td>Limestone</td>
<td>Ground</td>
</tr>
<tr>
<td>Huber</td>
<td>Q1T</td>
<td>1.1 µm</td>
<td>Stearic acid</td>
<td>Calcite</td>
<td>Rhombic</td>
<td>Limestone</td>
<td>Ground</td>
</tr>
<tr>
<td>Specialty Minerals</td>
<td>Super-Pflex</td>
<td>0.7 µm</td>
<td>Stearic acid</td>
<td>Calcite</td>
<td>Rhombic</td>
<td>Limestone</td>
<td>Precipitated</td>
</tr>
<tr>
<td>Specialty Minerals</td>
<td>Multifex-MM</td>
<td>0.07 µm</td>
<td>None</td>
<td>Calcite</td>
<td>Rhombic</td>
<td>Limestone</td>
<td>Precipitated</td>
</tr>
<tr>
<td>Specialty Minerals</td>
<td>Ultra-pflex</td>
<td>0.07 µm</td>
<td>Stearic acid</td>
<td>Calcite</td>
<td>Rhombic</td>
<td>Limestone</td>
<td>Precipitated</td>
</tr>
</tbody>
</table>
Table 3.3 Percentage of surface treatment

<table>
<thead>
<tr>
<th>Surface treatment</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultra-Pflex</td>
<td>2%</td>
</tr>
<tr>
<td>Super-Pflex</td>
<td>2%</td>
</tr>
<tr>
<td>Q1T, Q3T</td>
<td>2%</td>
</tr>
<tr>
<td>G3T</td>
<td>1%</td>
</tr>
</tbody>
</table>

PCC vs. GCC

<table>
<thead>
<tr>
<th>PCC</th>
<th>GCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>![PCC]</td>
<td>![GCC]</td>
</tr>
</tbody>
</table>

Figure 3.1 Precipitated calcium carbonate (PCC) vs. Ground calcium carbonate (GCC) (Specialty Minerals)

3.2 Experimental procedures

The experimental procedures, including the preparation of the samples and the characterization of the composites, are explained in this section.

3.2.1 Sample preparation

The preparation of the samples for the different PP/CaCO₃ composites included several steps including mixing, compression molding, grinding and injection molding.
3.2.1.1 Mixing

Compounding was done in a Brabender internal mixer with cam type rotors while monitoring the torque and temperature curves. The best mixing conditions for neat PP based on the dynamic viscosity (as explained in section 4.1) were found at 180°C, 60 RPM and a mixing time of 7 minutes (2 minutes for loading, 5 minutes for mixing).

Once the appropriate mixing conditions were found, the calcium carbonate was added to the polypropylene at 2%, 5%, 10% and 20% weight percentages. At first, it was intended to increase the calcium carbonate load further but beyond 20wt% the brabender started to have difficulties to melt the polypropylene properly and mix it with the calcium carbonate. Both rotors were surrounded by polypropylene but the separation between rotors avoided the contact between the material of each rotor and there was no mixing happening.

The mixing procedure consisted in first adding the polypropylene, wait for 1.5 minutes for the polypropylene to melt and finally add the calcium carbonate, the two steps took around two minutes, leaving the next five minutes for mixing.

3.2.1.2 Compression molding

The Wabash compression molding machine was used. After the mixing was finished, the chunk of soft material was taken and put between the two metal plates at room temperature. The compression molding machine compressed it up to 4000 psi.

The reason behind this procedure was the need to have a flat surface that could be cut easily with scissors in order to obtain samples for the SEM and X ray experiments. Another reason was that it was better to load the grinder with small pieces than with a big chunk of material which could damage the grinder.
3.2.1.3 Grinding

A WEIMA Grinder (Weima America Inc.) was used to grind the material into particles of the right size in order to feed the mini injection molder. There were not any parameters to control during grinding, except for the screen type which determined the final particle size obtained.

The procedure consisted in starting the machine, loading our sample and wait for a few minutes. After that, the material was recovered and the grinder was cleaned thoroughly before using it to grind the next sample.

3.2.1.4 Injection molding

After grinding the material, the DSM Injection Moulding Machine Research B. V. was used to mold samples for the mechanical and rheological testing. The air pressure was set at 6 bars, the temperature of the cylinder was 210°C and the mold temperatures were 50°C for the impact test samples and 80°C for the tensile test samples. The mold temperature of 50°C was found commonly used in the literature survey and 80°C was used to favor crystallization and improve tensile properties. Some experiments were done in order to compare these mold temperatures. It was found that the tensile properties obtained with a mold temperature of 80°C improved only slightly in comparison with 50°C. No further attention was paid to this variable.

The mass of polymer was different depending on the mold used. There were three molds, one for tensile testing (dumbbell), one for impact testing (rectangular) and one for dynamic mechanical testing (disk). The injection molder’s cylinder was filled with enough material to inject two samples for each mold.
The mass of material necessary for the composites filled with 0%, 2%, and 5% of CaCO$_3$ was lower than for the composites with 10% and 20% of CaCO$_3$. When the same mass of material was used for composites with 10wt% and 20wt% compositions, the mold was not filled properly. Table 3.4 indicates the mass of material used for each mold type.

For the dynamic mechanical test specimens, the polymer was loaded and four minutes were allowed for melting. After that, the material was compressed with the rod in order to take the air out and finally the cylinder was placed in position and the sample was injected into the mold. 30 seconds were allowed for cooling and then the sample was taken out. The second sample was injected right after in the same way.

For the tensile test and the impact test specimens, half of the material for each sample (approx. 2g) was added into the cylinder, four minutes were allowed for melting, and the material was pushed down with the rod. After that, the rest of the material was added, four minutes were allowed for melting again and finally the samples were injected. The material was divided in two loads because when the total amount of polymer was added, some bubbles or sometimes material that was not melted properly appeared in the samples.

Table 3.4 Mass of material used for each type of injection molded samples

<table>
<thead>
<tr>
<th></th>
<th>0%, 2%, 5% Calcium Carbonate</th>
<th>10%, 20% Calcium Carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile test samples load</td>
<td>4g</td>
<td>4.3g</td>
</tr>
<tr>
<td>Impact test samples load</td>
<td>3.8g</td>
<td>4.1g</td>
</tr>
<tr>
<td>Rheological test samples load</td>
<td>2g</td>
<td>2.3g</td>
</tr>
</tbody>
</table>
3.2.2 Characterization

Different characterization techniques were used to study the PP/CaCO$_3$ composites.

3.2.2.1 Dynamic Mechanical Testing (ARES)

In order to study the dynamic mechanical properties of the PP composites, the Advanced Rheometric Expansion System (ARES) was used. The specimens utilized were prepared previously in the mini injection molder. The dimensions of the specimens were 25mm of diameter and 1.2mm of thickness.

The test used was “dynamic frequency sweep - strain controlled” at 210°C and 2% of strain. The frequency range was 0.01 – 100 rad/s. The 25mm parallel plates were used and the separation between plates was set at 1mm.

The information obtained from the test included: the storage modulus G’, the loss modulus G”, the dynamic viscosity $\eta^*$ and the loss factor tan $\delta$.

3.2.2.2 Thermal Analysis (DSC)

A TA differential scanning calorimeter (DSC) Model 2920 was used to study the thermal properties of the PP composites. Non hermetic aluminum pans were used. For that reason, the preparation of the samples involved cutting thin slices of material with a mass of approximately 2 mg and put them into the pans. The slices were taken from the material cold compressed after mixing.

The heating rate used was ten degrees Celsius per minute (10°C/min). The temperature range for the scan was 30°C to 210°C. The information obtained through this analysis included the melting temperature, the heat of fusion obtained from integrating
the melting peak and the melting peak half width. All these values were obtained using the Universal Analysis software from TA Instruments.

The crystallinity of the sample, $X$, is equal to the heat of fusion of the sample, $\Delta H_f$, divided by the intrinsic value of the heat of fusion for completely crystalline polypropylene, of $\Delta H_f^0 = 234 \text{ J/g}^{161}$ times the polypropylene fraction in the sample (0 to 1).

$$X = \frac{\Delta H_f}{\Delta H_f^0 \times PP_{fraction}} \quad \text{Equation 3-1}$$

The DSC was also used to analyze the injection molded specimens prepared for the tensile and impact tests. In both cases, a small sample with mass between 2mg and 3mg was cut from the middle section of the specimens as shown in Figure 3.2.

![Figure 3.2 DSC samples for impact and tensile strength](image)

3.2.2.3 X-Ray Diffraction

A Brucker AXS D8 Discover X-Ray machine was used to analyze the $\alpha$-iPP and $\beta$-iPP phases in the PP composites. The X-Ray time was 60 seconds for most of the composites and 80 seconds for the ones filled with 20wt% of calcium carbonate. The distance to the objective was 15cm, the voltage was 40kV and the current 40mA.
Two types of samples were studied. The first were obtained from the cold compressed material after mixing in the Brabender internal mixer. The second samples were obtained from the injection molded samples for impact test. The objective was to quantify the amount of $\alpha$-iPP and $\beta$-iPP phases in the PP composites after mixing and after injection molding.

3.2.3 Particle dispersion and particle size distribution

In order to study the particle size distribution of calcium carbonate in the PP composites, the following procedure was used.

3.2.3.1 Scanning Electron Microscopy

The SEM JEOL JSM5310 machine was used to obtain photographs to study the dispersion, composition and particle distribution of CaCO$_3$ in the polypropylene matrix.

The preparation of the samples consisted in cutting 5 stripes (approx. 20mm x 3mm x 3mm) from the compressed material after mixing in the Brabender internal mixer. All the stripes were immersed into liquid nitrogen for 5 minutes in order to freeze them properly. Finally, the stripes were fractured and two surfaces were obtained.

The best two surfaces were selected based on appearance (especially flatness). Attention was also paid to select surfaces from stripes that were not adjacent to each other to provide images from different sections. The selected surfaces were then cut to the minimum height possible and then attached to the SEM mount using conductive copper tape.

A sputter coater Emitech K575x Turbo was used to deposit silver coating onto the surface of the samples before the SEM analysis. The sputter current was 55mA and the sputter time was 2 minutes.
When the samples were ready, they were introduced into the SEM chamber. Dr. Bojie Wang from the Polymer Science department operated the SEM machine at all times. For each sample of PP or PP composites, five photographs of the two different surfaces were taken. The best augmentation in order to compare all sizes of calcium carbonate was found to be 3000X. The voltage used in the SEM to analyze the samples was 10 kV.

3.2.3.2 Image Analysis

After obtaining the SEM photographs, the image analyzer software Image J originally developed by the National Institutes of health (NIH) was used to analyze them.

First, the image size was calibrated to show results in microns using the Calibrate command in the Process menu. After that, the appearance of SEM photographs was enhanced using the commands Brightness/Contrast, Window level and Threshold in the Image menu.

It was then essential to select the filler particles. Image J allows the selection of particles automatically. However, due to the lack of contrast obtained in the SEM photographs, it was necessary to manually select each particle. It was a tedious process that might be avoided experimenting with some parameters of the SEM machine or even adding some color to the polypropylene to differentiate it from the calcium carbonate.

After all the calcium carbonate particles were selected, the images were rendered binary using the Make Binary command in the Process menu. The command Subtract Background also in the Process menu was used to make the filler particles clearly visible in black and leaving the rest of the image in white. Finally, the commands Analyze particles and Distribution in the Analysis menu were used to obtain the area in µm² for
each particle selected. These results were used to calculate the approximate particle diameter and the particle size distribution in Chapter IV.

Figure 3.3 shows the Image J task bar and some of the options available for the Image and Analyze menus. Figure 3.4 shows an example of the image analysis results for PP composites filled with 2wt% of 0.07µm non treated calcium carbonate.

After obtaining the particle size distribution for each composite, the Image J software was used to fit the results with a mathematical model using the Curve Fitting tool in the Analyze menu. The Gamma Variant function proved to be the best fit and the $R^2$ values were calculated by the software together with the constants of the mathematical function. Figure 3.5 shows the particle size distribution result and the curve fit for the PP composite filled with 5wt% of treated 0.07µm particles.

Figure 3.3 Image and Analyze menus for the ImageJ software
Figure 3.4 Image analysis: (a) Original SEM photograph (b) Image obtained after software analysis
Figure 3.5 Particle size distribution analysis: (a) Histogram obtained from the image analysis (b) Curve fit obtained using the Gamma Variate function

3.2.4 Tensile test

The Instron 5567 tensile tester was used in order to study the tensile properties of the PP composites. The dumbbells or dogbones were previously prepared using the mini injection molding machine. Before the test each sample was cleaned properly from flash and their dimensions were measured using a caliper and micrometer.
The test was based on the ASTM D638 standard\textsuperscript{162} and the recommendations regarding sample preparation, sample conditioning, speed of testing, procedure and calculations were followed.

The specimens prepared were Type V and they were conditioned at room temperature and % humidity for not less than 40 h previous to the test according to ASTM D618\textsuperscript{163}.

The test parameters included gauge length 25.4mm and cross head speed of 12mm/min. Since the extensometer was not used, the gauge length was the distance between grips.

According with ASTM D638, the lowest speed of testing between 1, 10 or 100 mm/min +/- 25\% which gives rupture within $\frac{1}{2}$ and 5 minutes was required. After several tests it was determined that 12mm/min was the best option for the samples.

At least five samples per each type of composite were tested. The information obtained from the tensile test included the force in N and the extension in mm. From these values, the engineering stress, the true stress and strain were calculated and used to plot the stress versus strain curves. The slope of the stress versus strain curve was the elastic modulus of the composites. The tensile strength at yield and elongation at break were obtained directly from the Instron software.

The first tensile test results indicated that the 1kN load cell was the right one for our tests but it was found later that this load cell was not giving consistent results. For that reason the next results were obtained using the 10kN load cell. The results in Chapter IV will show that the values obtained for the elastic modulus are low compared with the values from the PP datasheet (1.2 GPa). Different experiments were performed in order
to find the reason for that behavior. Different load cells, injection molding machines, injection molding conditions were used but the elastic modulus remained low (between 0.7GPa and 1.1GPa). At the end the source for this behavior was narrowed down to Instron tensile tester or load cell malfunctioning and the specimen type. Perhaps the morphological structure formed with the type V specimen was not strong enough to reach a higher elastic modulus.

3.2.5 Impact test

In order to study the impact strength of the PP composites the tmi Impact Tester TMI NO 43-1 was used. The samples were prepared in the mini injection molder. Before the test each sample was cleaned from flash and measured with a caliper and micrometer.

The impact test was based on the ASTM D256-06a\textsuperscript{164}. The Test Method A for materials with impact strength higher than 27 J/m was used. According to the datasheet, the polypropylene used has impact strength of 32 J/m.

The average thickness of the samples was 1.95mm. According to the ASTM standard, it is recommended to test specimens with thickness above 6.35mm because thinner samples absorb more energy due to crashing, bending and twisting than do wider specimens.

The samples were notched following the recommendations from the ASTM D256-06a standard. At first, 10 specimens per each type of composite were prepared and they were all notched together using a tmi Notching Cutter Model TMI 22-05. This machine has knobs marked from 1 to 10 to change the cutter speeds and feed speed but no units are showed on the machine. After consulting with the manufacturer it was found out that the cutter speed ranges from 160 to 450 feet/min and the feed speed ranges from
0 to 5 inch/min. All those values are in the recommended range from the ASTM D256-06a standard. Different combinations for feed and cutter speeds were tried and the best results were obtained for the feed speed set at 9 and the cutter speed set at 7. The feed speed was high to avoid thermal damage of the material. High feed speed and slow cutter speed are recommended.

Before the impact test, the samples were carefully placed in the impact tester parallel to the pendulum path and at the height recommended in the ASTM D256-06a standard. The 2lb.ft pendulum was then released and the samples were hit and broken.

The results of the impact test were registered by means of a mechanical needle in lb.ft. The first results obtained for the impact strength of the PP composites were extremely low. To find the reason for this behavior, it was decided to test the same samples at Dynisco-Akron. The results obtained using their digital impact tester agreed with the PP datasheet.

After maintenance was performed in the tmi Impact Tester TMI NO 43-1, new samples were tested. However, this time due to lack of material, only 4 samples could be tested for each PP composite. The results obtained for PP this time agreed with the PP datasheet. The results for the PP composites are presented in Chapter IV.
CHAPTER IV
RESULTS AND DISCUSSION

4.1 Dynamic rheological properties of polypropylene (PP) and PP/CaCO$_3$ composites

Dynamic rheological properties can be used to represent the characteristics of multicomponent polymer systems such as the level of dispersion and distribution of fillers as well as processability. As mentioned before, the neat PP and PP/CaCO$_3$ samples were tested at 210°C and the elastic modulus (G’), loss modulus (G”), and dynamic viscosity ($\eta^*$) were obtained as a function of frequency at constant low strain (2%).

4.1.1 Polypropylene

The dynamic viscosity of neat PP at different mixing conditions is shown in Figure 4.1. The dynamic viscosity of PP processed at 200°C and 80rpm for 12 minutes was very low in comparison with the values for the PP processed at the other conditions in the internal mixer. The conditions to minimize degradation during mixing for 180°C were found to be at 60rpm or 80rpm and 7 minutes. The rotational speed of 60 rpm was selected over 80rpm because the addition of calcium carbonate would increase the shear and temperature during the mixing process. At 60rpm there would be better mixing with less degradation.

It was also observed that there is no clear viscoelastic linear regime for neat PP which confirms that the polypropylene used in this study has a high melting flow index (8 g/10 min) and thus low molecular weight.
4.1.2 Polypropylene/3.2\mu m CaCO_3 composites

The elastic modulus (G'), the loss modulus (G'') and the dynamic viscosity (|\eta^*|) of PP/CaCO_3 composites were obtained using different types and composition of calcium carbonate. All the composites were processed 7 minutes at 180°C and 60rpm.

4.1.2.1 Non treated 3.2\mu m particles of ground marble

Figure 4.2 (a) shows the elastic modulus (G') as a function of frequency for PP composite filled with 3.2\mu m non treated calcium carbonate of ground marble. The values
of G’ for the different compositions are very similar especially at higher frequencies. At low frequencies, the lowest elastic modulus was that of 5wt% CaCO₃ composite and the highest was that of 20wt% CaCO₃ composite. Also at low frequencies, the values for the G’ slopes are slightly higher than one.

Figure 4.2 (b) shows the loss modulus as a function of frequency for PP composites with 3.2µm non treated particles of ground marble. It revealed the same behavior as the elastic modulus.

Figure 4.2 (c) shows the dynamic viscosity as a function of frequency for PP composites filled with 3.2µm non treated particles of ground marble. The dynamic viscosity values of the PP composite filled with 20wt% and 2wt% CaCO₃ were the highest in the range of frequency analyzed. It was expected that the dynamic viscosity would increase with increasing amount of calcium carbonate. The reason why the composite with 2wt% CaCO₃ presents higher dynamic viscosity than 5wt% or 10wt% CaCO₃ may be related with the mixing process, at such low loading, it is not easy to create enough shear to break particles and achieve good dispersion. The sample tested in this experiment could have had large agglomerates that increased the dynamic viscosity.

Finally, there is no linear viscoelastic regime but it seems that there is a sharper shear thinning behavior with increasing amount of CaCO₃ which can be attributed to interfacial slippage as suggested by Osman et. al.¹⁵⁵.
Figure 4.2 Dynamic rheological properties for PP composites filled with non treated 3.2μm CaCO₃ particles from ground marble: (a) Elastic modulus G’ (b) Loss modulus G” (c) Dynamic viscosity |η*|. (×) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt%
4.1.2.2 Surface treated 3.2µm particles of ground marble

Figure 4.3 (a) shows the elastic modulus for PP composites filled with treated 3.2µm particles of ground marble. The PP composite with 20wt% CaCO₃ has the highest values for G’ and the PP composite with 2wt% CaCO₃ has the lowest values for G’. The same behavior is observed for the loss modulus and the dynamic viscosity as shown in Figure 4.3 (b) and Figure 4.3 (c) respectively.

The reason for the changes in G’, G” and |η*| (if compared with the previous section) may be related with the effect of surface treatment in reducing the agglomeration of particles in composites with low amount of CaCO₃. It seemed that the agglomerates formed with non treated particles could not be broken with the shear created during mixing.

Other important phenomena to observe are the change in elastic modulus and the dynamic viscosity for composites filled with 20wt% at low frequencies. The slope for G’ reduces in greater manner than the other composites.

The appearance of the semi plateau in the terminal region is considered to be induced by the formation of a higher order structure¹⁵¹ or as evidence for yield behavior¹⁵⁶. Another evidence for yield behavior is the change of slope in the dynamic viscosity. Above certain filler load and at low frequencies, the dynamic viscosity increases sharply and can reach a slope of 45°¹⁵⁶.

Even when a complete plateau for G’ or a 45° slope for |η*| were not observed, it can be expected that the changes in slope observed for these two properties are related with the formation of a higher structure or yield phenomena.
Figure 4.3 Dynamic rheological properties for PP composites filled with treated 3.2μm CaCO₃ particles of ground marble: (a) Elastic modulus $G'$ (b) Loss modulus $G''$ (c) Dynamic viscosity $|\eta^*|$. (×) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt%
4.1.2.3 Non treated 3.2µm particles of ground limestone

As it was mentioned before, different sources of calcium carbonate could result in different properties for the composites. In this section, PP was filled 3.2µm calcium carbonate of ground limestone to compare it with the results obtained for composites filled with ground marble.

Figure 4.4 (a) shows increasing elastic modulus with increasing composition of CaCO₃. The composites filled with 20wt% of CaCO₃ have the highest G’ and the composites filled with 2wt% of CaCO₃ have lowest G’. A sharper change in slope of the G’ curve at low frequencies is observed for the composite with 20wt% of CaCO₃ in comparison with the other curves. The loss modulus in Figure 4.4 (b) shows the highest G” for composites filled with 20wt% of CaCO₃ and the lowest for composites filled with 5wt% CaCO₃ although, starting at 5rad/s, the lowest G” was found for composites with 2wt% of CaCO₃.

The dynamic viscosity is highest for composites filled with 20wt% of CaCO₃ as shown in Figure 4.4 (c). |η*| is lowest for composites with 2wt% CaCO₃. A higher increase in slope for the dynamic viscosity is observed at low frequencies only for composites with 20wt% CaCO₃.

The changes observed in G’ and |η*| suggest the presence of a filler structure or agglomerates in the composites filled with 20wt% CaCO₃.
Figure 4.4 Dynamic rheological properties for PP composites filled with non treated 3.2μm CaCO₃ particles of ground limestone: (a) Elastic modulus $G'$ (b) Loss modulus $G''$ (c) Dynamic viscosity $|\eta^*|$. (×) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt%
4.1.2.4 Surface treated 3.2µm particles of ground limestone

Figure 4.5 shows the dynamic rheological properties of a series of PP composites filled with 3.2µm CaCO₃ of ground limestone. As seen in Figure 4.5 (a) the highest values for G’ was at 20wt% and the lowest was at 2wt% compositions. There is no clear variation of elastic modulus with composition for the frequency range analyzed except for the composite filled with 20wt% CaCO₃ at low frequencies. At low frequencies, the composite filled with 20wt% CaCO₃ shows a reduction in slope to 0.7 from a value of approximately 1.1 for all the other compositions.

The loss modulus in Figure 4.5 (b) shows the same behavior than that of the elastic modulus. Similar G’’ values for all compositions even at low frequencies. Figure 4.5 (c) shows the dynamic viscosity. The composite filled with 20wt% CaCO₃ had the highest |η*| and the one filled with 2wt% CaCO₃ had the lowest |η*| suggesting an increase of |η*| with increasing composition of CaCO₃. At low frequencies, the composite with 20wt% CaCO₃ demonstrates a sharper decrease of |η*| corresponding to a more pronounced shear thinning effect.

It is expected that the changes in slope for G’ and |η*| are evidence of the presence of agglomerates or a high order filler structure in the composites.
Figure 4.5 Dynamic rheological properties at 210°C for PP composites filled with treated 3.2μm CaCO₃ particles of ground limestone: (a) Elastic modulus G’ (b) Loss modulus G” (c) Dynamic viscosity |η*|. (×) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt%
4.1.3 Polypropylene/1.1µm CaCO₃ composites

The dynamic rheological properties of PP composites filled with 1.1µm and 0.7µm CaCO₃ particles are presented in this section.

4.1.3.1 Non treated 1.1µm particles of ground limestone

Figure 4.6 (a) shows the elastic modulus and Figure 4.6 (b) shows the loss modulus for PP composites filled with non treated 1.1µm particles. Changes in composition did not have a significant influence in the values for both G’ and G’”. Nevertheless, the composites filled with 10wt% and 20wt% CaCO₃ compete for the highest G’ and G” values and the composite filled with 2wt% CaCO₃ has the lowest G’ and G’”.

Figure 4.6 (c) shows the dynamic viscosity for PP filled with non treated 1.1µm particles. The same trend than that of G’ and G” is observed. The composites with different compositions have similar values of dynamic viscosity, the one with 2wt% CaCO₃ had the lowest |η*| and the one with 20wt% CaCO₃ had the highest |η*|.

4.1.3.2 Surface treated 1.1µm particles of ground limestone

At high frequencies, the elastic modulus G’ shown in Figure 4.7 (a) had similar values for the different calcium carbonate compositions. At low frequencies the composite with 20wt% CaCO₃ showed much higher elastic modulus and a clear reduction in slope in comparison to the other composites. This may indicate the presence of a filler structure in the composites. Figure 4.7 (b) shows the highest loss modulus for composites with 20wt% CaCO₃. Figure 4.7 (c) shows the highest dynamic viscosity for composites filled with 20wt% CaCO₃. For this composition there is a sharp increase of viscosity at low frequencies which indicates the yield behavior of this PP composite.
Figure 4.6 Dynamic rheological properties for PP composites filled with non treated 1.1μm CaCO\textsubscript{3} particles of ground limestone: (a) Elastic modulus G’ (b) Loss modulus G” (c) Dynamic viscosity |\eta^*|. (x) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt%
Figure 4.7 Dynamic rheological properties for PP composites filled with treated 1.1μm CaCO₃ particles of ground limestone: (a) Elastic modulus G’ (b) Loss modulus G” (c) Dynamic viscosity |η*|. (×) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt%
4.1.3.3 Surface treated 0.7µm particles of precipitated limestone

In order to compare precipitated and ground calcium carbonate, the rheological properties of PP composites filled with 0.7µm CaCO$_3$ of precipitated limestone were studied. Figure 4.8 (a) shows the elastic modulus and revealed that the PP composites filled with 20wt% CaCO$_3$ demonstrated the highest values at low frequencies and its slope changes drastically in comparison with high frequencies between 1rad/s and 500 rad/s. Figure 4.8 (b) shows the loss modulus with the same trend as seen for $G'$ and similarly a sharp change of slope was observed for the composite with 20wt% of CaCO$_3$. Figure 4.8 (c) shows the dynamic viscosity with the highest values for the PP composites filled with 20wt% CaCO$_3$ and a very sharp change of slope at low frequencies as seen in $G'$ and $G''$. This indicates the yield phenomena produced by high concentration of CaCO$_3$.

The elastic modulus, loss modulus and dynamic viscosity of PP composites did not increase with increasing amount of CaCO$_3$. The composite with 2wt% CaCO$_3$ has higher values than the composites with 5wt% and 10wt%. This may be related with agglomeration of particles. It seems surface treatment was not enough to avoid the agglomeration of 0.7µm particles. At the same time with such low amount of CaCO$_3$ the shear during mixing was not enough to break the agglomerates.
Figure 4.8 Dynamic rheological properties for PP composites filled with treated 0.7\(\mu\)m CaCO\(_3\) particles of precipitated limestone: (a) Elastic modulus \(G'\) (b) Loss modulus \(G''\) (c) Dynamic viscosity \(|\eta^*|\). (\(\times\)) 2wt\% (\(\Delta\)) 5wt\% (\(\Box\)) 10wt\% (\(\circ\)) 20wt\%
4.1.4 Polypropylene/0.07µm CaCO₃ composites

The dynamic rheological properties of PP composites filled with 0.07µm CaCO₃ particles are presented in this section.

4.1.4.1 Non treated 0.07µm particles of precipitated limestone

Figure 4.9 (a) shows the elastic modulus for a series of PP composites filled with 0.07µm non treated particles of precipitated limestone. Except for the composite filled with 20wt% CaCO₃ the G’ curves for the other composites indicate very similar values. At low frequencies the curve for 20wt% CaCO₃ shows a semi plateau in the frequency range of 0.05 rad/s to 0.5 rad/s.

Figure 4.9 (b) shows the loss modulus G”. A similar trend to G’ was observed. The highest values of G” in the frequency range used was that of the PP composites filled with 20wt% CaCO₃.

Figure 4.9 (c) shows the dynamic viscosity. The $|\eta^*|$ curve of the PP composite filled with 20wt% clearly reveals from the rest of the composites and has a 45° slope at low frequencies.
Figure 4.9 Dynamic rheological properties for PP composites filled with non treated 0.07μm CaCO₃ particles of precipitated limestone: (a) Elastic modulus $G'$ (b) Loss modulus $G''$ (c) Dynamic viscosity $|\eta^*|$. (×) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt%
4.1.4.2 Surface treated 0.07µm particles of precipitated limestone

Figure 4.10 (a) shows the elastic modulus for the PP composites filled with 0.07µm treated CaCO₃ particles. There is a clear difference in comparison with those of the PP composites filled with non-treated 0.07µm particles in Figure 4.9 (a). G’ increases with increasing amount of calcium carbonate. The plateau region of G’ appeared at the composite filled with 20wt% CaCO₃ in the range of frequencies from 0.05 rad/s to 0.5 rad/s. A very similar trend was observed in Figure 4.9 (b) for the loss modulus G” including the appearance of the plateau for the composite filled with 20wt% CaCO₃. The dynamic viscosity │η*│ increases with increasing load of calcium carbonate as shown in Figure 4.9 (c). The yield behavior appears in the │η*│ curve of the PP composite filled with 20wt% CaCO₃.
Figure 4.10 Dynamic rheological properties for PP composites filled with treated 0.07\,\mu m CaCO$_3$ particles from precipitated limestone: (a) Elastic modulus $G'$ (b) Loss modulus $G''$ (c) Dynamic viscosity $|\eta^*|$. (×) 2wt% (Δ) 5wt% (□) 10wt% (○) 20wt%
4.1.5 Effect of particle size, composition and surface treatment of calcium carbonate on the elastic modulus $G'$ and dynamic viscosity $|\eta^*|$ of PP/CaCO$_3$ composites

The results for the elastic modulus, loss modulus and dynamic viscosity for each type of calcium carbonate at low frequencies will be discussed in this section. In particular those at two frequencies such as 0.1 rad/s and 1 rad/s were used to compare the effects of the different size, surface treatment and composition of calcium carbonate in the PP composites.

Figure 4.11 (a) shows the elastic modulus $G'$ as a function of particle size for non treated particles at 0.1 rad/s. For the different particle sizes the highest $G'$ value was obtained for the composite filled with 0.07µm at 20wt% CaCO$_3$. The lowest value of $G'$ among the PP composites was observed at the PP composite filled with 3.2µm particles of ground limestone at 2wt% CaCO$_3$.

Figure 4.11 (b) shows the elastic modulus $G'$ for treated particles at 0.1 rad/s. The top $G'$ values were found for the composites filled with 20wt% CaCO$_3$. The highest $G'$ was found for PP composites with 20wt% of 0.07µm particles followed by those with 0.7µm of precipitated limestone, 1.1µm of ground limestone, 3.2µm of ground limestone and finally 3.2µm of ground marble also at 20wt% composition. For each particle size, the lowest $G'$ value tends to show at 2wt% CaCO$_3$ except for the composite with 0.7µm CaCO$_3$ particles. The lowest $G'$ value was observed for the composite filled with 2wt% of 0.07µm CaCO$_3$ particles.

Figure 4.12 (a) shows the dynamic viscosity $|\eta^*|$ for the composites filled with non treated particles at 0.1 rad/s. The highest $|\eta^*|$ value was located for the composites
Figure 4.11 Elastic modulus $G'$ vs. CaCO$_3$ median particle size at 0.1 rad/s for (a) non treated and (b) treated particles.
Figure 4.12 Dynamic viscosity vs. CaCO₃ median particle size at 0.1 rad/s for (a) non treated and (b) treated particles
filled with 0.07µm CaCO$_3$ particles at 20wt% and the lowest for the composite filled with 3.2µm particles of ground limestone at 2wt% CaCO$_3$.

Figure 4.12 (b) shows the dynamic viscosity for composites filled with treated particles at 0.1 rad/s. The highest $|\eta^*|$ values for all filler types was found for PP composites filled with 20wt% of 0.07µm CaCO$_3$. The lowest $|\eta^*|$ was found for PP composites filled with 0.7µm at 10wt% CaCO$_3$.

When the results for non treated and treated particles are compared, the highest value for G’ was found for PP composites filled with treated 0.07µm particles at 20wt% CaCO$_3$ and the lowest for non treated 3.2 µm particles from ground limestone at 2wt% CaCO$_3$. The same results were obtained when comparing the elastic modulus G’ for treated and non treated particles at 1 rad/s.

Figure 4.13 (a) and Figure 4.13 (b) show the elastic modulus G’ for treated and non treated particles at 1 rad/s respectively. These graphs show the same behavior than that of the one observed at 0.1 rad/s.

Figure 4.14 (a) and Figure 4.14 (b) show the dynamic viscosity for treated and non treated particles at 1 rad/s respectively with the same behavior than that of the PP composites filled with treated and non treated particles at 0.1 rad/s.

When the dynamic viscosity for non treated and treated particles at 0.1rad/s and 1 rad/s were compared, it was observed that the highest $|\eta^*|$ value was found for the composites filled with 0.07µm particles at 20wt% CaCO$_3$ and the lowest with 3.2µm CaCO$_3$ particles from ground limestone at 2wt% composition.

The main difference between the graphs for 0.1 rad/s and 1 rad/s is that for composites with the same particle size, the G’ values at different compositions are less
Figure 4.13 Elastic modulus $G'$ vs. CaCO$_3$ median particle size at 1 rad/s for (a) non treated and (b) treated particles
Figure 4.14 Dynamic viscosity vs. CaCO₃ median particle size at 1 rad/s for (a) non treated and (b) treated particles.
scattered at 1 rad/s than at 0.1 rad/s. The same phenomenon was observed for the dynamic viscosity $|\eta^*|$

There are important conclusions that can be obtained from the different graphs presented for the elastic modulus and dynamic viscosity of PP/CaCO$_3$ composites as a function of frequency, particle size and calcium carbonate composition.

Dynamic rheological properties are important to characterize multicomponent polymer systems$^{151,152}$. According to previous studies$^{155,157,158,165}$, when polymer composites have a critical amount of filler, the elastic modulus $G'$ and the loss modulus $G''$ become almost independent of frequency at the low frequency region. There is a plateau or semi plateau that appears in the terminal region and is considered to be induced by the formation of a higher order filler structure$^{151}$ or evidence for yield behavior$^{156}$. A similar yield behavior is shown in the dynamic viscosity. Previously, it was found that for PP composites filled with 0.8µm$^{155}$ and 0.044µm$^{158}$ CaCO$_3$, above 25wt% and at low frequencies, $G'$ showed a plateau and the dynamic viscosity appeared unbound and showed a increased slope close to $45^\circ$.

After analyzing our results, at 0.1 rad/s, the highest values for elastic modulus $G'$ and dynamic viscosity $|\eta^*|$ were found at 20wt% of treated calcium carbonate. This indicates that treated particles tend to form higher order structures that show thixotropic behavior. The lowest values for $G'$ and $|\eta^*|$ were found for the treated CaCO$_3$ particles at low compositions. At low compositions, treated particles disperse better and help to reduce viscosity and $G'$ in comparison with non treated particles.

These results agree with the studies from Gong et. al.$^{158}$ who suggested that at higher loads, well dispersed coated nanoparticles have a more important effect on
restricting the macromolecular chain motion than the large aggregates formed due to insufficient surface treatment.

For the same type of calcium carbonate at different compositions different behaviors were observed as follows. It was expected that $G'$ and $|\eta^*|$ would increase with increasing composition of calcium carbonate but the behavior depended on the different particle type. Increasing the composition of calcium carbonate did not necessarily increase the elastic modulus or the dynamic viscosity. That trend was observed clearly only for 0.07µm treated particles. For the other types of calcium carbonate, the elastic modulus and dynamic viscosity were influenced by other factors, including the formation of agglomerates that can cause increased shear during mixing. This shear can cause the reduction of viscosity due to degradation of polypropylene.

The comparison of the viscosity data for the composites with 3.2µm particles from ground marble with those from ground limestone showed that the increase of viscosity with increasing filler composition is more evident with treated particles from ground marble and for non treated particles from ground limestone. The reasons for this behavior could be related with the fact that marble quality is considered to enhance dispersion of particles in the matrix. Non treated ground limestone may form aggregates or contain impurities that can increase shear during mixing and result in improving dispersion at low compositions.

The lowest values of elastic modulus and dynamic viscosity for ground limestone at high loads could mean that this type of calcium carbonate produces more agglomeration, increased shear during mixing and causes severe degradation of the polypropylene matrix.
The importance of increased shear during mixing can be demonstrated with the results for the PP composites filled with 1.1µm particles. There is not much difference in the viscosity and elastic modulus for treated and non treated particles from ground limestone. This might be due to low shear during mixing.

Comparison of the effect of 0.7µm precipitated and 1.1µm ground calcium carbonate when added to PP shows a more pronounced plateau and unbound dynamic viscosity for the precipitated calcium carbonate. Precipitated calcium carbonate has a narrower particle size distribution and would produce better dispersion of particles in the polypropylene matrix. For that reason, it is possible that precipitated calcium carbonate is more effective inducing the formation of filler structures than ground calcium carbonate.

Finally, when the elastic modulus and dynamic viscosity are compared for the four particle sizes of calcium carbonate, they show similar values at low compositions. The large differences between different particle sizes are observed at 10wt% and especially at 20wt% compositions.
Figure 4.15 (a) Elastic modulus and (b) Dynamic viscosity vs. CaCO$_3$ (wt %) at 0.1 rad/s for non treated and treated particles
4.2 Thermal Characterization Studies

DSC analysis was used to characterize the crystallinity and crystallinity changes caused by the addition of calcium carbonate with different particle size, with and without surface treatment and at different compositions into polypropylene. The melting peak half width of the DSC curves was determined to discuss the spherulite size distribution. The wider the half width, the broader the spherulite size distribution became\textsuperscript{166}.

The DSC scans shown were taken after the material was grinded. The PP/CaCO\textsubscript{3} composite was prepared in a Brabender internal mixer and then it was cold compressed before grinding.

4.2.1 Polypropylene

Figure 4.16 shows the DSC traces for polypropylene prepared from pellets and neat PP mixed in the Brabender internal mixer at 180°C and 60 rpm. The DSC curves in the graph follow the same order as the legend on the right. As it is indicated, the first trace corresponds to the first run and the second to the second run.

Only one melting peak was observed in both cases. Table 4.1 shows the table of results for the melting point, % crystallinity and melting peak half width. The highest % crystallinity corresponded to the second run of PP pellets. The melting peak half width values did not differ too much. The narrowest half width corresponded to the second run trace of PP pellets and resulted in the narrower spherulite size distribution.
4.2.2 Polypropylene/3.2µm CaCO₃ composites

The DSC results for the PP composites filled with 3.2µm CaCO₃ particles are shown in this section.

4.2.2.1 Non treated 3.2µm particles of ground marble

Figure 4.17 shows the DSC traces of the PP composites filled with non treated 3.2µm particles of ground marble. It was observed that for all different compositions of CaCO₃ the first DSC run showed first a small shoulder peak close to a second large peak resulting in two melting temperatures. The first melting temperature appeared in all the first run scans despite of the CaCO₃ compositions. The first melting temperature was

![Figure 4.16 DSC plot for PP from pellets and after mixing in brabender](image)

Table 4.1 Thermal properties of neat PP pellets and neat PP mixed in Brabender internal mixer at 180°C

<table>
<thead>
<tr>
<th></th>
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<th></th>
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<tr>
<td></td>
<td>Tm₁ (°C)</td>
<td>Tm₂ (°C)</td>
<td>ΔH (J/g)</td>
<td>% Cryst.</td>
<td>Half width (°C)</td>
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<tr>
<td>PP Pellets</td>
<td>-</td>
<td>164</td>
<td>80.0</td>
<td>34.2</td>
<td>10.8</td>
</tr>
<tr>
<td>PP Brabender</td>
<td>-</td>
<td>163</td>
<td>77.8</td>
<td>33.2</td>
<td>10.4</td>
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<td>Tm₁ (°C)</td>
<td>Tm₂ (°C)</td>
<td>ΔH (J/g)</td>
<td>% Cryst.</td>
<td>Half width (°C)</td>
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<td>80.6</td>
<td>34.4</td>
<td>10.7</td>
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</tbody>
</table>
approximately 147-149°C for all compositions. In the second scans, the second melting
temperature peaks became broader and shifted slightly to lower temperature for all
compositions.

![DSC plot for PP mixed with non treated 3.2µm particles of ground marble](image)

**Table 4.2 DSC results for PP mixed with non treated 3.2µm particles of ground marble**

<table>
<thead>
<tr>
<th>First run</th>
<th>3.2µm Non treated Ground Marble</th>
<th>Tm₁ (°C)</th>
<th>Tm₂ (°C)</th>
<th>ΔH (J/g)</th>
<th>% Cryst.</th>
<th>Half width (°C)</th>
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<tr>
<td>2 wt%</td>
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<td>161</td>
<td>80.4</td>
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<td>5 wt%</td>
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<td>161</td>
<td>83.7</td>
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<td>10 wt%</td>
<td>149</td>
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<tr>
<td>20 wt%</td>
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<td>162</td>
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<td>39.4</td>
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<th>3.2µm Non treated Ground Marble</th>
<th>Tm₁ (°C)</th>
<th>Tm₂ (°C)</th>
<th>ΔH (J/g)</th>
<th>% Cryst.</th>
<th>Half width (°C)</th>
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<tr>
<td>2 wt%</td>
<td>-</td>
<td>161</td>
<td>82.4</td>
<td>35.9</td>
<td>10.8</td>
<td></td>
</tr>
<tr>
<td>5 wt%</td>
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<tr>
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</tr>
<tr>
<td>20 wt%</td>
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<td>160</td>
<td>76.1</td>
<td>40.7</td>
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Table 4.2 summarizes the thermal properties of these composites based on the DSC results including the first and second melting temperatures. The highest % crystallinity was found for the PP composites filled with 5wt% CaCO$_3$. The half width of the second melting peak increased during the second DSC scan for all loads which indicated that the spherulite size distribution became broader due to the thermal treatment process.

4.2.2.2 Surface treated 3.2µm particles of ground marble

Figure 4.18 shows the DSC traces for the first and second scans for PP composites filled with treated 3.2µm particles of ground marble. Two melting peaks were observed on the first DSC scan for all CaCO$_3$ compositions. The first peaks disappeared during the second DSC scan.

![DSC plot for PP mixed with treated 3.2µm particles of ground marble](image)

Figure 4.18 DSC plot for PP mixed with treated 3.2µm particles of ground marble
Table 4.3 summarizes the DSC results shown in Figure 4.18. The first melting temperature was 148°C for all compositions. The highest % crystallinity was shown for the PP composite with 5wt% CaCO$_3$ followed by the one with 10wt% CaCO$_3$ for both treated and non treated particles. The melting peak half width again increased during the second DSC scan for all composites.

Table 4.3 DSC results for PP mixed with treated 3.2µm particles of ground marble

<table>
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<tr>
<th>3.2µm Treated Ground Marble</th>
<th>Tm 1 (ºC)</th>
<th>Tm 2 (ºC)</th>
<th>ΔH (J/g)</th>
<th>% Cryst.</th>
<th>Half width (ºC)</th>
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<tr>
<td>2 wt%</td>
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<td>40.1</td>
<td>8.5</td>
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<tr>
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<td>148</td>
<td>161</td>
<td>77.9</td>
<td>37.0</td>
<td>8.1</td>
</tr>
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<td>161</td>
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<table>
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<th>3.2µm Treated Ground Marble</th>
<th>Tm 1 (ºC)</th>
<th>Tm 2 (ºC)</th>
<th>ΔH (J/g)</th>
<th>% Cryst.</th>
<th>Half width (ºC)</th>
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<td>68.2</td>
<td>36.4</td>
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4.2.2.3 Non treated 3.2µm particles of ground limestone

Figure 4.2 shows the first and second DSC scans for the PP composites filled with non treated 3.2µm particles of ground limestone. In this system, two melting peaks were observed clearly only for the PP composite filled with 5wt% CaCO$_3$.

Table 4.4 summarizes the DSC results shown in Figure 4.19. The highest % crystallinity was found for the PP composite with 5wt% CaCO$_3$. The % crystallinity was low in comparison with the results for the PP composites filled with non treated 3.2µm particles from ground marble. The melting peak half width increased for the second scan.
Figure 4.19 DSC plot for PP mixed with non treated 3.2µm particles of ground limestone

Table 4.4 DSC results for PP mixed with non treated 3.2µm particles of ground limestone

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<tr>
<th>3.2µm Non Treated Ground Limestone</th>
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<th>Tm₂ (ºC)</th>
<th>ΔH (J/g)</th>
<th>% Cryst.</th>
<th>Half width (ºC)</th>
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<td>10.7</td>
</tr>
<tr>
<td>5 wt%</td>
<td>-</td>
<td>161</td>
<td>83.40</td>
<td>37.5</td>
<td>10.4</td>
</tr>
<tr>
<td>10 wt%</td>
<td>-</td>
<td>162</td>
<td>62.76</td>
<td>29.8</td>
<td>10.2</td>
</tr>
<tr>
<td>20 wt%</td>
<td>-</td>
<td>161</td>
<td>55.01</td>
<td>29.4</td>
<td>9.6</td>
</tr>
</tbody>
</table>
4.2.2.4 Surface treated 3.2µm particles of ground limestone

Figure 4.20 shows the first and second DSC scans for PP composites filled with surface treated 3.2µm particles of ground limestone. The first melting peaks were slightly visible for the PP composites with 2wt% and 5wt% CaCO₃ for the first scan and surprisingly a first melting peak was observed for the PP composite with 20wt% for the second scan. Table 4.5 summarizes the results obtained from the DSC scans. The % crystallinity was higher for the 2wt% and 20wt% compositions. The half widths of the melting peak increased again for the second DSC scan which indicated that the spherulites size distribution increased.

![Figure 4.20 DSC plot for PP mixed with treated 3.2µm particles of ground limestone](image)
Table 4.5 DSC results for PP mixed with treated 3.2µm particles of ground limestone

<table>
<thead>
<tr>
<th>3.2µm Treated Ground Limestone</th>
<th>Tm₁ (ºC)</th>
<th>Tm₂ (ºC)</th>
<th>ΔH (J/g)</th>
<th>% Cryst.</th>
<th>Half width (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 wt%</td>
<td>146</td>
<td>162</td>
<td>73.33</td>
<td>32.0</td>
<td>9.4</td>
</tr>
<tr>
<td>5 wt%</td>
<td>146</td>
<td>163</td>
<td>63.62</td>
<td>28.6</td>
<td>9.5</td>
</tr>
<tr>
<td>10 wt%</td>
<td>-</td>
<td>163</td>
<td>56.36</td>
<td>26.8</td>
<td>8.3</td>
</tr>
<tr>
<td>20 wt%</td>
<td>-</td>
<td>161</td>
<td>55.26</td>
<td>29.5</td>
<td>9.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3.2µm Treated Ground Limestone</th>
<th>Tm₁ (ºC)</th>
<th>Tm₂ (ºC)</th>
<th>ΔH (J/g)</th>
<th>% Cryst.</th>
<th>Half width (ºC)</th>
</tr>
</thead>
<tbody>
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<td>-</td>
<td>161</td>
<td>63.37</td>
<td>28.5</td>
<td>10.1</td>
</tr>
<tr>
<td>10 wt%</td>
<td>-</td>
<td>161</td>
<td>56.54</td>
<td>26.8</td>
<td>9.9</td>
</tr>
<tr>
<td>20 wt%</td>
<td>145</td>
<td>161</td>
<td>56.81</td>
<td>30.3</td>
<td>9.8</td>
</tr>
</tbody>
</table>

Figure 4.21 shows the % crystallinity as a function of calcium carbonate composition for the PP composites filled with 3.2µm CaCO₃ from ground marble and ground limestone. The % crystallinity for the PP composites with ground marble was higher in comparison with the composites filled with ground limestone. This may be related with impurities found in ground limestone. There was no direct relation between increasing filler load and % crystallinity.

For the composites with 3.2µm from ground marble the highest % crystallinity was found for PP composites with 5wt% of non treated particles. For 3.2µm from ground limestone, the highest % crystallinity was found for PP composites with 5wt% of non treated particles. For the other compositions, treated and non treated particles did not show a large difference in % crystallinity. The % crystallinity was higher than that of neat PP for ground marble and lower than that of neat PP for ground limestone.
Figure 4.21 % Crystallinity as a function of composition (wt %) for 3.2µm calcium carbonate particles

4.2.3 Polypropylene/1.1µm CaCO₃ and Polypropylene/0.7µm CaCO₃ composites

The DSC results for the PP composites filled with 1.1µm and 0.7µm CaCO₃ particles are shown in this section.

4.2.3.1 Non treated 1.1µm particles of ground limestone

Figure 4.22 shows the first and second DSC scan for PP composites filled with non treated 1.1µm particles of ground limestone. A first melting peak for the first scan was hardly observed with 5wt% and 10wt% CaCO₃ compositions. Table 4.6 summarizes the results obtained from the DSC scans. The % crystallinity was highest for the PP composite with 20wt% CaCO₃. For the first time the peak half width decreased for the second run but only for the 2wt% CaCO₃ composition.
Figure 4.22 DSC plot for PP mixed with non treated 1.1µm particles of ground limestone

Table 4.6 DSC results for PP mixed with non treated 1.1µm particles of ground limestone

<table>
<thead>
<tr>
<th>1.1µm Non Treated Ground Limestone</th>
<th>Tm₁ (°C)</th>
<th>Tm₂ (°C)</th>
<th>ΔH (J/g)</th>
<th>% Cryst.</th>
<th>Half width (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First run</td>
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<td></td>
</tr>
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<td>2 wt%</td>
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<td>58.44</td>
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<td>9.2</td>
</tr>
<tr>
<td>5 wt%</td>
<td>148</td>
<td>162</td>
<td>66.03</td>
<td>29.7</td>
<td>7.6</td>
</tr>
<tr>
<td>10 wt%</td>
<td>148</td>
<td>161</td>
<td>60.73</td>
<td>28.8</td>
<td>9.5</td>
</tr>
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<td>-</td>
<td>163</td>
<td>62.42</td>
<td>33.3</td>
<td>7.5</td>
</tr>
<tr>
<td>Second run</td>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
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</tr>
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<td>65.16</td>
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<td>10.9</td>
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<td>-</td>
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<td>59.02</td>
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<td>20 wt%</td>
<td>-</td>
<td>161</td>
<td>62.11</td>
<td>33.2</td>
<td>8.8</td>
</tr>
</tbody>
</table>
4.2.3.2 Surface treated 1.1µm particles of ground limestone

Figure 4.23 shows the first and second DSC scans for the PP composites filled with treated 1.1µm particles of ground limestone. A clear first melting peak for the first scan was observed only for PP composites with 10wt% CaCO₃.

Table 4.7 presents the results obtained from the DSC scans. The highest % crystallinity occurred for PP composites filled with 10wt% CaCO₃. The melting peak half width increased with the second scan. The half width increase was of 30% for 2wt% CaCO₃ composition and almost 40% for the 20wt% CaCO₃ composition.

![Figure 4.23 DSC plot for PP mixed with treated 1.1µm particles of ground limestone](image_url)
Table 4.7 DSC results for PP mixed with treated 1.1µm particles of ground limestone

<table>
<thead>
<tr>
<th></th>
<th>Tm 1 (ºC)</th>
<th>Tm 2 (ºC)</th>
<th>ΔH (J/g)</th>
<th>% Cryst.</th>
<th>Half width (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>First run</strong></td>
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<td>66.06</td>
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</tr>
<tr>
<td>5 wt%</td>
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<td>162</td>
<td>73.11</td>
<td>32.9</td>
<td>10.2</td>
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<tr>
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<td>-</td>
<td>162</td>
<td>71.40</td>
<td>38.1</td>
<td>7.6</td>
</tr>
<tr>
<td><strong>Second run</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 wt%</td>
<td>-</td>
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<td>64.18</td>
<td>28.0</td>
<td>10.9</td>
</tr>
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<td>68.17</td>
<td>30.7</td>
<td>10.5</td>
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<td>88.57</td>
<td>42.1</td>
<td>10.6</td>
</tr>
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<td>20 wt%</td>
<td>-</td>
<td>159</td>
<td>70.79</td>
<td>37.8</td>
<td>10.6</td>
</tr>
</tbody>
</table>

4.2.3.3 Surface treated 0.7µm particles of precipitated limestone

Figure 4.24 shows the first and second DSC scan for PP composites filled with treated 0.7µm particles from precipitated limestone. This filler was used in order to compare precipitated and ground calcium carbonate. The first melting peak for the first scan was observed only for the PP composite with 2wt% CaCO₃.

Table 4.8 shows the results obtained from the DSC scans. The % crystallinity was similar for 2wt%, 5wt% and 10wt% CaCO₃ compositions and lowest for 20wt% CaCO₃ composition. The melting peak half widths were similar for the first and second scans. There was an increase of half width of 10% only for 2wt% CaCO₃ composition.
Figure 4.24 DSC plot for PP mixed with non treated 0.7µm particles of precipitated limestone

Table 4.8 DSC results for PP mixed with treated 0.7µm particles of precipitated limestone

<table>
<thead>
<tr>
<th>0.7µm Treated Precipitated Limestone</th>
<th>Tm 1 (ºC)</th>
<th>Tm 2 (ºC)</th>
<th>ΔH (J/g)</th>
<th>% Cryst.</th>
<th>Half width (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 wt%</td>
<td>147</td>
<td>162</td>
<td>78.44</td>
<td>34.2</td>
<td>9.0</td>
</tr>
<tr>
<td>5 wt%</td>
<td>-</td>
<td>163</td>
<td>72.39</td>
<td>32.6</td>
<td>10.4</td>
</tr>
<tr>
<td>10 wt%</td>
<td>-</td>
<td>162</td>
<td>72.61</td>
<td>34.5</td>
<td>10.4</td>
</tr>
<tr>
<td>20 wt%</td>
<td>-</td>
<td>164</td>
<td>55.86</td>
<td>29.8</td>
<td>11.1</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>0.7µm Treated Precipitated Limestone</th>
<th>Tm 1 (ºC)</th>
<th>Tm 2 (ºC)</th>
<th>ΔH (J/g)</th>
<th>% Cryst.</th>
<th>Half width (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 wt%</td>
<td>-</td>
<td>161</td>
<td>78.41</td>
<td>34.2</td>
<td>10.2</td>
</tr>
<tr>
<td>5 wt%</td>
<td>-</td>
<td>161</td>
<td>74.22</td>
<td>33.4</td>
<td>10.1</td>
</tr>
<tr>
<td>10 wt%</td>
<td>-</td>
<td>161</td>
<td>76.56</td>
<td>36.4</td>
<td>10.5</td>
</tr>
<tr>
<td>20 wt%</td>
<td>-</td>
<td>163</td>
<td>57.91</td>
<td>30.9</td>
<td>10.8</td>
</tr>
</tbody>
</table>
Figure 4.25 shows the % crystallinity as a function of calcium carbonate composition for PP composites filled with 1.1\(\mu\)m treated and non treated particles of ground limestone and with 0.7\(\mu\)m from precipitated limestone. For PP filled with 1.1\(\mu\)m non treated particles the % crystallinity was observed to increase with 20wt\% CaCO\(_3\). For the other compositions the % crystallinity did not change clearly. For the PP filled with 1.1\(\mu\)m treated particles the % crystallinity increased with increasing amount of CaCO\(_3\) up to 10wt\% and then decreased with 20wt\% CaCO\(_3\).

For the PP composites filled with 0.7\(\mu\)m treated particles the % crystallinity was similar with 2wt\%, 5wt\% and 10wt\% CaCO\(_3\) and decreased sharply with 20wt\% CaCO\(_3\). Except for the PP composite filled with 10wt\% of 1.1\(\mu\)m treated particles, the rest of values for % crystallinity obtained were lower than that of neat PP.

Figure 4.25 Crystallinity as a function of composition (wt %) for 1.1\(\mu\)m and 0.7\(\mu\)m calcium carbonate particles
4.2.4 Polypropylene/0.07µm CaCO₃ composites

The DSC results for the PP composites filled with 0.07µm CaCO₃ particles are shown in this section.

4.2.4.1 Non treated 0.07µm particles of precipitated limestone

Figure 4.26 shows the first and second DSC scans for PP composites filled with non treated 0.07µm particles from precipitated limestone. The first melting peaks for the first scan were observed with 2wt% and 5wt% CaCO₃. For the second scan a first melting peak was observed slightly with 2wt% CaCO₃.

![DSC plot for PP mixed with non treated 0.07µm particles from precipitated limestone](image)

**Table 4.9** summarizes the results obtained from the DSC scans. The highest values for % crystallinity correspond to the PP composites with 2wt% and 20wt% CaCO₃.
CaCO$_3$. Except for the composite filled with 2wt% CaCO$_3$, the melting peak half width decreased for the second run.

Table 4.9 DSC results for PP mixed with non treated 0.07µm particles from precipitated limestone

<table>
<thead>
<tr>
<th></th>
<th>0.07µm Non Treated Precipitated Limestone</th>
<th>Tm$_1$ (°C)</th>
<th>Tm$_2$ (°C)</th>
<th>ΔH (J/g)</th>
<th>% Cryst.</th>
<th>Half width (°C)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>164</td>
<td>96.4</td>
<td>42.0</td>
<td>10.1</td>
</tr>
<tr>
<td></td>
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<td>147</td>
<td>164</td>
<td>84.3</td>
<td>37.9</td>
<td>10.4</td>
</tr>
<tr>
<td></td>
<td>10 wt%</td>
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<td>162</td>
<td>78.4</td>
<td>37.2</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
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<td>-</td>
<td>162</td>
<td>79.2</td>
<td>42.3</td>
<td>8.1</td>
</tr>
<tr>
<td>Second run</td>
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<td>43.5</td>
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<td>161</td>
<td>79.7</td>
<td>37.9</td>
<td>8.2</td>
</tr>
<tr>
<td></td>
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<td>-</td>
<td>162</td>
<td>83.7</td>
<td>44.7</td>
<td>7.0</td>
</tr>
</tbody>
</table>

4.2.4.2 Surface treated 0.07µm particles from precipitated limestone

Figure 4.27 shows the first and second DSC scans for PP composites filled with treated 0.07µm particles from precipitated limestone. A first melting peak was observed for the first scan at all compositions. On Table 4.10 the highest % crystallinity was shown for PP composites with 10wt% and 20wt% CaCO$_3$. The melting peak half width increased during the second scan especially for PP composites with 2wt% and 5wt% CaCO$_3$.

Figure 4.28 shows the % crystallinity as a function of calcium carbonate load for PP composites filled with treated and non treated 0.07µm. The effect of increasing amount of CaCO$_3$ was similar for both particles. It only differed clearly at 10wt% composition. Treated particles increased the % crystallinity and non treated particles did
not produce a significant change in it. For all compositions of CaCO$_3$ the % crystallinity was similar or higher than the values for neat PP.

Figure 4.27 DSC plot for PP mixed with treated 0.07μm particles from precipitated limestone

Table 4.10 DSC results for PP mixed with treated 0.07μm particles from precipitated limestone

<table>
<thead>
<tr>
<th>0.07μm Treated Precipitated Limestone</th>
<th>Tm 1 (°C)</th>
<th>Tm 2 (°C)</th>
<th>ΔH (J/g)</th>
<th>% Cryst.</th>
<th>Half width (°C)</th>
</tr>
</thead>
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<tr>
<td>First run</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>163</td>
<td>93.87</td>
<td>40.9</td>
<td>9.4</td>
</tr>
<tr>
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<tr>
<td>Second run</td>
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<td>10.7</td>
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<td>43.2</td>
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</tr>
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<td>-</td>
<td>160</td>
<td>81.91</td>
<td>43.8</td>
<td>8.4</td>
</tr>
</tbody>
</table>

121
The results for each type of calcium carbonate are combined in graphs that show the % crystallinity as a function of particle size.

Figure 4.29 shows the % crystallinity for non treated and treated particles during the first and second DSC scans respectively. A cluster of data points was observed for each type of calcium carbonate.

For the first DSC scan, the highest % crystallinity was found for the PP composite filled with 0.07µm particles at 10wt% composition followed by the PP composite with 1.1µm particles at the same composition. The lowest crystallinity was found for composites with 3.2µm particles of ground limestone at 10wt% composition.
For the second DSC scan, the highest % crystallinity was found for PP composites filled with 0.07µm treated and non treated particles at 20wt% composition. The lowest % crystallinity was found for PP composites with 3.2µm treated particles with 10wt% composition.

4.2.5 Effect of calcium carbonate on the % crystallinity of PP/CaCO₃ composites.

The main effect of fillers on polypropylene morphology is their ability to act as nucleating agents⁶⁹. Nucleating effect can be identified with increasing crystallization temperature, increasing crystallization rate and reduced spherulitic size⁴⁰. The % crystallinity varies proportionally with the nucleation effect observed for PP filled with micro CaCO₃⁴⁰. Nano calcium carbonate was shown to increase the nucleation effect when added to PP, however it does not produce a clear increase in %crystallinity¹³⁹. The reason for that behavior is that nanoparticles act as nucleating agents to enhance crystallization but at the same time act as obstacles to the chain movement to reduce the crystallization¹⁶⁷.

The experiments in this section focused on the % crystallinity of the PP/CaCO₃ composites and how it was influenced by the different types of calcium carbonate used. The % crystallinity was calculated using the heat fusion obtained from the melting peak from the DSC scan using the theoretical value of 234J/g for 100% crystalline polypropylene¹⁶¹. Each sample was analyzed two times in order to erase the thermal history after the first run.
Figure 4.29 % Crystallinity vs. median particle size of CaCO₃ for the first DSC scan: (a) Non treated particles (b) Treated particles
Figure 4.30 % Crystallinity vs. median particle size of CaCO₃ for the second DSC scan for: (a) Non treated particles (b) Treated particles
The melting peaks for the first and second run differed in shape. In many cases the first run scan had two melting peaks, one at lower melting temperature and the other at higher melting temperature. Also, the larger melting peak for the first run was thinner and sharper than the melting peak for the second run in almost every case.

The explanation for the two melting peaks in the first DSC scan might be related with the appearance of two crystalline forms of iPP. As mentioned before, polypropylene can form α phase at higher melting temperature and β phase at lower melting temperature\(^{168}\). The small peaks represent the small portion of β phase in the composite. The addition of calcium carbonate induces the formation of β phase\(^{139,134,136}\) because calcium carbonate is a very weak α nucleating agent\(^{24}\).

The first DSC scan was done after mixing and pelletizing the PP/CaCO\(_3\) composites. The β phase was formed during the mixing process of PP and CaCO\(_3\). The mixing conditions were 180°C, 60rpm and 7 minutes.

After the first DSC scan, the samples were cooled to 30°C using liquid nitrogen and then placed for the second DSC scan. It was observed that after the second scan the low temperature melting peak was not shown anymore. Also, the high temperature melting peak observed was wider than the one found after the first DSC run. A wider peak is an indication of a broader spherulite size distribution in the samples.

The reason for the disappearance of the second melting peak might be related with the β to α recrystallization. The β phase is susceptible to recrystallization only if it was cooled below the critical temperature of approx. 105°C according to studies from Varga\(^{28}\). Our samples were cooled down to 30°C, it was then expected that β-iPP would recrystallize into α-iPP.
4.2.5.1 Effect of particle size and shape of calcium carbonate

Four different particle sizes of calcium carbonate were studied: 3.2µm from ground marble and ground limestone, 1.1µm from ground limestone, 0.7µm from precipitated limestone and 0.07µm from precipitated limestone.

According to the data sheets provided by suppliers, the different types of calcium carbonate used in these experiments are rhombic calcite although calcium carbonate exhibits polymorphism (calcite-aragonite) especially when obtained by precipitation.

When the results for all types of calcium carbonate were combined, clusters of data points were observed for each particle size. The highest % crystallinity was found for PP composites filled with 0.07µm CaCO₃. The lowest % crystallinity was found for PP composites filled with 1.1µm particles and for PP composites filled with 10wt% of treated 3.2µm particles from ground limestone.

The explanation for these results might be related with the dispersion of calcium carbonate particles in the polypropylene matrix. The extent of aggregation is determined by the relative magnitude between adhesive and shear forces during compounding and it is more pronounced with decreasing particle size.

The compounding conditions are the same for the different types of calcium carbonate, thus aggregation and formation of filler structures during mixing are considered the most important influence over the %crystallinity. The 0.07µm particles have a strong tendency to agglomerate. Thio et. al. showed that a large number of agglomerates were observed for 0.07µm even at low loadings.

Previous studies by Kowalewski and Galeski showed that single small calcite particles acted as nucleation centers and that aragonite acted as nucleation centers only
when it formed large aggregates. According to this, calcite calcium carbonate particles should act as nucleation centers at lower loads when appropriately dispersed. At higher loads the calcite particles agglomerate and do not favor nucleation.

The reasons why the 1.1µm particles and the 3.2µm particles from ground limestone had the lowest % crystallinity might be related with the origin of the two calcium carbonates. Both calcium carbonates come from ground limestone. As mentioned before the particle distribution of the ground limestone is broader and a higher amount of bigger particles are present as shown in Figure 3.1. Larger calcium carbonate particles do not act as nucleation centers. Limestone is also considered less pure than marble thus the impurities present could also influence the % crystallinity.

There are certain changes in the % crystallinity between the first and second DSC scans. Sometimes % crystallinity increases and other times it decreases. The reason for this might be related with how the dispersion of particles and molecular chains rearrange when the composite was melted, crystallized and melted again.

4.2.5.2 Effect of surface treatment of calcium carbonate

Calcium carbonate particles treated with stearic acid were used in these experiments. Stearic acid is the most common treatment for commercial calcium carbonate due to reduced cost. Different amounts of stearic acid are used for each type of calcium carbonate as shown in Table 3.3. Rybnikar suggested that stearic acid surface treatment reduced the nucleation effect of calcium carbonate. McGenity et. al. showed that with addition of stearic acid the % crystallinity of 40wt% of CaCO₃ mixed with PP was not affected.
For PP composites filled with 3.2µm calcium carbonate of ground marble and ground limestone the surface treatment did not increase the %crystallinity.

For the PP composites filled with 1.1µm calcium carbonate, the largest increase of % crystallinity was found for the composite with 10wt% of calcium carbonate. No important reduction of % crystallinity was observed.

For the PP composites filled with 0.07µm calcium carbonate the largest increase of % crystallinity was found for the composite with 10wt% CaCO₃. The largest reduction in % crystallinity corresponds to the composite with 2wt% CaCO₃.

In summary, the PP composites with all three sizes of treated calcium carbonate increased their % crystallinity at 10wt% composition. For composites filled with 20wt% CaCO₃ the surface treatment did not show an important influence in the % crystallinity.

It seems there is a certain load limit after which the surface treatment will not have a clear effect increasing the % crystallinity. That limit should be above 10wt% of calcium carbonate.

4.2.5.3 Effect of composition

PP composites filled with 2wt%, 5wt%, 10wt% and 20wt% CaCO₃ were prepared for each particle size. Previous studies have found that micro CaCO₃ particles show little nucleating effect for polypropylene and that when calcium carbonate is added to polypropylene only a small fraction of the calcium carbonate particles act as nuclei\textsuperscript{39}.

In general, the smaller the average particle size will result in greater number of particles. For the same content, the number of nanoparticles of calcium carbonate is very large in comparison with micro particles. If those particles are well dispersed in the polypropylene matrix and part of them become nucleation sites, the number of spherulites
will increase dramatically and the size of the spherulites will reduce significantly\textsuperscript{134}. Greater number of well dispersed calcium carbonate would then favor the increase of \% crystallinity. However, as mentioned before, nanoparticles can at the same time favor and block crystallization\textsuperscript{167}.

Another issue to consider is that high loads of calcium carbonate can increase the melt viscosity and that the friction during mixing can remove the stearic acid treatment from the particles\textsuperscript{138}. This will result in increased interaction between the \text{CaCO}_3 particles and PP and increased nucleation effect.

In order to consider the mixing conditions influence in the crystallinity results, the values of average torque for the different composites are shown in Figure 4.31. It does not seem that the average torque could influence the \% crystallinity. The value for the average torque is very similar for the different types of calcium carbonate. The only difference is found for composites with 20wt\% \text{CaCO}_3. The highest average torque in this case corresponds to the composites filled with 0.07\textmu m non treated particles and the lowest for the composites filled with 3.2\textmu m treated particles.

4.2.6 \% Crystallinity for tensile and impact tests

Some of the injection molded samples prepared for the tensile and impact tests were analyzed to obtain \% crystallinity. The results are presented in Table 4.11. They will be used to discuss the effect of \% crystallinity on the tensile and impact properties in sections 4.5 and 4.6 respectively.
Figure 4.31 Average torque for the Brabender mixing for PP composites filled with different types of calcium carbonate

Table 4.11 % Crystallinity for tensile and impact samples from injection molding

<table>
<thead>
<tr>
<th>Surf. Treat.</th>
<th>Particle Size (µm)</th>
<th>% wt</th>
<th>% Crystallinity IMPACT</th>
<th>% Crystallinity TENSILE</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP Pellet</td>
<td></td>
<td></td>
<td>32.5</td>
<td>39.0</td>
</tr>
<tr>
<td>PP Brab.</td>
<td></td>
<td></td>
<td>35.9</td>
<td>34.4</td>
</tr>
<tr>
<td>PP Brab. Non Treated</td>
<td>0.07</td>
<td>2</td>
<td>36.0</td>
<td>43.2</td>
</tr>
<tr>
<td>PP Brab. Non Treated</td>
<td>0.07</td>
<td>5</td>
<td>36.1</td>
<td>31.0</td>
</tr>
<tr>
<td>PP Brab. Non Treated</td>
<td>0.07</td>
<td>20</td>
<td>37.8</td>
<td>33.9</td>
</tr>
<tr>
<td>PP Brab. Treated</td>
<td>0.07</td>
<td>2</td>
<td>36.2</td>
<td>39.6</td>
</tr>
<tr>
<td>PP Brab. Treated</td>
<td>0.07</td>
<td>5</td>
<td>34.6</td>
<td>40.8</td>
</tr>
<tr>
<td>PP Brab. Treated</td>
<td>0.07</td>
<td>20</td>
<td>34.3</td>
<td>38.5</td>
</tr>
<tr>
<td>PP Brab. Non Treated</td>
<td>1.1</td>
<td>5</td>
<td>35.1</td>
<td>27.0</td>
</tr>
<tr>
<td>PP Brab. Non Treated</td>
<td>1.1</td>
<td>20</td>
<td>31.5</td>
<td>37.7</td>
</tr>
<tr>
<td>PP Brab. Treated</td>
<td>1.1</td>
<td>5</td>
<td>30.7</td>
<td>33.6</td>
</tr>
<tr>
<td>PP Brab. Treated</td>
<td>1.1</td>
<td>20</td>
<td>34.5</td>
<td>34.8</td>
</tr>
<tr>
<td>PP Brab. Non Treated</td>
<td>3.2</td>
<td>5</td>
<td>33.2</td>
<td>41.1</td>
</tr>
<tr>
<td>PP Brab. Non Treated</td>
<td>3.2</td>
<td>20</td>
<td>34.2</td>
<td>34.9</td>
</tr>
<tr>
<td>PP Brab. Treated</td>
<td>3.2</td>
<td>5</td>
<td>35.5</td>
<td>33.2</td>
</tr>
<tr>
<td>PP Brab. Treated</td>
<td>3.2</td>
<td>20</td>
<td>33.7</td>
<td>36.4</td>
</tr>
</tbody>
</table>
4.3 Wide Angle X-ray diffraction

Wide angle X-ray diffraction (WAXD) was used to determine the different phases in the crystalline structure of iPP. As mentioned in the previous section two melting peaks were observed during the DSC scans for some of the PP/CaCO$_3$ composites. According to previous studies$^{26,168}$, the lower melting temperature peak corresponds to the β-phase of iPP. Using WAXD we can determine if there is a correlation between the melting peak at low temperatures and the X-ray pattern obtained.

Figure 4.33 shows a comparison between a WAXD pattern from samples of iPP with α form and a mixture of α and β forms determined by Turner and Jones$^{169}$. There are three strong α crystalline form peaks $H_\alpha(110)$, $H_\alpha(040)$, and $H_\alpha(130)$ and $H_\beta$ is the height of the β crystalline form peak (300). Turner and Jones$^{169}$ also proposed to measure the relative content of β phase based on the $k$ parameter using the equation below. The value of $k$ tends to zero when no β form is present, and to unity when α form is absent.

$$K = \frac{H_\beta}{(H_\beta + H_\alpha + H_{\alpha2} + H_{\alpha3})}$$

Some 2θ values for $\alpha_1$, $\alpha_2$ and $\alpha_3$ peaks were found by Dou and Lou$^{170}$ at 2θ = 14.1, 16.9, and 18.9° respectively and $\beta_1$ peak at 2θ =16°. Morrow et. al.$^{42}$ found a slightly different 2θ value for $\alpha_3$ at 18.6°. Figure 4.32 shows the WAXD θ scan for the α, β and γ forms of iPP. Figure 4.33 shows the WAXD θ scan for a mixture of α and β forms of iPP.
Figure 4.32 WAXD diagram for α, β and γ forms of iPP (Reproduced with permission from A. Turner-Jones, J. M. Aizlewood, D. R. Beckett, Makromolecular Chemie, 75, 134. Copyright 1964, John Wiley & Sons)

Figure 4.33 WAXS θ scan for iPP with a mixture of α and β forms (Reproduced with permission from A. Turner-Jones, J. M. Aizlewood, D. R. Beckett, Makromolecular Chemie, 75, 134. Copyright 1964, John Wiley & Sons)

4.3.1 Polypropylene

Figure 4.34 shows the WAXD scan for our sample of neat PP after mixing it using the Brabender internal mixer together with a table with the 2θ values for the strongest reflections. A very similar pattern than that of Figure 4.32 was observed for α-iPP except for the presence of a H_{β1} peak. The calculated value of k is 0.18. This value will serve as a reference to compare it with the k values found when CaCO₃ was added to
the composites. It seems interesting that even without the presence of nucleating agents the \( k \) value is relatively high. Dragaun et al.\textsuperscript{171} showed that without nucleating agents, \( \beta \)-iPP formed at shear rates higher than 300s\(^{-1}\). It seems that the mixing process reached that threshold.

![Graph showing intensity vs. 2\( \theta \)](image)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Plane</th>
<th>( \alpha )</th>
<th>( \alpha )</th>
<th>( \alpha )</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane</td>
<td>(1 0 0)</td>
<td>14.1</td>
<td>16.9</td>
<td>18.9</td>
<td>16.0</td>
</tr>
<tr>
<td>2( \theta ) from previous studies</td>
<td>(0 4 0)</td>
<td>16.9</td>
<td>18.9</td>
<td>16.0</td>
<td></td>
</tr>
<tr>
<td>2( \theta )</td>
<td>(1 3 0)</td>
<td>18.9</td>
<td>16.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2( \theta )</td>
<td>(3 0 0)</td>
<td>16.0</td>
<td>16.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( k = 0.18 \)

Figure 4.34 2\( \theta \) scan of neat PP after mixing in Brabender internal mixer

4.3.2 Polypropylene/3.2\( \mu \)m CaCO\(_3\) composites

The X-Ray diffraction results for the PP composites filled with 3.2\( \mu \)m CaCO\(_3\) particles are shown in this section.

4.3.2.1 Surface treated 3.2\( \mu \)m particles of ground marble

Figure 4.35 shows the 2\( \theta \) scan for PP filled with surface treated 3.2\( \mu \)m particles of ground marble at different compositions, the table with the 2\( \theta \) values for the intensity peaks and the \( k \) values for each composition. The 2\( \theta \) values were very similar to the ones
found by Dou and Lou\textsuperscript{170}. The intensity decreased clearly with increasing amount of CaCO\textsubscript{3} especially at 20wt%, this could be due to the decreasing amount of PP matrix and the fact that CaCO\textsubscript{3} interfered with the Xrays. Finally, the highest value for k was found for composites with 2wt% composition followed by 10wt% composition. Based on the k value, only 2wt% CaCO\textsubscript{3} seemed to have increased the β phase in the composites.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.35.png}
\caption{2θ scan for PP filled with treated 3.2μm particles of ground marble}
\end{figure}

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
Phase & Plane & α (1 0 0) & α (0 4 0) & α (1 3 0) & β (3 0 0) \\
\hline
2θ from previous studies & 14.1 & 16.9 & 18.9 & 16.0 \\
2θ & 14.1 & 16.8 & 18.6 & 16.0 \\
\hline
\end{tabular}
\end{table}

2wt% k=0.29  
5wt% k=0.16  
10wt% k=0.20  
20wt% k=0.17
4.3.2.2 Non treated 3.2µm particles of ground limestone

Figure 4.36 shows the 2θ scan for PP composites filled with surface treated 3.2µm particles of ground marble at different compositions, the 2θ values for the highest intensity peaks and the k values for each composition. The intensity for the composite with 20wt% CaCO₃ almost disappeared in comparison with the other compositions. The k values for the composites with 5wt% and 10wt% were the same and the highest was found with 2wt% CaCO₃.

<table>
<thead>
<tr>
<th>Phase</th>
<th>2θ values from previous studies</th>
<th>2θ for non treated 3.2 µm particles of ground limestone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane</td>
<td>(1 0 0)</td>
<td>(0 4 0)</td>
</tr>
<tr>
<td></td>
<td>(1 3 0)</td>
<td>(3 0 0)</td>
</tr>
<tr>
<td>2θ from previous studies</td>
<td>14.1</td>
<td>16.9</td>
</tr>
<tr>
<td>2θ</td>
<td>14.1</td>
<td>16.7</td>
</tr>
</tbody>
</table>

2wt%  k=0.23  
5wt%  k=0.20  
10wt% k=0.20  
20wt% k=0.17

Figure 4.36 2θ scan for PP filled with non treated 3.2µm particles of ground limestone
4.3.2.3 Surface treated 3.2µm particles of ground limestone

Figure 4.37 shows the 2θ scan for PP composites filled with surface treated 3.2µm particles of ground marble at different compositions, the 2θ values for the highest intensity peaks and the k values for each composition. The intensity reduced with increasing CaCO₃ composition and the highest value for k was found at 2wt% CaCO₃.

<table>
<thead>
<tr>
<th>Phase</th>
<th>α</th>
<th>α</th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane</td>
<td>(1 0 0)</td>
<td>(0 4 0)</td>
<td>(1 3 0)</td>
<td>(3 0 0)</td>
</tr>
<tr>
<td>2θ from previous studies</td>
<td>14.1</td>
<td>16.9</td>
<td>18.9</td>
<td>16.0</td>
</tr>
<tr>
<td>2θ</td>
<td>14.1</td>
<td>16.8</td>
<td>18.5</td>
<td>16.0</td>
</tr>
</tbody>
</table>

2wt% k=0.27  
5wt% k=0.23  
10wt% k=0.20  
20wt% k=0.19

Figure 4.37 2θ scan for PP filled with treated 3.2µm particles of ground limestone

4.3.3 Polypropylene/1.1µm CaCO₃ composites

The X-Ray diffraction results for the PP composites filled with 1.1µm CaCO₃ particles are shown in this section.
4.3.3.1 Non treated 1.1µm particles of ground limestone

Figure 4.38 shows the 2θ scan for PP composites at different compositions of 1.1µm CaCO$_3$, the 2θ values for the highest intensity peaks and the k values for each composition. Each intensity reduced with increasing composition but the peaks were still visible even at 20wt% CaCO$_3$. The k values were low for all compositions which suggests that this type of particle did not favor the formation of β-iPP.

<table>
<thead>
<tr>
<th>Phase</th>
<th>α</th>
<th>α</th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane</td>
<td>(1 0 0)</td>
<td>(0 4 0)</td>
<td>(1 3 0)</td>
<td>(3 0 0)</td>
</tr>
<tr>
<td>2θ from previous studies</td>
<td>14.1</td>
<td>16.9</td>
<td>18.9</td>
<td>16.0</td>
</tr>
<tr>
<td>2θ</td>
<td>14.0</td>
<td>16.8</td>
<td>18.5</td>
<td>16.0</td>
</tr>
</tbody>
</table>

2wt%  k=0.19  
5wt%  k=0.15  
10wt% k=0.19  
20wt% k=0.14

Figure 4.38 2θ scan for PP filled with non treated 1.1µm particles of ground limestone
4.3.3.2 Surf–ace treated 1.1µm particles of ground limestone

The 2θ scan for this type of CaCO$_3$ was not presented because the results were very similar to the non treated 1.1µm with very low values of k. This was also expected due to the lack of low melting peak seen in the DSC scan.

4.3.4 Polypropylene/0.07µm CaCO$_3$ composites

The X-Ray diffraction results for the PP composites filled with 0.07µm CaCO$_3$ particles are shown in this section.

4.3.4.1 Non treated 0.07µm particles of precipitated limestone

Figure 4.38 shows the 2θ scan for PP filled with different compositions of 0.07µm CaCO$_3$, the 2θ values for the highest intensity peaks and the k values for each composition. Each intensity reduced with increasing composition but the peaks were still visible even at 20wt% CaCO$_3$. The k values were low for all compositions which suggests that this type of particle did not favor the formation of β-iPP.

4.3.4.2 Surface treated 0.07µm particles of precipitated limestone

Figure 4.40 shows the 2θ scan for PP filled with different compositions of 0.07µm CaCO$_3$, the 2θ values for the highest intensity peaks and the k values for each composition. The intensity remained almost constant after increasing the composition from 2wt% to 5wt%. At the same time the k values for 2wt%, 5wt% and 10wt% were above 0.3 which suggests that this type of calcium carbonate favors the formation of β-iPP.
<table>
<thead>
<tr>
<th>Phase</th>
<th>α</th>
<th>α</th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plane</td>
<td>(1 0 0)</td>
<td>(0 4 0)</td>
<td>(1 3 0)</td>
<td>(3 0 0)</td>
</tr>
<tr>
<td>2θ from previous studies</td>
<td>14.1</td>
<td>16.9</td>
<td>18.9</td>
<td>16.0</td>
</tr>
<tr>
<td>2θ</td>
<td>14.1</td>
<td>16.9</td>
<td>18.5</td>
<td>16.1</td>
</tr>
</tbody>
</table>

2wt%  k=0.21  
5wt%  k=0.30  
10wt% k=0.13  
20wt% k=0.15  

Figure 4.39 2θ scan for PP filled with non treated 0.07µm particles from precipitated limestone
Figure 4.40 WAXS for PP mixed with treated 0.07µm particles from precipitated limestone

Table 4.12 shows a summary of the k values for the different composites together with the variation of k in comparison with the value for neat PP. There were only six composites that caused a drastic (above 50%) change in k, three of them filled with treated 0.07µm CaCO₃ particles. Five of those six composites had a composition of 2wt% and 5wt% CaCO₃. The results suggest that lower amounts of CaCO₃, especially of small particle size favor the formation of β-iPP phase.

These results agree with the k values from previous studies. Jingjiang et al.¹⁷² found values of k ranging from 0.14 to 0.37 with concentrations of wollastonite of
3.2\%\text{vol} to 17.7\%\text{vol} within a copolymer of ethylene and polypropylene. McGenity et al.\textsuperscript{110} reported \(k\) values ranging from 0.06 to 0.12 in PP filled with coated CaCO\(_3\). Lozano et. al.\textsuperscript{173} studied the effect of dispersion on the formation of \(\beta\)-iPP and obtained \(k\) values ranging from 0.06 to 0.25 for different compositions of calcium carbonate. It was suggested that good filler dispersion and high shear forces\textsuperscript{171} led to the formation of \(\beta\)-iPP and that surface treatment produced high levels of \(\beta\)-iPP even at elevated contents of CaCO\(_3\).

Table 4.12 \(k\) values and variation of \(k\) in comparison with neat PP for all PP composites

<table>
<thead>
<tr>
<th>%wt CaCO(_3)</th>
<th>(k)</th>
<th>(\Delta k(%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP after Brabender mixing</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>3.2(\mu m) Treated G-M</td>
<td>2wt%</td>
<td>0.29</td>
</tr>
<tr>
<td>5wt%</td>
<td>0.16</td>
<td>-11%</td>
</tr>
<tr>
<td>10wt%</td>
<td>0.20</td>
<td>11%</td>
</tr>
<tr>
<td>20wt%</td>
<td>0.17</td>
<td>-6%</td>
</tr>
<tr>
<td>3.2(\mu m) Non Treated G-L</td>
<td>2wt%</td>
<td>0.23</td>
</tr>
<tr>
<td>5wt%</td>
<td>0.20</td>
<td>11%</td>
</tr>
<tr>
<td>10wt%</td>
<td>0.20</td>
<td>11%</td>
</tr>
<tr>
<td>20wt%</td>
<td>0.17</td>
<td>-6%</td>
</tr>
<tr>
<td>3.2(\mu m) Treated G-L</td>
<td>2wt%</td>
<td>0.27</td>
</tr>
<tr>
<td>5wt%</td>
<td>0.23</td>
<td>28%</td>
</tr>
<tr>
<td>10wt%</td>
<td>0.20</td>
<td>11%</td>
</tr>
<tr>
<td>20wt%</td>
<td>0.19</td>
<td>6%</td>
</tr>
<tr>
<td>1.1(\mu m) Non Treated G-L</td>
<td>2wt%</td>
<td>0.19</td>
</tr>
<tr>
<td>5wt%</td>
<td>0.15</td>
<td>-17%</td>
</tr>
<tr>
<td>10wt%</td>
<td>0.19</td>
<td>6%</td>
</tr>
<tr>
<td>20wt%</td>
<td>0.14</td>
<td>-22%</td>
</tr>
<tr>
<td>0.07(\mu m) Non Treated P-L</td>
<td>2wt%</td>
<td>0.21</td>
</tr>
<tr>
<td>5wt%</td>
<td>0.30</td>
<td>67%</td>
</tr>
<tr>
<td>10wt%</td>
<td>0.32</td>
<td>78%</td>
</tr>
<tr>
<td>20wt%</td>
<td>0.21</td>
<td>17%</td>
</tr>
</tbody>
</table>
4.3.5 The k parameter for impact test samples

The same procedure was used to calculate the k parameter for the impact test samples. The results obtained will be discussed with the impact properties in section 4.6.
4.4 Particle dispersion and particle size distribution of calcium carbonate in PP/CaCO₃ composites

SEM photographs were used in order to study the particle size distribution of the calcium carbonate particles in the PP matrix.

4.4.1 Polypropylene

Figure 4.41 shows the SEM photograph of the fracture surface of the neat PP used in this study after mixed in the Brabender internal mixer. The surface was relatively smooth except for the hesitation lines generated by the procedure to obtain the fracture surface. It seems to have one smooth phase.

Figure 4.41 SEM photograph of the fractured surface of neat PP after mixed in the Brabender internal mixer

The SEM photographs for the PP composites filled with six different types of CaCO₃ were analyzed using the Image J software. The compositions selected were 5wt% and 20wt% of CaCO₃. However, for the PP composites with 0.07µm CaCO₃, it was extremely difficult to obtain a clear fracture and the compositions chosen in that case were 2wt% and 5wt%. The decision was also based on the fact that nanoparticles are rarely used at those high compositions.
In the next pages, two SEM photographs for different sections of each composite labeled (a) and (b) are presented together with their particle size distribution histogram obtained from the software analysis. These results will be used in section 4.3.5 to obtain the average particle size, % composition and a curve fit.

4.4.2 Polypropylene/3.2µm CaCO₃ composites

The SEM results for the PP composites filled with 3.2µm CaCO₃ particles are shown in this section.

4.4.2.1 Non treated 3.2µm particles of ground limestone

Figure 4.42 SEM image and particle distribution for PP filled with 5wt% of non treated 3.2µm calcium carbonate for two different sections (a) and (b)
Figure 4.43 SEM image and particle distribution for PP filled with 20wt% of non treated 3.2µm calcium carbonate for two different sections (a) and (b).

Figure 4.42 and Figure 4.43 show the SEM photograph and histograms of PP composites filled with 5wt% and 20wt% of non treated 3.2µm CaCO₃ from ground limestone respectively. It was possible to see large CaCO₃ particles and some spaces left by the particles that were pulled out when breakage occurred. The particle size distribution became broader with increasing composition of CaCO₃. The mode frequency did not increase drastically with increasing composition.
4.4.2.2 Surface treated 3.2µm particles of ground limestone

Figure 4.44 SEM image and particle distribution for PP filled with 5wt% of treated 3.2µm calcium carbonate for two different sections (a) and (b)

Figure 4.44 and Figure 4.45 show the SEM photograph and histograms of PP composites filled with 5wt% and 20wt% of treated 3.2µm CaCO₃ of ground limestone respectively. The SEM photographs in Figure 4.44 of two sections of the PP composite appeared very different, with large particles in (a) and smaller particles in (b). However, the histograms did not differ clearly except for a slightly broader distribution for the (b)
photograph. Something similar occurred with Figure 4.45, the particle distribution was very similar for both sections.

Finally, there was a large difference in the mode frequency between the two compositions. As it was expected, the number of particles increased with increasing composition.

Figure 4.45 SEM image and particle distribution for PP filled with 20wt% of treated 3.2µm calcium carbonate for two different sections (a) and (b)
4.4.3 Polypropylene/1.1\,\mu m \, \text{CaCO}_3 \, \text{composites}

The SEM results for the PP composites filled with 1.1\,\mu m \, \text{CaCO}_3 \, \text{particles} are shown in this section.

4.4.3.1 Non treated 1.1\,\mu m \, \text{particles} \, \text{of} \, \text{ground limestone}

(a)
(b)

Figure 4.46 SEM image and particle distribution for PP filled with 5wt\% of non treated 1.1\,\mu m \, \text{calcium carbonate} \, \text{for} \, \text{two} \, \text{different} \, \text{sections} \, \text{(a) \, and} \, \text{(b)}

Figure 4.46 and Figure 4.47 show the SEM photograph and histograms of PP composites filled with 5wt\% and 20wt\% of non treated 1.1\,\mu m \, \text{CaCO}_3 \, \text{from} \, \text{ground limestone} \, \text{respectively}. \, \text{The} \, \text{SEM} \, \text{photographs} \, \text{of} \, \text{the} \, \text{two} \, \text{sections} \, \text{(a) \, and} \, \text{(b)} \, \text{for} \, \text{both}
compositions are very similar. On the other hand, the particle distribution and especially the frequency modes show a clear variation even for the two sections of same composition. This variation could indicate the difficulty to achieve good dispersion with these particles.

Figure 4.47 SEM image and particle distribution for PP filled with 20wt% of non treated 1.1µm calcium carbonate for two different sections (a) and (b)
4.4.3.2 Surface treated 1.1µm particles of ground limestone

Figure 4.48 SEM image and particle distribution for PP filled with 5wt% of treated 1.1µm calcium carbonate for two different sections (a) and (b).

Figure 4.48 and Figure 4.49 show the SEM photograph and histograms of PP composites filled with 5wt% and 20wt% of treated 1.1µm CaCO$_3$ from ground limestone respectively. Sections (a) and (b) of Figure 4.48 showed some agglomerates but their particle size distribution was very similar. The SEM photographs in Figure 4.49, for the composite with 20wt% composition, showed some large particles. The mode frequency...
found in the particle size distribution for the two sections (a) and (b) was clearly different.

The similar particle distribution for different sections at 5wt% composition supports the idea that surface treated particles improve dispersion at low composition. However, when 20wt% of CaCO$_3$ was added to PP, the surface treatment did not improve dispersion which was shown with the different particle size distributions for different sections at that composition.

Figure 4.49 SEM image and particle distribution for PP filled with 20wt% of treated 1.1µm calcium carbonate for two different sections (a) and (b)
4.4.4 Polypropylene/0.07µm CaCO₃ composites

The SEM results of the PP composites filled with 0.07µm CaCO₃ particles are shown in this section.

4.4.4.1 Non treated 0.07µm particles of precipitated limestone

![SEM image and particle distribution for PP filled with 2wt% of non treated 0.07µm calcium carbonate for two different sections (a) and (b)](image)

Figure 4.50 SEM image and particle distribution for PP filled with 2wt% of non treated 0.07µm calcium carbonate for two different sections (a) and (b)

Figure 4.50 and Figure 4.51 show the SEM photographs and histograms of PP composites filled with 5wt% and 20wt% of treated 0.07µm CaCO₃ of precipitated limestone respectively. All the SEM photographs showed agglomerates. A few
agglomerates of very similar size were observed for the composites with 2wt% composition. Less number of agglomerates were observed for the composites with 5wt%, however the size of those agglomerates were clearly larger than the ones for the composites with 2wt% CaCO₃.

The particle size distribution was similar for the same composition. There was a clear increase in the frequency of the mode with increasing composition but as it was expected, the variation was small compared with the variation observed with increasing composition from 5wt% to 20wt%.

Figure 4.51 SEM image and particle distribution for PP filled with 5wt% of non treated 0.07µm calcium carbonate for two different sections (a) and (b)
4.4.4.2 Surface treated 0.07µm particles of precipitated limestone

Figure 4.52 SEM image and particle distribution for PP filled with 2wt% of treated 0.07µm calcium carbonate for two different sections (a) and (b)

Figure 4.52 and Figure 4.53 show the SEM photographs and histograms of PP composites filled with 5wt% and 20wt% of treated 0.07µm CaCO₃ from precipitated limestone respectively. All the SEM photographs showed agglomerates and uneven distribution of the particles for the same composition. The same observation was obtained from the particle size distributions. For the same composition, the particle size distribution of the two sections (a) and (b) are very different in shape and mode

155
frequency. Comparing the particle size distribution for non treated and treated particles, it was observed that the frequency clearly increased.

![Graphs showing particle distribution](image)

Figure 4.53 SEM image and particle distribution for PP filled with 5wt% of treated 0.07µm calcium carbonate for two different sections (a) and (b)

After obtaining these results, a Gamma Variate function was used to fit the particle distribution histograms. The equation for the Gamma Variate is:

\[
y = a \times (x - b)^c \times \exp\left(-\frac{x - b}{d}\right)
\]

where \(x \geq b\) and \(a, c\) and \(d\) are parameters that describe the shape of the function.
Table 4.13 Particle size average, median and mode and $R^2$ and Standard deviation from the Gamma Variate fit

<table>
<thead>
<tr>
<th>wt%</th>
<th>Area%</th>
<th>Particle size (µm)</th>
<th>Gamma Variate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Average</td>
<td>Median</td>
</tr>
<tr>
<td>Q3</td>
<td>3.2µm Non Treated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>6.6%</td>
<td>0.900</td>
<td>0.650</td>
</tr>
<tr>
<td>5%</td>
<td>6.0%</td>
<td>0.740</td>
<td>0.500</td>
</tr>
<tr>
<td></td>
<td>6.3%</td>
<td>0.820</td>
<td>0.575</td>
</tr>
<tr>
<td>20%</td>
<td>10.4%</td>
<td>1.000</td>
<td>0.750</td>
</tr>
<tr>
<td>20%</td>
<td>20.3%</td>
<td>1.170</td>
<td>0.900</td>
</tr>
<tr>
<td></td>
<td>15.4%</td>
<td>1.085</td>
<td>0.825</td>
</tr>
<tr>
<td>Q3T</td>
<td>3.2µm Treated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>11.2%</td>
<td>0.990</td>
<td>0.500</td>
</tr>
<tr>
<td>5%</td>
<td>2.7%</td>
<td>0.590</td>
<td>0.550</td>
</tr>
<tr>
<td></td>
<td>7.0%</td>
<td>0.745</td>
<td>0.525</td>
</tr>
<tr>
<td>20%</td>
<td>8.6%</td>
<td>0.610</td>
<td>0.500</td>
</tr>
<tr>
<td>20%</td>
<td>14.4%</td>
<td>0.610</td>
<td>0.450</td>
</tr>
<tr>
<td></td>
<td>11.5%</td>
<td>0.610</td>
<td>0.475</td>
</tr>
<tr>
<td>Q1</td>
<td>1.1µm Non Treated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>6.1%</td>
<td>0.700</td>
<td>0.600</td>
</tr>
<tr>
<td>5%</td>
<td>3.3%</td>
<td>0.470</td>
<td>0.400</td>
</tr>
<tr>
<td></td>
<td>4.7%</td>
<td>0.585</td>
<td>0.500</td>
</tr>
<tr>
<td>20%</td>
<td>9.0%</td>
<td>0.650</td>
<td>0.550</td>
</tr>
<tr>
<td>20%</td>
<td>9.7%</td>
<td>0.550</td>
<td>0.450</td>
</tr>
<tr>
<td></td>
<td>9.4%</td>
<td>0.600</td>
<td>0.500</td>
</tr>
<tr>
<td>Q1T</td>
<td>1.1µm Treated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>6.0%</td>
<td>0.700</td>
<td>0.650</td>
</tr>
<tr>
<td>5%</td>
<td>7.5%</td>
<td>0.720</td>
<td>0.650</td>
</tr>
<tr>
<td></td>
<td>6.8%</td>
<td>0.710</td>
<td>0.650</td>
</tr>
<tr>
<td>20%</td>
<td>8.9%</td>
<td>0.530</td>
<td>0.450</td>
</tr>
<tr>
<td>20%</td>
<td>17.5%</td>
<td>0.560</td>
<td>0.450</td>
</tr>
<tr>
<td></td>
<td>13.2%</td>
<td>0.545</td>
<td>0.450</td>
</tr>
<tr>
<td>MF</td>
<td>0.07µm Non Treated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2%</td>
<td>1.4%</td>
<td>0.290</td>
<td>0.250</td>
</tr>
<tr>
<td>2%</td>
<td>2.4%</td>
<td>0.330</td>
<td>0.300</td>
</tr>
<tr>
<td></td>
<td>1.9%</td>
<td>0.310</td>
<td>0.275</td>
</tr>
<tr>
<td>5%</td>
<td>2.9%</td>
<td>0.340</td>
<td>0.350</td>
</tr>
<tr>
<td>5%</td>
<td>2.3%</td>
<td>0.340</td>
<td>0.350</td>
</tr>
<tr>
<td></td>
<td>2.6%</td>
<td>0.340</td>
<td>0.350</td>
</tr>
<tr>
<td>UF</td>
<td>0.07µm Treated</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2%</td>
<td>1.9%</td>
<td>0.310</td>
<td>0.300</td>
</tr>
<tr>
<td>2%</td>
<td>4.3%</td>
<td>0.390</td>
<td>0.400</td>
</tr>
<tr>
<td></td>
<td>3.1%</td>
<td>0.350</td>
<td>0.350</td>
</tr>
<tr>
<td>5%</td>
<td>3.1%</td>
<td>0.280</td>
<td>0.300</td>
</tr>
<tr>
<td>5%</td>
<td>4.6%</td>
<td>0.370</td>
<td>0.300</td>
</tr>
<tr>
<td></td>
<td>3.9%</td>
<td>0.325</td>
<td>0.300</td>
</tr>
</tbody>
</table>
The results are presented in Table 4.13 for all PP composites together with the average particle size and other parameters for each composite. The first column in Table 4.13, from the left to the right shows Wt%, the amount of CaCO$_3$ that was added to PP during mixing, either 2wt%, 5wt% or 20wt%. The second column shows the Area%, which is the percentage of area occupied by CaCO$_3$ in the images after analyzing them using the Image J software.

There were a few cases where the Area% was very similar to the Wt% which demonstrated how difficult is to obtain a perfect correlation between the amount of CaCO$_3$ added to PP and the one found using the image analysis. The Area% result was probably influenced by the image analysis. No particles on the borders were included on the analysis because it was not possible to know the real size of those particles.

![Graph](image.png)

**Figure 4.54** Comparison between the amount of CaCO$_3$ added to PP and the value found using SEM image analysis
Figure 4.54 compares Wt% and Area%. The dashed line represents the linear correlation. It is observed that the higher the composition of CaCO₃ the larger the difference between these two values.

The next three columns in Table 4.13 show the average, median and mode particle size found for the different composites. The median is the most common parameter to address particle size. The average particle size presented in the CaCO₃ datasheets corresponds to the median of the particles distribution. Figure 4.55 shows the resultant average particle size after mixing vs. the original average particle size from the CaCO₃ datasheets.

![Graph showing median particle size from image analysis vs. the median particle size from the datasheet](image)

For the composites filled with non treated and treated 0.07µm CaCO₃ particles at two different compositions 2wt% and 5wt%. Increasing composition from 2wt% to 5wt%
increased the average particle size for non treated particles and reduced it for treated particles. At 2wt% CaCO$_3$ non treated particles had a lower particle size of 0.28µm compared with 0.35µm for treated particles. At 5wt% CaCO$_3$ the opposite occurred, average particle size was 0.35µm for non treated and 0.3µm for treated particles. There was no clear effect of surface treatment for the 2wt% and 5wt% compositions. However, it can be suggested that at 5wt% composition the surface treatment helped to reduce the final average particle size.

If the particle distributions of treated and non treated particles are compared, it was observed that the number of particles found (frequency) increased up to 50% for treated particles at 5wt% and up to 30% for treated particles at 2wt%. This could be an indication of improved particle dispersion for treated particles.

For composites filled with non treated and treated 1.1µm CaCO$_3$ at 5wt% and 20wt%. Increasing composition did not change the average particle size for non treated particles but reduced it for treated particles. At 5wt%, non treated particles had a lower average particle size of (0.5µm) than treated particles (0.65µm). At 20wt% composition, PP composites with treated particles had a lower average particle size (0.45µm) compared with 0.5µm for composites with non treated particles. Again, it seemed that surface treatment helped to reduce the average particle size when increasing the composition of CaCO$_3$ to 20wt%.

The frequency of the particle size distribution for non treated particles decreased up to 30% at 5wt% composition and increased up to 37% at 20wt% composition.

For composites filled with non treated and treated 3.2µm CaCO$_3$ at 5wt% and 20wt%. It was observed that increasing composition increased the average particle size
for non treated particles and decreased it for treated particles. At 5wt% and 20wt% compositions, treated particles had a lower average particle size. The surface treatment reduced the average particle size at higher compositions.

The frequency of the particle distributions remained the same at 5w% but increased three times at 20wt% composition. The latter can suggest improved particle dispersion.

The effect of increasing particle size can be observed for the PP composites filled with 5wt% CaCO$_3$. For non treated particles at this composition, the average particle size obtained after mixing increased with increasing datasheet particle size from 0.35µm to 0.58µm. For treated particles it increased from 0.3µm to 0.65µm and then reduced to 0.53µm for the 3.2µm particles. At 20wt% composition, non treated and treated particles increased the average particle size obtained with increasing datasheet particle size.

It was observed that the PP composites with 0.07µm, 1.1µm and 3.2µm have a very similar average particle size after mixing for the same SEM augmentation. This may be due to the increased shear that 1.1µm and 3.2µm particles can cause during mixing resulting in further reduction of their original particle size. On the other hand, the composites filled with 0.07µm particles have a calculated average particle size between 0.25µm and 0.30µm, around four times their original value found in the datasheets. This suggests that these particles are agglomerating.

After obtaining the histograms showed previously, it was tried to fit them using a mathematical function. The Image J software allows the curve fit using different functions including polynomial, exponential, power, logarithmic, rodbard, Gaussian and
gamma variate. After trying all the different possibilities, the gamma variate function was clearly the best fit. The results for $R^2$ and standard deviation are showed in Table 4.13.

Figure 4.56 shows the variation of the correlation coefficient $R^2$ with average particle size from the datasheets. Higher $R^2$ indicates better curve fit. For PP composites filled with 0.07 particles at 2wt% and 5wt%, increasing composition improved the curve fit for treated particles but reduced it for non-treated particles. At 2wt% composition non-treated particles have a better fit. At 5wt% composition treated particles have a better fit.

For PP composites filled with 1.1µm at 5wt% and 20wt%, increasing composition improved the curve fit for non-treated but especially for treated particles. At 5wt% composition non-treated particles have a better fit and at 20wt% composition treated particles have a better curve fit.

![Figure 4.56](image)

Figure 4.56 $R^2$ calculated from the Gamma Variate
For PP composites filled with 3.2µm at 5wt% and 20wt%, increasing composition decreased the curve fit for non treated particles. Increasing composition did not have effect on the curve fit for treated particles.

It was observed that at 5wt% composition, the $R^2$ value for PP composites filled with non treated particles decreased with increasing particle size. For PP filled with treated particles, $R^2$ decreased with increasing particle size from 0.07µm to 1.1µm and then increased with 3.2µm particles.

$R^2$ decreased with increasing particle size for composites with 20wt% composition for treated and non treated particles. In general it was observed that the curve fit was better with the smallest particle size.
4.5 Tensile properties of PP/CaCO₃ composites

The tensile test results for the PP/CaCO₃ composites filled with different types of calcium carbonate are presented in this section. All the samples were first injection molded using the mini injection molder machine, and then, deflashed when necessary. The Instron tensile tester was used, with 12mm/min of cross head speed.

4.5.1 Polypropylene

Table 4.14 shows the results for tensile properties for neat polypropylene. The first group of samples was molded from PP pellets and the second from grinded PP after mixing it in the Brabender internal mixer. The data obtained from the tensile tester was analyzed to obtain the elastic modulus, tensile strength at yield and elongation at break. There was no significant difference in tensile strength and elastic modulus for PP from pellets and from the Brabender but the % elongation at break for PP after mixed in the Brabender was almost twice the value found for PP pellets.

Table 4.14 PP tensile properties from pellets and after mixed in the Brabender

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile strength at yield (MPa)</th>
<th>Modulus of elasticity (MPa)</th>
<th>% Elongation at break</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP Pellet</td>
<td>38.8</td>
<td>759</td>
<td>357</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>1.1</td>
<td>38.4</td>
<td>269</td>
</tr>
<tr>
<td>PP Brabender</td>
<td>37.8</td>
<td>767</td>
<td>765</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>1.2</td>
<td>30.8</td>
<td>337</td>
</tr>
</tbody>
</table>

4.5.2 Polypropylene/3.2µm CaCO₃ composites

The tensile properties for the PP composites filled with 3.2µm CaCO₃ particles are shown in this section.
4.5.2.1 Non treated and surface treated 3.2µm particles of ground marble

Figure 4.52 (a) shows the tensile strength as a function of calcium carbonate load for 3.2µm treated and non treated particles from ground marble. The tensile strength values for composites with treated and non treated particles were very similar and they decreased with increasing amount of calcium carbonate. The error bars and the standard deviation were also depicted on the graph, as seen, the error is very small. In the same graph the values for neat PP are shown. The tensile strength of the composites at low calcium carbonate was very similar to that of neat PP.

Figure 4.52 (b) shows the elastic modulus as a function of calcium carbonate load. A similar behavior for the composites filled with treated and non treated particles was observed except for the composites with 2wt% composition for which composites with

Figure 4.57 Tensile properties vs. CaCO₃ (wt %) for PP composites filled with 3.2µm particles of ground marble: (a) Tensile strength, (b) Elastic modulus
non treated particles had a higher value for modulus. The modulus for composites with both treated and non treated particles seemed to increase with increasing composition of filler. The error bar shown in this graph is also very small. Finally, in comparison with that of neat PP, higher values for the PP/CaCO$_3$ composites were observed.

Figure 4.53 shows the % elongation at break as a function of calcium carbonate compositions. The behavior for the PP composites filled with treated and non treated particles differed especially at 5wt% and 10wt% CaCO$_3$ compositions. The % elongation at break seemed to decrease with increasing filler composition. In general, there was a very high error bar.

![Figure 4.58](image)

Figure 4.58 % Elongation at break vs. CaCO$_3$ (wt %) of 3.2µm particles from ground marble
4.5.2.2 Non treated and surface treated 3.2µm particles of ground limestone

Figure 4.59 (a) shows the tensile strength as a function of calcium carbonate composition. The behavior for the PP composites filled with treated and non treated particles was very similar, they both decreased with increasing filler load. At 2wt% composition, both composites had similar tensile strength than that of neat PP. The error bar was again very small.

Figure 4.59 (b) shows the elastic modulus. It was observed that increasing the filler compositions did not change the elastic modulus in great manner. The modulus was slightly higher than for neat PP. The error bar was small.

Figure 4.59 Tensile properties vs. CaCO₃ (wt %) for PP composites filled with 3.2µm particles of ground marble: (a) Tensile strength, (b) Elastic modulus
Figure 4.60 shows the % elongation at break for different compositions. It was observed that for the PP composites filled with both treated and non treated particles the addition of filler did not change the % elongation at break in great manner. There was a very high error bar observed.

Figure 4.60 % Elongation at break vs. CaCO$_3$ (wt %) for 3.2µm particles from ground limestone

4.5.3 Polypropylene/1.1µm and Polypropylene/0.7µm CaCO$_3$ composites

The tensile properties for the PP composites filled with 1.1µm and 0.7µm CaCO$_3$ particles are shown in this section.

4.5.3.1 Non treated and treated 1.1µm particles of ground limestone

Figure 4.61 (a) shows the tensile strength for PP composites filled with 1.1µm treated and non treated particles. The results obtained for both fillers were similar, tensile
strength decreased with increasing filler composition. PP composites filled with non treated particles had a slight higher tensile strength for all loads. The error bar was very low. The tensile strength for composites filled with 5wt% of CaCO$_3$ and above was lower than that of neat PP.

Figure 4.61 (b) shows the elastic modulus as a function of filler composition. Increasing amount of treated particles did not increase the elastic modulus further than the value found for neat PP. PP composites filled with non treated particles reached higher elastic modulus than neat PP for 10wt% and 20wt% compositions.

Figure 4.61 Tensile properties vs. CaCO$_3$ (wt %) for PP composites filled with 1.1µm particles of ground marble: (a) Tensile strength, (b) Elastic modulus

Figure 4.62 shows the elongation at break as a function of filler composition. Surprisingly both treated and non treated particles increased their % elongation at break
up to 10wt% load and then clearly reduced it for 20wt% load. This behavior may be related with the increasing shear obtained with increasing amount of CaCO₃. Higher shear improves dispersion and as a result the mechanical properties of the composites. The error bar for elongation at break was very high.

![Elongation at break vs. CaCO₃ (wt %) for 1.1µm particles from ground limestone](image)

Figure 4.62 %Elongation at break vs. CaCO₃ (wt %) for 1.1µm particles from ground limestone

4.5.3.2 Surface treated 0.7µm particles of precipitated limestone

Figure 4.63 (a) shows the tensile strength for PP composites filled with 0.7µm particles as a function of filler load. There was a reduction in tensile strength with increasing amount of calcium carbonate. The error bar was larger than that of the PP composites filled with previous types of calcium carbonate.
Figure 4.63 Tensile properties vs. CaCO$_3$ (wt %) for PP composites filled with 0.7µm particles of ground marble: (a) Tensile strength, (b) Elastic modulus

Figure 4.64 %Elongation at break vs. CaCO$_3$ (wt %) for 0.7µm particles from precipitated limestone
Figure 4.63 (b) shows the elastic modulus of the composites. There was an increase of modulus with increasing composition of CaCO$_3$ from 2wt% to 5wt%. Above that composition the elastic modulus remained the same.

Figure 4.64 shows the % elongation at break for the composites. It was observed that the % elongation at break remains almost constant for 2wt% and 5wt% compositions and increased with 10wt% and especially for 20wt% CaCO$_3$. The error bar was still very high.

4.5.4 Polypropylene/0.07µm CaCO$_3$ composites

The tensile properties for the PP composites filled with 0.07µm CaCO$_3$ particles of are shown in this section.

4.5.4.1 Non treated and treated 0.07µm particles of precipitated limestone

Figure 4.65 (a) shows the tensile strength for the PP composites with treated and non treated 0.07µm particles. The tensile strength decreased with increasing amount of calcium carbonate. It was observed that at 2wt% composition, the tensile strength for the composite with treated and non treated particles was higher than of neat PP. The error bar was very small.

Figure 4.65 (b) shows the elastic modulus. The PP composites filled with both treated and non treated particles improved the elastic modulus with increasing amount of CaCO$_3$ but the best results were obtained with treated particles. The error bar was small.

Figure 4.66 shows the % elongation at break for the PP composites. There was a general decrease of elongation at break with increasing filler load. PP composites filled with treated and non treated particles differed clearly at 2wt% and 5wt% compositions but behaved similarly at 10wt% and 20wt% compositions. The error bar was very high.
Figure 4.65 Tensile properties vs. CaCO$_3$ (wt %) for PP composites filled with 0.07µm particles of ground marble: (a) Tensile strength, (b) Elastic modulus

Figure 4.66 %Elongation at break vs. CaCO$_3$ (wt %) for 0.07µm particles
4.5.5 Effect of calcium carbonate on the tensile properties of PP/CaCO₃ composites

As mentioned before, the addition of rigid filler particles like calcium carbonate increases the modulus of polypropylene especially when there is good adhesion or even with poor adhesion when different thermal coefficients impose a squeezing force on the filler¹¹². Yield stress is reduced with addition of fillers because the rigid particles reduce the matrix section and facilitate failure at lower external load⁷¹. Elongation at break reduces drastically with addition of calcium carbonate because all deformation comes from the polypropylene matrix⁶².

Treatment of calcium carbonate particles improves dispersion but also decreases matrix-polymer interaction which results in decreased yield stress and strength and improved deformability⁷¹. The tendency for agglomeration is more pronounced with decreasing particle size because of the high surface energy of very small particles which can be reduced by surface treatments¹³⁷. The advantage of nanofillers can only be exploited if particles are distributed homogeneously in the matrix¹⁴⁴.

The tensile strength and elastic modulus results for the PP composites are shown together in Figure 4.67 (a) and (b) respectively. The highest tensile strength, roughly 40MPa and only 5% higher than that of neat PP, was found for the PP nanocomposites filled with 0.07µm particles at 2wt% and 5wt%. The lowest tensile strength, 20% lower than that of neat PP, was observed for the PP composites filled with 3.2µm particles from ground limestone at 20wt% composition.

The highest elastic modulus, up to 30% higher than that of neat PP, was obtained for PP nanocomposites filled with 0.07µm particles, especially with treated calcium carbonate. The second best results were found for the PP composites filled with 3.2µm
particles. As seen in the graph, several PP composites had elastic modulus similar than that of neat PP. The lowest elastic modulus was 5% lower than neat PP.

The % elongation at break results are shown in Figure 4.68. In general there was a reduction of % elongation at break with increasing filler composition. The lowest % elongation at break was found for the PP composites filled with 0.7µm and 3.2µm particles from ground limestone.
Figure 4.67 Tensile properties vs. CaCO₃ median particle size (a) Tensile Strength, (b) Elastic modulus
Figure 4.68 %Elongation at break vs. CaCO₃ median particle size
4.5.5.1 Effect of the particle size of calcium carbonate

The results for the modulus showed a clear increase of modulus with reduction of particle size from 3.2µm to 0.07µm. These results agree with previous studies made by Kawasaki et. al.\textsuperscript{121}. The reason why the 1.1µm and 0.7µm particles showed lower modulus than the 3.2µm might be related with the mixing process and with the effect of the different particle sizes creating shear during mixing. The different origins of the calcium carbonate, marble or limestone and the manufacturing process ground or precipitated calcium carbonate did not seem to affect the modulus of the composites.

The values obtained for tensile strength at yield in Figure 4.17 showed the same tendency than modulus. The main difference was the lower difference in values between neat PP and the PP/CaCO\textsubscript{3} composites. Also the 1.1µm and 0.7µm, calcium carbonate particles added to PP seemed to perform better for tensile strength than for modulus. In general, tensile strength did not vary in great manner with particle size but it was clear that the best results were obtained when 0.07µm particles were added to PP especially at low composition.

Finally, particle size did not seem to play an important role in the variation of % elongation at break. The four particle sizes seem to behave the same way, all of them showed a wide range of values and very high error bars.

4.5.5.2 Effect of the surface treatment of calcium carbonate

The influence of surface treatment on the modulus and tensile strength was previously shown for each type of calcium carbonate.

According to those results, the influence of surface treatment on the modulus of the PP composites differed depending on the type of calcium carbonate. For the 0.07µm
particles, surface treatment seemed favorable and increased the elastic modulus of the composites up to 10% with 20wt% of calcium carbonate.

In the case of 1.1µm and 3.2µm particles, surface treatment did not seem to improve modulus. It actually decreased it slightly in most of the cases and down to 10% with 10wt% calcium carbonate for 1.1µm particles. This behavior may be related with reduced filler-PP interaction due to addition of stearic acid or due to the large shear produced with larger particles that removed the surface treatment.

In conclusion, surface treatment is beneficial for the elastic modulus only for the PP composites filled with 0.07µm particles, it seemed to reduce particle agglomeration and improve dispersion.

Tensile strength did not seem to be influenced by surface treatment. The only important reduction in tensile strength is produced with 10wt% for 1.1µm particles.

4.5.5.3 Effect of composition

The elastic modulus as expected improved with increasing composition of calcium carbonate. Modulus is measured at very low load and strain. Despite the poor adhesion between the filler and the polypropylene matrix, low loads are not enough to cause debonding, the different thermal coefficients from polypropylene and calcium carbonate allow the particles to be trapped and support load without debonding increasing the modulus.

Tensile strength at yield reduced with increased load of calcium carbonate. Yield is measured at higher loads and strain. High loads and strains produce debonding of the particles from the polypropylene matrix reducing the tensile strength.
Finally, as expected, there was a reduction of % elongation at break with increasing amount of calcium carbonate.

4.5.5.4 Effect of the %crystallinity

The % crystallinity calculated from the DSC scans for the tensile test samples was compared with the tensile properties obtained after tensile testing.

Figure 4.69 shows the tensile strength as a function of % crystallinity. The best results were obtained for PP composites filled with 0.07µm non treated particles at 43% crystallinity. It was observed that the maximum values for tensile strength were found above 38% crystallinity for PP nanocomposites.

Figure 4.70 shows the elastic modulus as a function of % crystallinity. The best results were obtained with approximately 40% crystallinity for PP composites with 0.07µm particles, treated and non treated. The highest elastic modulus was found with 39% crystallinity for PP nanocomposites with 20wt% of treated particles.

Figure 4.71 shows the % elongation at break as a function of % crystallinity. The best results were obtained for PP nanocomposites filled with 0.07µm particles at 2wt% and 5wt% compositions.

In general, the best results for tensile strength and elastic modulus were found for high values of crystallinity.

These results agree with the previous studies. The influence of % crystallinity on modulus and tensile strength is related with the failure mechanism of polypropylene. At low strains, characteristic of modulus and tensile strength, the crystallites serve as cross links holding the material together but once higher strain are reached, these crystallites
start to deform and finally fail\textsuperscript{57,58,59,60}. Crystallinity should increase the stiffness and as a result the tensile strength and elastic modulus of the PP composites.

The \% elongation at break in Figure 4.71 shows values dispersed broadly in both axis. It was difficult to obtain a relation between \% crystallinity and higher \% elongation at break.
Figure 4.69 Tensile strength vs. % crystallinity
Figure 4.70 Elastic modulus vs. % crystallinity
Figure 4.71 %Elongation at break vs. % crystallinity
4.5.6 Comparison of the elastic modulus results with semi empirical models

An attempt was made to compare the results obtained for the elastic modulus with two of the semi empirical models used to predict this property\textsuperscript{174}. As shown in Figure 4.72, the results agree with the model predictions. One of the reasons for this good fit is that both models predict values based on filler volume fraction. It was not possible to go further than 0.08 volume fraction for these experiments. However, it was observed that the PP composites filled with 0.07µm particles showed higher elastic modulus than that of the model predictions and that the composites filled with 1.1µm particles had lower elastic modulus than the ones calculated with the models.

![Figure 4.72 Comparison of elastic modulus results with the Chantler and Halpin Tsai models](image-url)
4.6 Impact properties of PP/CaCO$_3$ composites

The impact test results for the PP/CaCO$_3$ composites filled with different types of calcium carbonate are presented in this section. The samples were injection molded using the mini injection molder machine, then deflashed and finally notched using the tmi notching machine. The samples were tested using the tmi impact tester with the 2lb load.

4.6.1 Polypropylene

Table 4.15 shows the impact resistance for polypropylene injected directly from pellets and for polypropylene injected after mixing it in the Brabender internal mixer. It was observed that the impact resistance for both samples was very similar.

Table 4.15 Polypropylene’s impact resistance

<table>
<thead>
<tr>
<th></th>
<th>Breaking Energy (ft lb)</th>
<th>Breaking Energy (J)</th>
<th>Impact resistance (ft lb/in)</th>
<th>Impact resistance (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP Pellets</td>
<td>0.063</td>
<td>0.086</td>
<td>0.796</td>
<td>42.5</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.010</td>
<td>0.014</td>
<td>0.123</td>
<td>6.6</td>
</tr>
<tr>
<td>PP Brabender</td>
<td>0.065</td>
<td>0.088</td>
<td>0.817</td>
<td>43.6</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.006</td>
<td>0.008</td>
<td>0.067</td>
<td>3.6</td>
</tr>
</tbody>
</table>

4.6.2 Polypropylene/3.2µm CaCO$_3$ composites

Figure 4.73 shows the impact resistance of PP composites filled with treated and non treated 3.2µm particles of ground limestone. The highest impact resistance was found for the PP composites filled with 2wt% of treated particles and 5wt% of non treated particles. At 20wt% composition, the composites filled with treated particles clearly had higher impact strength. The error bar was high. For PP composites filled with both treated and non treated particles at different loads, the impact resistance was up to 70% higher than that of neat PP.
Figure 4.73 Impact strength for PP composites filled with 3.2µm particles of ground limestone

4.6.3 Polypropylene/1.1µm CaCO₃ composites

Figure 4.74 shows the impact resistance for PP composites filled with treated and non treated 1.1µm particles. There was a clear difference in impact resistance especially for composites filled with treated particles. At high filler compositions, the impact resistance for non treated particles was similar to that of neat PP. Treated particles improved impact resistance by almost 75% compared with neat PP. The error bar was high.
4.6.4 Polypropylene/0.07μm CaCO₃ composites

Figure 4.75 shows the impact resistance for PP composites filled with treated and non treated 0.07μm particles. The impact resistance for the PP composites filled with treated particles was clearly higher than the PP composites filled with non treated particles. Treated particles improved the impact strength up to 43%.

It was observed that increasing the composition of filler reduced the impact strength, especially for treated particles. The impact strength reached the value for neat
PP at 20wt% composition of treated particles and at 10wt% composition of non treated particles. Non treated particles only enhanced the impact strength at 2wt% composition.

![Figure 4.75 Impact strength for PP composites filled with 0.07µm particles](image)

**Figure 4.75 Impact strength for PP composites filled with 0.07µm particles**

4.6.5 Effect of calcium carbonate on the impact properties of PP/CaCO₃ composites

The main factors that contribute to impact properties for polypropylene filled with calcium carbonate include good filler dispersion, the ability of calcium carbonate to block cracks and particle debonding.¹¹⁶ The latter is especially important for nanoparticles. Debonding followed by massive plastic deformation seem responsible for the great
improvements in impact strength found for nanocomposites\textsuperscript{134,136}. In addition to those factors, presence of β-iPP should improve impact strength. The impact strength and toughness exceeds those of α-iPP\textsuperscript{36,37}. The formation of small quantities of β-iPP has been shown previously with the DSC and X ray experiments.

4.6.5.1 Effect of the particle size of calcium carbonate

Figure 4.76 (a) and (b) shows the impact strength vs. calcium carbonate particle size. According to these results the impact strength of the PP composites decreased with decreasing particle size due to agglomeration, especially for the composites filled non treated 0.07µm calcium carbonate. Besides dispersion, the reason for that behavior, may be the presence of two different mechanisms to avoid fracture. The larger 3.2µm particles were probably more effective blocking cracks and the 0.07µm particles producing debonding together with massive crazing. Agglomerates of nanoparticles reduce the later mechanism and the impact strength of the PP composites. It seemed that blocking cracks was more effective in improving impact strength for these composites.

4.6.5.2 Effect of the surface treatment of calcium carbonate

The impact strength of the PP composites can be compared based on surface treatment. It was clear from Figure 4.76 that surface treatment improved the impact strength for the three particle sizes used in these experiments, especially for the PP composites filled with 0.07µm and 1.1µm particles. For these two particle sizes, surface treatment may improve dispersion and prevent agglomeration. In the case of 0.07µm particles, surface treatment seem to have favored debonding, massive crazing and plastic deformation which improved impact strength.
Figure 4.76 Impact resistance vs. median particle size of calcium carbonate for PP composites filled with (a) non treated and (b) treated particles.
Surface treatment did not seem to have an important effect on PP composites filled with 3.2µm particles. It seemed agglomeration of 3.2µm particles is less frequent. However it could also mean that the surface treatment was not enough to be effective or perhaps due to the high shear produced during mixing the surface treatment was removed from the particles and it was no longer effective.

4.6.5.3 Effect of composition

The effect of composition was shown in graphs previously for the composites with different types of calcium carbonate. It was observed that impact strength of the PP composites seemed to decrease with increasing composition of CaCO₃. However the PP composites showed higher impact strength than that of neat PP for most of the types of calcium carbonate at different compositions. From Figure 4.76 it was observed that the lowest impact strength was found for PP composites filled with 20wt% of non treated 0.07µm CaCO₃.

4.6.5.4 Effect of % crystallinity

Higher crystallinity increases stiffness (modulus and yield strength) but also reduces elongation to break which results in toughness reduction. Figure 4.77 shows the impact strength of the PP composites as a function of % crystallinity obtained from injection molded samples using DSC. It was observed that the highest impact strength is obtained with 30% crystallinity. The highest % crystallinity resulted in low impact strength especially for nanoparticles.
Figure 4.77 Impact Strength of PP composites vs. % crystallinity
4.6.5.5 Effect of β-iPP

Table 4.16 shows the impact strength for the PP composites and PP nanocomposites together with their % crystallinity and k parameters. The k obtained from the impact specimens (k impact) is compared with the k parameter found after mixing (k mix). It was observed that k impact value for the best four impact strengths is approximately 0.25. The crystallinity for those composites is above 30%.

The high impact strength for the PP nanocomposites was found with 0.07µm treated particles at 2wt% and 5wt% compositions, with k impact=0.22 and k impact=0.25 respectively. The crystallinity was approximately 35%.

The top values for impact strength and k parameter are highlighted in Table 4.16. It was observed that in most cases the composites with highest impact strength also have the highest values of the k parameter.

The values for k impact and k mixing were compared to address the formation of β-iPP after mixing and after injection molding. For the majority of the PP composites, the k impact value is higher than the k mixing. The reason for that may be related with processing conditions (shear) and cooling conditions. Cooling was faster after mixing. Formation of β-iPP with injection molding was studied by Varga33.

Finally, a different variation of k (Δk) between k impact and k mixing was observed with different particle size. The k impact value seemed greater than k mixing especially for 3.2µm and 1.1µm particles and lower for 0.07µm particles.
Table 4.16 Impact strength as a function of % crystallinity, k mixing (after mixing) and k imp (from impact specimens)

<table>
<thead>
<tr>
<th>Median Particle Size(µm)</th>
<th>%wt</th>
<th>Surf. Treat.</th>
<th>% Cryst.</th>
<th>Impact test (J/m)</th>
<th>k impact</th>
<th>k mixing</th>
<th>Δk(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP Brab.</td>
<td>1.1</td>
<td>5</td>
<td>Treated</td>
<td>30.7</td>
<td>75.9</td>
<td>0.25</td>
<td>0.19</td>
</tr>
<tr>
<td>PP Brab.</td>
<td>3.2</td>
<td>2</td>
<td>Treated</td>
<td>35.5</td>
<td>75.2</td>
<td>0.24</td>
<td>0.27</td>
</tr>
<tr>
<td>PP Brab.</td>
<td>3.2</td>
<td>5</td>
<td>Non Treated</td>
<td>33.2</td>
<td>74.3</td>
<td>0.25</td>
<td>0.20</td>
</tr>
<tr>
<td>PP Brab.</td>
<td>3.2</td>
<td>10</td>
<td>Non Treated</td>
<td>34.2</td>
<td>69.3</td>
<td>0.26</td>
<td>0.20</td>
</tr>
<tr>
<td>PP Brab.</td>
<td>3.2</td>
<td>20</td>
<td>Treated</td>
<td>33.7</td>
<td>67.6</td>
<td>0.23</td>
<td>0.19</td>
</tr>
<tr>
<td>PP Brab.</td>
<td>1.1</td>
<td>20</td>
<td>Treated</td>
<td>34.5</td>
<td>67.1</td>
<td>0.20</td>
<td>0.19</td>
</tr>
<tr>
<td>PP Brab.</td>
<td>3.2</td>
<td>5</td>
<td>Treated</td>
<td>35.5</td>
<td>63.5</td>
<td>0.25</td>
<td>0.23</td>
</tr>
<tr>
<td>PP Brab.</td>
<td>0.07</td>
<td>2</td>
<td>Treated</td>
<td>36.2</td>
<td>62.5</td>
<td>0.22</td>
<td>0.31</td>
</tr>
<tr>
<td>PP Brab.</td>
<td>0.07</td>
<td>5</td>
<td>Treated</td>
<td>34.6</td>
<td>59.7</td>
<td>0.25</td>
<td>0.31</td>
</tr>
<tr>
<td>PP Brab.</td>
<td>1.1</td>
<td>5</td>
<td>Non Treated</td>
<td>35.1</td>
<td>50.7</td>
<td>0.16</td>
<td>0.15</td>
</tr>
<tr>
<td>PP Brab.</td>
<td>3.2</td>
<td>20</td>
<td>Non Treated</td>
<td>34.2</td>
<td>50.2</td>
<td>0.24</td>
<td>0.17</td>
</tr>
<tr>
<td>PP Brab.</td>
<td>0.07</td>
<td>2</td>
<td>Non Treated</td>
<td>36.0</td>
<td>45.0</td>
<td>0.16</td>
<td>0.30</td>
</tr>
<tr>
<td>PP Brab.</td>
<td>35.9</td>
<td>43.6</td>
<td>0.16</td>
<td>0.18</td>
<td>-11%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP Brab.</td>
<td>0.07</td>
<td>5</td>
<td>Non Treated</td>
<td>36.1</td>
<td>42.5</td>
<td>0.20</td>
<td>0.30</td>
</tr>
<tr>
<td>PP Brab.</td>
<td>0.07</td>
<td>20</td>
<td>Treated</td>
<td>34.3</td>
<td>42.5</td>
<td>0.23</td>
<td>0.21</td>
</tr>
<tr>
<td>PP Pellet</td>
<td>32.5</td>
<td>42.5</td>
<td>0.18</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PP Brab.</td>
<td>1.1</td>
<td>20</td>
<td>Non Treated</td>
<td>31.5</td>
<td>37.2</td>
<td>0.19</td>
<td>0.14</td>
</tr>
<tr>
<td>PP Brab.</td>
<td>0.07</td>
<td>20</td>
<td>Non Treated</td>
<td>37.8</td>
<td>36.5</td>
<td>0.17</td>
<td>0.15</td>
</tr>
</tbody>
</table>
CHAPTER V

CONCLUSIONS

In this study, composites of polypropylene and calcium carbonate were prepared in a Brabender internal mixer. Different types of calcium carbonate were used including treated and non treated particles with 3.2µm, 1.1µm and 0.07µm median particle sizes. The dynamic, thermal, morphological and mechanical properties of the PP composites at different compositions were investigated.

At high loads of calcium carbonate, the high values of dynamic viscosity and elastic modulus at low frequencies showed that treated nanoparticles can restrict the mobility of the PP melt in a greater manner than microparticles. At the same time, treated and better dispersed nanoparticles can have a more significant effect on the restriction of macromolecular chain motion than non treated particles.

Calcium carbonate nanoparticles increase crystallinity of iPP to higher levels than microparticles. However, even when nanoparticles can act as strong nucleating agents, they can also be obstacles to the chain movement to reduce crystallization. Blocking the chain movement and the formation of agglomerates can prevent iPP to reach higher levels of crystallinity with addition of calcium carbonate nanoparticles. There is a slight increase of crystallinity with surface treatment of the calcium carbonate particles.

Formation of higher amounts of β-iPP suggested by the higher k parameter was observed with addition of calcium carbonate nanoparticles in comparison with
microparticles. There was a correlation between the presence and size of a low temperature melting peak in the DSC traces of the PP composites with the value of k found using X-Ray diffraction. However, the k parameter was also found for neat PP mixed in the Brabender without filler. The DSC scan in that case did not show a low temperature melting peak. This indicated that without addition of fillers, high shear was an important factor in the formation of β-iPP during mixing.

Elastic modulus was highest with addition of 20% of calcium carbonate nanoparticles and there was an increase of up to 30% in comparison with that of neat PP. Increasing composition from 5wt% to 20wt% increased the elastic modulus by roughly 13%. The elastic modulus was highest with approximately 40% crystallinity. The best results for microcomposites are 9% higher than neat PP.

Tensile strength was also highest with the addition of 2wt% and 5wt% nanoparticles but the improvement was only 5% compared with neat PP. High crystallinity of 40% was necessary to obtain higher values of tensile strength. The highest tensile strength for PP microcomposites shows no improvement compared with neat PP.

Impact strength was higher with addition of calcium carbonate microparticles. Increment of above 70% was found for PP composites with 1.1µm and 3.2µm treated particles at 5wt% composition. Surface treated nanoparticles at 2wt% composition with k=0.22 and 5wt% composition with k=0.25 proved to improve the impact strength of PP above 40% compared with neat PP.

The best combination of mechanical properties was found for PP nanocomposites filled with 2wt% of 0.07µm treated particles.
The SEM photographs verified the presence of agglomerates and uneven distribution of nanoparticles on the composites. The SEM image analysis was performed using the Image J software. It was not possible to use an automatic analysis, in other words, taking an SEM picture from which the software could recognize the particles and find the particle distribution directly. The similar color of the calcium carbonate particles and the PP matrix did not allow it. It was necessary to manually select the particles and obtain the particle distribution.

The median particle size found after the image analysis suggested that calcium carbonate microparticles reduced their original median particle size while the nanoparticles agglomerate to an average of four times their original size.

The particle size distribution obtained with image analysis can show how difficult is to obtain good dispersion depending on the particle size of the filler added. Particle distributions for the same particle size and composition became irregular with reduction of particle size.

Surface treatment of particles can be shown in the particle size distribution. There is an increment in the number (frequency) of calcium carbonate particles found in the samples. This can suggest better dispersion obtained with treated particles.

It was possible to find a mathematical function that fit the particle size distributions obtained from the image analysis. The function was the Gamma Variant. The correlation coefficient $R^2$ was found to be above 0.99 for nanoparticles at 2wt% and 5wt% compositions.

Further studies are needed to verify if the Gamma Variant is valid to describe the particle distribution of calcium carbonate nanoparticles in PP. If this is verified, more
work can be done in relating this function with the filler characteristics and perhaps with the mixing conditions used to prepare the PP nanocomposites.

Many papers have tried to study and improve impact strength of PP/CaCO₃ nanocomposites, and a few of them indicated the formation of β-iPP in their composites. However, there was not much information about the relation between addition of nanoparticles to PP and their effect on formation of β-iPP. β-iPP is known to have better impact properties than α-iPP. Some studies can be done to learn how to promote the formation of β-iPP with calcium carbonate nanoparticles to improve impact strength of PP.
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