UNIVERSITY OF CINCINNATI

Date: April 16th, 2009

I, Xiujuan Zhang, hereby submit this original work as part of the requirements for the degree of: Doctor of Philosophy in Chemistry

It is entitled:

Improvements in the Mechanical Properties of Some Biodegradable Polymers & Bimodal Poly(dimethylsiloxane) Hydrogels and Surface Hydrophilic Treatments

Student Signature: Xiujuan Zhang

This work and its defense approved by:

Committee Chair: Dr. James E. Mark
Dr. William R Heineman
Dr. Bruce S. Ault

Approval of the electronic document:

I have reviewed the Thesis/Dissertation in its final electronic format and certify that it is an accurate copy of the document reviewed and approved by the committee.

Committee Chair signature: Prof. James E. Mark
Improvements in the Mechanical Properties of Some Biodegradable Polymers & Bimodal Poly(dimethylsiloxane) Hydrogels and Surface Hydrophilic Treatments

A dissertation submitted to the Graduate School of the University of Cincinnati in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in the Department of Chemistry of the College of Arts and Sciences by

Xiujuan Zhang

M.S., University of Cincinnati, USA, 2007
Committee Chair: Professor James E. Mark
Abstract

The first part presents the improvements in the mechanical properties of a couple of biodegradable polymers, the first one is poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHx) by introducing several nano-fillers (clay, mica, talc, expanded graphite) to prepare nanocomposites. Solution mixing and melt bending are the two preparation methods used. The resulting nanocomposites were characterized by X-ray diffraction measurements (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and INSTRON measurements. The results showed that PHBHx/clay and PHBHx/graphite nanocomposites were obtained with remarkable improvements in mechanical properties even at very low filler content. The improvements were mostly attributed to the intercalated, even exfoliated state of the clay in PHBHx.

Another Biodegradable polymer was studied in this work is glycerol-derived alkyd resin. One set of the resin/clay nanocomposites was successfully prepared by melt blending the resin precursors with organoclays. The clay using here is clay30B, and clay30BT (further treated ones of clay30B). Mica and talc were also used to prepare nanocomposites for comparison. The morphologies, thermostabilities, and mechanical properties of the resulting nanocomposites were investigated, indicating that resin/clay nanocomposites were obtained with remarkable improvements in thermostability and mechanical properties even at very low loadings.
The second part focused on the preparation and characterization of silicone hydrogels based on poly(dimethylsiloxane) (PDMS) and hydrophilic block copolymer, and some surface modifications of PDMS.

The first two series of bimodal silicone hydrogels successfully prepared are PDMS-poly(ethylene glycol) (PEG) hydrogels, which were prepared by end-linking a combination of long and short chains and a couple of hydrophilic functional crosslinker respectively. In both cases longer hydrophilic chains clearly migrated to the surfaces of the resulting PDMS-PEG hydrogels to give decreases of static contact angles (CA) from 105° to 80° for the first series, and to 40° for the second. The longer hydrophilic chains were found to give larger decreases in CA values and larger equilibrium water contents as expected.

Several other series of PDMS amphiphilic conetworks (APCNs) were prepared including by bonding a hydrophilic macromer, hydroxyl-terminated linear PEG, hydroxyl-terminated linear PDMS with the crosslinker bis[(3-methyldimethoxysilyl)propyl]-polypropylene oxide (BMPPO), which also functioned as a compatibilizer. The CA values decreased significantly from 105° in PDMS to 55° in the PEG/PDMS APCN (10/1 mol ratio), and the swelling degrees of the APCNs increased from about 0 to 60 % when the mol ratio was larger than 4/1. A couple of other series APCNs with very high and long lasting hydrophilicity and good mechanical properties were also obtained.

Secondly, several surface treatments methods were applied to make PDMS networks surface hydrophilic, including (1) introduction of an ultra thin layer of silica on the surfaces through the sol-gel process, (2) a UV/ozone method for bimodal networks consisting of some vinyl-substituted chains, poly(vinylmethyldisiloxane) (PVMS), along with those of PDMS; (3) treatment of PDMS networks by UV/ozone, followed by grafting of polyethylene
glycol based silane directly onto the surfaces, (4) grafting a hydrophilic monomer, N-isopropylacrylamide by the UV radiation, (5) plasma polymerization of acrylic acid (AA) onto the surface of the PDMS.

**Keywords:** poly(3-hydroxybutyrate-co-3-hydroxyhexanoate); clay; expanded graphite; carbon nanotube; poly(dimethylsiloxane); poly(ethylene glycol); amphiphilic conetworks; hydrophilicity; mechanical properties; end-linking; alkoxy silanes; Hydrogels; surface properties; contact angles; swelling; surface treatments.
Acknowledgements

My deepest appreciation goes to my advisor, Dr. James E. Mark. I thank him for his constant supervision, recommendations and suggestions during all these years involved in my research. I would like to thank him for his incredible support, and for providing me with a lot of opportunities and independence by giving me the freedom to develop myself as a truly independent researcher with creativity, by developing my ideas into novel executable projects, and sharing his knowledge and expertise in the area of polymer science. His professional and personable attitude has made my stay at University of Cincinnati a very rewarding and memorable experience. It is my great pleasure and honor to be his student.

I am also deeply grateful to my committee members Prof. Bruce S. Ault and Prof. William R. Heineman for their time, advice, help and guidance in my research and Ph. D. program.

Acknowledgements are particularly due to Dr. Isao Noda and Dr. Sai Kumar for their great help, cooperation and discussions.

This work was funded by the financial support provided Dr. James E. Mark by the National Science Foundation through Grant DMR-0314760 (Polymers Program, Division of Materials Research), CIBA Vision Corporation, Atlanta, GA and Procter & Gamble Company, Cincinnati, OH. I would also like to acknowledge the financial support provided by Dr. Mark for research assistantship, and the Department of Chemistry for a teaching assistantship, and University of Cincinnati for a graduate Scholarship.

I appreciate a lot the support provided by JEM group members, friends, and staff and
faculty of the University of Cincinnati for their help and assistance.

    Special thanks to my family, my husband Dr. Gui Lin and my little girl, Grace Lin, for bringing me such great happiness.

VI
Table of contents

Abstract ................................................................................................................................. I
Acknowledgements ................................................................................................................ V
Table of contents .................................................................................................................. VII
List of figures ......................................................................................................................... XV
List of tables ......................................................................................................................... XXII
List of abbreviations and symbols .................................................................................... XXIII

Chapter 1. Improvements in the mechanical properties of the biodegradable polymer, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) ... 1

1.1 Introduction ..................................................................................................................... 1
1.2 Experimental .................................................................................................................. 3
  1.2.1 Materials .................................................................................................................. 3
  1.2.2 Preparations of the PHBHx nanocomposites ......................................................... 5
    1.2.2.1 Solution mixing .................................................................................................. 5
    1.2.2.2 Extrusion blending .......................................................................................... 7
  1.2.3 Characterizations ...................................................................................................... 7
    1.2.3.1 Stress-strain .................................................................................................... 7
    1.2.3.2 X-ray diffraction ............................................................................................. 8
    1.2.3.3 Thermogravimetric analysis ............................................................................ 8
    1.2.3.4 Differential scanning calorimetry .................................................................... 8

VII
1.3 Results and discussion .................................................................................................. 10

1.3.1 PHBHx nanocomposites prepared by solution mixing ............................................. 10

1.3.1.1 Dispersion of the layered silicates ................................................................. 10

1.3.1.2 Mechanical properties .................................................................................... 17

1.3.1.3 Thermal stabilities ........................................................................................ 19

1.3.2 PHBHx nanocomposites prepared by melt blending ............................................. 21

1.3.2.1 Dispersion of layered silicate and expanded graphite ..................................... 21

1.3.2.2 The crystallinity of PHBHx/layered filler nanocomposites .............................. 31

1.3.2.3 The mechanical properties .............................................................................. 33

1.3.2.4 The thermal stabilities .................................................................................... 35

1.3.2.5 Conductivity of PHBHx/EG ........................................................................... 37

1.4 Conclusions ................................................................................................................... 39

Chapter 2. Improvements in the mechanical properties of a biodegradable thermoset based on glycerol-derived alkyd resin by layered .. 41

2.1 Introduction ................................................................................................................... 41

2.2 Experimental ................................................................................................................. 43

2.2.1 Materials ................................................................................................................. 43

2.2.2 Treatment of the clay ............................................................................................. 44

2.2.3 Preparation of the alkyd nanocomposites ............................................................. 45

2.2.4 Characterizations ..................................................................................................... 46
2.4.1 X-ray diffraction .................................................................46
2.4.2 Transmission electron microscopy ..................................46
2.4.3 Thermogravimetric analysis ............................................46
2.4.4 Differential scanning calorimetry ......................................46
2.4.5 Mechanical properties ......................................................47

2.3 Results and discussion .........................................................47
  2.3.1 The dispersion of layered silicate ......................................47
  2.3.2 Thermal stability ..............................................................54
  2.3.3 Mechanical properties ......................................................57

2.4 Conclusions ............................................................................59

Chapter 3. Preparation and characterization of hydrophilic bimodal
hydrogels based on PDMS .................................................................61

3.1 Introduction ..............................................................................61
3.2 Experimental .............................................................................64
  3.2.1 Materials .............................................................................64
  3.2.2 Preparation of the polysiloxane hydrogels .......................65
  3.2.3 Characterizations .................................................................66
    3.2.3.1 Static contact angles .........................................................66
    3.2.3.2 Equilibrium water contents ............................................66
    3.2.3.3 Differential scanning calorimetry ..................................66
    3.2.3.4 Mechanical properties ....................................................67
    3.2.3.5 Fourier transform infrared spectroscopy .......................67
    3.2.3.6 X-ray diffraction patterns ...............................................67
3.2.3.7 Environmental scanning electron microscopy ........................................67

3.3 Results and discussion ........................................................................................................... 68
3.3.1 Crosslinked hydrogels using the poly(ethylene oxide)–trialkoxysilanes ..................68
3.3.2 Thermal characteristics ...................................................................................................71
3.3.3 Morphology of the hydrogels .......................................................................................73
3.3.4 Hydrophilicities .............................................................................................................75
3.3.5 Equilibrium water contents .........................................................................................77
3.3.6 Mechanical properties ...................................................................................................79

3.4 Conclusions ......................................................................................................................... 81

Chapter 4. Preparation of bimodal hydrogels based on PDMS networks crosslinked by hydrophilic silane on the main chains .................................................. 83

4.1 Introduction.......................................................................................................................... 83

4.2 Experimental section ......................................................................................................... 84
4.2.1 Materials and preparation .............................................................................................84
4.2.2 Characterization ...............................................................................................................85
4.2.2.1 Fourier transform infrared spectroscopy .................................................................85
4.2.2.2 Differential scanning calorimetry ...........................................................................85
4.2.2.3 Contact angles ..........................................................................................................86
4.2.2.4 Equilibrium water content ......................................................................................86
4.2.2.5 Mechanical properties ............................................................................................86

4.3 Results and discussion ....................................................................................................... 86
4.3.1 Formation of silicone hydrogel networks ......................................................................86
4.3.2 Thermal characteristics ................................................................................................89
4.3.3 Hydrophilicity ........................................................................................................90
4.3.4 Mechanical properties ..........................................................................................93
4.4 Conclusions and further work ...................................................................................94

Chapter 5. Improving hydrophilicity from poly(ethylene glycol) in amphiphilic conetworks with poly(dimethylsiloxane) .............................................95

5.1 Introduction ................................................................................................................95
5.2 Materials and experimental methods .........................................................................98
5.2.1 Materials and preparation of amphiphilic conetworks ...........................................98
5.2.2 FTIR .......................................................................................................................99
5.2.3 Differential scanning calorimetry ........................................................................100
5.2.4 X-ray diffraction ...............................................................................................100
5.2.5 Static contact angles ........................................................................................100
5.2.6 Water swelling kinetics .......................................................................................100
5.2.7 Mechanical properties ......................................................................................101
5.2.8 Characterization of morphologies ......................................................................101
5.3 Results and discussion .............................................................................................101
5.3.1 Preparation of the PDMS-PEG amphiphilic conetworks .....................................101
5.3.2 Surface and bulk morphologies ........................................................................104
5.3.3 Thermal properties ...........................................................................................106
5.3.4 Surface hydrophilicity ......................................................................................108
5.3.5 Water-swelling kinetics ....................................................................................110
5.3.6 Mechanical properties ......................................................................................111
5.4 Conclusions .............................................................................................................112
### Chapter 6. Preparation of bimodal hydrogels based on PDMS and amphilic PDMS-poly(alkyl oxide) copolymers

- **6.1 Introduction** ................................................................. 114
- **6.2 Experimental** ................................................................. 114
  - **6.2.1 Materials and preparation** ........................................ 114
  - **6.2.2 Characterization** .................................................... 117
    - **6.2.2.1 Static contact angles** ........................................ 117
    - **6.2.2.2 FTIR** ............................................................ 117
    - **6.2.2.3 Differential scanning calorimetry** ..................... 117
    - **6.2.2.4 Equilibrium water contents** ............................ 118
- **6.3 Results and discussion** ................................................ 118
- **6.4 Conclusions and further work** ....................................... 123

### Chapter 7. Surface hydrophilic treatments of PDMS-based bimodal networks

- **7.1 Improvement in surface hydrophilicity of polysiloxane networks by introducing poly(N-isopropylacrylamide) via ultraviolet polymerization** ................................................ 124
  - **7.1.1 Introduction** .......................................................... 124
  - **7.1.2 Experimental** ....................................................... 125
    - **7.1.2.1 Materials** ...................................................... 125
    - **7.1.2.2 Preparation of PDMS-PVMS bimodal silicone networks** ...................... 125
    - **7.1.2.3 Ultraviolet polymerization grafting** ........................ 126
    - **7.1.2.4 Characterization** ............................................ 127
  - **7.1.3 Results and discussion** .......................................... 127
7.1.3.1 Surface treatments to make surface hydrophilic................................. 127
7.1.3.2 Surface hydrophilicity........................................................................... 131
7.1.4 Conclusions and further work................................................................. 132
7.2 Surface modification by covalent bonding of hydrophilic silane directly onto the surface of polysiloxane networks.................................................................................. 132
  7.2.1 Introduction.............................................................................................. 132
  7.2.2 Experimental.......................................................................................... 133
    7.2.2.1 Materials ......................................................................................... 133
    7.2.2.2 Surface treatment............................................................................. 133
    7.2.2.3 Contact angle .................................................................................. 134
    7.2.2.4 FTIR ............................................................................................... 134
  7.2.3 Results and discussion............................................................................ 134
    7.2.3.1 Surface modification ........................................................................ 134
    7.2.3.2 Surface hydrophilicity..................................................................... 137
  7.2.4 Conclusion.............................................................................................. 139
7.3 Introducing a colloidal silica gradient onto the surface of bimodal PDMS networks using a sol-gel reaction......................................................................................... 139
  7.3.1 Introduction.............................................................................................. 139
  7.3.2 Experimental.......................................................................................... 140
    7.3.2.1 Materials ......................................................................................... 140
    7.3.2.2 Preparation process......................................................................... 140
    7.3.2.3 Characterization............................................................................... 141
  7.3.3 Results and discussion............................................................................ 142

XIII
7.3.3.1 Formation of silica on surfaces ................................................................. 142
7.3.3.2 Surface hydrophilicity .............................................................................. 143
7.3.4 Conclusions............................................................................................... 144
7.4 Surface modification of bimodal PVMS-PDMS films by plasma polymerization..... 145
  7.4.1 Introduction............................................................................................... 145
  7.4.2 Experimental............................................................................................. 147
    7.4.2.1 Materials ............................................................................................ 147
    7.4.2.2 Preparation of PDMS-PVMS bimodal silicone networks............... 147
    7.4.2.3 Plasma polymerization of PAA on the surfaces of a PVMS-PDMS networks 148
    7.4.2.4 Characterization ............................................................................... 148
  7.4.3 Results and discussion ............................................................................. 149
    7.4.3.1 Formation of PAA layers on PVMS-PDMS networks ....................... 149
    7.4.3.2 Surface hydrophilicity ....................................................................... 150
  7.4.4 Conclusions and further work ................................................................. 151

Chapter 8. Overall conclusions and future work ............................................. 153
  8.1 Summary....................................................................................................... 153
  8.2 Future work.................................................................................................. 157

References.......................................................................................................... 159

Publications and contributions ........................................................................ 180
List of figures

**Figure 1.1** Molecular structure of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), 11-13 mol% of hydroxyhexanoate................................................................................................................. 3

**Figure 1.2** Chemical structures of natural clays, the cations in quaternary ammonium salts as the surfactants in the treating process of clay20A, clay30B and clay25A, respectively, where HT is hydrogenated tallow (≈65% C18, ≈30% C16, ≈5% C1)................................................................................. 4

**Figure 1.3** The dispersion state of clay in chloroform (a), clay30B in water (b), mica (c), mica in chloroform (d), talc (e) and talc in chloroform (f)........................................................................................................... 7

**Figure 1.4** Schema of the solution mixing process to prepare the PHBx/layered silicates nanocomposites.......................................................................................................................... 7

**Figure 1.5** The setup used to measure electrical volume resistivity: (a) for high resistivity and (b) for low resistivity.................................................................................................................. 10

**Figure 1.6** X-ray diffraction patterns for neat PHBx, layered-silicate and PHBx /layered-silicate nanocomposites with various layered silicate loadings by solution intercalation. (a) clay20A, (b) clay25A, (c) mica, and (d) talc........................................................................................................... 11

**Figure 1.7** TEM images of PHBx/layered-silicate nanocomposites (a) clay20A -3%, (b) clay25A-3%, (c) mica-3%, and (d) talc-3%............................................................................................................... 13

**Figure 1.8** The SAXS results of layered silicate 30B in the chloroform solution. ............... 15

**Figure 1.9** SAXS results for PHBx/clay20A (a, b), PHBx/clay25A (c, d) and PHBx/30B nanocomposites (e)......................................................................................................................... 16

**Figure 1.10** Schema of the possible interaction between layered silicates with PHBx matrix (a) physical interaction; (b) hydrogen-bonded interaction. ............................................. 17
Figure 1.11 Effect of concentration on Young’s modulus (a), tensile strength (b), toughness (c, e), elongation at break (d, e) of PHBHx/layered silicates nanocomposites. -□-: PHBHx/clay20A; -○-: PHBHx/clay25A; -♦-: PHBHx/mica; -△-: PHBHx/talc, -▲-: Elongation at break of PHBHx/talc. ........................................................................................................... 19

Figure 1.12 Determination of onset and end set temperature from the thermogravimetric results on the PHBHx ........................................................................................................... 21

Figure 1.13 X-ray diffraction patterns for neat PHBHx, layered-silicate clay25A, and PHBHx/layered-silicate nanocomposites (a) and EG nanocomposites (b) at various loadings. ........................................................................................................... 24

Figure 1.14 Expanded graphite preparation and interaction with PHBHx................................. 25

Figure 1.15 FTIR results for graphite flake and expanded graphite........................................... 25

Figure 1.16 TEM results for graphite flakes and expanded graphite ........................................ 26

Figure 1.17 TEM images of PHBHx nanocomposites: (a) NC3, x6,000, 500 nm scale; (b) NC3, x10,000, 100 nm scale; (c) NG2, x6,000, 500 nm scale; and (d) NG2, x10,000, 100 nm scale. ........................................................................................................... 28

Figure 1.18 SAXS results for PHBHx/clay25A (a, b) and PHBHx/EG nanocomposites (c, d). ........................................................................................................... 31

Figure 1.19 DSC curves for neat PHBHx, (a) PHBHx/clay25A nanocomposites and (b) PHBHx/EG nanocomposites........................................................................... 33

Figure 1.20 Young’s modulus (a), tensile strength (b), toughness (c) and elongation at break (d) of nanocomposites based on PHBHx with layered silicate clay25A (■) and EG (▼)........................................................................................................... 34

XVI
Figure 1.21 Thermal stabilities of the nanocomposites based on PHBHx with clay25A (a) and EG (b)................................................................................................................................. 37

Figure 1.22 The electrical volume resistivity of the PHBHx/EG composites as a function of composition. .......................................................................................................................... 38

Figure 2.1 Schematic for the preparation of a glycerol-derived alkyd resin made from maleic anhydride and glycerol ................................................................. 44

Figure 2.2 Quaternary ammonium salt used to treat the clay. Here T is tallow (65% C18, 30% C16, 5% C14), and the anion is chloride................................................................. 44

Figure 2.3 Schema of the preparation glycerol-derived alkyd resin/layered filler hybrid thermoset nanocomposites ................................................................. 45

Figure 2.4 XRD results for alkyd resins reinforced with layered silicates. (a) Clay30B and its alkyd resin composites; (b) Clay30BT and its alkyd resin composites; (c) mica and its alkyd resin composites; (d) talc and its alkyd resin composites.............................. 49

Figure 2.5 Schematic of the reaction of alkyd resin precursor with the clay30B........... 51

Figure 2.6 Schema of the reaction of DGBEA with clay30B................................. 51

Figure 2.7 TEM results showing the dispersion of clay30B and clay30BT in the alkyd resin. (a) Alkyd resin/clay30B 5.0%; (b) Alkyd resin/clay30BT 5.0%; (c) alkyd resin/mica 5.0%; (d) Alkyd resin/talc 5.0% ................................................................................. 54

Figure 2.8 Determination of onset and end set temperature from the thermogravimetric results on an alkyd resin thermoset ........................................................................... 55

Figure 2.9 Mechanical properties of glycerol-derived alkyd resin/layered silicates (clay30BT, mica, talc) nanocomposites: (a) Young’s modulus, (b) tensile strength, (c) toughness. .................................................................................................................. 58

XVII
Figure 3.1 Structures of end-linkers S1 (upper sketch) and S2 (lower sketch). .......... 65

Figure 3.2 Schema reactions for end-linking the hydrogels by (a) S1 and (b) S2. .......... 69

Figure 3.3 FTIR results for the (a) T-S1 series the (b) T-S2 series of hydrogels. .......... 70

Figure 3.4 Differential calorimetry results for the (a) T-S1 series (b) T-S2 series of hydrogels. .................................................................................................................... 72

Figure 3.5 SEM images for the hydrogels: (a) surface of T-S1-2, (b) cross section of T-S1-2, (c) surface of T-S1-6, (d) cross section of T-S1-6, (e) surface of T-S2-2, (f) cross section of T-S2-2, (g) surface of T-S2-6, and (h) cross section of T-S2-6. ................................................................. 75

Figure 3.6 Effects of the end-linkers on the static contact angles with water for the T-S1 and T-S2 hydrogels. ■ the air-side surfaces, ● the mold-side surfaces; (a) end-linker S1 and (b) S2. ................................................................................................................................. 77

Figure 3.7 Effects of the end-linkers on equilibrium water contents. .......................... 79

Figure 3.8 Dependences of the stress-strain isotherms in elongation on the end-linker (a) S1, and (b) S2. ................................................................................................................................. 80

Figure 4.1 Schema of the preparation of bimodal silicone networks cocrosslinked by SIB1660 ........................................................................................................................................... 87

Figure 4.2 FTIR results for silicone hydrogels formed by hydrophilic crosslinkers placed into the main chains. ................................................................................................................................. 89

Figure 4.3 Schema of the hydrophilic chains’ distribution in the networks. ............... 89

Figure 4.4 DSC results for silicone hydrogels crosslinked by hydrophilic main chains.... 90

Figure 4.5 The contact angle results for silicone hydrogels crosslinked by hydrophilic crosslinkers on the main chains. ........................................................................................................ 91
Figure 4.6 EWC results of silicone hydrogels by hydrophilic crosslinkers into the main chains. (a) single-mole networks; (b) S12/different content of crosslinker................................. 92

Figure 5.1 Preparation of PDMS-PEG amphiphilic conetworks by chain coupling of hydroxyl-terminated PEG and hydroxyl-terminated PDMS with BMPPO and TEOS. The dots indicate coupling sites between the polymer chains, the bold lines represent BMPPO, the thin smooth lines, PEG; and wrinkled lines, PDMS................................................................. 103

Figure 5.2 FTIR results for the PEG-PDMS amphiphilic conetworks.................................................. 103

Figure 5.3 SEM images of PDMS-PEG APCNs (a) PDMS-PEG (1/8) surface; (b) PDMS-PEG (1/8) cross-section; (c) PDMS-PEG (1/4) surface; (d) PDMS-PEG (1/4) cross-section...... 105

Figure 5.4 XRD results of the PEG-PDMS amphiphilic conetworks.................................................. 106

Figure 5.5 DSC results of the PEG-PDMS amphiphilic conetworks.................................................. 108

Figure 5.6 Effect of the PEG content on the hydrophilicity, as gauged by values of the contact angle with deionized water................................................................. 109

Figure 5.7 Contact angle photographs for PDMS-PEG (1/2) (left), PDMS-PEG (1/6) (right) conetworks........................................................................................................ 110

Figure 5.8 Equilibrium water contents of the PDMS-PEG conetworks as a function of time.
.................................................................................................................................................... 111

Figure 6.1 Structure of carbinol-terminated poly(alkyl oxide)-PDMS- poly(alkyl oxide) triblock macromer used to prepare bimodal networks (a) PEO-PDMS-PEO; (b) PPO-PDMS-PPO................................................................. 115

Figure 6.2 Schema of the preparation of (a) PDMS-(PEO-PDMS-PEO) and (b) PDMS-(PPO-PDMS-PPO) bimodal amphiphilic networks with hydrophilic crosslinkers................... 117
Figure 6.3 FTIR spectra of (a) PDMS-(PEO-PDMS-PEO) and (b) PDMS-(PPO-PDMS-PPO) silicone networks. ................................................................. 119

Figure 6.4 DSC of PDMS-(PEO-PDMS-PEO) bimodal networks. ....................... 120

Figure 6.5 Contact angles of a bimodal network based on PDMS and PPO-PDMS-PPO with increasing time ................................................................................... 121

Figure 6.6 EWC results of the PDMS-(PEO-PDMS-PEO) silicone networks. .............. 122

Figure 7.1 Scheme preparation of bimodal PVMS-PDMS networks. Bold lines: short linear PVMS-PDMS; thin lines: long linear PDMS; side spot: vinyl side group in PVMS-PDMS; spot: crosslink point. ................................................................. 126

Figure 7.2 FTIR spectra of the surface of (a) PDMS and (b) PDMS-PVMS with the UV polymerization IPAA ......................................................................................... 129

Figure 7.3 Schema of PIPAAm polymerization onto the surface of PDMS (a) and PVMS-PDMS (b) network. ......................................................................................... 130

Figure 7.4 Contact angles of bimodal networks treated by PIPAA. (a) pristine PDMS, 1hr; (b) pristine PDMS, 2hrs; (c) pristine PDMS, 3hrs; (d) PDMS-PVMS, 1hr; (e) PDMS-PVMS, 2hrs; (f) PDMS-PVMS, 3hrs. ........................................................................................................................................................................ 131

Figure 7.5 FTIR spectrum of PVMS-PDMS networks surface treated with PEO-silane..... 136

Figure 7.6 Scheme of the chemical-bonding hydrophilic silane on the surface of PDMS-PVMS networks ................................................................................................. 137

Figure 7.7 The contact angle and its change with time of the pristine PDMS networks treated by ClSiMPEO. ........................................................................................................ 138

Figure 7.8 Preparation process for placing colloidal silica onto the surface of bimodal PDMS. ..................................................................................................................... 141

XX
Figure 7.9 Schema of the structure of silica gradient on a surface (upper portion) and the morphology of the gradient silica/PDMS networks (lower portion). ........................................ 143

Figure 7.10 Effect of colloid silica on the contact angles of bimodal PDMS surfaces. .......... 144

Figure 7.11 Schema preparation of bimodal PVMS-PDMS networks. Bold lines: short linear PVMS-PDMS; thin lines: long linear PDMS; side groups: vinyl groups in PVMS-PDMS; spot: crosslink point. ................................................................................................................. 148

Figure 7.12 Mechanism of plasma polymerization of acrylic acid on the surface of bimodal PDMS. ............................................................................................................................................................................. 150

Figure 7.13 Contact angles of PDMS-PVMS bimodal networks. -□- : native PDMS-PVMS; -○- : PDMS-PVMS deposited with poly(acrylic acid) after oxygen plasma treatment; -Δ- : PDMS-PVMS further treated by PEO after deposition of PAA. ......................................................... 151
List of tables

Table 1.1 The characteristics of natural clay, and treated layered silicates (20A, 25A, 30B), for the preparation of PHBHx nanocomposites ................................................................. 4

Table 1.2 Thermal stability parameters of various nanocomposite systems as determined from TGA .......................................................................................................................... 20

Table 2.1 Thermal stability parameters of various alkyd resin/layered silicates systems as determined from TGA ........................................................................................................ 56

Table 4.1 Formulation of bimodal silicone networks crosslinked by the hydrophilic crosslinkers into the main chains .................................................................................................. 84

Table 4.2 The mechanical properties of the silicone hydrogels crosslinked by hydrophilic crosslinkers in the main chains ......................................................................................... 93

Table 5.1 Synthesis details on the preparation of the PDMS-PEG conetworks .................. 99

Table 5.2 The mechanical properties of the PDMS-PEG conetworks ................................. 112

Table 6.1 Contact angles and transparencies of PDMS-(PEO-PDMS-PEO) bimodal networks ........................................................................................................................................ 121

Table 7.1 Absorption band assignment of FTIR spectra ......................................................... 129

Table 7.2 The static contact angles of PDMS, PVMS-PDMS .................................................. 138
List of abbreviations and symbols

**Polymers**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>APCN</td>
<td>Amphiphilic conetworks</td>
</tr>
<tr>
<td>ETS</td>
<td>[2-methyl(polyethyleneoxy)propyl]-trichlorosilane</td>
</tr>
<tr>
<td>PAA</td>
<td>poly(acrylic acid)</td>
</tr>
<tr>
<td>PDMS</td>
<td>Poly(dimethylsiloxane)</td>
</tr>
<tr>
<td>PEG</td>
<td>Poly(ethylene glycol)</td>
</tr>
<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PHA</td>
<td>Poly(3-hydroxyalkanoates)</td>
</tr>
<tr>
<td>PHBHx</td>
<td>Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)</td>
</tr>
<tr>
<td>PIPAAm</td>
<td>Poly(N-isopropylacrylamide)</td>
</tr>
<tr>
<td>PPO</td>
<td>Poly(propylene oxide)</td>
</tr>
<tr>
<td>PVMS</td>
<td>Poly(vinylmethylsiloxane)</td>
</tr>
</tbody>
</table>

**Fillers**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG</td>
<td>Expanded graphite</td>
</tr>
</tbody>
</table>

**Crosslinkers**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEOS</td>
<td>Tetraethoxysilane</td>
</tr>
<tr>
<td>TMOS</td>
<td>Tetramethoxysilane</td>
</tr>
<tr>
<td>BMPPO</td>
<td>Bis((3-methyl(dimethoxy)silyl)propyl)-polypropylene oxide</td>
</tr>
</tbody>
</table>
**Instruments**

- **AFM**  Atomic force microscopy
- **DSC**  Differential scanning calorimeter
- **FTIR**  Fourier transform infrared spectroscopy
- **SAXS**  Small angle X-ray scattering
- **SEM**  Scanning electronic microscopy
- **ESEM**  Environmental scanning electronic microscopy
- **TGA**  Thermogravimetric analysis
- **USAXS**  Ultra-small angle X-ray diffraction
- **UV**  Ultraviolet
- **UV/vis**  Ultraviolet/visible (light)
- **XPS**  X-ray photoelectron spectroscopy
- **XRD**  X-ray diffraction

**Properties**

- **CA**  Contact angle
- **EWC**  Equilibrium water content
- **LCST**  Lower critical solution temperature
Chapter 1. Improvements in the mechanical properties of the biodegradable polymer, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)

1.1 Introduction

Nowadays, biodegradable polymers are becoming an important research focus,[1-3] since they can be degraded by bioactive environments (such as those containing bacteria, fungi, or algae), or by hydrolysis in sea water or even buffer solutions. For this reason, such polymers can be used as attractive substitutes for many synthetic materials, thereby alleviating problems associated with solid waste disposal. Worldwide consumption of biodegradable polymers increased from 14 million kg in 1996 to an estimated 68 million kg in 2001.

Poly(3-hydroxyalkanoates) (PHA), a class of biodegradable and biocompatible polyesters, has in fact attracted much research interest and industrial attention as substitutes for synthetic materials.[4-8] These polymers can be produced directly from renewable resources by microbes which accumulate them as carbon and energy storage materials under unbalanced growth conditions. The copolyesters, poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHX) (Trade name: Nodax™), are some of the most important biodegradable semi-crystalline aliphatic polyesters in this PHA family. They provide a unique combination of properties such as superior thermo-plasticity, excellent biocompatibility, and biodegradability, etc.,[4,5] and are of interest for disposable packaging applications because of their being environmentally benign. However, there is a need for
more research for achieving improvements in the mechanical, thermal stability and barrier properties (to water and gases) when these PHBx materials are applied in more widespread areas.\cite{7, 8} One feasible method, described in some of our previous studies, applies the technique of orientation induced by pre-stretching to improve the mechanical properties of polymers.\cite{9, 10} Another relevant method is the preparation of hybrids made of PHBx and inorganic materials; such hybrids may circumvent these limitations on PHBx, and thereby expand its applications. The general goal would thus be to incorporate an environmentally acceptable filler to improve PHBx properties relevant to their use as packaging materials.

Incorporation of exfoliated layered silicates to prepare polymer/layered silicate nanocomposites has attracted considerable attention since the earliest work of some Toyota Corporation researchers.\cite{11} One of our previous studies showed that incorporating organically modified clay fillers by solution intercalation improved the mechanical properties of these promising copolyesters.\cite{12} In addition to clays, there are exfoliated layered particles such as expanded graphite (EG), a typical pseudo-two-dimensional solid in bulk form.\cite{13, 14} Similar to the clays, this EG could also provide very effective reinforcement of polymers at loading levels much smaller than required in the case of roughly spherical particles such as carbon black and silica.\cite{15-17} Moreover, it is a kind of electrically conductive filler.\cite{18-20} In the present investigation, some biodegradable nanocomposites based on PHBx and layered fillers, specifically organically modified clay or EG, were prepared by melt blending.
Chapter 1. Thermoplastic nanocomposites

The morphology and dispersion of the layered silicates and EG in PHBHx, and their effects on crystallinity, mechanical properties, thermal degradability, and conductivity of these materials were also investigated.

1.2 Experimental

1.2.1 Materials

PHBHx, whose molecular structure is shown in Figure 1.1, was provided by the Procter & Gamble Co., West Chester, OH and was used as received. Based on NMR results, it was a random copolymer consisting of 87~89 mol% 3-hydroxybutyrate, and 11-13 mol% 3-hydroxyhexanoate (based on NMR analysis). It had a number-average molecular weight of 500,000 - 600,000 g mol\(^{-1}\) and a polydispersity index \(M_w/M_n\) of 1.9 - 2.1 (based on polystyrene standards).

![Figure 1.1 Molecular structure of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), 11-13 mol% of hydroxyhexanoate.](image)

The layered-silicates, modified with quaternary ammonium cations, were purchased from Southern Clay Products Inc., Gonzales, Texas (with designations Cloisite 20A, 25A and 30B). The chemical structures of the cations used in the modification of 20A and 25A are
shown, respectively, in Figure 1.2. The average distances of the layers of these clays 20A and 25A were, respectively, about 24.2 and 18.6 Å.

Figure 1.2 Chemical structures of natural clays, the cations in quaternary ammonium salts as the surfactants in the treating process of clay20A, clay30B and clay25A, respectively, where HT is hydrogenated tallow (~65% C18, ~30% C16, ~5% C1).

Table 1.1 The characteristics of natural clay, and treated layered silicates (20A, 25A, 30B), for the preparation of PHBHx nanocomposites.

<table>
<thead>
<tr>
<th>Clay</th>
<th>Organic Modifier</th>
<th>Size: 10% less than</th>
<th>Size: 50% less than</th>
<th>Size: 90% less than</th>
<th>Specific Gravity, g/cc</th>
<th>d001 Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cloisite® Na⁺</td>
<td>-</td>
<td>2µ</td>
<td>6µ</td>
<td>13µ</td>
<td>-</td>
<td>11.7</td>
</tr>
<tr>
<td>Cloisite® 30B</td>
<td>MT2EtOT</td>
<td>2µ</td>
<td>6µ</td>
<td>13µ</td>
<td>1.98</td>
<td>18.5</td>
</tr>
<tr>
<td>Cloisite® 25A</td>
<td>2MHTL8</td>
<td>2µ</td>
<td>6µ</td>
<td>13µ</td>
<td>1.87</td>
<td>18.6</td>
</tr>
<tr>
<td>Cloisite® 20A</td>
<td>2M2HT</td>
<td>2µ</td>
<td>6µ</td>
<td>13µ</td>
<td>1.77</td>
<td>24.2</td>
</tr>
</tbody>
</table>

Note: The information from Southern Clay Company, TX.
Chapter 1. Thermoplastic nanocomposites

Mica (H₂Al₆K₂O₂₄Si₆, 325 mesh, water ground) and talc (3MgO·4SiO₂·H₂O) were the products of Spectrum Quality Products Inc., Garden, CA and the Aldrich Chemical Co. St Louis, MO, respectively. All organic solvents were high-performance liquid chromatography grades and were purchased from the Aldrich Chemical Co., St Louis, MO.

The graphite flakes had an average size of 500 μm and was used for preparing the EG. They were generously provided by Asbury Graphite Mills, Inc., Asbury, NJ. Concentrated sulfuric acid and concentrated nitric acid were obtained from Aldrich Chemical Co., St Louis, MO. All of these chemicals were used as received, without further purification.

**EG preparation.** The EG was prepared in the manner similar to that reported in the literature.[21, 22] Briefly, graphite flakes were first oxidized in a mixture solution of concentrated sulfuric acid and nitric acid, which had a volume ratio of 4:1, for 48 hours. Then the acid-treated graphite flakes were washed with enough distilled water until the pH of the solution was approximately 5-6. The solutions were filtered, and then dried at 100 °C to remove the remaining water. The dried graphite flakes were heated at 1000 °C for 30-60 s. The EG obtained had layered c-expansions of more than a hundred folds.

**1.2.2 Preparations of the PHBHx nanocomposites**

**1.2.2.1 Solution mixing**

PHBHx/layered silicate nanocomposites were prepared by solution intercalation. First, PHBHx and 1, 3, 5, 7, 10 and 15 wt% layered silicate (clays 20A, 25A, mica, and talc) were separately dissolved or dispersed in chloroform[23] and the two resulting dispersions stirred for 1hr, followed by ultrasonic treatment for another hour. Finally, the product was
dried and thermally compressed in preparation for the characterizations of morphology and properties.
Chapter 1. Thermoplastic nanocomposites

**Figure 1.3** The dispersion state of clay in chloroform (a), clay30B in water (b), mica (c), mica in chloroform (d), talc (e) and talc in chloroform (f).

![Image of dispersion states](image)

**Figure 1.4** Schema of the solution mixing process to prepare the PHBHx/layered silicates nanocomposites.

![Image of solution mixing process](image)

1.2.2.2 Extrusion blending

PHBHx/layered silicate nanocomposites and PHBHx/EG nanocomposites were prepared by melt extrusion. Firstly, PHBHx was separately mixed with various contents (1, 3, 5, 7 wt%) of layered silicate (Cloisite clay25A) and various contents (1, 2, 4, 6 wt%) of EG in a Brabender mixer for at least 15 min at 150 °C. Then the composites were thermally compressed into 1 mm films in thickness by using a standard hot press to prepare for the morphology and property measurements.

1.2.3 Characterizations

1.2.3.1 Stress-strain

The values of the modulus and tensile strength of samples having dimensions of 30 x 5 x 1 mm³ were measured using a fully computerized INSTRON mechanical tester (Model
1122, Acton, MA) at a cross-head speed of 5 mm/min with the initial gauge length being 20 mm at 25 °C. The tensile properties including Young’s modulus and tensile strength at break of each sample were determined from an average of at least five tests.

1.2.3.2 X-ray diffraction

WAXD patterns of neat PHBHand, the layered silicates, EG and the corresponding composites films were obtained using an X-ray generator (a Siemens D500 diffractometer) (monochromatized Cu-Kα radiation, with 30 mA, 40 kV, λ = 1.5406 Å). Data were collected with a 2θ scan range of 2° to 15° at room temperature with a step size of 0.05 degree and a time per step of 1 second.

1.2.3.3 Thermogravimetric analysis

TGA was performed using a TA Instruments (TGA 2050 Thermogravimetric Analyzer) with nitrogen as purging gas (30 ml/min) by increasing the temperature from 40 to 450 °C at a heating rate of 20 °C/min.

1.2.3.4 Differential scanning calorimetry

DSC measurements of the nanocomposites were performed with a TA Instrument (DSC 2010) with nitrogen as purging gas over a temperature range from -25 to 200 °C at a heating rate of 10 °C/min. The samples used for the DSC measurements were the same as those for the WAXD analysis.

1.2.3.5 Transmission electron microscope

TEM images were obtained using a JEM 1230 EX-II instrument (JEOL, Tokyo, Japan) operated with 1×10^4 magnification at an accelerating voltage of 80 kV. All of the ultrathin sections (less than 200 nm) were microtomed using a Super NOVA 655001 instrument.
Chapter 1. Thermoplastic nanocomposites

(Leica, Swiss) with a glass knife and were then subjected to TEM observation without staining.

1.2.3.6 Ultra Small angle X-ray scattering

SAXS data were collected using the equipment provided by Argon National Lab, IL. The wavelength of the beam was 1.489Å and the irradiated area was 1.5×0.5 mm². All data were collected at a sample-to-detector distance of 2.003 m. The scattered intensity was obtained as a function of the scattering vector q, between 7.5 x 10⁻³ and 0.3 Å⁻¹.

1.2.3.7 Electric conductivity

Electrical conductivity was measured using a Keithley 8009 test chamber combined with a 6517A electrometer using sheets (Figure 1.5a). Lower resistivity samples were measured using a 4-point fixture combined with a Keithley Digital multimeter 2000 electrometer (shown in Figure 1.5b) with different test fixtures: test fixture 8009 for sheets d=600 nm, thickness up to 1 mm; test fixture 8002A for filaments, strands and molded specimens; home-built unit for strip samples (ca. 40x5x1 mm³) on strips (3x20 mm²) cut from the sheets. Strips were usually cut from the sheets and measurements were made along the strip by means of a home-built sample fixture in combination with a digital multimeter.
Chapter 1. Thermoplastic nanocomposites

**Figure 1.5** The setup used to measure electrical volume resistivity: (a) for high resistivity and (b) for low resistivity.

### 1.3 Results and discussion

#### 1.3.1 PHBHx nanocomposites prepared by solution mixing

**1.3.1.1 Dispersion of the layered silicates**

Figure 1.6 shows the XRD patterns in the range $2\theta = 2-15^\circ$ for the neat PHBHx, clay20A, clay25A, mica, and talc, and their corresponding composites with various amounts of the layered silicates. The pattern of the neat PHBHx is displayed as a baseline to compare the existence of diffraction peaks coming from the layered silicate dispersed in the matrix. The peak of the neat PHBHx at $13^\circ$ corresponds to the crystallites in the matrix. There is no peak in the range $2\theta = 2-10^\circ$ in the PHBHx/clay20A composites in which the content of layered silicate is less than 7%. The result indicates that the d-spacings between layers are so large that the fillers formed exfoliated structures. This exfoliation may be caused by the side chains of the matrix dispersing into the spaces among layers to exfoliate the layers (facilitated by the compatibility between the tallow modifier chains of the clay20A and the PHBHx matrix). The characteristic peak of the neat clay20A is still evident in the composites when the content of clay20A is over 7%, which demonstrates that the clay20A was not well exfoliated in the matrix when its concentration is relatively high and thus forms only intercalated structures. The presence of the peak from the crystallites in the PHBHx matrix also indicates that the finely dispersed clay20A layered silicate does not strongly affect the crystalline regions during the thermal processing.
Figure 1.6 X-ray diffraction patterns for neat PHBh, layered-silicate and PHBh/layered-silicate nanocomposites with various layered silicate loadings by solution intercalation. (a) clay20A, (b) clay25A, (c) mica, and (d) talc.

The same phenomenon occurs in the clay25A composites. There is no discernible peak from the clay25A in the composites at the range $2\theta = 2$–$10^\circ$ when the content of the layered silicate is less than 7% (Figure 1.6 b), which means that the clay25A is almost completely exfoliated. The characteristic peak from clay25A in the PHBh/clay25A composites becomes weaker when the clay content is over 7%. The flat peak of the PHBh/clay25A composite compared to that of the neat clay25A indicates an increase in d-
Chapter 1. Thermoplastic nanocomposites

spacing and more intercalated structures in the polymer matrix. The presence of the peak of the crystalline regions in the neat PHBHx indicates the incorporation of layered silicates does not greatly decrease the crystallinity during the processing.

The XRD pattern of the PHBHx/mica composites (Figure 1.6 c) showed that the characteristic peak of mica disappeared in the PHBHx with 1% mica while it is still present in the other composites. The same results were obtained in the PHBHx/talc composites (Figure 1.6 d). These results indicate that the mica and talc could be intercalated and even exfoliated and well dispersed during the ultrasonic treatment at low concentration.

In addition to XRD, to validate the morphologies of the nanocomposites, the internal nanometer-scale structures were observed by TEM, which provides direct visualization of the morphology, atomic arrangement, spatial phase distribution, and structural features of a selected sample area. Figure 1.7 shows the TEM images of the nanocomposites: (a) PHBHx/clay20A – 3%; (b) PHBHx/clay25A – 3%; (c) PHBHx/mica – 3% and (d) PHBHx/talc – 3%, where the dark entities are intercalated silicate layers. From the TEM results in Figure 1.7 a and d, it is clear that the stacks of clay20A and clay25A forming the clay crystallites are now well dispersed in the polymer matrix. TEM results in Figure 1.7 c and d also indicate that mica and talc could be intercalated by polymer chains into platelet agglomerates although the surface properties are different from those of organically-modified clays.
Figure 1.7 TEM images of PHBHx/layered-silicate nanocomposites (a) clay20A-3%, (b) clay25A-3%, (c) mica-3%, and (d) talc-3%.
Chapter 1. Thermoplastic nanocomposites

SAXS results were shown to yield important characteristics of the filler structures such as primary particles size, surface roughness as well as the size and the fractal dimension of larger scattering entities (aggregates and agglomerates). The layered silicate in the chloroform solution (See Figure 1.8) could be clearly seen to be layered structure with slope -2 for q < 1 nm, and aggregate structure with diameter about 142 nm in q=10~100 nm, and the agglomerates structure in q > 100 nm.

Large scale dispersions of layered silicates (clay20A, clay25A, clay30B) in PHBHx were also characterized by SAXS in Figure 1.9. The diffraction peaks reveal the layer spacing and layer perfection of the multilayer stacks (tactoids). As the tactoids exfoliate and disperse, the layer peaks shift to smaller q and broaden. Therefore SAXS can also be employed to probe at large length scales and reveal the size and perfection of the individual platelets as well as the morphology of tactoids in polymer. It well showed in Figure 1.9 that low-q (q < 10^{-2} Å^{-1}) implied a larger fractal dimension \( d_m = -2.91 \) in clay20A, clay25A and \(-3.01\) in clay30B) corresponding to more compact crumpling. This value was close to 3, corresponding to a globular nonfractal cluster. However, large-q (q > 10^{-2} Å^{-1}) showed the short distance of layered silicates dispersion in matrix. Figure 1.9b and c showed the layer diffraction peaks at larger q in the PHBHx/clay20A and PHBHx/clay25A when PHBHx/clay was over 100/7, and the diffraction peaks were not showed with a slope \( d_m \approx -2 \) in the PHBHx/clay20A and PHBHx/clay25A (PHBHx/clay < 100/7). All these results were well corresponding to the XRD results.
Figure 1.8 The SAXS results of layered silicate 30B in the chloroform solution.
Figure 1.9 SAXS results for PHBHx/clay20A (a, b), PHBHx/clay25A (c, d) and PHBHx/30B nanocomposites (e).
Chapter 1. Thermoplastic nanocomposites

The well dispersion of clay30B in PHBHx than that of clay20A and clay25A could be well explained by that the hydroxyl in the quaternary amine salt may easily to form hydrogen bond with the ester group in the PHBHx (Figure 1.10 b), meanwhile, the long tallow chains in the quaternary amine salts in clay20A and clay25A could only physically twist with the PHBHx chains (Figure 1.10 a).

![Figure 1.10](image.png)

**Figure 1.10** Schema of the possible interaction between layered silicates with PHBHx matrix (a) physical interaction; (b) hydrogen-bonded interaction.

### 1.3.1.2 Mechanical properties

**Figure 1.11** shows the tensile properties obtained at 25 °C for the neat PHBHx and the PHBHx/layered silicate composites. The properties include (i) Young's modulus, (ii) tensile strength (defined as the stress at break), (iii) toughness, and (iv) elongation at break. As shown in **Figure 1.11**, both the Young's modulus and tensile strength of the nanocomposites were greatly improved compared to those for the pure PHBHx. Of particular interest is the observation that even very small amounts of the organoclays gave significant reinforcement of the PHBHx. Larger amounts of layered silicate (>5%) did not improve the Young's modulus and tensile strength much. In fact, the toughness of the composites decreased with increasing filler concentration except in the case of the PHBHx/talc composites, where toughness was greatly improved at low talc contents, and decreased only slightly with increasing content. The same trend was observed in the
Chapter 1. Thermoplastic nanocomposites

elongation at break for these PHB/Hx/talc composites. The values for the clay20A and the clay25A PHB/Hx composites increased slightly at contents below 1%, but decreased after that. The elongation at break of PHB/Hx/mica series increased slightly at contents less than 5%, and almost remained constant beyond that amount.
Figure 1.11 Effect of concentration on Young’s modulus (a), tensile strength (b), toughness (c, e), elongation at break (d, e) of PHBHx/layered silicates nanocomposites. -□-: PHBHx/clay20A; -○-: PHBHx/clay25A; -●-: PHBHx/mica; -Δ-: PHBHx/talc, -▲-: Elongation at break of PHBHx/talc.

1.3.1.3 Thermal stabilities

The thermal stabilities of the PHBHx/layered silicate composites series were determined from the thermogravimetric results.

Figure 1.12 shows an example of a TGA trace obtained for the neat PHBHx system. The onset and the end set temperature were determined from the intersection of the two tangents, and the peak degradation temperatures were determined from the inflection points on the curves. Table 1.2 presents values for the (i) onset temperature, (ii) the end set temperature, (iii) the temperature interval ΔTemp between these two temperatures, (iv) the degradation peak temperature, and (v) the total weight loss at 350 °C. The results showed that the onset temperature was slightly decreased with increasing layered silicates concentration in these composites. Compared with that of neat PHBHx, the end set
temperature was greatly improved at concentrations of fillers less than 5%, for all four silicates. Less improvement and even worsening of properties at higher concentrations obviously resulted from changes in the structures of the nanocomposites, specifically from filler exfoliation at low filler contents to less-effective intercalation at the higher contents. Slight decreases in the end set temperature were also observed with increasing concentration of the layered silicates. The interval between degradation onset and end set showed a slight broadening for the PHBHx/clay20A series but remained nearly constant around a value of 27 °C for the other three series. However, the interval temperatures were increased by about 11 °C compared with that for the neat PHBHx.

**Table 1.2** Thermal stability parameters of various nanocomposite systems as determined from TGA

<table>
<thead>
<tr>
<th>Filler</th>
<th>Filler loading</th>
<th>Onset temp (°C)</th>
<th>End set temp (°C)</th>
<th>ΔTemp (°C)</th>
<th>Degradation peak (°C)</th>
<th>Total wt. loss @ 350 °C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0</td>
<td>289.5</td>
<td>305.5</td>
<td>16.0</td>
<td>295.0</td>
<td>99.8</td>
</tr>
<tr>
<td>Clay 20A</td>
<td>1</td>
<td>286.2</td>
<td>316.7</td>
<td>20.5</td>
<td>300.4</td>
<td>99.4</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>278.8</td>
<td>308.7</td>
<td>29.9</td>
<td>294.9</td>
<td>97.6</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>277.0</td>
<td>307.4</td>
<td>29.6</td>
<td>292.0</td>
<td>96.2</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>272.7</td>
<td>302.7</td>
<td>30.0</td>
<td>287.7</td>
<td>94.9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>247.9</td>
<td>292.5</td>
<td>44.6</td>
<td>272.6</td>
<td>90.7</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>247.9</td>
<td>289.2</td>
<td>41.3</td>
<td>270.4</td>
<td>87.5</td>
</tr>
<tr>
<td>Clay 25A</td>
<td>1</td>
<td>285.2</td>
<td>311.4</td>
<td>26.2</td>
<td>299.3</td>
<td>98.8</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>284.3</td>
<td>310.0</td>
<td>25.7</td>
<td>297.9</td>
<td>97.3</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>286.4</td>
<td>312.6</td>
<td>26.2</td>
<td>300.1</td>
<td>96.4</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>281.6</td>
<td>304.4</td>
<td>22.8</td>
<td>294.5</td>
<td>94.4</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>280.7</td>
<td>303.8</td>
<td>23.1</td>
<td>293.0</td>
<td>92.3</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>272.5</td>
<td>303.0</td>
<td>30.5</td>
<td>290.2</td>
<td>89.5</td>
</tr>
<tr>
<td>Mica</td>
<td>1</td>
<td>286.1</td>
<td>312.1</td>
<td>26.0</td>
<td>300.5</td>
<td>98.7</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>286.3</td>
<td>312.5</td>
<td>26.2</td>
<td>300.3</td>
<td>97.9</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>287.7</td>
<td>314.5</td>
<td>26.8</td>
<td>300.9</td>
<td>96.4</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>286.5</td>
<td>314.3</td>
<td>27.8</td>
<td>300.9</td>
<td>94.1</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>286.7</td>
<td>311.6</td>
<td>24.9</td>
<td>300.5</td>
<td>86.9</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>282.4</td>
<td>309.8</td>
<td>27.4</td>
<td>297.4</td>
<td>88.1</td>
</tr>
<tr>
<td>Talc</td>
<td>1</td>
<td>289.0</td>
<td>315.8</td>
<td>26.8</td>
<td>304.2</td>
<td>99.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>286.5</td>
<td>314.5</td>
<td>28.0</td>
<td>299.7</td>
<td>96.2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>285.4</td>
<td>311.4</td>
<td>26.0</td>
<td>300.1</td>
<td>95.3</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>286.1</td>
<td>315.2</td>
<td>29.1</td>
<td>300.1</td>
<td>94.7</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>285.1</td>
<td>312.1</td>
<td>26.0</td>
<td>300.5</td>
<td>92.1</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>282.4</td>
<td>309.8</td>
<td>27.4</td>
<td>298.9</td>
<td>88.9</td>
</tr>
</tbody>
</table>
Chapter 1. Thermoplastic nanocomposites

![Graph showing weight percentage vs temperature](image)

**Figure 1.12** Determination of onset and end set temperature from the thermogravimetric results on the PHBHx.

The total weight losses of the composites at 350°C were not generally in direct proportion to the amount of layered silicates incorporated. Reductions of weight loss with increases in layered silicate concentration were of course observed, as expected.

1.3.2 PHBHx nanocomposites prepared by melt blending

1.3.2.1 Dispersion of layered silicate and expanded graphite

The WAXD patterns for the neat PHBHx, the clay25A, and their corresponding composites in the range of 2θ=2-20° are presented in **Figure 1.13(a)**. These results are consistent with known structural features, as summarized below. Each nanolayer of this smectite clay consisted of two tetrahedral sheets (mainly Si and occasionally Al) and a central octahedral sheet (occupied by Mg, Al, etc.), with a lateral dimension of 0.2-2 μm and
Chapter 1. Thermoplastic nanocomposites

a thickness of about 1 nm. The stacking of nanolayers forms tactoids (similar to

crystallites) that are typically 0.1–1 μm thick.[26] This layered silicate exhibits a net

negative charge on the lamellar surface, which enables it to absorb cations, such as Na+ or
Ca2+, and occupies the gallery space between nanolayers in the naturally occurring mineral.

Because the negative charge originates in the silicate layer, the cationic head group of the

alkylammonium molecule preferentially resides at the layer surface going from hydrophilic
to organophilic. Additionally, the organic cations can contain various functional groups that
react with the polymers and improve adhesion between the reinforcement particles and
the matrix, thus producing nanocomposites with high dispersion in organic solvents.

Natural Na+-clay has also been extensively used for nanocomposites via the emulsion
polymerization method.[27, 28] The cation molecule structure of the quaternary ammonium

salt used in clay25A was shown in Figure 1.2. The WAXD results showed the regular

arrangements of silicates layers in intercalated forms, and the irregular arrangements in

the case of complete exfoliations of the layers. As usual, the 2θ values can be converted to

layered spacing d values through the Bragg relationship (λ=2dsinθ), where λ is the

wavelength of the radiation. The interaction of alkylammonium cations with clay usually

increases the interlayer spacing relative to that of the pure clay, leading to a shift in X-ray
diffraction peak toward a lower angle. The d spacing of the original clay25A expanded to

1.81 nm.

The pattern of the neat PHBHx is displayed as a baseline to compare the existence of
diffraction peaks coming from layered silicate dispersed in the matrix. The peak of the neat

PHBHx at 13.9° corresponds to the crystallites in the matrix. The interaction of polymer
chains with the alkylammonium cation on the surface of clay usually also increases the
interlayer spacing relative to that in the original clay. The significant layer expansion associated with intercalated structures resulted in a new basal reflection that corresponded to the layer gallery height of the intercalated nanocomposites. The d spacing of the clay expanded significantly, from 1.81 nm to 3.06 nm for NC7 and to 3.26 nm for NC5. It is also clear that the intensities of the WAXD peaks almost disappear in NC3 and NC1, which means that there is no intercalated structure in the matrix.
Figure 1.13 X-ray diffraction patterns for neat PHB/Hx, layered-silicate clay25A, and PHB/Hx/layered-silicate nanocomposites (a) and EG nanocomposites (b) at various loadings.

The XRD patterns for the series of neat PHB/Hx, EG, and their corresponding composites in the range of $2\theta$=2-20° are presented in Figure 1.13(b). As for the WAXD pattern of the pure EG, there were sharp (001) peaks at $d=1.12$ nm ($2\theta=7.90^\circ$) and some other peaks with less intensity at $d=3.604$ nm ($2\theta=2.42^\circ$) and $d=1.52$ nm ($2\theta=5.81^\circ$), which means that EG has multiple ordered platelet structures. It is suggested that, as shown in Figure 1.14, after oxidization with concentrated sulfuric acid and nitric acid, and heating at high temperature, many polar groups such as hydroxyl, carboxyl etc. were introduced onto the surface of the graphite. This gave the expansion in the c-direction and led to the peak moving to lower angles in the WAXD results. Figure 1.13(b) also shows that there is no peak in the WAXD results for NG1, NG2, NG4, and NG6, which clearly indicates
that there is almost no ordered EG in the matrix. It thus suggests that the EG was extensively exfoliated into disordered layers. The unusual peak shown here suggests the existence of PHBHx crystallites in the nanocomposites.

Figure 1.14 Expanded graphite preparation and interaction with PHBHx.

Figure 1.15 FTIR results for graphite flake and expanded graphite.
Figure 1.16 TEM results for graphite flakes and expanded graphite.

The nanometer-scale structure was also studied by TEM, which provides direct visualization of the morphology, atomic arrangement, spatial phase distribution, and structural effects of a selected sample area. Figure 1.17 shows the TEM images of the PHBHx nanocomposites (a) NC3 (x6,000), (b) NC3 (x10,000), (c) NG2 (x6,000), and (d)
NG2 (x10,000). The dark entities in Figure 1.17 (a) and (b) are exfoliated clay layers. From the TEM results, it is clear that stacks of the clay25A layers are extensively dispersed and exfoliated into layers in the polymer matrix although groups of ordered platelets may form upon increase in the amount of clay loaded.[29] The WAXD results thus indicate that the clay is well exfoliated into sheets that should reinforce the polymers. It is supposed that the interaction between the alkyl chains or the tallow chains on the quaternary ammonium compound and the polymer chains may help to improve compatibility, and force the polymer chains to intercalate into layers, leading to exfoliation of the clay during melt blending.
Figure 1.17 TEM images of PHBhx nanocomposites: (a) NC3, x6,000, 500 nm scale; (b) NC3, x10,000, 100 nm scale; (c) NG2, x6,000, 500 nm scale; and (d) NG2, x10,000, 100 nm scale.
Chapter 1. Thermoplastic nanocomposites

From the TEM results in Figure 1.17(c) and (d), the dark entities are EG layers. It is obvious that the EG is further dispersed and exfoliated into layers in the polymer matrix even when the parts per hundred loading of EG was increased to 100/6. It is known that after oxidation with concentrated sulfuric acid, some functional groups such as hydroxyl, carbonyl and ether embedded in carbon sheets in EG lamella make graphite hydrophilic, and also produce strong interactions. This readily leads to insertions of polar polymers, and also enables it to exhibit rich interaction chemistry, as shown in Figure 1.14. This would easily lead to insertion of polar polymers into lamellae to formexfoliated nanocomposites. These results suggest the presence of strong molecular forces between the EG and the polymer chains, such as hydrogen bonding and Coulombic forces.[30] Similar results were found for the system based on EG and polymers such as Nylon 6,[31, 32] poly(ethylene oxide),[33] poly(vinyl alcohol),[34] poly(vinyl acetate),[30] poly(diallyldimethyl ammonium chloride),[35] even poly(furfuryl alcohol),[36] and several others.[37]

The extensive dispersion of clay25A and EG in PHBHx by melting blend were characterized by SAXS (Figure 1.18). The low-q (q < 10^{-2} \text{ Å}^{-1}) indicated a larger fractal dimension (d_m = -3.3 in clay25A and -3.01 in EG) corresponding to more compact crumpling. This value was close to 3, corresponding to a globular nonfractal cluster, which seemed true in the case of PHBHx/clay25A with TEM images in Figure 1.17. The large-q (q > 10^{-2} \text{ Å}^{-1}) showed more detail exfoliated/intercalated state of layered fillers in PHBHx. In PHBHx/clay25A, the broaden peaks at q = 2\times10^{-2} \text{ Å}^{-1} were also showed up even in the case of PHBHx/clay25A (100/1.0). The SAXS results for PHBHx/clay25A over 100/7 were well
Chapter 1. Thermoplastic nanocomposites

corresponding to the XRD results Figure 1.13 a, which indicated the intercalated state of layered silicate of clay25A. The peaks at $q = 2 \times 10^{-2} \text{Å}^{-1}$ at PHB/HxClay25A (100/1.0) somewhat conflicted to XRD results. In case of PHB/Hx/EG, the slope of the cures in the range of large-$q$, was about $d_m = -2$, well corresponding to the XRD results in Figure 1.13 a that the EG was exfoliated into layered pieces in PHB/Hx.
Chapter 1. Thermoplastic nanocomposites

**Figure 1.18** SAXS results for PHBHx/clay25A (a, b) and PHBHx/EG nanocomposites (c, d).

### 1.3.2.2 The crystallinity of PHBHx/layered filler nanocomposites

As can be seen in the XRD results shown in Figure 1.13, the crystalline part of PHBHx is characterized by a broad maximum located around 2θ=20°, whereas the crystalline zones display two diffraction peaks near 14° and 17.5°. According to the DSC results in Figure 1.19, there are two melting temperatures (around 136 and 152°C) and two glass transition temperatures (around 0 and 50°C) for the pure PHBHx. These values agree with the results reported for poly(3-hydroxybutyrate-co-3-hydroxyhexanoate).\(^{[38]}\) The appearance of intermediate states of PHBHx has been suggested by a small but wide endothermic pre-melting peak around 60°C in the DSC results. The present DSC results for
the PHBHx does show peak around 60.8°C for the bulk samples, which agrees with results reported elsewhere.\textsuperscript{[38-41]}
The DSC curves for the NC series and the NG series of nanocomposites are shown in Figure 1.19(a) and (b), respectively. It is clear that the two glass transition temperatures of PHBHx are only slightly affected by the exfoliated clay in the matrix. However, the two melting peaks, especially the peak near 136°C, are broadened compared with those of the neat PHBHx. That is, the incorporation of the exfoliated clay increased the melting temperature of the polymer, and this is consistent with results reported by Chen.\textsuperscript{[41]} The exfoliated clay may act as the heat barrier that retards the transfer of heat to melt the crystallites in the polymer, and this leads to an apparent higher melting temperature.

As shown in Figure 1.19 (b), the same trend was observed in the NG series of nanocomposites. That is, the glass transition temperatures were only slightly affected by the incorporation of EG. However, the melting peaks were also broadened with increasing amounts of EG in the polymer matrix. It is suggested that the polar groups on the surface of the EG may increase compatibility with the matrix, and the surface may provide nucleation centers for lamellar growth.\textsuperscript{[42]}

### 1.3.2.3 The mechanical properties

The reinforcement by clay or EG in PHBHx is illustrated by values of the Young's modulus, tensile strength (defined as the stress at break), toughness, and elongation at break, as shown in Figure 1.20. The Young's modulus, presented in Figure 1.20(a), was greatly improved compared to that of the neat PHBHx, especially at very small loadings (less than 100/3) of organoclay or EG. However, the Young's modulus decreased somewhat
with increasing layered filler content when the amounts of the layered fillers were over 100/3. The improvement of Young’s modulus by EG is higher than that obtained using the corresponding amount of clay25A.

Figure 1.20 Young’s modulus (a), tensile strength (b), toughness (c) and elongation at break (d) of nanocomposites based on PHBhx with layered silicate clay25A (■) and EG (▼).
Chapter 1. Thermoplastic nanocomposites

The tensile strength increased a little with increasing loadings of the exfoliated clay or EG when the amount of layered fillers was less than 100/1, as shown in Figure 1.20(b). However, the tensile strength of the NC series decreased when the amount of layered silicate was over 100/1 and again increased slightly when the amount of clay25A was over 100/4. The tensile strengths in the NG series decreased when the amount of EG was over 100/1.

There is an obvious trend of decreasing toughness of the NC and NG series with increasing filler concentration, as shown in Figure 1.20(c). The elongation at break of the NC and NG series increased slightly at contents less than 100/1 and decreased with increasing layered fillers when the content was larger than 100/1, as shown in Figure 1.20(d). The fine dispersion of layered fillers in the matrix may decrease the chains’ mobilities during tensile extensions. Recently, a reduction in elongation at break with increasing layered silicate content was also reported for thermoplastic/layered silicate systems.[20]

1.3.2.4 The thermal stabilities

The TGA results for the NC and NG series of nanocomposites are shown in Figure 1.21(a) and (b), respectively. The onset of thermal degradation point was taken to be the temperature at 5% weight loss. There was a decrease in the onset of thermal degradation temperature with increasing amount of dispersed silicate layers. The onset of thermal degradation temperature decreases up to approximately 22°C in the NC series, compared with that of the neat PHBHx. The residual weight, calculated as the weight at 320°C, of course increases with the increasing amount of clay; it was, however, not proportional to the amount of clay incorporated. This could be explained by assuming that the addition of
clay enhanced the performance by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition. At the same time, a small amount of clay may also restrict thermal motion of the polymer on the surface of the silicate layers, which is actually the absorbed or chemically bonded polymer matrix on the surface of the layered fillers.[43] Therefore, the residual weights are also somewhat more than the corresponding amount of layered fillers incorporated. This kind of improvement in thermal stability was also observed in other systems, such as the intercalated nanocomposites prepared by emulsion polymerization.[27]
Figure 1.21 Thermal stabilities of the nanocomposites based on PHBHx with clay25A (a) and EG (b).

As shown in Figure 1.21(b), similar trends were observed for the onset thermal degradation temperature, and the residual weight at 320°C for the NG series. However, the onset of thermal degradation temperature decreased up to about 10°C compared with that of the neat PHBHx. This could also be explained by the fact that the fine dispersion of EG in the PHBHx matrix, the strong physical and chemical interactions between EG and PHBHx, and the heat conductivity of graphite layers may help to transfer the heat inside, which would lead to less heat accumulation for degradation than in the NC series.

1.3.2.5 Conductivity of PHBHx/EG

As shown in Figure 1.22, the resistivity of the NG series is still in the range $10^{15} \sim 10^{16}$ Ohm-cm with the amounts of EG used to improve the other properties of this
nanocomposite. Since only those materials with resistivity values lower than $10^4$ Ohm-cm can be regarded as electrically conductive, the PHBHx/EG nanocomposites with filler content less than 100/10 would not be in this category at present.

![Graph showing electrical volume resistivity vs. ratio of PHBHx/EG](image)

**Figure 1.22** The electrical volume resistivity of the PHBHx/EG composites as a function of composition.

The electrical conductivity of EG/polymer nanocomposites is strongly related to filler-filler networking in the polymer matrix, which depends on the nature of the particle dispersion, the EG particle sizes, the amount of the EG, and processing conditions during extrusion blending and hot compression. EG consists of sheets, which should be favorable in giving low values of the percolation threshold concentration necessary for conducting pathways. At the same time, numerous other research studies also concluded that the
electric conductivity of hybrid systems are strongly related to the conditions used in the preparation and mixing procedures applied,\cite{44-46} and to the temperature and hydrostatic pressure during sheet formation.\cite{47} Although, the TEM results clearly showed that the successful achievement of nanoscale dispersions of EG in PHBHx, which also showed that the sheets are completely separated from each other, which seems reasonable to expect the high resistivity values. Potschke’s results\cite{44} also demonstrated that the resistivity value less than $10^4$ Ohm-cm could be reached in polycarbonate/EG nanocomposites only when the EG content was over 17.5 wt\% prepared under certain conditions. In the case of the present system, future work should be carried out for the conversion of such EG dispersions to ones yielding filler-filler networks that show electrical conductivity.

1.4 Conclusions

Solution intercalation methods were developed for preparing novel nanocomposites based on the PHBHx biodegradable polyester and layered silicates (specifically two organically modified clays, mica, and talc). Exfoliated structures of these fillers in the matrixes are produced at low filler concentrations, but intercalated structures are probably predominant at higher loadings. The major benefits from these nanoparticles are the increase in the modulus and toughness at surprisingly low concentrations of the layered silicates. The thermal stability of the PHBHx polymer decreased slightly with the incorporation of fillers but the interval temperature characterizing the degradation was broadened, especially in the case of some of the clay nanocomposites. Overall, clay nanocomposites have better mechanical properties than those formed from mica and talc mainly because the two kinds of clay used here are organically modified ones which have
Chapter 1. Thermoplastic nanocomposites

much better compatibility with PHBHx polymer than do mica and talc. As for thermal
stabilities, in some cases, these layered fillers slightly increased the degradability of the
PHBHx in agreement with studies on other reinforced biodegradable polymers [17].

Novel nanocomposites based on the biodegradable polyester PHBHx and layered
silicate clay25A or EG, were successfully prepared by melt blending. The WAXD and TEM
results clearly demonstrated that the clay25A and EG were exfoliated in the polymer
matrix, especially at low filler contents. The major benefit was the considerable increase in
the Young’s modulus and tensile strength of PHBHx/clay25A and PHBHx/EG
nanocomposites, particularly at very low filler contents. The introduction of clay25A and
EG decreases the onset thermal degradation temperature and increases the thermal
degradation rate of the PHBHx. The exfoliated state of EG in the PHBHx matrix does not
help to form the filler-filler network to make the NG nanocomposites electrically conductive
at the loadings used to improve other properties of these materials. Further research in the
effect of exfoliated clay and EG on the biodegradability of these interesting and important
materials is ongoing, with some of the focus being on electrical conductivity,
biodegradation mechanisms, chemical syntheses, and additional mechanical properties. [48-
51]
Chapter 2. Improvements in the mechanical properties of a biodegradable thermoset based on glycerol-derived alkyd resin by layered

2.1 Introduction

There is currently considerable interest in biodegradable polymers that can be used as alternatives to petroleum-based plastics to reduce environmental problems.[1, 2] For example, such polymers can be derived from (a) sources such as poly(butylene succinate), poly(E-caprolactone), poly(vinyl alcohol), aliphatic polyester and aliphatic-aromatic copolyesters, or (b) from renewable resources such as polyglycolide, polylactides, chitosan derivatives, or (c) from biosources such as corn, wood cellulose, etc, or (d) from small molecules like butyric acid or valeric acid that give polyhydroxybutyrate and polyhydroxyvalerate and their copolymers (including Procter & Gamble’s Nodax™ resins) by bacterial reactions.[3-6] Obviously, biodegradable polymers made from renewable resources or natural sources are attracting much more attention because of the eco-friendliness resulting from their origins, in contrast to the fully petroleum-based biodegradable polymers, mainly because they have environmental and economic advantages.[7, 8] Glycerol-derived alkyd resins are also a kind of biodegradable polymer, and are products of polycondensation reactions between a polybasic acid and polyhydric alcohol modified with fatty acid or drying oil.[9, 10] In recent years, the increasing low-cost supply of glycerol from the production of biofuels has led to increasing interest in glycerol-based alkyd resins, particularly since they might be a useful type of biodegradable polymer.
Chapter 2. Thermoset nanocomposites

Traditionally, alkyd resins, as oil modified polyesters, are among the most widely used resins in exterior solvent-based inexpensive coatings applications because of their high gloss and durability.\textsuperscript{[11-13]} Alkyd resins possess flexibility to certain extents because of the long-chain fatty acid of the oil used in the modification procedures. The availability of better performing acrylic resins caused alkyd resins to become relatively minor in importance. However, it is estimated that alkyd resins still constitute 70\% of the conventional binders used in surface coatings today.\textsuperscript{[8]} Such thermoset resins could be very important in a wide range of applications, not only because of their excellent high gloss and durability, but also because of their being made from natural materials. Thus, alkyd resins are currently considered to be among the most promising biodegradable plastics because of their low production costs and easy processibility in large-scale production. However, some of the properties such as brittleness, low heat distortion temperature, high gas permeability, and low melt viscosity for further processing etc. restrict their applications. Therefore, modification of the biodegradable alkyd resins through innovative technologies such as nanoreinforcement is an increasingly important challenge.

The introduction of layered silicates into polymeric materials have been a research focus for a number of years, since results from the Toyota Company showed that the introduction of only 2 vol\% of exfoliated clay into Nylon-6 leads to an 87°C increase in glass transition temperature and doublings in Young's modulus and tensile strength.\textsuperscript{[14-18]} The introduction of natural layered silicates such as clay, mica and talc into a biodegradable alkyd resin would mean that the resulting polymeric nanocomposites would be entirely made of nonpetroleum dependable sources.\textsuperscript{[19, 20, 52]}
Chapter 2. Thermoset nanocomposites

The present review gives a brief report on the preparations and morphologies of glycerol-based alkyd resin/layered silicates nanocomposites, as well as their thermal stabilities and mechanical properties.

2.2 Experimental

2.2.1 Materials

The glycerol-derived alkyd resin polymer, a kind of thermoset precursor material, was kindly provided by the Procter & Gamble Company. The precursor was maleic anhydride-glycerol oligomer (Figure 2.1). It is a sticky solid, and becomes sufficiently liquefied to pour when heated to 100°C. Southern Clay Products Inc. (Gonzales, Texas) provided commercially available clay, Cloisite 30B, which was a natural montmorillonite modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium chloride (Figure 2.2) (concentration of 90mg=100 g clay). The average d001 d-spacing of this silicate layer was about 18.5 Å diglycidyl ether of bisphenol A (DGEBA) was kindly provided by the Dow Chemical Company (Midland, MI). Mica (H₄Al₆K₂O₂₄Si₆, 325 mesh, water ground) and talc (3MgO·4SiO₂·H₂O) were products of Spectrum Quality Products Inc. (Garden, CA) and the Aldrich Chemical Co., St Louis, MO, respectively. All organic solvents were high-performance liquid chromatography grades and were purchased from the Aldrich Company.
Chapter 2. Thermoset nanocomposites

Figure 2.1 Schematic for the preparation of a glycerol-derived alkyd resin made from maleic anhydride and glycerol.

Figure 2.2 Quaternary ammonium salt used to treat the clay. Here T is tallow (65% C18, 30% C16, 5% C14), and the anion is chloride.

2.2.2 Treatment of the clay

To further enhance the polar interactions between the fillers and the alkyd resin matrix, the organoclay surfaces were further treated with a diepoxide, a diglycidyl ether of bisphenol A (DGEBA) with epoxy molar mass of 184 to 190 g/mol. The epoxy monomer was diluted in acetone with a volume ratio of 1:10. The organo-clay was first suspended in water, and then the desired amount of epoxy-acetone solution was poured into the mixture, which was then mechanically stirred at 50°C for 2 h. The mixture was completely dried in an oven, evaporating both the water and solvent. The weight ratio of DGEBA to alkyd resin in the finished composite was calculated from the molecular weight of epoxy and carboxyl contents of the resin.

44
2.2.3 Preparation of the alkyd nanocomposites

Several concentrations of the clay30B, clay30BT, mica, and talc in the alkyd resins were investigated, specifically 2.5, 5.0, 7.5, and 10 wt% (relative to the total weight of the glycerol-derived alkyd resin). Briefly, the desired amount of one of these layered silicates was added to the glycerol-derived alkyd resin and mechanically stirred for 20 min in a flask at 80–90°C. The mica and talc had been strongly milled to a fine state of homogenous powders before mixing. The samples were then placed into Teflon™ molds and degassed under vacuum at 100°C for about 60 min, and then held at 100 °C overnight. In many cases, undesirable bubbles formed, but this was generally avoidable by better degassing at a temperature that gave a decreased viscosity at which any bubbles easily escaped before the matrix solidified.

![Image](image_url)

**Figure 2.3** Schema of the preparation glycerol-derived alkyd resin/layered filler hybrid thermoset nanocomposites.
2.2.4 Characterizations

2.2.4.1 X-ray diffraction

X-ray diffraction (XRD) measurements of neat alkyd resin, the layered silicates, and the corresponding composites films were carried out at room temperature using an X-ray generator (a Siemens D500 diffractometer) (CuKa radiation, with 130 30 mA, 40 kV, k 46 1.5406A ). The 2θ scan range was 2° to 10°, with a step size of 0.05°, and a time per step of 1 sec.

2.2.4.2 Transmission electron microscopy

TEM images were obtained using a JEM 1230 EX-II instrument (JEOL, Tokyo, Japan) operated at an accelerated voltage of 80 kV. All of the ultrathin sections (less than 200 nm) were obtained by microtoming, using a Super NOVA 655001 instrument (Leica, Swiss) with a glass knife. They were subjected to TEM observation without staining.

2.2.4.3 Thermogravimetric analysis

TGA results of the alkyd thermoset and corresponding nanocomposites were carried out on a TA Instruments TGA 2050 Thermogravimetric Analyzer with nitrogen as purging gas at 130 ml/min. Tests were conducted from room temperature to 600°C at a heating rate of 20°C/min.

2.2.4.4 Differential scanning calorimetry

The thermal behavior of the all materials was characterized using DSC measurements on a TA Instruments DSC 2010 at 130 ml/min nitrogen flow at a thermal rate of 10°C/min from -150 to 100°C.
2.2.4.5 Mechanical properties

The values of the moduli and tensile strengths of samples having dimensions of 30x5x1mm$^3$ were measured at room temperature using a fully computerized INSTRON mechanical tester (Model 1122). The initial gauge length was 30 mm and the cross-head speed was 5 mm/min. The tensile properties of greatest interest were the Young’s moduli and tensile strengths, and the values were obtained based on an average of at least five measurements.

2.3 Results and discussion

2.3.1 The dispersion of layered silicate
Chapter 2. Thermoset nanocomposites
Figure 2.4 XRD results for alkyd resins reinforced with layered silicates. (a) Clay30B and its alkyd resin composites; (b) Clay30BT and its alkyd resin composites; (c) mica and its alkyd resin composites; (d) talc and its alkyd resin composites.

Figure 2.4 shows the XRD patterns in the range of $2\theta = 2-40^\circ$ for the alkyd resin, Clay30B, clay30BT, mica, and talc, and their corresponding composites containing various concentrations of the layered silicates.

The pattern of the neat alkyd resin is displayed as a baseline to compare the existence of diffraction peaks coming from the layered silicate dispersed in the matrix. The peak at $2\theta = 4-30^\circ$ of the neat glycerol-derived alkyd resin corresponds to the amorphous state of the matrix. There is no peak in the range of $2\theta = 2-15^\circ$, which is an important range with regard to analysis of peak changes upon the introduction of the layered silicates.
Chapter 2. Thermoset nanocomposites

Clay30B was the clay modified with methyl tallow bis-2-hydroxyethyl quaternary ammonium chloride with one alkyl tail, which increased the space between two layers. Specifically, the d001 distance increased from 11.7 Å in Cloisite Na+ to 18.7 Å in clay30B.

There was no peak in the range 2θ = 2–15° in the alkyd resin/clay30B composites in which the content of layered silicate was less than 7.5%. This result indicates that the d-spacings between layers are so large that the fillers formed exfoliated structures. This exfoliation may have been brought about by the side chains of the matrix dispersing into the spaces among layers to exfoliate the layers, which facilitated by the reaction between the tallow modifiers chains of clay30B and the alkyd resin matrix. The reaction between the maleic-anhydride and the hydroxyl groups in the methyl tallow 2-hydroxylethyl quaternary ammonium on the surface of clay30B was proposed in the schematic in Figure 2.5. The characteristic peak of the neat clay30B was still evident in the composites when the content of clay30B was over 5.0% but much lower than that of clay30B, which demonstrated that the clay30B was not well exfoliated in the matrix when its concentration was relatively high and thus formed only intercalated structures.
**Figure 2.5** Schematic of the reaction of alkyd resin precursor with the clay30B.

It is clearly indicated in **Figure 2.4b** that clay30BT was further delaminated by the reaction with DGEBA from 18.5 Å to 20.2 Å compared with clay30B. The proposed reaction mechanism could be explained by the sketch in **Figure 2.6**, in which the hydroxyl groups on the surface of clay30B may react with the epoxy of DGEBA. The introduction of DGEBA did indeed expand the d-spaces among the layers.

**Figure 2.6** Schema of the reaction of DGBEA with clay30B.

A similar phenomenon occurred in the clay30BT composites. There was no discernible peak from the clay30BT in the composites at the range 2–10° when the content of the clay30BT was less than 7.5%, which means that the clay30BT was almost completely exfoliated.

The characteristic peak for the clay30BT became weaker when the clay content was over 7.5%. The plain peak of the resin/clay30BT composite compared to that of the neat clay30BT indicates an increase in d-spacing and more intercalated structures in the
polymer matrix. The figure also clearly shows that there were weak peaks in the XRD result for resin/clay30BT nanocomposites, even in the resin/clay30BT composite with 10.0% of clay30BT, which indicated that the clay30BT was almost fully exfoliated in the alkyd resin matrix, since the crosslinking between maleic-anhydride and DGEBA could also happen.

The XRD pattern for the alkyd resin/mica composites (Figure 2.4 c) showed that the characteristic peak of mica was still present in the composites. The same results were obtained in the alkyd resin/talc composites (Figure 2.4 d). The results showed that the mica and talc could not be intercalated applying the usual melt blending methods. The results were somewhat different from the results reported in the PHBHx/mica and PHBHx/talc composites, in which mica and talc were intercalated or even exfoliated and well dispersed during ultrasonic treatment at low concentrations.\(^{[4]}\)

In order to check the nanometer-scale morphologies of the nanocomposites, XRD was supplemented by TEM, which provides direct visualization of the morphology, atomic arrangement, spatial phase distribution, and structural features in a selected sample area.
Chapter 2. Thermoset nanocomposites
Figure 2.7 TEM results showing the dispersion of clay30B and clay30BT in the alkyd resin. (a) Alkyd resin/clay30B 5.0%; (b) Alkyd resin/clay30BT 5.0%; (c) alkyd resin/mica 5.0%; (d) Alkyd resin/talc 5.0%.

Figure 2.7 shows the TEM images of the nanocomposites: (a) glycerol-derived alkyd resin/clay30B -5.0%; (b) glycerol-derived alkyd resin/clay30BT-5.0%; (c) glycerol-derived alkyd resin/mica -5.0% and (d) glycerol-derived alkyd resin/talc -5.0%, where the dark entities are intercalated silicate layers. From the TEM results in Figure 6a and b, it is clear that the stacks of clay30B and clay30BT forming the clay crystallites were now well dispersed in the polymer matrix. TEM results in Figure 2.7c and d also demonstrate that mica and talc could be dispersed into small agglomerates by the milling and shear during melt blending.

2.3.2 Thermal stability

The thermal stabilities of the alkyd resin/layered silicate composites series were determined from the thermogravimetric results. Figure 2.8 shows an example of a TGA trace obtained for the neat alkyd resin thermoset system. The onset and the end set temperature were determined from the intersection of the two tangents, and the peak degradation temperatures were determined from the inflection points on the curves.
**Figure 2.8** Determination of onset and end set temperature from the thermogravimetric results on an alkyd resin thermoset.

Table 2.1 presents values for the (i) onset temperature, (ii) the end set temperature, (iii) the temperature interval ΔTemp between these two temperatures, (iv) the degradation peak temperature, and (v) the total weight loss at 500°C. These results showed that the onset temperature was increased to ca. 345°C for the alkyd resin/clay30BT nanocomposite, to 330°C for the alkyd resin/mica composites, and to 342°C for the alkyd resin/talc composites, compared with the onset temperature 321.2°C for the neat alkyd resin thermoset. Similarly, the end temperature was increased to ca. 436°C for the alkyd resin/clay30BT nanocomposite, to 426°C for the alkyd resin/mica composites, and to 425°C for the alkyd resin/talc composites, compared with the onset temperature 344.7°C for the neat alkyd resin thermoset. The improvement of thermostability obviously results from the introduction of layered silicates, such as clay30BT, mica and talc. Specially, the
larger improvement in the alkyd resin/clay thermosets relative to the other two series is obviously from the exfoliated structure in alky resin/clay30BT as opposed to the less-effective intercalation in the alkyd/mica or alkyd resin/talc composites. The interval temperature between degradation onset and end set remained nearly constant around 90°C for the alkyd resin/clay30BT thermosets and alkydresin/mica thermosets, and ca. 80°C for the alkyd resin/talc thermosets. However, the interval temperatures were increased by about 65°C compared with that for the neat alkyd resin thermoset.

**Table 2.1** Thermal stability parameters of various alkyd resin/layered silicates systems as determined from TGA

<table>
<thead>
<tr>
<th>Filler</th>
<th>Filler loading</th>
<th>Onset temp (°C)</th>
<th>End set temp (°C)</th>
<th>ΔTemp (°C)</th>
<th>Degradation peak (°C)</th>
<th>Total wt. loss @500°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0</td>
<td>321.2</td>
<td>344.7</td>
<td>23.5</td>
<td>344.7</td>
<td>100.0</td>
</tr>
<tr>
<td>Clay30BT</td>
<td>2.5</td>
<td>349.2</td>
<td>437.1</td>
<td>87.9</td>
<td>403.0</td>
<td>79.6</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>345.8</td>
<td>437.8</td>
<td>92.0</td>
<td>407.2</td>
<td>78.1</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>346.5</td>
<td>437.1</td>
<td>90.6</td>
<td>408.0</td>
<td>76.5</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>345.0</td>
<td>436.2</td>
<td>91.3</td>
<td>408.0</td>
<td>75.6</td>
</tr>
<tr>
<td>Mica</td>
<td>2.5</td>
<td>335.9</td>
<td>432.1</td>
<td>96.2</td>
<td>393.1</td>
<td>78.1</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>336.7</td>
<td>427.1</td>
<td>90.3</td>
<td>395.6</td>
<td>76.6</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>336.6</td>
<td>426.3</td>
<td>89.8</td>
<td>394.1</td>
<td>76.4</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>328.4</td>
<td>426.3</td>
<td>97.9</td>
<td>394.5</td>
<td>74.1</td>
</tr>
<tr>
<td>Talc</td>
<td>2.5</td>
<td>342.8</td>
<td>431.9</td>
<td>89.1</td>
<td>402.8</td>
<td>79.8</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>344.3</td>
<td>425.6</td>
<td>81.4</td>
<td>398.1</td>
<td>75.9</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>344.3</td>
<td>425.6</td>
<td>81.4</td>
<td>399.7</td>
<td>74.4</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>344.3</td>
<td>425.0</td>
<td>80.7</td>
<td>400.4</td>
<td>72.2</td>
</tr>
</tbody>
</table>

The total weight losses of the composites at 500°C were not generally in direct proportion to the amount of layered silicates incorporated. Reductions of weight loss with increases in layered silicates concentration were of course observed, as expected.
2.3.3 Mechanical properties

![Modulus vs Filler Content](image1)

![Tensile Strength vs Filler Content](image2)
Figure 2.9 Mechanical properties of glycerol-derived alkyd resin/layered silicates (clay30BT, mica, talc) nanocomposites: (a) Young’s modulus, (b) tensile strength, (c) toughness.

Figure 2.9 shows the tensile properties obtained at 25°C for the neat alkyd resin and the alkyds resin/layered silicate composites. The properties include (i) Young’s modulus, (ii) tensile strength (defined as the stress at break) and (iii) toughness. As shown in Figure 8, there was almost no increase in the mechanical properties including Young’s modulus, tensile strength and toughness of alkyd resin/clay30BT composites compared those of pure alkyd resin thermoset. This is due to the fact that the fine dispersion and exfoliated layered clays in the alkyd resin may also act to improve the gas permeability of the matrix, which would prevent the low molecular weight molecules such as water from permeating through the matrix during crosslinking, especially when the matrix had a high viscosity.\textsuperscript{[53]} However, as shown in Figure 2.9, both the Young’s modulus and tensile strength of the composites were greatly improved in alkyd resin/mica and alkyd/talc composites.
Chapter 2. Thermoset nanocomposites

compared to those of the pure alkyd resin thermoset. Of particular interest is that even very small amounts of the mica or talc gave significant reinforcement of the alkyd resin thermoset. Large amounts of mica or talc (>5.0%) did not improve the Young's modulus and tensile strength as much. Similar results were obtained for the toughness of the alkyd resin/mica thermosets. However, the toughness of the alkyd resin/talc did increase with increasing amounts of talc.

2.4 Conclusions

Alkyd resin/clay nanocomposites were successfully prepared by melt blending maleic anhydride-glycerol precursors with organo/clays that had been pretreated with methyl tallow bis-2-hydroxyethyl ammonium chloride salt (clay30B) and the clay further treated with DGEBA (clay30BT). XRD and morphology results clearly indicated that 30BT was further delaminated by the DGEBA, and that the organoclays were mostly exfoliated and well dispersed in both series of alkyd resin nanocomposites, and this led to considerable improvements in thermostabilities. The mechanical properties including Young’s modulus, tensile modulus, and toughness, remained comparable to those of the corresponding neat alkyd resin thermoset. Although the mechanical properties of these glycerol-anhydrid alkyd resins were found to be greatly improved, there are still problems such as the need for further minimizing the formation of aggregates in the case of mica or talc in the polymer matrix.

Additional research also should be carried out to establish the morphologies, mechanical properties, and biodegradabilities of these interesting clay-based materials. It would also be important to investigate the modification by introducing in-situ silica by the
sol-gel method,[54, 55] and other layered inorganic fillers such as expanded graphite.[44, 46] Microcellular foams would also be of interest, particularly in the case of the graphite, since the percolation threshold concentration for electrical conductivity should be extremely low for such an anisometric filler.[11]
Chapter 3. Preparation and characterization of hydrophilic bimodal hydrogels based on PDMS

3.1 Introduction

Poly(dimethylsiloxane) (PDMS), with repeat unit [-Si(CH3)2-O-], has attracted great interest for many years since it can be widely used in microfluidic devices, microcontact printing technology, biocompatible devices (for example contact lenses), and drug delivery systems. These impressive ranges of applications have been due to the many attractive features of PDMS, including (i) high gas permeability, (ii) good optical transparency, (iii) high flexibility and low risk of loss or damage, (iv) nontoxicity and biocompatibility, (v) stability toward heat and chemicals, (vi) low curing temperature, (vii) moldability, and (viii) ease of sealing with other materials. Although PDMS has many advantages, there are some physical properties that limit its use in some applications, especially those involving biocompatible devices. PDMS is a hydrophobic polymer, and some other hydrophobic molecules, biopolymers and cells all irreversibly absorb to its surface. In addition, small hydrophobic molecules can actually be absorbed into the bulk of the PDMS. This has led to recognition of the need for modifying the surface of such polysiloxane materials to ameliorate problems of this type. Obviously, increasing the hydrophilicity of any polymer surface improves its’ wettability and this, in turn, improves its’ biocompatibility.

There have been a large number of patents and research reports that describe attempts to modify the strongly hydrophobic surfaces of PDMS to make them sufficiently hydrophilic to be useful in a number of biomedical applications. The required changes in surface energy
can be gotten by introducing various polar groups with corona discharges,\cite{70,71} ultraviolet irradiation in combination with ozone\cite{72-75} plasma treatments,\cite{76-78} irradiation with CO$_2$ pulsed lasers,\cite{79} and grafting or simple adsorption of polar polymers onto the surfaces.\cite{80-83} These methods have indeed given significant improvements in the wettability of PDMS surfaces. Three problems that have arisen, however, are (i) the loss of hydrophilicity from the migration of surface hydroxyl groups into the polymer bulk (to minimize surface free energies), (ii) physical damage to the surface of PDMS from cracks or other defects, and (iii) limited biocompatibility of PDMS surfaces after some of the more aggressive chemical treatments.\cite{71,75,81,84} Similar problems occurred upon either coating the surface with additives, or compounding the additives into the polymer (since they would subsequently diffuse to the surfaces). In one case, Binkert covalently immobilized lactic acid poly(ethylene glycol (PLL-g-PEG) onto the surfaces of contact lenses based on polysiloxane hydrogels via an intermediate aldehyde plasma polymer to form brush-like, protein-resistant surfaces.\cite{83} More hydrophilic surfaces and good optical quality were achieved, but reproducibility problems and inhomogeneities in the coatings were encountered.

Preparation of amphiphilic polymer conetworks has been a successful way to make the surfaces and interiors of a polysiloxane network more hydrophilic. Such amphiphilic conetworks consist of hydrophilic and hydrophobic chains covalently bonded to each other.\cite{85} The amphiphilic nature of these new cross-linked polymers is indicated by their swelling ability in both aqueous and organic media without losing their dimension stability and without encountering macroscopic phase separation or polymer leaching. For these reasons, amphiphilic polymer conetworks represent a relatively new class of promising materials for applications such as contact lenses, pervaporation membranes, drug delivery
systems, biomedical scaffolds for tissue engineering, and supports for catalysts. The amphiphilic conetworks based on PDMS and some hydrophilic components was shown to at least partly provide co-continuous or interpenetrating phase morphologies for long-term biocompatibility, with the resulting two phases acting as two different routes for transfer of oxygen and aqueous materials.\(^{85-89}\)

The hydrophilic component was poly(ethylene oxide) (PEO) or, nearly equivalently, poly(ethylene glycol) [-(CH\(_2\))\(_2\)O\(-\)] (PEG), both being polyethers already used in numerous applications involving biomaterials. Their advantages are their interfacial energies with water, relative structural stability, lack of binding sites for reactive proteins, high chain mobility, and steric stabilization effects.\(^{90-93}\) However, because of their incompatibilities with other polymers, phase separation almost always occurs in their mixtures and this can lead to opaqueness as well as reduced mechanical properties.\(^{94}\) Covalently crosslinking the polymer chains at least prevents demixing at the macroscopic level, leading to domains that remain in the nanoscale range.\(^{88,95-100}\)

An earlier part of this series of reports described using amphiphilic PDMS-PEG block copolymers as both compatilizers for these very different blocks, as well as sources of greatly increased hydrophilicity.\(^{101}\) The present study involves another novel method to prepare polysiloxane hydrogels by crosslinking hydroxyl-terminated PDMS by poly(ethylene oxide) functionalized trialkylsilanes having different chain lengths. Specifically, these materials were 2-methoxy(polyethyleneoxy)propyl-trimethoxysilane with 4-6 units of ethylene oxide, and N-(triethoxysilylpropyl)-O-polyethylene oxide urethane with 6-9 units of polyethylene oxide (from polycondensations at room temperature).\(^{102}\) The hydrophilic chains thus introduced would be dangling from the trifunctional crosslinks
and should have very favorable effects on surface hydrophilicities, equilibrium water contents, and mechanical properties.

3.2 Experimental

3.2.1 Materials

Samples of linear hydroxyl-terminated PDMS having average number-molecular weights, 22,600 g·mol⁻¹ and 880 g·mol⁻¹ (DMS-S31 and DMS-S12), were purchased from the Dow Corning Company. The crosslinkers were tetraethoxysilane (TEOS), N-(triethoxysilylpropyl)-O-polyethylene oxide urethane (brand name: SIT8192.0, designated here as S1), and methyloxy(polyethyleneoxy)propyl-trimethoxysilane (brand name: SIM6492.7, designated S2), and their structures are shown in Figure 3.1. These crosslinkers and the catalyst, stannous-2-ethylhexanoate (SNB1100), were all purchased from Gelest Inc, Morrisville, PA. The solvents, such as alcohol and toluene, were purchased from the Aldrich-Sigma Company, and were used directly without further purification. Deionized (DI) water was used in the measurements of static contact angles of the hydrogels. Additional details are given elsewhere.[103]

![Figure 3.1 Structures of end-linkers S1 (upper sketch) and S2 (lower sketch).](image-url)
3.2.2 Preparation of the polysiloxane hydrogels

The hydrogels were prepared with the constant mol ratio (5/95) of DMS-S31 as the long chains, to DMS-S12 as the short chains. The samples of hydroxyl-terminated chains were end-linked in the undiluted state with the stoichiometrically-required amounts of crosslinkers at the mol ratios of TEOS and S1 of (10/0, 8/2, 6/4, 4/6, 2/8) (designated T-0, T-S1-2, T-S1-4, T-S1-6, T-S1-8), and at the mol ratios of TEOS and S2 of (10/0, 8/2, 6/4, 4/6, 2/8) (designated T-0, T-S2-2, T-S2-4, T-S2-6, T-S2-8), respectively. The bimodal distributions of network chain lengths thus produced have been shown to give unusually good mechanical properties in a variety of elastomers. [19, 104-107]

Briefly, the mixtures were first stirred vigorously in air at room temperature for at least 2 hrs. The stannous-2-ethyl hexanoate catalyst was then introduced at 0.6 wt% of the total weight of the other components. The mixtures were then stirred for approximately 10 min before being poured into Teflon™ molds. The reactions were carried out at room temperature for three days, after which a vacuum was used to remove the by-products such as alcohol and water, and gas bubbles. The hydrogel sheets were then extracted with toluene for three days, and were then deswelled with methanol and finally dried under vacuum. The fraction of soluble polymers thus removed was very small, amounting to approximately only 2.5 wt%.

3.2.3 Characterizations

3.2.3.1 Static contact angles

The hydrophilicities of the surfaces of the hydrogels were characterized by values of the contact angles, the values of which were the average results taken from at least four
areas on the surfaces. The tests were carried out at room temperature with ca. 1 μl deionized water, and angles were visually determines using a VCA2000 digital camera with zoom capability.

3.2.3.2 Equilibrium water contents

Values of the EWC were obtained by immersing a piece of weighed hydrogel film measuring 1 cm × 1 cm × 0.2 cm in a large excess of distilled water at ambient temperature. The weights of the swollen samples were not recorded until they became constant. Values of the equilibrium volumetric degree of swelling $S_m$ were calculated from the equation $S_m = (W_t - W_d) / W_d \times 100\%$, where $W_t$ and $W_d$ were the swollen and dry weights, respectively.

3.2.3.3 Differential scanning calorimetry

A TA 1501 thermal analyzer (Thermal Analyzer Inc.) was used for determination of the thermal behaviors of the samples in an atmosphere of nitrogen flowing at a rate of 30 ml/min. A 5 - 10 mg sample of hydrogel film was sealed into an aluminum sample pan. The sample was then quickly heated above its glass transition temperature $T_g$ to irritate its thermal history, and was then quickly cooled to -150 °C. After a period for equilibration, it was then heated at a scan rate of 10 °C/min from -150 to 100 °C in a nitrogen environment.

3.2.3.4 Mechanical properties

The stress-strain behavior at ambient temperature was determined using a home-built tensile tester on samples having the dimensions 30 mm × 5 mm × 2 mm, at an elongation rate of 5 mm/min. Of particular interest were Young’s modulus, tensile strength, toughness, and elongation at break.
3.2.3.5 Fourier transform infrared spectroscopy

FTIR spectroscopy measurements were carried out to identify the functional groups present on the surfaces of the pristine hydrogel samples. This could be useful for analyzing the structures and reaction mechanism involved in the processing. The measurements were conducted using Digilab Excalibur FTIR equipment in the mid-IR range (4000 to 500 cm\(^{-1}\)). The resolution was 4 cm\(^{-1}\), and 16 scans per sample were analyzed using the Digilab Resolutions Software.

3.2.3.6 X-ray diffraction patterns

These measurements on the hydrogel films were carried out at room temperature using an X-ray diffractometer (Siemens D500) (Cu K\(\alpha\) radiation, with 30 mA, 40 kV, \(\lambda = 1.5406 \text{ Å}\)). The 2\(\theta\) scan range was 2 to 30\(^\circ\), with a step size of 0.05 degree and a time per step of 1 second.

3.2.3.7 Environmental scanning electron microscopy

Sample surfaces were cleaned with alcohol, and suitable cross sections were then obtained by immersing the samples in liquid nitrogen. The resulting brittle samples were then broken to obtain fresh surface areas. The morphologies of the surfaces and cross sections were measured using a Philips XL30 Environmental Scanning Electron Microscopy under high vacuum.
3.3 Results and discussion

3.3.1 Crosslinked hydrogels using the poly(ethylene oxide)–trialkoxyasilanes

The reactions involved are shown in Figure 3.2. The approach shown is based on the usual preparation of networks from linear hydroxyl-terminated PDMS end-linked by TEOS with stannous 2-ethylhexanoate as catalyst.\(^{108}\) In the present case, the crosslinkers were TEOS and a PEO derivative of trialkoxyasilane (S1 or S2). Specifically, there was a condensation reaction between hydroxyl end groups of the PDMS and the alkoxy groups on the TEOS and the trialkoxyasilane. In this way, the hydrophilic PEO sequences, on the S1 or S2 were attached to the crosslinks as dangling chains.

![Diagram of hydrogel crosslinking reactions](image)

Figure 3.2 Schema reactions for end-linking the hydrogels by (a) S1 and (b) S2.
The FTIR results for the T-S1 and T-S2 series of hydrogels are shown in Figure 3.3 (a) and (b), respectively, and confirmed the nature of the condensation reactions. The peaks at 2965 cm\(^{-1}\), 1263 cm\(^{-1}\) and 792 cm\(^{-1}\) were assigned to Si–CH\(_3\) groups, and the peak at 1012 cm\(^{-1}\) to Si–O–Si groups. These peaks, identified in the pristine PDMS, were assigned to the siloxane chains in the hydrogels. Figure 3.3 (a) compares the FTIR results for the pristine PDMS (T-0) with those for some of the hydrogels. New peaks appeared in the T-S1 series at 3357 cm\(^{-1}\), 2871 cm\(^{-1}\) and 1074 cm\(^{-1}\) in T-S1-2 and T-S1-4, and were assigned to the –NH–, –CH\(_2–\) and C–O–C groups, respectively. Figure 3.3 (b) shows the presence of new peaks assigned to the groups –CH\(_2–\) (2965 cm\(^{-1}\)) and C–O–C groups (1074 cm\(^{-1}\)) in the T-S2 series of hydrogels. These results confirmed that the hydrophilic chains, with their PEO sequences, were successfully introduced into the networks.
Figure 3.3 FTIR results for the (a) T-S1 series the (b) T-S2 series of hydrogels.
3.3.2 Thermal characteristics

The differential scanning calorimetry results for the T-0 and T-S1 series of hydrogels, shown in Figure 3.4 (a), demonstrated that there were two new values of the glass transition temperature, $T_{g1(PEO)}$ and $T_{g2(PEO)}$, in the range 10 - 30 °C in the T-S1 series. As is also shown in Figure 3.4, comparisons can be made with pristine PDMS networks, whose crystallization temperature $T_{c(PDMS)}$ is -86.6 °C and crystalline melting point $T_{m(PDMS)}$ is -65.0 °C. In the hydrogels, $T_{c(PDMS)}$ decreased slightly, while $T_{m(PDMS)}$ and $T_{m\text{ peak}}$ increased slightly with increase content of S1. $T_{g1(PEO)}$ and $T_{g2(PEO)}$ also decreased with increased content of S1. These results indicated that the S1 end-linker improved the compatibility of the two phases. The results on the T-S2 series of hydrogels, shown in Figure 3.4 (b), also clearly indicated that there were two new values of the glass transition temperature, $T_{g1(PEO)}$ and $T_{g2(PEO)}$, in the range 10 - 30 °C. Again, increase in S2 content decreased $T_{g1(PEO)}$ and $T_{g2(PEO)}$ and slightly increased $T_{m(PDMS)}$ and $T_{m\text{ peak}}$. However, the crystallization temperature of PDMS, $T_{c(PDMS)}$, was not discernible, possibly because of improved compatibility obtained from the long dangling chains of PEO in the networks. As expected, the longer dangling PEO chains in S2, gave more pronounced improvements in the compatibility between the PDMS and PEO.
Figure 3.4 Differential calorimetry results for (a) T-S1 series (b) T-S2 series of hydrogels.
3.3.3 Morphology of the hydrogels

The hydrophilic POE dangling chains in the T-S1 and T-S2 series obviously formed hydrophilic phases because of their limited compatibility with the hydrophobic PDMS in the networks. Additional information was provided by the electron microscopy, which provided direct visualization of the PDMS and PEG phases. This is illustrated in Figure 3.5 where the dark regions are the PEG phases, which are seen to be seen well dispersed in the PDMS. The ESEM images shown correspond to: (a) T-S1-2 surface, (b) T-S1-2 cross section, (c) T-S1-6 surface, (d) T-S1-6 cross section, (e) T-S2-2 surface, (f) T-S2-2 cross section, (g) T-S2-6 surface, and (h) T-S2-6 cross section. In the T-S1-2 and T-S1-4 hydrogels, there was not much difference in the surface and cross-section results, with the PEG forming spherical phases of diameter less than 5 μm. This was much less than the PEG phase diameters in the PDMS-PEG systems crosslinked by bis((3-methyldimethoxysilyl)propyl)-polypropylene oxide.\(^{101}\) It was also observed that the PEG phase diameters in T-S1-4 were somewhat larger than those in T-S1-2 because of the higher contents of PEG in T-S1-2. Similar results were reached in the T-S2-2 and T-S2-4 hydrogels, where the PEG phase diameters were less than 5 μm, slightly larger than those in T-S2-2. As expected, the morphologies of T-S1 and T-S2 depended on the mixing condition during the cross-linking process as well as on the lengths and the amounts of the hydrophilic chains.
Chapter 3. Hydrophilic bimodal networks
3.3.4 Hydrophilicities

One of the simplest available methods for probing the surface properties of materials involves measuring the contact angles (CA) a water droplet makes on these surfaces. Baier et al.[93, 109] have found empirically that minimal fouling of hydrophilic polymer surfaces is obtained for intermediate values of the critical surface tension, obtained from the contact angles of a series of different liquids. In the case of PDMS networks, low contact angles would confirm that water-miscible polymer was present at its surface. Figure 3.6 (a) shows the CA values for the T-S1 bimodal hydrogel networks. The results show that (i) the CA values were considerably less than that of pristine PDMS (c.a. 105°), and (ii) the CA values of hydrogels on what was the air-side surface during crosslinking were much lower than those of the mold-side surface, and (iii) the CA values for both sides of the hydrogels decreased with increased amounts of S1 (except for T-S2-6), decreasing up to 40° for the
air-side surfaces and up to 15° for the mold-side surfaces. The results certainly confirmed the presence of hydrophilic chains on the surfaces of the polysiloxane networks.
Figure 3.6 Effects of the end-linkers on the static contact angles with water for the T-S1 and T-S2 hydrogels. ■ the air-side surfaces, ● the mold-side surfaces; (a) end-linker S1 and (b) S2.

In some cases, the Teflon™ molds apparently expelled some hydrophilic dangling chains on the mold side surface into the bulk of the polysiloxane networks, decreasing the hydrophilicity of these surfaces. This demonstrated that the hyrophilicity of the hydrogels was strongly related to environmental conditions.

The corresponding results for the T-S2 series were very similar, as can be seen from Figure 3.6 (b). Again, the values of the contact angles were lower than that of the pristine PDMS. Also, the CA values of the air-side surface were much lower than those on the mold-side surfaces. The CA value decreased up to 85° for the mold-side surface and up to 55° for the air-side surfaces. The CA values for the T-S2 series were much lower than those on the T-S1 list, which was mainly due to the larger number of PEO units (6~9) in the end-linker S2 than in the S1 one (4~6). This suggests that the longer hydrophilic chains do form hydrophilic layers on the surfaces, but there may be a critical length which, when exceeded, leads to saturation of the desired changes.

3.3.5 Equilibrium water contents

The equilibrium degrees of swelling of the hydrogels are of obvious importance, since several applications require suitable water contents. It should be noted that attaching a conetwork to the surface of a hydrophobic material confines the swelling volume change to one dimension (normal to the surface), with obvious effects on swelling behavior. In the specific case of the present hydrogels, higher water contents were generally more
advantageous because they gave a higher permeability and biocompatibility. However, with increasing water content, the mechanical strengths of the hydrogels decreased and their transparencies could also decrease (as a consequence of a microscopic phase separations). The optimal situation would obviously be high mechanical strength, transparency, and sufficient water content, which is the ultimate goal of this series of investigations.\textsuperscript{[110,111]} The EWC values of the T-S1 series, shown in Figure 3.7 (a), increased in proportion to the S1/TEOS amount, up to 11.8 wt%. The same trend was observed in Figure 3.7 (b) for the T-S2 series, where the EWC values increased up to 29.8 wt%. These results thus confirmed that the larger the number of PEO repeat units in the hydrophilic trialkoxysilane, the higher the hydrophilicity of the resulting hydrogel.
Figure 3.7 Effects of the end-linkers on equilibrium water contents.

3.3.6 Mechanical properties

The stress-strain behaviors of the T-S1 series of hydrogels (Figure 3.8, a) showed that the tensile strengths and elongations at break increased with increased values of S1/TEOS (except T-S1-4), while the Young’s modulus remained almost the same. Similar results were obtained for the T-S2 series (Figure 3.8, b), except for Young’s moduli slightly decreasing instead of increasing. Comparing the Young’s moduli for the T-S1 and T-S2 series given in Fig. 8 shows that the dangling hydrophilic chains did not decrease the hydrogel mechanical properties until their lengths were over a critical value.
Figure 3.8 Dependences of the stress-strain isotherms in elongation on the end-linker (a) S1, and (b) S2.
Chapter 3. Hydrophilic bimodal networks

Some of these results parallel earlier results, particularly on bimodal elastomers.[107, 112] The mechanical properties of bimodal elastomers in general could readily be controlled by variation of the ratio of the short to long chains in the end-linked networks.[104, 107, 112] This suggests the importance of additional work to optimize the mechanical properties of the present hydrogels through changes in the relative amounts of short chains and long chains in the networks. As a specific goal, for example, the Young’s moduli for biomaterials used in soft contact lenses should be less than 1.0 MPa (preferably less than 0.70 MPa), and elongations at break should be larger than 250 %.[89] In this regard, optimization of the present materials is in progress.

3.4 Conclusions

Bimodal hydrogels were successfully prepared from hydroxyl-terminated long and short chains of poly(dimethylsiloxane) (PDMS), end-linked with TEOS and the hydrophilic trialkoxysilane cocrosslinkers, methoxy(polyethyleneoxy)propyltrimethoxysilane and N-(3-triethoxysilylpropyl)-0-gluconamide. The contact angles observed with water showed that the surface hydrophilicities did greatly increase with increasing proportions of PEO sequences of the hydrophilic chains. Equilibrium swelling results showed the same increases with increasing proportions of the end-linkers. The mechanical properties of the bimodal hydrogels did not suffer very much with introduction of the hydrophilicity. The hydrophilic phases were well dispersed but calorimetric results indicated that there was nonetheless some phase separation, into PDMS and PEO phases. The contact angles with water and equilibrium water contents were in the acceptable range for used as contact lenses material. Further work should focus on increasing the advantages of the
bimodalities, increasing the transparency and the oxygen and water permeability, and decreasing the extents of protein absorptions.
Chapter 4. Preparation of bimodal hydrogels based on PDMS networks crosslinked by hydrophilic silane on the main chains

4.1 Introduction

PDMS has attracted so wide attention to apply as biomaterial because of its biocompatibility. However, its hydrophobicity limits its broad applications such as microchips,[56, 58, 60, 102, 113] drug delivery,[66, 67], contact lenses and other materials that need hydrophilic surface, proper water content as well as controllable mechanical properties. The PDMS networks with controllable mechanical properties could be obtained via end-linking short linear chains with long linear chains with proper crosslinkers, which were called bimodal networks proposed by Mark.[106, 107] The introduction of hydrophilic block polymer into long chains, or short chains, or the crosslinker may improve its hydrophilicity.

Here the hydrophilic crosslinker, bis[(3-methyldimethoxy-silyl)propyl]polypropylene oxide (BMPPO), partially instead of TEOS, was applied to crosslink hydroxyl-terminated PDMS linear chains to prepare PDMS-PEO networks. The hydrophilicities, the equilibrium water contents, as well as the mechanical properties were investigated.
4.2 Experimental section

4.2.1 Materials and preparation

The linear hydroxyl-terminated PDMS utilized in this study had a number-average molecular weights $M_n = 880, 2,200, 6,000, 18,000, 22,600,$ and $36,000 \text{ g mol}^{-1}$ were purchased from Gelest, Inc., Midland, MI. The samples (listed in Table 4.1) were tetrafunctionally end-linked in the undiluted state with the stoichiometrically-required amounts of crosslinker, bis[(3-methyldimethoxy-silyl)propyl]polypropylene oxide (BMPPO) (Brand name: SIB1660, viscosity: 6000-10,000 cSt. $M_w$: 600-800 Gelest Inc., Midland, MI) and TEOS. The catalyst was 1.0 wt% stannous-2-ethyl hexanoate (Gelest Inc., Midland, MI). The reactions were run in Teflon™ molds at room temperature for 24 hrs. The resulting network sheets were extracted with toluene for three days, then deswelled with methanol, and finally dried under vacuum. The fraction of soluble polymer thus removed amounted to approximately 2.5 wt%.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>PDMS</th>
<th>S12</th>
<th>S15</th>
<th>S21</th>
<th>S27</th>
<th>I2</th>
<th>I3</th>
<th>I4</th>
<th>I5</th>
<th>I6</th>
</tr>
</thead>
<tbody>
<tr>
<td>S12/TEOS</td>
<td>2/1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S12/SIB1660.0</td>
<td>2/1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S15/SIB1660.0</td>
<td></td>
<td>2/1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S21/SIB1660.0</td>
<td></td>
<td></td>
<td>2/1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S27/SIB1660.0</td>
<td></td>
<td></td>
<td></td>
<td>2/1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S12/(TEOS/SIB1660)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4/1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S12/(TEOS/SIB1660)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3/2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.2.2 Characterization

4.2.2.1 Fourier transform infrared spectroscopy

FTIR spectroscopy measurements were carried out to identify the functional groups present on the surfaces of the pristine hydrogel samples. This could be useful for analyzing the structures and reaction mechanism involved in the processing. The measurements were conducted using Digilab Excalibur FTIR equipment in the mid-IR range (4000 to 500 cm⁻¹). The resolution was 4 cm⁻¹, and 16 scans per sample were analyzed using the Digilab Resolutions Software.

4.2.2.2 Differential scanning calorimetry

Thermal properties (i.e. glass transition temperature, $T_g$) of the amphiphilic conetworks were determined on a TA 1501 unit (Thermal Analyzer Inc.) under a nitrogen atmosphere. A 5-10 mg sample of the conetwork was sealed into an aluminum sample pan. The sample was quickly heated above its glass transition temperature $T_g$ to negate its thermal history and was then quickly cooled to -150 °C. After a period to allow for equilibration, the heating scan was started, at a rate of 10 °C/min from -150 to 100 °C with $N_2$ flow at 130 ml/min.
4.2.2.3 Contact angles

Static CA was visually measured using a digital camera (VCA2000) with zoom capability under room temperature with about 1 µl deionized water. The results were based at least five surface spots to get static contact angles.

4.2.2.4 Equilibrium water content

EWC was determined by testing the water absorbance of a 1 cm × 1 cm piece of bimodal network sheet before and after being placed into deionized water for 24 hr.

4.2.2.5 Mechanical properties

The stress-strain behavior was characterized by a homemade tester at the tensile rate 5 mm/min using a sample 30 mm × 5 mm × 2 mm at room temperature.

The bimodality of the network was dependent on the short linear chains and long linear chains that were used to prepare the crosslinked networks. Of course, the mechanical properties should be characterized compared with the normal networks to determine whether the bimodal networks did have the expected improved properties. Certainly, other properties such EWC and DSC should also be characterized.

4.3 Results and discussion

4.3.1 Formation of silicone hydrogel networks

The silicone networks were formed by end-linking hydroxyl-terminated linear PDMS (DMS-S12, DMS-S15, DMS-S21, DMS-S27) with the crosslinkers, TEOS and/or BМPPO, catalyzed by stannous-2-ethyl hexanoate was according to the classic reaction. The BMPPO has a structure similar to that of TEOS, with four ethoxy groups terminating it. Therefore, it was supposed that the same hydrolysis reactions between the hydroxyl
groups in PDMS with ethoxy groups in BMPPO occurred (shown in Figure 4.1). Therefore, the hydrophilic block polymer, poly(propylene oxide), was introduced into the main chains of the networks by chemical bonding.

Figure 4.1 Schema of the preparation of bimodal silicone networks cocrosslinked by SIB1660

FTIR results of polysiloxane networks crosslinked by BMPPO compared with that of the silicone networks crosslinked by TEOS are showed in Figure 4.2 (a). They indicated the pristine peaks of Si-O-Si (1000-1100 cm\(^{-1}\)) and CH\(_3\) (2960 cm\(^{-1}\), 1258 cm\(^{-1}\) and 803 cm\(^{-1}\)). The special peak 2860 cm\(^{-1}\) (CH\(_2\)) and 1080 cm\(^{-1}\) (C-O-C stretching vibration) reflected the component, PPO in the networks.\(^{[114]}\) However, the peaks were small because of the amount of BMPPO relative to the PDMS. Moreover, the PPO was in the main chains, which made it embed in the matrix (see Figure 4.3), and did not show on the surface and therefore difficult to detect.

Therefore, the linear PDMS S12 was chosen to prepare silicone networks crosslinked by BMPPO and TEOS. The FTIR results in Figure 4.2 (b) clearly showed the PPO
special peak (2860 cm\(^{-1}\), CH\(_2\)) with increasing BMPPO. The C-O-C could not be well
differentiated for it was also included in the peak of Si-O-Si.
Figure 4.2 FTIR results for silicone hydrogels formed by hydrophilic crosslinkers placed into the main chains.

Figure 4.3 Schema of the hydrophilic chains’ distribution in the networks.

4.3.2 Thermal characteristics

Typical thermal characteristics of PDMS/(BMPPO/TEOS) (I series) were characterized by DSC comparing them with that of PDMS crosslinked with TEOS. The pristine PDMS clearly showed the glass transition temperature, \( T_g = -128^\circ\text{C} \), an exothermic peak (for so-called cold crystallization) \( T_c \) near -100°C and a melting peak \( T_m \) near -50°C.[115] DSC curves for PDMS/(BMPPO/TEOS) showed a temperature transition near -128°C (the \( T_g \) of PDMS), one temperature transition near -70°C (belong to melting point of PDMS) and another transition (near -15°C, corresponding to glass transition of PPO)[116], with no cold crystallize or melting peak. The \( T_g \) near 15°C became more obvious with increasing content of BMPPO in the networks, which also revealed that the PPO were successfully introduced into the networks.
Figure 4.4 DSC results for silicone hydrogels crosslinked by hydrophilic main chains.

4.3.3 Hydrophilicity

The CA results of bimodal hydrogel networks based on PDMS and BMPPO (Figure 4.5a) decreased from 105° of pristine PDMS to 102.2°~97.1° in PDMS/(BMPPO/TEOS). The decrease in hydrophilicity was somewhat small since there was not many hydrophilic groups were likely distributed on the surface of the films. There were not many differences among the CA values for S7, S8, S9 and S10, since the values were determined by the density of hydrophilic groups on the surfaces. Similar CA results in the range 97.1°~103.0° (Figure 4.5 b) were reached when short linear PDMS were used to prepare the silicone hydrogels.
Figure 4.5 The contact angle results for silicone hydrogels crosslinked by hydrophilic crosslinkers on the main chains.

Comparing with the EWC result (i.e. 0%) for pristine PDSM crosslinked by TEOS, the EWC of PDMS/BMPO and PDMS/(BMPO/TEOS) (shown in Figure 4.6 a and b) increased
a little but very slightly (less than 5.3 wt%). Obviously the low content of PPO in the silicone networks and the water rejection of PDMS in the surface of matrix might be the main causes of the low equilibrium water content.

![Bar chart](image)

**Figure 4.6** EWC results of silicone hydrogels by hydrophilic crosslinkers into the main chains. (a) single-mole networks; (b) S12/different content of crosslinker.
4.3.4 Mechanical properties

The mechanical properties including Young's modulus, tensile strength, toughness and elongation at break are listed in Table 4.2. Comparing to that of the pristine PDMS (S12/TEOS), Young's modulus of PDMS/BMPO were greatly decreased from 3.92 MPa to 0.54 MPa or even less, and Young's modulus decreased with the increasing molecular weight of linear PDMS (S12, S15, S21). There were similar changes in the tensile strength of PDMS/BMPO comparing with that of S12/TEOS, except S27. However the elongation at break increased significantly. The toughness of PDMS/BMPO increased somewhat compared with PDMS/TEOS. The change in mechanical properties is probably caused by the functionality decrease of the crosslinking point from 4 in TEOS to 3 in BMPO. The linear PDMS molecules increase in the order S12, S15, S21 and S27 might cause the increase in its extensibility.

In the PDMS/(BMPO/TEOS) series, Young’s modulus and the tensile properties also decreased with increasing mol ratio of BMPO/TEOS. There were also somewhat increase in elongation at break and toughness (except for S12/(BMPO/TEOS 4/1)). The decrease in crosslinking functionality from 4 in TEOS to 3 in BMPO might be one of the main reasons.

Table 4.2 The mechanical properties of the silicone hydrogels crosslinked by hydrophilic crosslinkers in the main chains.
Chapter 4. Hydrophilic bimodal networks

<table>
<thead>
<tr>
<th>Unit</th>
<th>Modulus</th>
<th>Stress</th>
<th>at Break</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MPa</td>
<td>MPa</td>
<td>%</td>
</tr>
<tr>
<td>S12/TEOS</td>
<td>3.92</td>
<td>0.130</td>
<td>0.509</td>
</tr>
<tr>
<td>S12/SIB1660</td>
<td>0.39</td>
<td>0.344</td>
<td>0.282</td>
</tr>
<tr>
<td>S15/SIB1660</td>
<td>0.37</td>
<td>0.352</td>
<td>0.261</td>
</tr>
<tr>
<td>S21/SIB1660</td>
<td>0.14</td>
<td>0.118</td>
<td>0.155</td>
</tr>
<tr>
<td>S27/SIB1660</td>
<td>0.54</td>
<td>0.229</td>
<td>0.316</td>
</tr>
<tr>
<td>S12/(TEOS/SIB1660) (4/1)</td>
<td>3.31</td>
<td>0.040</td>
<td>1.433</td>
</tr>
<tr>
<td>S12/(TEOS/SIB1660) (3/2)</td>
<td>2.39</td>
<td>0.939</td>
<td>1.285</td>
</tr>
<tr>
<td>S12/(TEOS/SIB1660) (2.5/2.5)</td>
<td>2.06</td>
<td>0.300</td>
<td>0.696</td>
</tr>
<tr>
<td>S12/(TEOS/SIB1660)(2/3)</td>
<td>1.01</td>
<td>0.151</td>
<td>0.340</td>
</tr>
<tr>
<td>S12/(TEOS/SIB1660) (1/4)</td>
<td>0.51</td>
<td>0.470</td>
<td>0.330</td>
</tr>
</tbody>
</table>

4.4 Conclusions and further work

A hydrophilic polymer, poly(propylene oxide), was successfully introduced into silicone networks via hydrophilic crosslinkers, bis[(3-methyldimethoxy-
silyl)propyl]polypropylene oxide, which was partially or all used in place of TEOS in the preparation of end-linking silicone networks. The contact angles and equilibrium water contents increased somewhat but only slightly. The main problem might be the low content of block hydrophilic polymer in the systems and the hydrophilic copolymer being on the main chains and embedded in the networks instead of dangling outside of the surface.
Chapter 5. Improving hydrophilicity from poly(ethylene glycol) in amphiphilic conetworks with poly(dimethylsiloxane)

5.1 Introduction

Poly(dimethylsiloxane) (PDMS), with repeat unit [-Si(CH₃)₂-O-], has attracted great interest for years to be widely used as a biomaterial in many impressive applications such as microfluidic devices,[56-61] microcontact printing technology,[61-63] biocompatible devices (e.g. contact lenses),[64] and drug delivery systems,[65-68] because of its many attractive features, including (i) high gas permeability, (ii) stable and high optical transparency, (iii) high flexibility and low risk of loss or damage, (iv) nontoxicity and biocompatibility, (v) stability toward heat and chemicals, (vi) low curing temperature, (vii) moldability, and (viii) ease of sealing with other materials.[56-68] However, its hydrophobicity has limited its application in more broadened fields as biomaterials, especially those involving biocompatible devices, because hydrophobic molecules, biopolymers and cells all irreversibly absorb to its surface.[60, 117] In addition, small hydrophobic molecules can actually be absorbed into the bulk of the PDMS.[60]

Many researchers have long recognized the need to make PDMS hydrophilic to ameliorate problems of this type.[118, 119] One of the feasible methods is to modify the surface of silicone networks. Increasing the hydrophilicity of the silicone surface improves its wettability and this, in turn, improves the biocompatibility.[119] There have been a large number of patents and studies describing various surface modifications to increase the
Chapter 5. Improve Hydrophilicity from PEG in APCNs with PDMS

hydrophilicity of the intrinsically inert and hydrophobic PDMS surface.[120, 121] Such changes in surface energy can be obtained by introducing various polar groups, by corona discharges,[71, 81, 122] ultraviolet irradiation in combination with ozone,[72-75] and plasma treatments [57, 76, 77, 80-82, 123]. Generally, the hydrophilic surfaces of oxidized PDMS are not stable with time and a hydrophobic recovery will gradually occur after exposure, even though the bulk properties of the PDMS are not changed.[71, 75, 81, 84] Coating the surface or compounding the polymer with additives that subsequently diffuse to the surface can also raise this problem.[83, 84] Also, such surface modification could not increase the water content in the matrix to satisfy the special requirements of some biomaterials such as the hydrogels for drug delivery and contact lenses.[68].

Thus research on double network hydrogels or amphiphilic conetworks attracts more attention to make PDMS more biocompatible. Amphiphilic polymer conetworks, consisting of hydrophilic and hydrophobic chains covalently bonded to each other, represent a relatively new class of promising materials for applications such as pervaporation membranes, contact lenses, drug delivery systems, biomedical scaffolds for tissue engineering, and supports for catalysts.[86] The amphiphilic nature of these new crosslinked polymers is indicated by their swelling extents in both aqueous and organic media without losing their dimensional stability and without encountering macroscopic phase separation or polymer leaching.[124, 125] The amphiphilic conetworks based on PDMS and some hydrophilic components have shown to at least partly provide bicontinuous or interpenetrating phase morphologies for long-term biocompatibility.[86-89] In brief, amphiphilic polymer conetworks have been a successful way to make the surfaces and interiors of a polysiloxane network more hydrophilic.
Chapter 5. Improve Hydrophilicity from PEG in APCNs with PDMS

With regard to the hydrophilic component, poly(ethylene oxide) (PEO) with repeat unit \[-(CH₂)₂O-\] or poly(ethylene glycol) (PEG) (with hydroxyl end group) is a hydrophilic polyether which has received much attention for applications in biomaterials because of its low interfacial energies with water, relative structural stability, lack of binding sites for reactive proteins, high chain mobility, and steric stabilization effects. Moreover, PEG is of interest also because of its low degrees of protein adsorption and cell-adshesion.\[90-93\] However, because of its incompatibility with other polymers, phase separation always occurs in their mixtures and thus leads to opaqueness as well as reduced mechanical properties.\[94\] Covalently crosslinking two types of polymer chains at least can prevent a macroscopic demixing, and this method may result in a phase-separated morphology with domains that remain in the nanoscale range.\[95, 97-100, 126\] Baron introduced PEG into PDMS to form tri-block copolymers, to prepare contact lenses that had the required oxygen permeability and water content balance.\[88\] Kennedy et al. combined vinyl-telechelic PDMS and allyl-telechelic PEG by hydrosilation using pentamethylcyclopentasiloxane (D₅H), a novel multifunctional co-crosslinker.\[95-100\]

An earlier part of this series of reports described PDMS-PEG bimodal amphiphilic networks prepared via crosslinking hydroxyl-terminated linear PDMS with poly(ethylene oxide) functionalized trialkoxysilanes of various chain lengths.\[127\] The hydrophilic chains have very favorable effects on surface hydrophilicities, and equilibrium water contents. At the same time, the bimodal PDMS network was used as the basic network because the network chain lengths could be controlled through end-linking, and the bimodal network gives unusually good mechanical properties in a variety of elastomers.\[104, 105, 108, 128-131\] Here a tetrafunctional crosslinker BMPPO is also used as the compatibilizer to improve the
miscibility between PDMS and PEG, yielding some novel and attractive hydrophilic network structures. The physical properties and the hydrophilicity were also investigated for possible use as biomaterials.

## 5.2 Materials and experimental methods

### 5.2.1 Materials and preparation of amphiphilic conetworks

PEG- PDMS amphiphilic conetworks (0/1, 2/1, 4/1, 6/1, 8/1, and 10/1 in mol ratios) were prepared from linear hydroxyl-terminated PEG (number-average molecular weight $M_n = 300$ g·mol$^{-1}$, Aldrich Chemical Co., St Louis, MO.) and hydroxyl-terminated PDMS ($M_n = 18,000$ g·mol$^{-1}$, Gelest Inc., Midland, MI.). The combined materials were tetrafunctionally end-linked in the undiluted state with the stoichiometrically-required amounts of bis((3-methyldimethoxy-silyl)propyl)-polypropylene oxide (BMPPO) (Gelest Inc., Midland, MI.) and tetraethoxysilane (TEOS) $[\text{Si(OC}_2\text{H}_5)_4]$ (Gelest Inc., Midland, MI.) in a standard condensation reaction. Details are given in Table 5.1. Stoichiometric amounts of BMPPO and TEOS were employed according to the corresponding PEG/PDMS ratio. The mixtures were first vigorously stirred in air at room temperature for at least 2 hrs. The catalyst stannous-2-ethyl hexanoate (used as received, Gelest Inc., Midland, MI.) was then introduced at 1.0 wt% of the total weight of the other components. The mixtures were then stirred for approximately 10 min before being poured into Teflon™ molds. They were then put under vacuum for 20 min to remove air bubbles and low molecular weight materials such as alcohol and water. The reactions were run in these molds at room temperature for 24 hrs. The resulting network sheets were extracted with toluene (Analysis pure, Aldrich-Sigma Inc.) for three days, and then deswelled with methanol, and
Chapter 5. Improve Hydrophilicity from PEG in APCNs with PDMS

finally dried under vacuum. The fraction of soluble materials thus removed was very small (amounting to approximately only 2.5 wt%).

Table 5.1 Synthesis details on the preparation of the PDMS-PEG conetworks

<table>
<thead>
<tr>
<th>PDMS/PEG (mol/mol)</th>
<th>1/0</th>
<th>1/2</th>
<th>1/4</th>
<th>1/6</th>
<th>1/8</th>
<th>1/10</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMS-S27 (x10^−3mol)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>PEG (x10^−3mol)</td>
<td>1.0</td>
<td>2.0</td>
<td>3.0</td>
<td>4.0</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>BMPPO (x10^−3mol)^a</td>
<td>0.6</td>
<td>1.2</td>
<td>1.8</td>
<td>2.4</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>TEOS (x10^−3mol)</td>
<td>0.48</td>
<td>0.58</td>
<td>1.20</td>
<td>1.78</td>
<td>2.40</td>
<td>2.98</td>
</tr>
<tr>
<td>Tin catalyst (g)</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Note: a The total amount of the crosslinker (BMPPO and TEOS) was about 1.1 of the stoichiometrically-required for the crosslink of the APCNs, and the ratio of BMPPO/TEOS was corresponding to the PEG/PDMS ratio.

5.2.2 FTIR

Fourier transforms infrared (FTIR) spectroscopy measurements were carried out to identify the functional groups present on the surfaces of the pristine PEG-PDMS samples. This would be useful for analyzing the structures and reaction mechanism involved in the processing steps. The measurements were conducted using Digilab Excalibur FTIR equipment and were analyzed with the Digilab Resolutions Software. The measurements were recorded in the mid IR range 4000 to 500 cm⁻¹ at a resolution of 4 cm⁻¹ and at 16 scans per sample.
5.2.3 Differential scanning calorimetry

Thermal properties (i.e. glass transition temperature, $T_g$) of the amphiphilic conetworks were determined on a TA 1501 unit (Thermal Analyzer Inc.) under a nitrogen atmosphere. A 5-10 mg sample of the conetwork was sealed into an aluminum sample pan. The sample was quickly heated (30 °C/min) above its glass transition temperature $T_g$ (c.a. 100 °C) to negate its thermal history and was then quickly cooled with liquid nitrogen to -150 °C. After a period (c.a. 5 min) to allow for start equilibration, the heating scan was started, at a rate of 10 °C/min from -150 to 100 °C with $N_2$ flow at 130 ml/min.

5.2.4 X-ray diffraction

XRD measurements on the amphiphilic conetwork films were carried out using an X-ray diffractometer (Siemens D500) (Cu K$_\alpha$ radiation, with 30 mA, 40 kV, $\lambda = 1.5406$ Å). The 2θ scan range was 2 to 30°, with a step size of 0.05 degree and a time per step of 1 sec.

5.2.5 Static contact angles

Static CA values were visually determined at room temperature using a VS2000 digital camera with zoom capability with approximately 1 μl deionized water after 15 seconds of the drop contact with the surface. At least five areas were tested to obtain average CA values.

5.2.6 Water swelling kinetics

Water swelling extents were obtained by immersing a weighed amphiphilic conetwork in a large excess of distilled water at ambient temperature, with the weights of the swollen samples being recorded with different time. The weight swelling degree $S_m$ was calculated from

$$S_m = \frac{(Wt_s-Wt_d)}{Wt_s} \times 100\%$$

(1)
where $W_{ts}$ and $W_{td}$ are the weights of the swollen state and the dry samples, respectively.

### 5.2.7 Mechanical properties

The tensile mechanical properties of the APCNs in dry state, including Young’s modulus, tensile strength, toughness, and elongation at break, were determined by the average of 5 samples using a home-built tensile tester (Model 11, Honeywell Sensotec Inc. Columbus, OH). The sample dimensions were 30 mm × 5 mm × 2 mm, and the strain-stress properties were measured at an elongation rate of 5 mm/min at 23~25 °C.

### 5.2.8 Characterization of morphologies

The surface and the cross-section morphologies of the APCNs in dry state were characterized using a Philips XL30 Environmental Scanning Electron Microscopy (ESEM) in high vacuum. The fresh cross-sections of the APCNs were obtained by freezing the samples in liquid nitrogen for several minutes and then broken quickly.

### 5.3 Results and discussion

#### 5.3.1 Preparation of the PDMS-PEG amphiphilic conetworks

The crosslinking reactions involved here are outlined in Figure 5.1. The preparation of the amphiphilic conetworks was based on the usual preparation of polymer networks from linear hydroxyl-terminated PDMS end-linked by TEOS with the catalyst stannous 2-ethylhexanoate.[133, 134] The hydroxyl groups at the terminal of PDMS and PEG chains hydrolyzed with the alkoxy groups in TEOS or BMPPO to form the APCNs and corresponding small molecules (ethanol or methanol). The crosslinker BMPPO is poly(propylene oxide) terminated, by (3-methyldimethoxysilyl)propyl groups, and it plays two key roles in the reactions. The primary role is to function as a crosslinking agent to
Chapter 5. Improve Hydrophilicity from PEG in APCNs with PDMS

initiate the crosslinking reaction between the hydroxyl groups of PEG or PDMS and the methoxy groups in the BMPPO, since it has the same characteristics as TEOS to couple the hydroxyl groups in the polymer, especially in silicone chains. The same reaction occurred between the hydroxyl groups in the PEG or PDMS and the ethoxy groups in TEOS. The secondary role of BMPPO was a compatibilizer to physically improve the compatibility between PDMS and PEG by reducing the interfacial tension forces at the interface between hydrophobic and hydrophilic phases,\textsuperscript{[135-140]} so that the phases in the compounds would remain in the micro range or even smaller scale in the final networks. The extraction fraction of the final APCNs by toluene and other solvents was about 2.5 wt\%, which demonstrated the formation of the networks. The fact also indicated that the free hydroxyl groups of PEG and PDMS were activated by the stannous di-2-ethylhexanoate to hydrolyze with the alkoxy groups in TEOS and BMPPO, forming the PDMS-PEG amphiphilic conetworks, though they may be unstable in aqueous environment.\textsuperscript{[138-140]} The FTIR results, in Figure 5.2, clearly showed the presence of the groups –CH\textsubscript{2}– (~2943 cm\textsuperscript{-1}) and CH\textsubscript{2}-O-CH\textsubscript{2} (1108 ~1249 cm\textsuperscript{-1}) in the PDMS-PEG APCNs. This could be explained by the fact that there were both of these groups at the surface, and the PEG and PDMS components were bonded by BMPPO or TEOS, via Si-O-CH\textsubscript{2} bonds to form PDMS-PEG APCNs. The PDMS-PEG APCNs in dry state were stable in room temperature. The extraction experiment indicated the APCNs were also stable in toluene and methanol for over 30 days. Meanwhile the continuous swelling in water showed the APCNs may be degradable. Additional relevant information is given in the following section.
Chapter 5. Improve Hydrophilicity from PEG in APCNs with PDMS

**Figure 5.1** Preparation of PDMS-PEG amphiphilic conetworks by chain coupling of hydroxyl-terminated PEG and hydroxyl-terminated PDMS with BMPPO and TEOS. The dots indicate coupling sites between the polymer chains, the bold lines represent BMPPO, the thin smooth lines, PEG; and wrinkled lines, PDMS.

**Figure 5.2** FTIR results for the PEG-PDMS amphiphilic conetworks.
5.3.2 Surface and bulk morphologies

The PDMS-PEG APCNs morphologies were elucidated by the SEM results gotten on their surfaces and cross-sections, since this method provides direct visualization of the PDMS and PEG phases. Figure 5.3 shows the SEM images of the APCNs: (a) PDMS-PEG (1/8) surface; (b) PDMS-PEG (1/8) cross-section; (c) PDMS-PEG (1/4) surface; (d) PDMS-PEG (1/4) cross-section. The dark entities are the PEG phases, which can be seen to be homogeneously dispersed in the PDMS. In PDMS-PEG (1/4) APCN, there is not much difference in the surface and cross-section results, with the PEG forming spherical phases with diameters around 10μm. Meanwhile, in PDMS-PEG (1/8) APCN, the PEG domains on the surface were much smaller than those in the cross-sectional parts, with diameters less than 5 μm. This may be due to the aggregation of the PEG from the surface during the crosslinking, which led to some voids in the matrix. It can also be clearly seen in the SEM images that there are interphases between the dark phases (PEG) and the white phases (PDMS) in PDMS-PEG (1/4) and (1/8) APCNs. This could be explained by the previously mentioned roles of BMPO in improving the compatibility of PDMS and PEG, and chemical bonding between the PDMS and PEG by dehydration during the crosslinking.
Figure 5.3 SEM images of PDMS-PEG APCNs (a) PDMS-PEG (1/8) surface; (b) PDMS-PEG (1/8) cross-section; (c) PDMS-PEG (1/4) surface; (d) PDMS-PEG (1/4) cross-section.

The XRD results, as illustrated in Figure 5.4, clearly indicated the presence of two amorphous phases, corresponding to the range $2\theta = 8\sim16^\circ$ and $16\sim30^\circ$, which are associated with the homogenous amorphous phases of PDMS and PEO, respectively.[93] The amorphous peak in the range of $2\theta = 16\sim30^\circ$ increased with increase in the mol ratio
5.3.3 Thermal properties

Typical DSC results of the PDMS-PEG APCNs are shown in Figure 5.5. The APCNs were studied at a heating rate of 10°C min⁻¹ from -150°C to 100°C after quickly cooling down from 100°C to eliminate the effect of heat history during the preparation process. The cooling curves were not collected while the heating curves identified the glass transition temperature $T_g$, the crystallization temperature $T_c$, and the melting temperature $T_m$. The pure PDMS (i.e. PDMS/PEG 1/0) gave $T_g = -128°C$ (which is not shown in the figure). There was also an exothermic peak (for so-called cold crystallization) $T_c$ near -100°C, and a
Chapter 5. Improve Hydrophilicity from PEG in APCNs with PDMS

melting peak $T_m$ near -50°C.\cite{115} The pure PEG gave glass transition temperature, $T_g = -60^\circ$C, crystalline temperature $T_c = -30 \sim -20^\circ$C and melting temperature $T_m = -11^\circ$C.\cite{93} DSC curves of PEG-PDMS APCNs reported thus far show one distinctive exothermic peak in -100 \sim -80^\circ$C, and one glass transition temperature near -60 °C corresponding to that of PDMS and PEG, respectively, indicating the presence of at least two phases of the hydrophilic and hydrophobic polymer chains.\cite{134} The two values moved closer together with increase in the ratio PEG/PDMS, which is consistent with the formation of ordered-domain morphologies.\cite{141} It can also be seen that the glass transition temperature of PEG was significantly higher with increased amounts of PEG in the conetworks. This suggested that low molecular weight PEG chains did have some compatibility with the conetworks, since the existence of separated PEG domains was conclusively indicated by the nature of the glass transition temperature of PEG in the case of the conetworks. The values of $T_g$ were shifted to lower values, to about 25 °C for PEG in the corresponding PEG-PDMS conetworks. Moreover, the APCNs showed one distinct glass transition temperature in the range of -30 \sim -20^\circ$C and two transition temperatures ($T_1$ and $T_2$) in the range 10 \sim 30^\circ$C. For example, for APCN (PDMS/PEO: 8/1): $T_g = -29.4$ °C, $T_1 = 11.9$ °C, $T_2 = 23.7$°C. These transition temperatures may be attributed to the interphase between PDMS and PEGs in APCNs. Similar results were observed in the other PDMS-PEG APCNs. The transition temperatures increased slightly and the $T_m$ of the PDMS decreased slightly with increasing content of PEG. These shifts can most likely be attributed to the effect of the amphiphilic BMPPO crosslinker. This means that the crosslinker BMPPO did improve the compatibility between PDMS and PEG, although there were still two fine-dispersed phases present but with very small dimensions.\cite{125}
Figure 5.5 DSC results of the PEG-PDMS amphiphilic conetworks.

5.3.4 Surface hydrophilicity

One of the simplest available methods for probing the surface properties of a material involves the measurement of the contact angles of pure water on these surfaces. In this case, the static CA values for deionized water droplets at approximately 1µl were used to characterize the surface hydrophilicity. The CA results of the APCNs for values of the mol ratio of PEG to PDMS are shown in Figure 5.6. The static contact angle of water on PDMS network surface decreased from 105° to 75° by addition of the amphiphilic co-crosslinker BMPPO in APCNs (PDMS/PEG: 1/2) (Figure 5.7, a). The decrease in CA varied sharply with increase in the PEG/PDMS mol ratio from 0/1 to 4/1. The static contact angle decreased down to 55° in APCNs (PDMS/PEG: 1/6) (Figure 5.7, b) and almost stayed constant when
Chapter 5. Improve Hydrophilicity from PEG in APCNs with PDMS

the PEG/PDMS mol ratio was larger than 6/1. In the case of PDMS networks, low contact angles provided an indication that water-soluble polymer was present at the surface of the material. This may be attributed to the distribution of the hydrophilic domains, that is, the PEG chains, which may easily aggregate outside the matrix and distribute on the surface of the conetworks even after the conetworks formed, and the PEG density on the surface increased with the increase in PEG/PDMS mol ratio. The results also mean that the significant decreases in the contact angles were obtained with the tetrafunctional crosslinker BMPPO and the hydrophilic PEG.

Figure 5.6 Effect of the PEG content on the hydrophilicity, as gauged by values of the contact angle with deionized water.
Chapter 5. Improve Hydrophilicity from PEG in APCNs with PDMS

Figure 5.7 Contact angle photographs for PDMS-PEG (1/2) (left), PDMS-PEG (1/6) (right) conetworks.

5.3.5 Water-swelling kinetics

The water content of the APCN is of obvious importance, since several applications in biomaterials require suitable water contents.[64, 68, 142] The water swelling kinetics of the PDMS-PEG APCNs is shown in Figure 5.8. It obviously showed that there was no increase in water in the pure PDMS networks (APCN PDMS/PEG: 1/0) because of its high hydrophobicity. Meanwhile, the PDMS-PEG APCNs swelled quickly during the first several days, and the APCNs swelled slightly after the first state. The final water content also increased with increasing PEG/PDMS mol ratio. The water content increase became particularly significant, which was up to 40 wt% in the PEG/PDMS (4/1) APCN and even up to 60 wt% in PEG/PDMS (10/1) APCN. This may be explained by the fact that the hydrophilicity of APCN greatly depended on the amounts of PEG as well as the distributing state of PEG in the APCNs bulk. Chemical coupling of a hydrophobic network to another hydrophilic network confines the volume change to all dimensions, thus altering the swelling behavior. [110] APCNs with higher water content were generally more advantageous because they show a higher water and gas permeability and biocompatibility.
Chapter 5. Improve Hydrophilicity from PEG in APCNs with PDMS

![Figure 5.8](image)

**Figure 5.8** Equilibrium water contents of the PDMS-PEG conetworks as a function of time.

### 5.3.6 Mechanical properties

Table 5.2 shows the mechanical properties of the present PDMS-PEG APCNs in dry state. The results indicated that Young’s modulus decreased from 0.74 MPa in pure silicone network to 0.39 MPa in PDMS/PEG (1/10) APCN, while the toughness, the tensile strength and the elongation at break increased from 0.29 MPa, 0.34 MPa, 137 % to 1.15 MPa, 0.61MPa, 328 % respectively, in PDMS/PEG (1/10) APCN. It indicated that the introduction of short linear chains, PEG with molecular weight 300, into the PDMS networks did not make the network stiffer, but did make the amphiphilic network softer and tougher. These APCNs, with such mechanical properties as well as the hydrophilicity, may be possibly as
biomaterials in many biological applications. Further investigation on the biocompatibility is still ongoing in our current research.

### Table 5.2 The mechanical properties of the PDMS-PEG conetworks

<table>
<thead>
<tr>
<th>PDMS/PEG (mol/mol)</th>
<th>Young modulus, MPa</th>
<th>Toughness, MPa</th>
<th>Tensile strength, MPa</th>
<th>Elongation at break, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/0</td>
<td>0.74</td>
<td>0.29</td>
<td>0.34</td>
<td>137</td>
</tr>
<tr>
<td>1/2</td>
<td>0.44</td>
<td>0.57</td>
<td>0.39</td>
<td>236</td>
</tr>
<tr>
<td>1/4</td>
<td>0.61</td>
<td>0.70</td>
<td>0.56</td>
<td>204</td>
</tr>
<tr>
<td>1/6</td>
<td>0.58</td>
<td>0.86</td>
<td>0.57</td>
<td>253</td>
</tr>
<tr>
<td>1/8</td>
<td>0.56</td>
<td>0.55</td>
<td>0.47</td>
<td>189</td>
</tr>
<tr>
<td>1/10</td>
<td>0.39</td>
<td>1.15</td>
<td>0.61</td>
<td>328</td>
</tr>
</tbody>
</table>

### 5.4 Conclusions

A new approach, specifically, a chain-coupling strategy, was successfully utilized to synthesize a series of novel PEG-PDMS amphiphilic conetworks from the corresponding telechelic polymers, i.e., from the immiscible hydrophilic hydroxyl-telechelic PEG and the strongly hydrophobic hydroxyl-telechelic PDMS with an amphiphilic crosslinker BMPPO. This successfully produced a new generation of structurally-unique APCNs, with well-dispersed junction points from the BMPPO amphiphilic crosslinker. The PEG-PDMS conetworks exhibited amphiphilic character, and the swelling behavior of these APCNs depended on the compositions and the crosslink density. The APCNs did exhibit phase separation, but not on a macroscopic level. These properties and water contents were in
Chapter 5. Improve Hydrophilicity from PEG in APCNs with PDMS

the desirable range for some biomaterial applications. These new conetworks are expected to be useful in a variety of applications ranging from drug delivery to separation membranes, which should encourage further investigations of their properties.
Chapter 6. Preparation of bimodal hydrogels based on PDMS and amphilic PDMS-poly(alkyl oxide) copolymers

6.1 Introduction

When high molecular hydroxyl-terminated linear PDMS is blended with low molecular hydroxyl-terminated linear PDMS and end-linked, the bimodal PDMS network will have good mechanical performances and high transparencies. Bimodal PDMS is gradually becoming a research focus in polymer fields because of its excellent mechanical properties. However, bimodal PDMS networks could not be directly applied as a biocompatible material because of its hydrophobicity. PEO is popularly used to incorporate onto silicone surface to suppress protein absorption.[132, 143-146] If parts of the PDMS macromoers for the bimodal networks could be replaced by the amphiphilic PEO-PDMS-PEO triblock polymers, tough bimodal hydrogel networks based on PEG-PDMS could be obtained.

6.2 Experimental

6.2.1 Materials and preparation

The linear hydroxyl-terminated PDMS (DMS-S12) utilized in this study had a number-average molecular weight of \( M_n = 880 \ \text{g mol}^{-1} \) and was purchased from Gelest, Inc. The linear hydroxyl-terminated PEO-PDMS-PEO triblock polymer (DBE-C25, Figure 6.1 a), PPO-PDMS-PPO triblock polymer (DBP-C22, Figure 6.1 b), purchased from Gelest, Inc., had a \( M_n = 3000 \sim 5000 \ \text{g mol}^{-1} \) and a \( M_n \) of 2,200 ~ 3,500 g mol\(^{-1}\), respectively. The samples
were tetrafunctionally end-linked in the undiluted state by the stoichiometrically-required amounts of TEOS (Gelest, Inc. Midland, MI). The catalyst was 1.0 wt% stannous-2-ethyl hexanoate (Gelest, Inc. Midland, MI). Various mole ratios of short chains to long chains were employed (see Table 6.1). The reactions were run in Teflon™ molds at room temperature for 24 hrs. The resulting network sheets were extracted with toluene for three days, then deswelled with methanol, and finally dried under vacuum. The fraction of soluble polymer thus removed amounted to only approximately 2.5 wt%.

Figure 6.1 Structure of carbinol-terminated poly(alkyl oxide)-PDMS- poly(alkyl oxide) triblock macromer used to prepare bimodal networks (a) PEO-PDMS-PEO; (b) PPO-PDMS-PPO.
Chapter 6. Hydrophilic bimodal networks

(a)

(b)
6.2.2 Characterization

6.2.2.1 Static contact angles

The hydrophilicities of the surfaces of the hydrogels were characterized by values of water contact angles, the values of which were the average results taken from at least four areas on the surfaces. The tests were carried out at room temperature with ca. 1 μl deionized water, and angles were visually determines using a VCA2000 digital camera with zoom capability.

6.2.2.2 FTIR

The surface components of the bimodal networks, PDMS-(PEO-PDMS-PEO) and PDMS-(PPO-PDMS-PPO) were characterized using FTIR spectroscopy (AA 2024-T3) in the mid-IR range from 4000 to 550 cm⁻¹. All spectra were obtained at an incident angle of 90 degrees to the surfaces of the specimens, with a spectral resolution of 4 cm⁻¹ and sixteen scans were taken.

6.2.2.3 Differential scanning calorimeetry

Thermal properties (i.e. glass transition temperature, T_g) of the amphiphilic conetworks were determined on a TA 1501 unit (Thermal Analyzer Inc.) under a nitrogen atmosphere. A 5-10 mg sample of the conetwork was sealed into an aluminum sample pan. The sample was quickly heated above its glass transition temperature T_g to negate its thermal history and was then quickly cooled to -150 °C. After a period to allow for
equilibration, the heating scan was started, at a rate of 10 °C/min from -150 to 100 °C, with a N₂ flow at 130 ml/min.

### 6.2.2.4 Equilibrium water contents

Values of the EWC were obtained by immersing a piece of weighed hydrogel film measuring 1 cm × 1 cm × 0.2 cm in a large excess of distilled water at ambient temperature. The weights of the swollen samples were not recorded until they became constant. Values of the equilibrium volumetric degree of swelling $S_m$ were calculated from the equation $S_m = (W_{ts} - W_{td})/W_{ts} \times 100\%$, where $W_{ts}$ and $W_{td}$ were the swollen and dry weights, respectively.

### 6.3 Results and discussion

The CA results for the bimodal networks based on hydroxyl-terminated PDMS and hydroxyl-terminated linear tripolymer PPO-PDMS-PPO, shown in Figure 6.5, clearly indicated that the contact angles were very low (about 15 °) with regard to the wettability of PDMS (CA approximately 105 °). These results also showed that the contact angle of the samples remained almost constant with time, up to at least 28 days. The CA results for the bimodal networks based on PDMS and PEO-PDMS-PEO, shown in Table 6.1, also indicated that the wettability was really high. In fact, the deionized water spread so quickly that the image of the deionized water drop on the surfaces could not be captured by the camera. The hydrophilic surface obtained was greatly dependent on the presence of the poly(alkyl oxide) chains, which had most likely migrated to the surface since poly(alkyl oxide) was incompatible with PDMS. However, both kinds of bimodal networks were only semi-transparent, according to visual observations.
Figure 6.3 FTIR spectra of (a) PDMS-(PEO-PDMS-PEO) and (b) PDMS-(PPO-PDMS-PPO) silicone networks.
Figure 6.4 DSC of PDMS-(PEO-PDMS-PEO) bimodal networks.
Figure 6.5 Contact angles of a bimodal network based on PDMS and PPO-PDMS-PPO with increasing time

Table 6.1 Contact angles and transparencies of PDMS-(PEO-PDMS-PEO) bimodal networks

<table>
<thead>
<tr>
<th>Sample#</th>
<th>DBE/PDMS mol ratio</th>
<th>Transparence</th>
<th>Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>S21</td>
<td>10/90</td>
<td>Semi-transparent</td>
<td>Almost 0 degree</td>
</tr>
<tr>
<td>S22</td>
<td>13/87</td>
<td>Semi-transparent</td>
<td>Almost 0 degree</td>
</tr>
<tr>
<td>S23</td>
<td>16/84</td>
<td>Semi-transparent</td>
<td>Almost 0 degree</td>
</tr>
</tbody>
</table>
Figure 6.6 EWC results of the PDMS-(PEO-PDMS-PEO) silicone networks.
6.4 Conclusions and further work

Two series of bimodal networks with excellent hydrophilic properties were successfully prepared via crosslinking hydroxyl-terminated PDMS with hydroxyl-terminated linear triblock polymer, PDMS-PEO and PDMS-PPO macromers, respectively. The right amount of hydrophilic poly(alkyl oxide), in this case are PEO and PPO, in the system, which may immigrate out onto the surface of the bimodal network, clearly contributed to the significant decreases in contact angles.

Further work on the morphology, the mechanical properties, transparency, equilibrium water content, oxygen and water permeability, and extents of protein absorption should be investigated to establish whether these materials are really appropriate as biomaterial for any biomedical application.
Chapter 7. Surface hydrophilic treatments of PDMS-based bimodal networks

7.1 Improvement in surface hydrophilicity of polysiloxane networks by introducing poly(N-isopropylacrylamide) via ultraviolet polymerization

7.1.1 Introduction

The modification of polymer surfaces is a topic of great theoretical and practical interest. In principle, this approach allows the production of polymer surfaces of desired composition and structures.[147, 148] Poly(N-isopropylacrylamide) (PIPAAm) has been suggested as a polymer for the recovery of cells from tissue culture substrata without the need for proteolytic enzymes to digest the matrix responsible for cell attachment,[147-149] because PIPAAm in water shows a full expanded chains conformation below the lower critical solution temperature (LCST) of 32 °C and a collapsed, compact conformation at temperatures above the LCST. Recently PIPAAm has been extensively studied on controlled drug release applications as a biocompatible and hydrophilic polymer. Several methods have been suggested to produce PIPAAm-coated surfaces from electron beam and UV grafting.[150, 151] Irrespective of the surface modification methods used, the surface characteristics of PIPAAm in solution are maintained when the polymer is grafted to a substrate surface.
Chapter 7. Surface hydrophilic treatments

Here PIPAAm is used as biomaterials introduced onto polysiloxane networks by UV-grafting to investigate the effect of the thin layers on the wetting properties of the polysiloxane networks.

7.1.2 Experimental

7.1.2.1 Materials

The linear hydroxyl-terminated PDMS, (DMS-S27, Gelest Inc. Midland, MI) had a number average molecular weight corresponding to \( M_n \sim 18,000 \text{g/mol} \). The hydroxyl-terminated linear siloxane copolymer (VDS-2513, Gelest Inc. Midland, MI) was composed of 25~30 mol\% vinylmethylsiloxane and 70~75 mol\% dimethylsiloxane. TEOS (SIT7110.0 Gelest Inc. Midland, MI) was used as the tetrafunctional crosslinker. Stannous-2-ethylhexanoate (SNB1100, Gelest Inc. Midland, MI) was used as the catalyst for the bimodal PVMS-PDMS, and acrylic acid, purchased from the Aldrich Company (St Louis, MO), was employed as the monomer for polymerization. Polyethylene oxide (PEO), hydroxyl terminated, \( M_n \sim 300 \text{g/mol} \), was also purchased from the Aldrich Company (St Louis, MO). N-isopropylacrylamide (IPAAm) (98% pure) was purchased from Kodak, Japan. NaIO\(_3\) and benzyl alcohol were purchased from Aldrich Chemical Co. (St Louis, MO).

7.1.2.2 Preparation of PDMS-PVMS bimodal silicone networks

A series of bimodal silicone networks with various vinyl groups were prepared by employing different mol ratios of PVMS to PDMS amounts of (0:100, 5:95, 10:90, 15:85, 20:80), corresponding to the short chains and long chains, respectively. The short chains and long chains were tetrafunctionally end-linked in the undiluted state with the stoichiometrically-required amounts of TEOS and the catalyst, stannous-2-ethylhexanoate, 0.6 wt\% (Figure 7.11). The reactions were run in Teflon™ molds at room temperature for
three days for completion of the crosslinking. The resulting network sheets were extracted with toluene for three days, then deswelled with methanol, and finally dried under vacuum.

The number of vinyl groups depended on the molar concentration of PVDS used to prepare the samples. It could be determined by FTIR, NMR and titration, etc.

![Scheme preparation of bimodal PVMS-PDMS networks](image)

**Figure 7.1** Scheme preparation of bimodal PVMS-PDMS networks. Bold lines: short linear PVMS-PDMS; thin lines: long linear PDMS; side spot: vinyl side group in PVMS-PDMS; spot: crosslink point.

### 7.1.2.3 Ultraviolet polymerization grafting

PDMS-PVMS films were immersed in an aqueous solution containing NaI0₄ (0.5 mM), benzyl alcohol (0.5 wt %), and IPAAm at the concentrations and ratios indicated in the text. After immersion, the films were placed in a custom-built irradiator (200-W mercury lamp) for various time. The distance between the sample and the lamp was 5 cm. Uniform UV exposure was carried out by rotating the films (10 rpm) under the UV source. The samples were then washed in distilled water at 80 °C under constant stirring for 24 h to remove adsorbed monomer and polymer. The PDMS-PVMS films were then vacuum-dried (0.01 atm, 23 °C). The graft density was defined as the difference in the film weight before and after grafting divided by the total surface area of the film. For these
measurements of the graft density, the PDMS sample was approximately 4.5 cm × 2.5 cm × 0.2 cm.

7.1.2.4 Characterization

7.1.2.4.1 Static contact angle

The surface hydrophilicity was characterized by the static contact angles. The CA values were average results basing on at least four areas of the surfaces. The tests were carried out with ca. 1 μl deionized water visually measured with VCA optima at room temperature after 15 sec after the drop contact the surface, using a digital camera with zoom capability.

7.1.2.4.2 FTIR

The surface components of the pristine bimodal PDMS-PVMS and the samples grafted with PIPAA by UV polymerization were characterized using FTIR spectroscopy (AA 2024-T3) in the mid-IR range from 4000 to 550 cm⁻¹. All spectra were obtained at an incident angle of 90 degrees to the surfaces of the specimens, with a spectral resolution of 4 cm⁻¹. Sixteen scans were taken.

7.1.3 Results and discussion

7.1.3.1 Surface treatments to make surface hydrophilic

The surface composition of the PIPAAm-grafted PDMS and PVMS-PDMS networks together with the pristine polysiloxane were tested with FTIR, with the results shown in Figure 7.2. The surface of the pristine PDMS contained only CH₃ groups (2960 cm⁻¹ and 1240 cm⁻¹, 785-815 cm⁻¹) and Si-O groups (1015 cm⁻¹) (see Figure 7.2 a). The surface of PVMD-PDMS contained CH₃ groups (2960 cm⁻¹ and 1240 cm⁻¹, 785-815 cm⁻¹), Si-O group
Chapter 7. Surface hydrophilic treatments

(1015 cm⁻¹) and CH₂=CH- (1599 cm⁻¹) (Figure 7.2b). No traces of contaminants or extraneous groups were detected.

After PIPAAm grafting, the surface composition was close to the composition expected for the polymers, PIPAAm and PDMS with the appearance of peaks at 1370, 1640 and 3310 cm⁻¹. The grafted PIPAAm amounts on the surfaces could be evaluated from the FTIR measurements. There were clear increases in the relative intensity of the PIPAAm specific peak with increasing UV exposure time. From a surface chemistry point of view, it must be noted that in the present case, no direct evidence exists that the polymerized acrylate was, indeed, covalently grafted to the substrate surface. A strong physical interaction or entanglement between the UV-treated PDMS surface and the PIPAAm chains could explain the observed results as well. Meanwhile, it is important to note that the PIPAAm surface coating could successfully withstand overnight extraction in water.

![FTIR spectrum](image)
Figure 7.2  FTIR spectra of the surface of (a) PDMS and (b) PDMS-PVMS with the UV polymerization IPAA

<table>
<thead>
<tr>
<th>IR region (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>614</td>
<td>Si-CH=CH₂</td>
</tr>
<tr>
<td>785-815</td>
<td>-CH₃ rocking and Si-C stretching in Si-CH₃</td>
</tr>
<tr>
<td>1015</td>
<td>Si-O-Si asymmetric stretching (doublet)</td>
</tr>
<tr>
<td>825-865</td>
<td>Si-O stretching in Si-OH</td>
</tr>
<tr>
<td>1025-1150</td>
<td>In-phase and out-of-phase wagging vibrations of –(CH₂)- in Si-(CH₂)₃-Si and Si-CH₂-Si</td>
</tr>
<tr>
<td>1055-1090</td>
<td>Asymmetric Si-O-Si stretching in [–(CH₂)₂Si-O]</td>
</tr>
<tr>
<td>1245-1270</td>
<td>Symmetric –CH₃ stretching in Si-CH₃</td>
</tr>
</tbody>
</table>
Chapter 7. Surface hydrophilic treatments

<table>
<thead>
<tr>
<th>Wavenumber</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1370</td>
<td>C-N and N-H</td>
</tr>
<tr>
<td>1400-1450</td>
<td>Asymmetric –CH₃</td>
</tr>
<tr>
<td>1599</td>
<td>C=C stretching in CH₂=CH-</td>
</tr>
<tr>
<td>1640-1650</td>
<td>C=O</td>
</tr>
<tr>
<td>2855</td>
<td>-CH₂- in PEO</td>
</tr>
<tr>
<td>2912</td>
<td>C-H symmetric stretching in sp³ CH₃</td>
</tr>
<tr>
<td>2964-2967</td>
<td>C-H asymmetric stretching in sp³ and –CH₃ in Si-CH₃</td>
</tr>
<tr>
<td>3020</td>
<td>=CH₂ symmetric stretching in CH₂=CH-</td>
</tr>
<tr>
<td>3060</td>
<td>=CH₂ asymmetric stretching in CH₂=CH-</td>
</tr>
<tr>
<td>3050-3700</td>
<td>-OH stretching in Si-OH, possibly also in C-OH (3610-3640 cm⁻¹)</td>
</tr>
<tr>
<td>3310</td>
<td>N-H stretching</td>
</tr>
</tbody>
</table>

Note \([147, 151, 152]\)

**Figure 7.3** Schema of PIPAAm polymerization onto the surface of PDMS (a) and PVMS-PDMS (b) network.
7.1.3.2 Surface hydrophilicity

The CA results of native PDMS and PDMS-PVMS networks by UV treatment for 1hr, 2hrs and 3hrs, respectively, shown in Figure 7.4, indicated that the CA were decreased significantly compared with that of pure PDMS, contact angle of 105°. However, CA of pristine PDMS increased with increase in duration of the UV treatment. The same was true for the PDMS-PVMS. The FTIR results in Figure 7.2 also indicated that the PIPAA was grafted onto the surface of the pristine PDMS and the PDMS-PVMS. The surface wettability greatly depended on the thickness and amount of the grafted hydrophilic groups on the surface. There should be an optimum content of grafted PIPAAm to exhibit the balance of transparency, protein deposition, and wettability properties.

![Figure 7.4 Contact angles of bimodal networks treated by PIPAA. (a) pristine PDMS, 1hr; (b) pristine PDMS, 2hrs; (c) pristine PDMS, 3hrs; (d) PDMS-PVMS, 1hr; (e) PDMS-PVMS, 2hrs; (f) PDMS-PVMS, 3hrs.](image-url)
Chapter 7. Surface hydrophilic treatments

7.1.4 Conclusions and further work

The UV polymerization PIPAAm deposition onto the surface of pristine PDMS and PDMS-PVMS bimodal networks significantly improved the hydrophilicity. The treatment of the silicone networks by UV polymerization was carried out in a solution with the hydrophilic monomers at various concentrations. This environment was much easier to control compared with that of a plasma treatment, which is carried out in a vacuum. The concentration of the hydrophilic monomers depended greatly on their volatility.

Further work could be done on characterizing the morphologies and compositions of the surfaces by AFM and XPS. The transparency, and oxygen and water permeability, should also be investigated. More biocompatible hydrophilic monomers with vinyl groups could be introduced onto the surfaces by plasma polymerizations.

7.2 Surface modification by covalent bonding of hydrophilic silane directly onto the surface of polysiloxane networks

7.2.1 Introduction

PDMS has been intensively used as a fabrication material for medical devices in many fields of application due to its remarkable gas permeability and biocompatibility.[153] However, PDMS medical devices are hampered due to its hydrophobic nature favoring adsorption of nonpolar molecules and unwanted adsorption of biomolecules. Thus control of surface properties (hydrophilicity) in biomaterials systems is an indispensable prerequisite for successful applications of a critical material, PDMS, in medical fields.
Chapter 7. Surface hydrophilic treatments

PEO is gaining widely recognition as a biomaterial due to its non-interaction with proteins or cells. As a result, there have been many attempts to create PEO surfaces for use in biomedical applications. [83, 143-146, 153]

In this section, we propose to coat PDMS surfaces with PEO. The native PDMS is pretreated by exposure to UV irradiation or to oxygen plasma, and the possible covalent linkage of PEO-silane was investigated. FTIR results were used to characterize the surface component and contact angle measurements were applied to measure the homogeneous attachments of PEO to the PDMS surfaces.

7.2.2 Experimental

7.2.2.1 Materials

The materials and preparation process for PDMS-PVMS networks were described in the previous section. 2-[methoxy(polyethyleneoxy)propyl]-trichlorosilane (ClSiMPEO, MW = 426-588 g/mol, Brand code: SIM6492.66, Gelest, MI) (designed as Cl₃SiMPEO) were used as the hydrophilic silane for surface treatment. Other solvent materials were purchased from Aldrich Chemical Co. St Louis, MO.

7.2.2.2 Surface treatment

The PVMS-PDMS networks surface were first treated by UV light in ambient atmosphere. The PVMS-PDMS films were placed in an UVO cleaner (model 42-220, Jetlight, USA) for 30 min under ambient atmosphere. The PVMS-PDMS networks were immersed in a 2 mM solution of ClSiMPEO immediately after UV treatments in a glove-box filled with N₂ for 24 hrs. The samples were thoroughly washed in water and dried in a stream of N₂.
7.2.2.3 Contact angle

A contact angle goniometer (VCA Optima, AST Product Inc. 2000 Billerica, MA) was used to determine the wettability of the modified PVMS-PDMS by saline. The static contact angle was measured at several spots. The resulting values were averaged with an absolute error of less than 4°.

7.2.2.4 FTIR

FTIR measurements were conducted using Digilab Excalibur FTIR equipment in the mid-IR range (4000 to 500 cm\(^{-1}\)) to determine the surface components in the PVMS-PDMS and surface treated networks. The resolution was 4 cm\(^{-1}\), and 16 scans per sample were analyzed using the Digilab Resolutions Software.

7.2.3 Results and discussion

7.2.3.1 Surface modification

The successful grafting of C\(_2\)SiMPEO onto the oxidized PDMS and PVMS-PDMS networks was first confirmed by FTIR spectrum in Figure 7.5, which demonstrated the surface characteristics of the untreated pristine PDMS, the treated PDMS and PVMS-PDMS. The peaks near 2855 cm\(^{-1}\) was the fingerprint of aliphatic carbon atoms involved with the symmetric and asymmetric stretching vibrations of CH\(_2\) in the C\(_2\)SiMPEO, see Table 7.2. This spectral change clearly indicated that the SiCl groups of the C\(_2\)SiMPEO molecules were strongly reacting with SiOH groups at the polysiloxane surface, and therefore, the hydrophilic PEO covalently bonded onto the surfaces. The absorption bands at 1270 and 800 cm\(^{-1}\), which were attributed to the SiCH\(_3\) groups, were not altered by the surface treatment because the SiCH\(_3\) groups were mostly irradiated by UV/ozone oxidation. The peak near 2855 cm\(^{-1}\) almost kept constant with increase of vinyl groups in PVMS-PDMS
Chapter 7. Surface hydrophilic treatments

also indicated that the vinyl groups, similarly to CH₃ in the networks, possibly formed SiOH groups under UV/ozone treatment, therefore the formation the hydrophilic layers made of linear PEO on the surfaces. Figure 7.6 (1st Step) showed the mechanism of PDMS-PVMS treated with UV/ozone. UV treatment of PVMS-PDMS in ambient atmosphere for 30 min reduced the contact angle of native PVMS-PDMS (105°) only slightly to 102°. PDMS networks treated with reactive oxygen (irradiated by plasma or UV/ozone) was described in the references as resembling glass surfaces in their chemical properties due to the creation of silanol groups on the surface. 30 min UV/ozone treatments significantly enhanced the hydrophilicity of the PVMS-PDMS surface, but since cracks occurred in the PDMS, these surfaces were not stable because the broken chains and hydroxyl groups diffused or sank into the matrix. All this indicated that UV treatment may not be suitable for long-term hydrophilicity improvement. Therefore, the covalent bonding hydrophilic chains were proposed to react with the silanol group to form a thin hydrophilic layer. Figure 7.6 (2nd Step), showed the covalent attachment of PEO onto PDMS. ClSiMPEO likely coupled to the silanol groups on the oxidized PDMS-PVMS surface.¹⁵⁴,¹⁵⁵
Figure 7.5 FTIR spectrum of PVMS-PDMS networks surface treated with PEO-silane.
Figure 7.6 Scheme of the chemical-bonding hydrophilic silane on the surface of PDMS-PVMS networks

7.2.3.2 Surface hydrophilicity

The Cl3SiMPEO treated the pristine PDMS, shown in Figure 7.7, exhibited the contact angle of 65.5° which was lower than that of the pristine PDMS and PVMS-PDMS networks, 105°. The contact angles decreased to near 20° when the contact time was 360 sec. The contact angles of ClSiMPEO treated PVMS-PDMS networks almost the same, near 62° with the increase in content of vinyl groups in PVMS-PDMS networks. With the ClSiMPEO as a silane coupling agent, the ethoxy group was hydrophilic and the ClSiMPEO treatment provided the hydrophilic surface. The absorbance of water by the PEO in the surface layers changed the saline drop contact angles formation to lower value. It is noteworthy that the surface of polysiloxane networks could be controlled by this ClSiMPEO coupling agent from hydrophobic to hydrophilic.
Figure 7.7 The contact angle and its change with time of the pristine PDMS networks treated by ClSiMPEO.

Table 7.2 The static contact angles of PDMS, PVMS-PDMS

<table>
<thead>
<tr>
<th>PVMS/PDMS</th>
<th>Static contact angle / degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>0/100</td>
<td>65.5 ± 2.0</td>
</tr>
<tr>
<td>5/95</td>
<td>60.6 ± 3.4</td>
</tr>
<tr>
<td>10/90</td>
<td>61.2 ± 2.7</td>
</tr>
<tr>
<td>15/85</td>
<td>63.2 ± 3.6</td>
</tr>
<tr>
<td>20/80</td>
<td>62.5 ± 2.7</td>
</tr>
</tbody>
</table>
7.2.4 Conclusion

Hydrophilic surface layers made of linear PEO were successfully introduced to PDMS and PVMS-PDMS networks through covalent reaction between ClSiMPEO and silanol groups on the surface firstly by UV/ozone treatment. The controlled surface hydrophilicity, near 60–65° in static contact angles were obtained.

7.3 Introducing a colloidal silica gradient onto the surface of bimodal PDMS networks using a sol-gel reaction

7.3.1 Introduction

Protein is one of major classes of contaminants for hydrophilic contact lenses. When a protein solution contacts another phase (a solid, liquid, or a gas) with which it is immiscible, protein molecules tend to accumulate at the interface between the two phases. The deposition of protein on the surface of contact lenses is strongly related to the surface characteristics of the materials. Therefore, functional surfaces are very important for biomaterial technologies. The introduction of colloidal silica by a sol-gel reaction on the surface of PDMS is frequently used to improve the hydrophilicity of surfaces. Roman’s research showed that metal oxide-modified PDMS surfaces were significantly more hydrophilic than pristine PDMS and that the inorganic coatings were stable over a period of at least 95 days. Here we would like to introduce silica onto bimodal networks to improve the surface hydrophilicility via a sol-gel reaction. Obviously, the
metal-oxide layer should be thin enough to maintain transparency for this optical application.

7.3.2 Experimental

7.3.2.1 Materials

The linear hydroxyl-terminated PDMS had number-average molecular weights corresponding to $M_n \sim 22,600 \text{ g mol}^{-1}$ and $\sim 880 \text{ g mol}^{-1}$ and was obtained from Gelest Inc., Midland, MI. These two samples were used as the long chains and short chains of bimodal PDMS networks, respectively. TEOS (SIT7110.0 Gelest Inc. Midland, MI) was used as the crosslinker and the precursor to generate the colloidal silica. Stannous-2-ethylhexanoate (Gelest Inc. Midland, MI) was used as the catalyst for the PDMS crosslinking, and diethylamine (Aldrich Chemical Co. St Louis, MO) was used as the catalyst for the sol-gel formation. Other materials such as hexane were all purchased from Aldrich Chemical Co. St Louis, MO.

7.3.2.2 Preparation process

7.3.2.2.1 Preparation of bimodal PDMS networks

The mol ratio of long linear chains and short linear chains employed to prepare bimodal PDMS was 10/90 in all cases. The linear hydroxyl-terminated PDMS chains were tetrafunctionally end-linked in the undiluted state with the stoichiometrically-required amounts of TEOS and the catalyst stannous-2-ethylhexanoate, present at 0.6 wt%. The preparative procedure was described in detail elsewhere.[129] Briefly, the reactions were run in Teflon™ molds at room temperature for three days. The resulting network sheets were extracted with toluene for three days, then deswelled with methanol, and finally dried
under vacuum. The fraction of soluble polymer thus removed amounted to approximately 3.0 wt%.

7.3.2.2.2 **Sol-gel reaction to introduce gradient silica**

The bimodal PDMS samples were immersed in a TEOS solution in hexane for swelling for various times, from 0 ~ 24 hrs, immediately thereafter, the samples were immersed into a 2 wt% diethylamine solution for about 2 hrs at room temperature to carry out the hydrolysis reaction. The samples were then washed with deionized water for several times, and dried under vacuum before characterization. **Figure 7.8** describes the detailed process.

**Figure 7.8** Preparation process for placing colloidal silica onto the surface of bimodal PDMS.

7.3.2.3 **Characterization**

7.3.2.3.1 **Contact angle**

The hydrophilicities of the surfaces were characterized by contact angles, the values of which were average results taken from at least four areas of the surfaces. The tests were carried out at room temperature with ca. 1 μl deionized water visually measured, using a digital camera with zoom capability.
7.3.3 Results and discussion

7.3.3.1 Formation of silica on surfaces

Figure 7.9 (upper portion) describes the preparation process for the gradient silica on the PDMS networks. TEOS, the precursor of the gradient silica, was first introduced into the PDMS network by swelling the PDMS networks, which were compatible with TEOS.\textsuperscript{159, 160} Different swelling degrees of the PDMS networks were obtained since the swelling degree depended on the time of PDMS films immersion in the TEOS/hexane solution. After the immediate immersion of the swelled PDMS networks into the diethylamine solution, the sol-gel process, TEOS hydrolyzing into silica with the catalyst (Eqn 7.1) quickly occurred on the top surface and sub-surface of the PDMS networks.\textsuperscript{161, 162} A gradient silica layer on the top of PDMS networks was obtained (Figure 7.9 lower portion). At the same time, diethylamine also diffused into the PDMS networks helps to the formation of silica in the sub-surface of the PDMS networks. The longer of the immersion of PDMS networks in TEOS, the more silica sol generated at or near the surface of PDMS films, and therefore, the higher the density of in-situ silica formation.
Figure 7.9 Schema of the structure of silica gradient on a surface (upper portion) and the morphology of the gradient silica/PDMS networks (lower portion).

\[
\text{Si(OC}_2\text{H}_5)_4 + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 4\text{C}_2\text{H}_5\text{OH} \quad \text{(Equation 7-1)}
\]

7.3.3.2 Surface hydrophilicity

CA results of the PDMS networks shown in Figure 7.10, indicated that the CA gradually decreased with increasing time of the samples immersed in TEOS solution, from 105° in the pristine PDMS network to about 72° in the samples which was immersed for 24h. This means that the surface wettability was improved through the introduction of the hydrophilic silica on the surface, and the wettability improved with increased density of silica on the surface. It was obvious that the hydrophilicity of the surface was greatly dependent on the density of polar groups on the surface. The introduction of silica onto the surfaces of bimodal PDMS networks increased the numbers of such hydrophilic groups (i.e. hydroxyl groups) which, therefore, improved the hydrophilicity.
Figure 7.10 Effect of colloid silica on the contact angles of bimodal PDMS surfaces.

7.3.4 Conclusions

Introducing of in-situ silica onto the surfaces of bimodal PDMS networks improved the hydrophilicity. The CA decreased nearly 30° when the PDMS networks had been immersed in TEOS for 24 hours.

Additional work will include dispersion of colloidal silica into bulk bimodal PDMS, characterizing the chemical bonding between the colloidal silica coating with changing the kind of polar groups and their exposition on the surface (which may affect the hydrophilicity of bimodal PDMS). Other work were focused on introduction of hydrophilic silica by the sol-gel process. The inorganic coatings could be derivatized with various organic functionalities including oligoethylene oxide (OEO), amino, perfluoro, or mercap to groups (using some involving silane chemistry). (The introduction of hydrophilic silica
could be carried out by first swelling the polymer with an amphiphilic macromonomer,\textsuperscript{143,163} and then using the sol-gel method.) The transparency, equilibrium water content and extent of protein deposition should also be considered to determine whether the sol-gel reaction method could be realistically applied to surface modification for contact lenses.

7.4 Surface modification of bimodal PVMS-PDMS films by plasma polymerization

7.4.1 Introduction

Contact lenses made from silicone-containing materials have been investigated for a number of years. Such materials can generally be subdivided into two major classes, namely hydrogels and non-hydrogels. Non-hydrogels do not absorb appreciable amounts of water, whereas hydrogels can absorb and retain water in an equilibrium state. Regardless of their type, both non-hydrogel and hydrogel silicone contact lenses tend to have relatively hydrophobic, non-wettable surfaces. Those skilled in the art have long recognized the need for modifying the surface of such silicone contact lenses so that they are comfortable on the eye. It is known that increased hydrophilicity of the contact lens surface improves the wettability. This in turn is associated with improved wear comfort. Additionally, the surface of the lens can affect the lens's susceptibility to depositions, particularly protein and lipid depositions from the tear fluid during lens wear. Accumulated deposition can cause eye discomfort or even inflammation. In the case of extended wear lenses, the surface is especially important since extended wear lens must be designed for high standards of comfort over an extended period of time, without requiring daily removal of the lens before
Chapter 7. Surface hydrophilic treatments

sleep. Thus the regimen for the use of extended wear lenses would not provide a daily period of time for the eye to recover from any discomfort or other possible adverse effects of lens wear.

There are many surface treatments disclosed in the literature for making the surfaces of silicone lenses more hydrophilic and more wettable, including changing the chemistry of the surface layer, coating the surface\cite{164}, and compounding the polymer with additives that subsequently diffuse to the surface.

Among chemical surface modification techniques are non-polymeric plasma treatments and corona treatments. This includes etching or the selective destruction of a surface layer. Surface modification techniques also include the introduction of functional groups onto a surface layer, for example the introduction of oxygenated functions (hydroxyl, carboxyl, etc.) at the surface of organic polymeric materials for the purpose of increasing hydrophilicity, thereby promoting increased wettability. Such techniques may employ flame treatments, corona treatments, or plasma treatments. Plasma treatments have been increasingly studied for the modification of surfaces\cite{164}. The plasma gas can include many species, such as free radicals and energetic electrons and ions. Depending on the gas or vapor used in the plasma and the process conditions, the effects of non-polymeric or non-depositing plasma treatment include surface etching or ablation, oxidation, the formation of reactive groups, and combinations thereof.

Silicone lenses have been subjected to plasma surface treatment to improve their surface properties, e.g., surfaces have been rendered more hydrophilic, deposit resistant, scratch resistant, etc. Examples of previously disclosed plasma surface treatments include subjecting contact lens surfaces to plasmas comprising an inert gas or oxygen.
Chapter 7. Surface hydrophilic treatments

Here, we discuss the introduction of functional groups absent in the parent polymer using plasma polymerization onto a surface to promote the hydrophilicity.

7.4.2 Experimental

7.4.2.1 Materials

The linear hydroxyl-terminated PDMS, (DMS-S27, Gelest Inc. Midland, MI) had a number average molecular weight corresponding to $M_n \sim 18,000$ g/mol. Hydroxyl-terminated linear siloxane copolymer (VDS-2513, Gelest Inc. Midland, MI) was composed of 25~30 mol% vinylmethylsiloxane and 70~75 mol% dimethylsiloxane. TEOS (SIT7110.0 Gelest Inc. Midland, MI) was used as the tetrafunctional crosslinker, and the stannous-2-ethylhexanoate (SNB1100, Gelest Inc. Midland, MI) was used as the catalyst for bimodal PVMS-PDMS. Acrylic acid, purchased from the Aldrich Company Co. St Louis, MO, was employed as the monomer for polymerization. Polyethylene oxide (PEO), hydroxyl terminated, $M_n \sim 300$ g/mol, was also purchased from the Aldrich Company, St Louis, MO.

7.4.2.2 Preparation of PDMS-PVMS bimodal silicone networks

A series of bimodal silicone networks with various vinyl groups were prepared by employing different mol ratios of PVMS to PDMS (0:100, 5:95, 10:90, 15:85, 20:80), corresponding to the short chains and long chains, respectively. The short chains and long chains were tetrafunctionally end-linked in the undiluted state with the stoichiometrically-required amounts of TEOS and the catalyst, stannous-2-ethylhexanoate, 0.6 wt% (Figure 7.11). The reactions were run in Teflon™ molds at room temperature for three days for completion of the crosslinking. The resulting network sheets were extracted with toluene for three days, then deswelled with methanol, and finally dried under vacuum.
The number of vinyl groups depended on the molar concentration of PVDS used to prepare the samples. It could be determined by FTIR, NMR and titration, etc.

**Figure 7.11** Schema preparation of bimodal PVMS-PDMS networks. Bold lines: short linear PVMS-PDMS; thin lines: long linear PDMS; side groups: vinyl groups in PVMS-PDMS; spot: crosslink point.

### 7.4.2.3 Plasma polymerization of PAA on the surfaces of a PVMS-PDMS networks

PDMS-PVMS bimodal networks were first activated by the oxygen present in the reactor in oxygen plasma, which led to a partial oxidation of the topmost layer. This pretreatment also led to better adhesion of the deposited film. Plasmas of acrylic acid were subsequently used to deposit an acrylic acid coating on the pretreated PDMS-PVMS networks. The plasma treatments of the PDMS-PVMS bimodal networks were carried out in a plasma reactor at 0.2 mbar at 60 W for 15 min. Some of the samples were immediately immersed into a PEO water solution for further treatment.

### 7.4.2.4 Characterization

#### 7.4.2.4.1 Contact angle

The hydrophilicity of surface was characterized by static contact angles, the values of which were the average results based on at least 4 areas of the surfaces. The CA values
were analyzed from the images which were taken 15 sec after ca. 1 µl deionized water contacted the film surface using a digital camera with zoom capability at room temperature.

7.4.2.4.2 Transparencies

UV-Vis transmittance measurements of the samples were performed on a Shimadzu UV-Vis 160A spectrophotometer in the wavelength range 200-1200 nm.

7.4.3 Results and discussion

7.4.3.1 Formation of PAA layers on PVMS-PDMS networks

PVMS-PDMS bimodal networks were obtained through end-linking hydroxyl-terminated PVMS-PDMS linear short chains and hydroxyl-terminated PDMS linear long chains with TEOS, as catalyzed by stannous-2-ethylhexanoate. The crosslinking mechanism is the same to that of bimodal PDMS networks.

The vinyl groups in the PVMS-PDMS networks here were used as the original points for homo- or block polymerization. The plasma polymerization was carried out to deposit PAA, hydrophilic polymer, on the surface of PVMS-PDMS, (see Figure 7.12).
Chapter 7. Surface hydrophilic treatments

Figure 7.12 Mechanism of plasma polymerization of acrylic acid on the surface of bimodal PDMS.

7.4.3.2 Surface hydrophilicity

Figure 7.13 shows the CA results for (i) native PDMS-PVMS bimodal networks, (ii) PDMS-PVMS deposited poly(acrylic acid) (PAA) after air plasma treatment, and (iii) PDMS-PVMS further treated by PEO. The CA of PDMS-PVMS remained large upon increase in the number of vinyl groups, which means that vinyl groups did not greatly influence the hydrophobicity. The CA obviously decreased greatly with increasing treatment time with the AA plasma. Especially, the CA decreased significantly with increasing number of vinyl groups from 100/0 to 85/15 in the PDMS-PVMS samples, but only slightly when the PDMS/PVMS molar ratio was less than 85/15. Further PEO treatment of the PDMS-PVMS after AA plasma polymerization did not improve the CA. The experimental results obviously indicated that the PAA plasma polymerization on the surface of PDMS-PVMS improved the wettability of the surfaces. This improvement of the wettability was strongly related to the number of vinyl groups, and further PEO treatment had only a slight effect on
the wettability. A proposed mechanism of PAA grafted onto the surface of PDMS-PVMS is shown in Figure 7.12.

Figure 7.13 Contact angles of PDMS-PVMS bimodal networks. -□- : native PDMS-PVMS; -○- : PDMS-PVMS deposited with poly(acrylic acid) after oxygen plasma treatment; -△- : PDMS-PVMS further treated by PEO after deposition of PAA.

7.4.4 Conclusions and further work

The plasma polymerization giving PAA deposition on the surface of PDMS-PVMS bimodal networks significantly improved their hydrophilic properties.

Further work could be done on the morphology and composition of the surfaces by AFM, XPS, and FTIR. The transparency and oxygen and water permeability should also be investigated. More hydrophilic monomers with vinyl groups, which are biocompatible, could be introduced onto the surfaces by such plasma polymerizations.
Chapter 7. Surface hydrophilic treatments

The uniformity and stability of the plasma treatment was strongly related to the nature of the treatment and the controlled plasma environment. Actually, many US patents [121, 165-167] describe plasma treatments of contact lenses.
Chapter 8. Overall conclusions and future work

8.1 Summary

The first part presents the improvements in the mechanical properties of a couple of biodegradable polymers, the first one is poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHx) by introducing several nano-fillers (clay, mica, talc, expanded graphite) to prepare nanocomposites. There were two preparation methods applied in this research. One is solution mixing, in which the nanocomposites were prepared by exfoliation-adsorption technique, and the other is extrusion blending, which involves pre-heating the polymer, mixing in the nano-fillers, and then extruding them. The resulting nanocomposites were characterized by X-ray diffraction measurements (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) to determine the dispersion of the layered silicate in the matrix; by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) to determine their thermal characteristics and stability; and by the INSTRON measurements to determine their mechanical properties. In both methods, XRD results showed a transition in the nanocomposites structure from exfoliation to intercalation, and the transition degree depended on the surface characteristics of the organoclay. PHBHx/clay (clay30B, clay25A, clay20A), PHBHx/expanded graphite (EG) had higher values of the Young’s modulus, toughness, yield stress, and tensile strength compared with those of PHBHx/mica and PHBHx/talc, even at very low content of the fillers. The changes in the mechanical properties were mostly attributed to the intercalated, even exfoliated state of the clay in PHBHx because of the physical compatibility including hydrogen bonding between the fillers and the matrix. The good dispersion of the layered
silicate did not affect the crystallinity of PHBHx, but somewhat slightly decreased its thermal stability.

Another biodegradable polymer was studied in this work is glycerol-derived alkyd resin, which was synthesized from glycerol and maleic anhydride by polycondensation reactions. One set of glycerol-derived alkyd resin/clay nanocomposites was successfully prepared by melt blending maleic anhydride-glycerol precursors with organoclays. These clays had been pretreated with methyl tallow bis-2-hydroxyethyl ammonium chloride salt (yielding a nanocomposite designated clay30B), and some samples of the clay30B were further treated with the diglycidyl ether of bisphenol A (DGEBA) (clay30BT). Resin/mica and resin/talc nanocomposites were also prepared, in the same way, to yield materials for purposes of comparison. The morphologies, thermostabilities, and mechanical properties of the resulting nanocomposites were investigated in detail. XRD results and transmission electron microscopy images clearly indicated that 30BT was further delaminated by the DGEBA, and that the clay30B and clay30BT were mostly exfoliated and finely distributed sheets in the alkyd resin matrices. These layered silicate fillers gave remarkable improvements in thermostability and mechanical properties even at very low loadings. Minimizing aggregation was more of a problem in the case of the mica and the talc, at least in this matrix.

The second part of this research work focused on the preparation and characterization of silicone hydrogels based on poly(dimethylsiloxane) (PDMS) and hydrophilic block copolymer, and some surface modifications of PDMS to make its surface hydrophilic.
Chapter 8. Conclusions

The first two series of bimodal silicone hydrogels were successfully prepared with highly improved surface hydrophilicity through the introduction of hydrophilic components into the PDMS network in the side chains and in the main chains, respectively.

In this way a strongly hydrophobic polymer was converted into a hydrogel by introducing sufficient lengths and amounts of hydrophilic side chains of sufficient length to overcome the hydrophobicity but sufficiently well dispersed to avoid disadvantages such as loss of the transparency required in some biomaterial applications. Specifically, PDMS-poly(ethylene glycol) (PEG) hydrogels were successfully prepared by end-linking a combination of long and short chains to give the bimodal distributions of network chain lengths that generally give unusually good mechanical properties. The end-linkers were chosen to be using trialkoxysilanes R'Si(OR)₃ having R’ side chains that are hydrophilic of variable lengths and of sufficient hydrophilicity to produce the desired hydrogels. The first trialkoxy silane was N-(triethoxysilylpropyl)-O-polyethylene oxide urethane (S1) with 4 to 6 units of ethylene glycol, and the second was [methoxy(polyethyleneoxy)propyl]-trimethoxysilane (S2) with 6 to 9 units of ethylene glycol, and they were used to end-link hydroxyl-terminated PDMS chains in standard room-temperature condensation reactions. It was possible to introduce the hydrophilic side chains into the hydrophobic networks without discernible phase separation. These linear side chains increased equilibrium water contents, from 0 to 11.2 wt% in the first series and from 0 to 29.8 wt% in the second. Longer hydrophilic chains clearly migrated to the surfaces of the resulting PDMS-PEG hydrogels to give decreases of static contact angles from 105° to 80° for the first series, and to 40° for the second. The longer hydrophilic chains were found to give larger decreases in the contact angles and larger equilibrium water contents as expected. The mechanical

155
properties demonstrated that the Young's moduli of the hydrogels did not change upon introduction of the S1 hydrophilic crosslinker, but did decrease from the presence of the S2. The tensile strength and elongation at break were relatively insensitive to the amounts of either of the hydrophilic groups.

The other series of PDMS-PEG amphiphilic conetworks (APCNs) were prepared by bonding a hydrophilic macromer, hydroxyl-terminated linear PEG, into another highly hydrophobic macromer, hydroxyl-terminated linear PDMS with the crosslinker, tetraethoxysilane (TEOS) and bis[(3-methyldimethoxysilyl)propyl]polypropylene oxide (BMPPPO), which also functioned as a compatibilizer. Fourier transform infrared (FTIR) results clearly demonstrated the occurrence of the hydrolysis reactions between the terminal hydroxyl groups of the two polymer chains and the ethoxyl groups in TEOS and BMPPPO. DSC and XRD results clearly showed the presence of the two phases in the conetworks. The contact angle (CA) indicated the wettability of the conetworks increased, that is, CA values decreased significantly from 105° in PDMS to 55° in the PEG/PDMS APCN (10/1 mol ratio), and the swelling degrees of the APCNs increased from about 0 to 60 % when the PEG/PDMS mol ratio was larger than 4/1. The APCNs with such high hydrophilicity and the good mechanical properties should be useful as some biomaterials.

Secondly, several surface treatments methods were applied to make PDMS networks hydrophilic, including (1) introduction of an ultra thin layer of silica on the surfaces through the sol-gel process, (2) a UV/ozone method for bimodal networks consisting of some vinyl-substituted chains, poly(vinylmethylsiloxy) (PVMS), along with those of PDMS; (3) treatment of PDMS networks by UV/ozone, followed by grafting of polyethylene glycol based silane directly onto the surfaces, (4) grafting a hydrophilic monomer, N-
Chapter 8. Conclusions

isopropylacrylamide by the UV radiation, (5) plasma polymerization of acrylic acid (AA) onto the surface of the PDMS networks. The static CA, SEM and FTIR were applied to characterize the surface hydrophilicity, surface components and surface morphologies of the hydrogels, respectively. These experiments illustrated the fact that all these approaches made the PDMS surfaces significantly more hydrophilic by introducing polar groups onto the surfaces.

8.2 Future work

The biodegradable polymer nanocomposites based on PHB/Hx/layered silicates were prepared via solution mixing and extrusion blending, respectively. This research may broaden the applications of these biodegradable polymer nanocomposites in packaging, medical and other routine plastic products that cause environmental concerns. The melt extrusion method may be preferred since it could be carried out to manufacture continuously, and this method does not need large amounts of the solvents to assist the formation of the biodegradable nanocomposites. The processibility, the rheology, the biodegradability as well as the special requirements of the products should be further investigated before their final industrialization.

Glycerol-derived alkyl resin/layered fillers hybrid nanocomposites were successfully prepared through thermal polycondensation and crosslinking. Future work should be pay more attention to the dispersion of layer fillers in the precursors, and the techniques on get rid of air bubbles during the formation of final products.
Chapter 8. Conclusions

The hydrophilic chains were successful introduced into the main chains or side chains of PDMS networks to improve the hydrophilicity and the water contents in the hydrogels. These amphiphilic conetworks or hydrogels may be applied in areas such as biomaterials in drug delivery, medical, microchips, and contact lenses. The biocompatibilities of these products need to be further investigated before their final applications.

Some surface treatments and modifications were greatly helped to improve the hydrophilicity as well as the wettability of the PDMS networks. These methods may be used as a further step of the APCNs or hydrogels to improve the hydrophility. Obviously, these methods could also be applied to many other kinds of films or membranes to improve their wettability or the hydrophilicity.
References


15. Pinnavaia TJ and Beall G. Polymer-clay nanocomposites. Chichester: John Wiley & Sons Ltd., **2000**.


References


64. Meijs GF and Laycock BG. Polymerizable siloxane macromonomers. US Patent 5,981,615, **1999**.


103. Zhang X. Improvements in the mechanical properties of biodegradable poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) and bimodal poly(dimethylsiloxane) hydrogels & treatments for making poly(dimethylsiloxane) network surfaces hydrophilic. University of Cincinnati. PhD. **2008**


120. Heiler DJ, Groemminger SF, Denick JJ, and Simpson LC. Surface treatment of silicone hydrogel contact lenses. US Patent 6,348,507, **2002**.

121. Chen RY. Process for putting a hydrophilic coating on a hydrophobic contact lens. US Patent 4143949, **1979**.


141. Mark JE. Polymer Data Handbook: Oxford University Press, Inc, **1999**.


170. Lin G, Zhang X, Kumar S, and Mark JE. Improved hydrophilicity from poly(ethylene glycol) in amphiphilic conetworks with poly(dimethylsiloxane) Silicon 2009;Accepted.


Publications and contributions

Journal publications


2. Lin G, Zhang X, Kumar S, and Mark JE. Improved hydrophilicity from poly(ethylene glycol) in amphiphilic conetworks with poly(dimethysiloxane) Silicon 2009; Accepted.


**Presentations and posters**


14. Lin G, **Zhang X**, Li Y, Allen WM, Noda I, and Mark JE Some nanocomposites based on a glycerol-derived alkyd resin and layered silicates IXth International Conference on Frontiers of Polymers and Advanced Materials, Cracow, Poland, **2007**


17. **Zhang X**, Lin G, Allen WM, Noda I, and Mark JE Some nanocomposites based a glycerol-derivated alkdy resin and layered silicates Osper Conference in University of Cincinnati, Cincinnati, OH, **2007**

18. **Zhang X**, Lin G, and Mark JE Bimodal poly(dimethylsiloxane) hydrogels and treatments for making poly(dimethylsiloxane) network surfaces hydrophilic Osper Conference in University of Cincinnati, Cincinnati, OH, **2006**

**Book chapters**


Please see the references [4, 127, 168-170], [161, 162, 171-174] [175, 176]