TPU NANOCOMPOSITES WITH 1D AND 2D CARBONEOUS FILLERS

by

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TPU Nanocomposites with 1D and 2D Carbaceous Fillers

Abstract

by

DIAN YUAN

In this work thermoplastic polyurethane (TPUs) nanocomposites incorporating carbon nanotubes (CNTs) were prepared via melt blending and compression molding and their physical and mechanical properties were characterized. TPU-CNTs systems exhibited extensive filler agglomeration, which resulted in a significant decrease in strength and ductility. Since shear mixing was not effective enough to disentangle CNTs, surfactant was combined with the CNTs via sonication. TPU-CNT surfactant nanocomposites exhibited significantly higher tensile mechanical and dynamic mechanical properties comparing with nanocomposites prepared without surfactant, thanks to the better filler dispersion, as indicated by scanning electron microscopy (SEM) morphological studies. Thermogravimetric analyses (TGA) shed some light on a second mechanism of improvement in the mechanical properties: the well-dispersed nanofillers can also favor higher phase separation in TPUs, leading to a better microstructure which is able to enhance the load transfer effects and maximize the mechanical properties of the material. Synergistic effects were observed when 1D CNTs were combined with 2D graphene nanoplatelets in TPU hybrid composites. Higher tensile mechanical and dynamic mechanical properties were observed with respect to the systems incorporating individual CNT and graphene, especially when combining graphene and CNTs at a ratio of 6:4. The synergistic mechanism was
hypothesized to occur due to the combination of two fillers with different shape and aspect ratio, with the long tortuous CNTs limiting graphene aggregation and bridging adjacent graphene platelets in order to form a more efficient network. Hybrid (6:4) nanocomposites showed the highest creep resistance and recovery ability since the network formed by 1D CNT and 2D graphene can hinder the movement of TPU chains, leading to a decrease in viscoelastic and viscous deformation.

The TPUs developed in this study exhibit remarkably improved tensile and viscoelastic properties, which are highly demanded for this type of TPUs. Additional multifunctional properties can be potentially displayed, including electrical and thermal conductivity, self-healing mechanisms and shape-memory form effects, in order to extend the TPU use to many other technological applications.
Chapter 1

Introduction

1.1 Thermoplastic polyurethanes

1.1.1 Synthesis of TPUs

Thermoplastic polyurethanes (TPUs) represent a family of copolymers produced by polymerization reaction of a diisocyanate (NCO–R–NCO), a long-chain diol, and a short-chain diol (acts like chain extender). The reaction mechanism of urethane group is shown in Fig 1.1.

There are various methods that can be used to produce TPUs. TPUs can be obtained in solution and bulk, or by a different addition sequence of reactants it can be considered as one-step or two-step polymerization reaction. The main difference between this two reaction methods is the chain build-up of TPUs. In the one-step polymerization procedure, polyol, diisocyanate and chain extender are added at once at the beginning of the reaction, which yields random block sequences. The one-step reaction is widely used in industry since it is faster, easier and more reproducible. On the other hand, the two-step method produces a more regular hard–soft–hard–soft chain sequence with fewer side reactions (Fig 1.2). TPUs synthesized by the two-step reaction generally show higher mechanical properties since the high structural regularity enhances aggregation and crystallization of the hard segments\(^1\).become much easier.
1.1.2 Microstructure of TPUs

TPU block polymers contain alternating soft and hard segments linked by covalent bonds. Hard segments are rigid at room temperature and are produced by the reaction of diisocyanate with the short-chain diol, rendering a high density of urethane groups. On the other hand, soft segments consist of flexible chains produced by the reaction of diisocyanate and the long-chain diol, producing longer polymer chains and lower density of urethane groups by comparison with the hard segments\(^1\). **Fig 1.3** shows the characteristic structure of TPU chains with soft and hard segments.

The polarity of urethane groups in the hard segments attracts each other in order to promote a high degree of aggregation. Crystallized hard segments embedded in soft segments forms generate the so-called phase separation in TPUs. This crystalline areas act like physical crosslinks, giving the TPU a rubber-like elasticity\(^1\). **Fig 1.4** shows the typical microstructure of TPU block copolymers. The difference in polarity and chemical nature between the soft and hard segments induces phase separation in TPUs. The current literature reports that when the content of hard segment increases, the mean domain size increases from 10 to 20 nm. Moreover, the shape of the hard domains varies from spheres with diameter of 5–20 nm to long needles 5 nm thick and 50-300 nm long \(^1\).

Several factors can influence the formation of the domains and the degree of phase separation, including the type of the diisocyanate, polyol and chain extender; molecular weight of the soft segments\(^2\); nature size of the soft and hard domains; the reaction conditions and manufacturing process \(^3\) and the introduction of nanofillers \(^4\).
For example, annealing can favor the formation of stronger hydrogen bonds and promote a more uniform TPU network, so that the physical and mechanical properties are improved.

Several techniques can be used to study the phase preparation of TPUs, from small angle X-ray scattering (SAXS), scanning electron microscopy (SEM), atomic force microscopy (AFM) to neutron scattering.

1.1.3 Physical properties of TPUs

This special phase separated structure is responsible for the excellent physical properties exhibited by TPUs. For instance, when stress is applied to a TPU sample, the soft domains are flexible and easy to be stretched while hard domains can absorb and store the energy coming from the stress. This rubber-like elasticity also gives TPU excellent abrasion resistance and high tear strength.

TPU has good chemical resistance due to the counterbalance between polar and nonpolar domains in the TPU structure. Moreover, TPUs also show excellent low temperature performance and grease resistance. By changing the micro domain structure, we can properly tailor the properties of TPUs from very hard to very soft depending on the final application.
1.2 Carboneous fillers

Fullerenes, nanotubes, graphene, graphite, are all different allotropes of carbon, with different shape and dimensionality varying from 0D to 3D. These carbon materials exist in various forms, from powders to fibres and can have different dimension, from nano to micro. Due to their structure, most carbon materials show good mechanical properties and excellent electrical and thermal conductivities. Typical examples of carbon nanomaterials are graphite and graphene, carbon black and carbon nanotubes (CNT). Carbon nanostructured materials are widely used as reinforcing fillers to improve properties of various polymer matrixes. Fig 1.5 shows carbon nanofillers with different dimensionalities. Below is a brief presentation of the carbon nanofiller which have been used in this research work.

1.2.1 Carbon nanotubes

Carbon nanotubes (CNTs) are carbon material with cylindrical nanostructure. CNTs have much higher length to diameter ratio comparing with other carbon materials; this ultrahigh aspect ratio (up to 132,000,000:1) endows CNTs with exceptional properties.

Based on the number of rolled layers, CNTs are categorized as multi-walled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs). Single-walled nanotubes can be fabricated in a variety of ways. The most common synthetic methods include laser ablation; chemical vapor deposition (CVD) and decomposition of CO. MWCNTs are usually produced by CVD method. Although
MWCNTs made by this method have large quantities of defects which significantly affect their properties, high output production still makes it the most widely used method in the industry.

The multi-walled nanotubes have a diameter in the range from 2.5 to 30 nm, and length range from several nanometers to few micrometers. **Fig 1.6** shows typical dimensions of A) single-walled carbon nanotubes and B) multi-walled carbon nanotubes.

SEM can be used to get some indications on the nanotubes morphology, while other techniques can be applied to determine the mechanical properties of MWCNTs\(^8\), with Young’s modulus ranging from 270 to 950 GPa, and tensile strength from 11 to 63 GPa. However, it is shown that the mechanical properties of MWCNTs are very sensitive to the concentration and type of defects present on the surface\(^9\).

CNTs not only have excellent mechanical properties but also show great potential in electrical\(^10\) and thermal conductivity\(^11\). Specifically, the CNT electrical conductivity was measured as higher than \(10^3\) S/cm at room temperature and the thermal conductivity shows up to 3500 W/mK\(^12\).

Chemically modified carbon nanotubes also attracted a lot of attention since the functional groups can improve the filler dispersion in solvents or polymer matrix. Moreover, the functionalization can also help to enhance the interfacial interactions between fillers and matrix, which in turn affect the properties of the resultant material. In 1994 S. C. TSANG removed the caps of nanotube by treating with hot nitric acid, as a result of oxidation of the pentagonal rings\(^7\). Then the modification methods were
optimized by using acid–base titration to induce the formation of carboxylic acid and other groups on the surface of nanotubes. However, oxidation can cause the formation of some defects on CNT surface, which decrease the electrical and thermal conductivities. Further research is required to investigate more successful functionalization for CNTs in order to effectively improve the filler dispersion and maximize the property enhancement in nanocomposites, while keeping a low filler concentration.

1.2.2 Graphene

Graphene is a monolayer of carbon material (thickness ~0.34 nm) with carbon atoms arranged in sp² bonded six-membered rings. Graphene can be regarded as layers exfoliated from graphite with large theoretical specific surface area up to 2630 m² g⁻¹. This two-dimensional carbon material has outstanding mechanical (Young’s modulus ~1.0 TPa), thermal (thermal conductivity ~5000 Wm⁻¹K⁻¹) and electrical (electronic mobility 15000 cm²·V⁻¹·s⁻¹) properties¹³. Fig 1.7 shows the characteristic structure of graphene (single layer of graphite).

There are four common ways to synthesis graphene: chemical vapor deposition (CVD)¹⁴, mechanical exfoliation, exfoliation in solvent by ultrasonication¹⁵ and chemical process starting from graphite¹⁶. However, the CVD method requires transferring of the graphene from one substrate to another, mechanical exfoliation cannot produce graphene with large specific area, and the yield of exfoliation in solvent is low. Therefore, although the chemically derived
Graphene from graphite shows some defects on the filler surface, the process high productivity still make it the most widely applied method in the industry.

Graphene with unique band structure and high electron mobility on the surface is widely used in the electronic field. Since graphene has high optical transmittance, it can be potentially applied in transparent conductive films. The conductivity of graphene is changed by changing its surface adsorption, so that graphene plates can also be used as sensors to detect other molecules, such as gases. Graphene shows also potential applications in solar cells since the electronic structure of graphene exhibits high sensitivity to doping\textsuperscript{17}.

1.2.3 Graphene oxide (GO)

The structure of GO can be seen as one layer of graphene with oxygen functional groups located on both sides of the surface. The presence of the functional groups on the surface makes GO thicker than one layer of graphene, with thickness of 1–1.4 nm. These oxygen functional groups are not distribute randomly on the surface, but with carbonyl, carboxyl, and lactone decorating the edge and epoxy and hydroxyl groups present on the basal plane\textsuperscript{16}. Fig 1.8 shows the chemical structure model of GO.

An ideal graphene is perfectly flat and consists of only trigonally bonded sp\textsuperscript{2} carbon atoms. However, a GO sheet contains some of sp\textsuperscript{3} carbon atoms displaced slightly below or above the plane. Although the overall size of GO is similar to graphene, the carbon atoms attached with functional groups are still slightly displaced.
GO’s chemical compositions is changed based on the preparation method, ranging from $C_8O_2H_3$ to $C_8O_4H_5$ with a C:O ratio of 4:1 to 2:1$^{16}$. Reduction can enhance the C:O ratio to approximately 12:1.

The synthesis of graphene oxide consists in placing graphite into a mixture of nitric and sulfuric acid with strong oxidation agent like potassium chlorate inside. The product of oxidation is GO, following with ultrasonication in order to exfoliate the packed GO to well-exfoliated GO.

The properties of GO can be tuned by changing its chemical composition, which depends on the degree of oxidation. The conductivity of GO is reduced comparing with graphene, since oxidation introduces defects on the surface of the plane. However, functional groups on GO can hydrolyze in water and become negatively charged, which makes GO easily and homogeneously dispersible in solvents like water. This makes GO relatively easy to process during preparation of polymer composites.

GO reduced by chemical or thermal processes in order to reestablish the chemical structure of graphene, and restore their high electrical and thermal conductivity. GO can thus be applied in photonic devices such as photovoltaics, electroluminescent cells and photodetectors. The resistance of reduced GO (rGO) increases when rGO is exposed to some chemical species, showing good molecular sensing. For practical applications, it can act as sensor for selective molecules.
In the case of polymer nanocomposites, GO can be first easily dispersed in the matrix and subsequently reduced by thermal treatment via in-situ reduction\textsuperscript{18}.

1.3 TPU nanocomposites

Taking into account the above considerations and the evidence reported in the current literature, carbon nanofillers like CNT, graphene, GO with high aspect ratio and excellent mechanical properties, outstanding thermal and electrical conductivities are excellent candidates as reinforcing fillers for TPUs.

1.3.1 Preparation of TPU nanocomposites

Typically there are three mixing processing methods to produce TPU composites. Each mixing method enables to achieve a different degree of dispersion. 1) \textit{In situ polymerization}, where fillers are mixed with monomers or pre-polymers and mixing occurs prior and during polymerization. 2) \textit{Solvent mixing}, where fillers are incorporated into the polymer solutions and mixed at low viscosity, while the solvent can be removed subsequently. 3) \textit{Melt mixing}, where the nanofiller is mixed with the molten polymer in a mixer or extruder. This method generally shows a lower degree of dispersion compared with the previous two methods, but it is widely used in the industry\textsuperscript{19}.

1.3.2 Physical properties of TPU nanocomposites
By adding functionalized graphene into TPU matrix, the Young’s modulus was reported to improve up to 7 times with more than 50% improvement in toughness\textsuperscript{20}. Improvement in mechanical properties not only comes from load transfer from matrix to fillers, but the filler itself will also influence the morphology of TPUs improving its properties. For example, MWCNT- TPU nanocomposites exhibit higher glass transition temperature ($T_g$) and crystallinity comparing with neat TPUs, showing that the nanotubes are able to (i) interact with the molecular chains limiting their mobility and (ii) act as nucleation agent to improve crystallinity of TPUs\textsuperscript{4}.

Combining high aspect ratio with good conductivities, carbon nanofillers can form networks in a TPU matrix at very low loadings. These networks allow the transfer of electrons and phonons thus improving the electrical\textsuperscript{21} and thermal\textsuperscript{22} performance of TPUs. In MWCNT/TPU composite systems, the percolation threshold was measured around 3–4 wt.%\textsuperscript{23}.

The filler dispersion and its interactions with the host polymer matrix are two main issues encountered in the preparation of TPU nanocomposites. In particular, strong van der Waals attractions tend to aggregate graphene sheets, while long CNTs are easily entangled with each other, causing poor dispersion. Therefore, achieving good filler dispersion is important to maximize the reinforcing effect in nanocomposites. Moreover, good interactions result in high load transfer, which also enables to improve the mechanical properties of polymers. Surfactants can be used as dispersion agents to help the dispersion of nanofillers in different matrices\textsuperscript{24}. 
To help the interaction between nanofillers and polymers, surface modification of fillers is widely used. In the specific case of TPU composites, CNT and graphene are typically modified with oxygen functional group on the surface, since oxygen groups can form strong hydrogen bonding with urethane groups\textsuperscript{20, 25}. Fig 1.9 shows the hydrogen bonding formed between MWCNT and TPU matrix. On the other hand, polymeric chains can be properly grown on the graphene surface to prevent aggregation and improve the interactions with the matrix\textsuperscript{26}.

Taking into account that filler dispersion and interactions with the matrix depend on the filler shape and aspect ratio, incorporation of two different fillers might further optimize the properties in hybrid polymer nanocomposites. For instance, graphene can act as dispersion agent for CNTs, and the combination of 1D CNTs with 2D graphene can also form an efficient network to decrease the percolation threshold of nanofillers in matrix. CNTs and graphene were reported to show synergistic effects when used in certain proportion in nanocomposites\textsuperscript{27}.

1.3.3 Novel applications of TPU nanocomposites

TPU nanocomposites exhibit functional properties to be applied in novel applications. Graphene-TPU nanocomposites are good gas barrier materials since 2D graphene can act like layers to prevent the permeation of gases\textsuperscript{21}. It was shown that 90% decrease in nitrogen permeation of TPU was achieved with only 3wt% of graphene added to the matrix.
Functionalized graphene (FG)-TPU composites also exhibit outstanding self-healing properties. In particular, fractured TPU/graphene nanocomposites can be healed by three different methods: exposure to conventional infra-red (IR) lamp, voltage application to the fractured FG-TPU samples and exposure to electromagnetic waves. The FG-TPU nanocomposites show healing efficiencies higher than 98% with healing time between 15 and 20 s, and can be healed more than 20 times without property lose. The FG can transfer energy to heat and transport it to the matrix, thus the polymer chains can diffuse and entangle again to heal the fracture\textsuperscript{28}.

CNT-TPU nanocomposites are also a voltage-triggered shape-memory material. For instance, when a constant voltage was applied to a deformed nanocomposites, its shape changed spontaneously into the original shape in 20s with nearly 90–95% recovery\textsuperscript{29}. In the specific case of TPUs, hard segments act like frozen phase to memorize the original shape and soft segment act like reversible phase, which have a drop in modulus upon heating. It is the high conductivity of TPU nanocomposites that induces the thermal stimulation, which can heat the TPU sample above the glass transition temperature of the soft segments. The consequent decrease in modulus enables the shape recovery.
1.4 Objective of this research

TPUs are employed as seal materials in various applications due to their structure, excellent dimensional stability, good dynamic behavior and outstanding abrasion resistance. Pressure, media and temperature are three main factors influencing the performance of TPU s in sealing applications.

In this project, we study the use of carbon nanofillers with high aspect ratio and excellent mechanical properties to reinforce TPU s and augment the composites mechanical behavior. Moreover, due to the filler outstanding thermal and electrical properties, we also expect carbon fillers to improve the high temperature performance and thermal stability of TPU s, thus extending the operating temperature range for composites when used as seal materials.

We also explore the use of hybrid fillers instead of single fillers to reinforce TPU s. In this case graphene could act as dispersion agent to help the dispersion of CNTs in the polymer matrix and the combination of 1D nanotube and 2D graphene may show some synergistic effects to decrease the overall percolation threshold.

Therefore, the overall goal of this research is to enhance the physical and mechanical properties of TPU by adding different carbon nanofillers or their combination. The target properties are the mechanical properties, high temperature performance and thermal stability. When considering hybrid composites, we expect to observe synergistic effects in some properties. Therefore further research is necessary to understand the mechanisms responsible for synergy.
1.5 References


\[ R-\text{NCO} + R'-\text{OH} \rightarrow R-\text{NH-COO-R}' \]

**Fig 1.1** Reaction mechanism of urethane group
Fig 1.2 Schematic of the TPUs two-step polymerization reaction
Fig 1.3 The characteristic structure of TPU chains
Fig 1.4 Microstructure of TPU block copolymer

( • chain extender ; □ isocyanate ; — polyol )
A) 2D graphene  
B) 3D graphite  
C) 1D nanotube  
D) 0D fullerene

Fig 1.5 Carbon nanofillers with different dimensions. 2D graphene A) 3D graphite B) 1D nanotube C) 0D fullerene D)
Fig 1.6 Typical dimensions of single-walled carbon nanotube A) and multi-walled carbon nanotube B)
Fig 1.7 Structure of a single layer graphene
Fig 1.8 Chemical structure mode of graphene oxide
Fig 1.9 Hydrogen bonding formed between MWCNT and TPU matrix\textsuperscript{25}
Chapter 2

Experimental Section

2.1 Materials

A commercially-available thermoplastic polyurethane comprised of a polyester-based polyol and an aromatic diisocyanate was used as the polymer matrix in this project. Carbon nanofillers used included multi-wall carbon nanotubes (MWCNTs) having an average diameter of 9.5 nm and average length of 1.5 µm, and graphene nanoplatelets (GNPs) (1~3 monolayers graphene) with lateral size of ~10 µm and thickness of 1.0~1.2 nm. Graphene oxide was synthesized by Hummers method\(^1\). Surfactant BYK 333 was provided by ALTANA chemical company. Fig 2.1 shows information about BYK333.

2.2 TPU Nanocomposites preparation

2.2.1 Preparation of graphene oxide powder

3.0g graphite powder was mixed with 70mL concentrated H\(_2\)SO\(_4\) and 1.5g NaNO\(_3\) in ice bath conditions. Then 9.0g KMnO\(_4\) were added to the mixture. The mixture was kept in a water bath in order to maintain the temperature at 35°C for 2 hours.

150mL DI-water were slowly added after 2 hours, followed by the addition of 500mL DI-water to the mixture. Then 15mL H\(_2\)O\(_2\) (30%) were slowly added\(^{1a}\). The mixture was filtered and washed with HCl and DI-water. The washed mixture underwent dialysis with DI-water for at least one week. Graphite oxide was obtained
by ultra-sonication. Finally, freeze GO powder was obtained by freeze-drying for four days.

2.2.2 Preparation of CNT-Surfactant (CNT-S) filler

300mg MWCNTs were mixed with 900mg BYK333 (surfactant) in 45ml DI water. The mixture was sonicated for 10min (on 4s, off 4s, amplitude 30%). Freeze-drying was finally carried out with dry ice for four days in order to get CNT-S powder.

2.2.3 Preparation of TPU nanocomposites

TPU granules were first dried in vacuum oven at 105°C for 16 hours. An internal batch mixer with roller rotors was used for melt mixing at rotor speed of 60 rpm and mixing temperature of 210°C. The mass of TPU granules in the internal batch mixer was fixed to 50g. Fig 2.2 shows a schematic illustration of the twin-rotor batch mixer. Nanocomposites with different filler types were prepared using the same procedure using different loadings and mixing times as shown in Table 2.1

Note:

**GO/TPU nanocomposites:** GO was prepared by Hummers method and mixed with TPU granules in the mixer for 7min.

**CNT/TPU nanocomposites:** CNT used as received and mixed with TPU granules in the mixer for 7min.

**Graphene/TPU nanocomposites:** Graphene used as received. First TPU granules
were melt in mixer for 7min then graphene powder was added and mixed with the molten polymer for another 7min.

**CNT-S/TPU nanocomposites:** CNT-S powder was prepared by sonication, fixing the ratio between CNT and surfactant to 1:3. The CNT-S filler was mixed with TPU granules in mixer for 7min.

**CNT-S/Graphene hybrid TPU nanocomposites:** The ratio between CNT and surfactant was fixed to 1:3, the CNT-S filler was mixed first with TPU granules in mixer for 7min then graphene was added in the mixer and mixing was carried out for another 7min.

For all samples prepared by melt mixing, hot pressing was used to prepare the TPU films at a temperature of 230°C for 9min and applying a pressure of 10 bar. **Fig 2.3** shows the schematics of the hot pressing procedure. Finally, all samples were annealed in a vacuum oven at 120 °C for16h. Aging of the samples was performed at room temperature for 24h. **Fig 2.4** shows the schematics of composites preparation procedure.

### 2.3 Characterization

**AFM**

The size and morphology of GO platelets were characterized by using atomic force microscope (AFM; MultiMode, Veeco Instruments,) in tapping-mode configuration. Samples were prepared by depositing GO aqueous solution on a Si substrate, followed by water evaporation.
FTIR

The Fourier transform infrared spectroscopy (FTIR) spectrum of the synthesized GO was obtained by using an FTS 2000 FTIR. GO powder obtained by freeze-drying was mixed with KBr powder following by compression molding to prepare a KBr tablet.

SEM

The morphology of TPU nanocomposites was observed by scanning electron microscopy (SEM; Nova NanoLab 200). The samples were fractured in liquid nitrogen and the fractured surface was coated with gold before testing.

Mechanical Testing

The mechanical properties of the TPU nanocomposites were determined by using a universal testing machine (Model 2525-806, MTS System Corporation, Minnesota, USA) equipped with a 1000N load cell. Tests were carried out setting a crosshead speed of 50mm/min and a gauge length of 10mm. Testing samples were cut into a dumbbell shape after hot pressing, with dimensions of 30mm in length, 4.5mm in width and 0.6mm in thickness. At least five specimens were tested for each sample at 25°C.

DMA

The viscoelastic behavior of TPU nanocomposites was studied by using dynamic mechanical analysis (DMA; Q800, TA Instruments). The measurements were made under a multi-frequency-strain mode with frequency of 1 Hz, amplitude of 20 µm and preload force of 0.01N. Strip samples with dimensions of 10mm in length,
4.5mm in width and 0.6 mm in thickness were tested starting from an equilibrium temperature of -100°C and increasing the temperature to 200°C with a heating rate of 3°C/min.

TGA

Thermogravimetric analysis (TGA; Q500, TA Instruments) was used to measure the thermal stability of the TPU nanocomposites. Samples with weight of 5~10mg were heated from room temperature to 600°C with a heating rate of 10°C/min under nitrogen.

DSC

Differential scanning calorimetry (DSC; Q100, TA Instruments) was used in the temperature range from -80 to 200 °C with a heating rate of 10°C /min. Samples with 1~5mg weight were tested with nitrogen applied during the whole experiments.

Electrical Conductivity

The electrical conductivity of the TPU nanocomposites was measured by eleven-probe station (PRS-801, PROSTAT) on TPU films after hot press.
2.4 References


<table>
<thead>
<tr>
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<th>Nanofillers</th>
<th>Filler loading</th>
<th>Mixing time</th>
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<tr>
<td>CNT/TPU system</td>
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<td>0.1wt%</td>
<td>7min</td>
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<tr>
<td></td>
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<td>7min</td>
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<td></td>
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<td>0.5wt%</td>
<td>7min</td>
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<td>7min</td>
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<td>7min</td>
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<td></td>
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<td>Graphene</td>
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**Table 2.1** TPU nanocomposites with different fillers and different mixing times
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<th><strong>BYK333</strong></th>
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<td><strong>Composition</strong></td>
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<tr>
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</tr>
<tr>
<td><strong>Water solubility</strong></td>
<td>Completely miscible</td>
</tr>
<tr>
<td><strong>Ignition temperature</strong></td>
<td>&gt;200°C (&gt;392°F)</td>
</tr>
<tr>
<td><strong>Initial boiling point</strong></td>
<td>&gt; 200 °C (&gt; 392.00 °F)</td>
</tr>
<tr>
<td><strong>Density (20 °C)</strong></td>
<td>1.04 g/ml</td>
</tr>
</tbody>
</table>

Fig 2.1 Information about BYK333(ALTANA chemical company)
Fig 2.2 Schematic illustration of the twin rotor batch mixer²
Fig 2.3 Schematics of hot press procedure – A final TPU square film with side of 70 mm and average thickness of 0.6 mm was obtained starting from melt compounded TPU chips.
Fig 2.4 Schematics of composites preparation procedures
3.1 Optimization of mixing processing parameters

Mixing temperature in the internal batch mixer was chosen as 210°C based on a previous study in this group (210°C is the temperature set on the computer). During melt mixing, the friction heat generated by the solid granule contacting the mixer wall will increase the temperature up to 230°C, which is the real temperature the polymer experienced during mixing. During processing, the viscosity of the polymer decreased with increasing temperature. While lower viscosity results in reduced energy consumption and easier nanoparticles dispersion in the polymer matrix\textsuperscript{1} on one hand, the decomposition of the polymer might occur on the other hand.

Although previous studies in this group showed that the TPU can melt and well mix with nanofillers at 210°C (set temperature), there is no evidence showing that TPUs are stable and no degradation happened at this temperature. So in the first part of this study, we used TGA to investigate the thermal stability of TPUs at the mixing temperature (~230°C, real temperature) Fig 3.1 a) and over a time correspondent to the mixing time (i.e. less than 20min) Fig 3.1 b)

As shown in Fig 3.1 a), TPU starts to decompose at 288°C (more than 5% weight loss occurred), indicating that the chosen mixing temperature (230°C) does not lead to significant degradation over the mixing time. In order to give further evidence, the TPU sample was kept isothermally at 230°C for 45min, noticing a weight loss
lower than 2wt% (safety range in industry, less than 5wt%), as shown in Fig 3.1 b), thus indicating that mixing time lower than 45min is acceptable.

3.2 GO/TPU Nanocomposites

3.2.1 Characterization of GO

The size and morphology of GO platelets were characterized by using atomic force microscopy (AFM). **Fig 3.2.1** shows (A) the AFM image of the GO sheet on the surface of silicon substrate and (B) the thickness profile of the GO sheet, measured by AFM. From the analysis of these figures two important morphological features can be obtained: the size of a single layer graphene is about 100 nm (Fig 3.2 (A)) and the thickness of two or three graphene layers is 3~4 nm (Fig. 3.2 (B)), which is consist with the literature data (i.e. thickness of a monolayer GO sheet is approximately 1~1.4 nm).

**Fig 3.2.2** shows the FTIR spectrum of GO synthesized by Hummers method. FTIR bands at 1722, 1629, 1420, 1251 and 1060 cm$^{-1}$ correspond to the vibration modes of C=O, C=C, C-OH, C-O-C and C-O respectively$^3$. Comparing the spectrum of GO and graphite, it is confirmed that the Hummers method can be effectively used to oxidize graphite by attaching oxygen functionalities on the graphite surface in order to obtain GO.

3.2.2 Thermal Stability of Nanocomposites
Fig 3.2.3 shows thermogravimetric analyses (TGA) curves of Neat TPU and TPU-0.2wt%GO nanocomposites. From the derivative curves, we can observe that the decomposition of TPUs occurs in two steps between 300°C and 500°C. Based on the literature, the first stage happened between 300°C and 375°C, representing the dissociation of the urethane groups of the hard segments. CO₂ was released during the degradation with the formation of diisocyanate and diol. The second stage happened between 375°C and 500°C, and is ascribed to the decomposition of the soft segments. Mixture of molecular species coming from polyol segments was released during this stage⁴,⁵,⁶,⁷. The TGA curve of the TPU-GO nanocomposites is shifted to higher temperature comparing with Neat TPU, indicating a significant improvement in thermal stability by addition of GO, mainly attributed to the excellent thermal conductivity of GO. Therefore exposing the sample to high temperatures may induce GO aggregates to agglomerate on the surface of the molten polymer, thus, creating a barrier that physically protects the rest of the polymer and limits the volatilization of the oligomers during the combustion.

3.2.3 Decomposition of GO during mixing

TGA curve of GO shows that there are two decomposition stages of GO upon heating. The first stage happening between 200°C and 300°C, is the degradation of oxygen functional groups, while the second stage is originated from the sublimation of the carbon backbone, which happened at 650 °C⁸. Since the melt mixing temperature is about 230°C, the decomposition of GO during mixing was taken into consideration. Fig 3.2.4 shows the FTIR spectrum of GO, Neat TPU and TPU-GO nanocomposites.
For Neat TPU, bands arise at 1714 and 1666 cm$^{-1}$ correspondent to the free $\text{C}=\text{O}$ and amide group (HN-C=O) stretching vibrations, respectively$^9$. FTIR spectrum of TPU-GO nanocomposites is similar to that of Neat TPU, however when compared with GO spectrum it can be noticed that the bands at 1420 and 1251 cm$^{-1}$ disappeared, which indicates the removal of C-OH, C-O-C group on the GO surface, confirming that decomposition occurs during mixing.

Although GO has good interactions with TPU matrix$^{10}$ and can enhance its thermal stability, the decomposition will (1) release gases which form bubbles in the polymer matrix, (2) decrease the interactions between GO and TPU and (3) cause a progressive GO reduction whose extent is difficult to control during mixing.

### 3.3 CNT/TPU Nanocomposites

#### 3.3.1 Tensile Mechanical Properties

The experimental results were compared to the predictions according to two models reported in the current literature in order to describe the mechanical properties of composites: the rule of mixtures and the Halpin–Tsai model. Noteworthy, both models were originally developed to predict the mechanical properties in the case of composites reinforced with micro-sized fibres, however these models have been widely applied also in the case of nano-reinforced polymer composites.

According to the rule of mixtures, the composite Young’s modulus $Y_C$, is given by:
\[ Y_C = (Y_f - Y_m)V_f + Y_m \]  \hspace{1cm} \text{[Equ. 3.1]} 

where \( Y_f \) is the modulus of fibre, \( Y_m \) is the modulus of matrix and \( V_f \) is the volume fraction of fibre. However, this describes an ideal situation where all fibres are aligned and span the full length of the specimen and have perfect bonding with the matrix. If we consider that the fibres are short and non-aligned, composite modulus is given by:

\[ Y_C = (\eta_0 \eta_1 Y_f - Y_m)V_f + Y_m \]  \hspace{1cm} \text{[Equ. 3.2]} 

where \( \eta_0 \) is the orientation efficiency factor, when fibres are randomly oriented, \( \eta_0 = 0.2^{11} \). \( \eta_1 \) is the length efficiency factor, which can be described by\(^{12} \):

\[ \eta_0 = 1 - \frac{Tanh(aL/D)}{aL/D} \]  \hspace{1cm} \text{[Equ. 3.3]} 

\[ a = \sqrt{\frac{3y_m}{2y_f lnV_f}} \]  \hspace{1cm} \text{[Equ. 3.4]} 

where \( D \) is the fibre external diameter and \( L \) is the fibre length. In our case, the modulus of CNT \( Y_f = 270 \text{GPa}^{13} \), modulus of TPU matrix \( Y_m = 25.5 \text{MPa} \) and \( D = 9.5 \text{nm}, L = 1.5 \text{ mm.} \)

The following equation shows the relation between CNT volume fraction \( V_f \) and weight fraction \( M_f \):

\[ V_f = \left[ 1 + \left( \frac{\rho_f}{\rho_m} \right) \left( \frac{1 - M_f}{M_f} \right) \right]^{-1} \]

where \( \rho_f \) is the density of MWCNT (2.1 g/cm\(^3\)), \( \rho_m \) is the density of TPU (1.2 g/cm\(^3\)).
The calculated Young’s modulus of nanocomposites based on rule of mixtures are shown in Table 3.1

For randomly oriented filler composites the expression of Young’s modulus using the Halpin–Tsai model is:

\[
\frac{Y_C}{Y_m} = \frac{2}{8} \left[ 1 + \frac{1+\xi \eta f}{1-\eta f} \right] + \frac{5}{8} \left[ 1 + \frac{1+2\eta f}{1-\eta f} \right] 
\]  

[Equ. 3.5]

where

\[
\xi = \frac{2l}{D}
\]

\[
\eta f = \frac{Y_f/Y_m-1}{Y_f/Y_m+\xi} 
\]

[Equ. 3.6]

and

\[
\eta T = \frac{Y_f/Y_m-1}{Y_f/Y_m+2}
\]

[Equ. 3.7]

The calculated Young’s modulus of nanocomposites based on Halpin–Tsai model are also shown in Table 3.1

In both models, the stiffness is scaled with both volume fraction and aspect ratio, thus an improvement of modulus with increasing volume fraction\(^{14}\). In particular, when external stresses are applied to the composite, the stress can be efficiently transferred to the nanotubes, allowing CNTs to share the load.

As shown in Fig 3.3.1, by adding CNTs in TPU matrix, Young’s modulus proportionally increases reaching the maximum at 0.5wt% CNT loading (from 25MPa to 29MPa). However, the modulus starts to decrease for higher filler contents, but still remains higher than that of the neat TPU at 0.7wt%. Finally, the modulus at 1.0wt%
decreases below that of the neat polymer (i.e. 22MPa). The experimental values are lower than those calculated by the two models, since in these two models, nanotubes are presumed to be uniformly dispersed and well interacting with the matrix individually to achieve a good interfacial stress transfer. However, in the case of melt compounding, the highly viscous polymer melt and CNTs are mixed by shear mixing that makes the entanglement of nanotubes inevitable\textsuperscript{15}. Entanglement will decrease the effective CNTs aspect ratio thus reducing the reinforcing effects. Specifically, when the CNTs loading increases, the entanglement of CNTs will form aggregation, changing the 1D tube to 0D spherical carbon material, thus decreasing the reinforcing effect dramatically\textsuperscript{16}. Moreover, the CNT entanglements can act like defects which make the sample easier to break at low stress. This mechanism can explain the first increase and subsequent decrease trend in experimental modulus with increasing filler amount.

3.3.2 Dynamic Mechanical Analysis

Fig 3.3.2 shows DMA measurements of TPU-CNT nanocomposites. The storage modulus curve shows that incorporation of CNTs into TPU leads to better viscoelastic performances at high temperatures. However when the loading of CNTs goes beyond 0.5wt% the storage modulus starts to decrease due to filler aggregation.

The glass transition temperature (Tg) can be determined from the maximum of the Tangent delta (tan δ) curve. As widely shown in the literature, incorporation of nanofillers including CNTs can result in a significant shift of Tg towards higher temperatures. This is attributed to the fact that CNTs interact with the polymeric
chains and restrict their motion\textsuperscript{17}. However the experimental results show a decrease in Tg, which is another indication of poor dispersion of CNTs.

3.3.3 Electrical conductivity behavior

Excluded volume theory as proposed by Balberg was used to predict the electrical percolation threshold of cylindrical particles with high aspect ratio mixed in a polymer matrix\textsuperscript{18,19,20,21}.

The volume fraction at percolation can be determined as:

$$\phi_c = \frac{\rho_c V_{cyl}}{V_{tot}}$$ \hspace{1cm} \text{[Equ. 3.8]}

where $V_{cyl}$ is the volume of particle:

$$V_{cyl} = \frac{4}{3} \pi r^3 + \pi l r^2$$ \hspace{1cm} \text{[Equ. 3.9]}

$$\rho_c \propto (V_{ex})^{-1}$$ \hspace{1cm} \text{[Equ. 3.10]}

And

$$V_{ex} = \frac{32}{3} \pi r^3 + 8 \pi l r^2 + 4 l^2 r (\sin(\gamma))$$ \hspace{1cm} \text{[Equ. 3.11]}

Here $V_{ex}$ is the excluded volume for capped cylinders, $\sin(\gamma)$ represents the degree of alignment of the rods, $\gamma$ is equal to $\frac{\pi}{4}$ for isotropic samples. $l$ and $r$ represent the length and radius of nanotube respectively. $V_{tot}$ is the total volume of the sample, and will be rescaled to 1 in the calculations\textsuperscript{22}.

In our case, the radius of CNT $r = 4.75$ nm, length $l = 1.5$ mm. The calculated volume fraction at percolation $\phi_c = 0.287 \text{vol\%}$, weight fraction $M_f = 0.5 \text{wt\%}$
However, Fig 3.3.3 shows the electrical conductivity of TPU-CNT nanocomposites and indicates that TPU-CNT nanocomposites start to be conductive at a filler loading beyond 4wt%, which is much higher than the calculated threshold. Noteworthy, the excluded volume theory takes into account individual CNTs dispersed homogeniously in TPU matrix. However, this is not the case, as previous results on the mechanical properties evidenced diffuse CNTs agglomeration at high loadings. Therefore, agglomeration decreases the contact points between CNTs, limiting the ability of forming a network that can enable the movement of electrons\textsuperscript{23}.

### 3.4 Graphene/TPU Nanocomposites

#### 3.4.1 Tensile Mechanical Properties

Halpin and Thomas developed an approach to predict the elastic behavior of a composite with ribbon-shaped reinforcements\textsuperscript{24}. The ribbon-shaped filler is relevant to graphene. In their theory, the filler is aligned, and the Young’s modulus of the nanocomposites is predicted to be:

\[
\frac{Y_c}{Y_m} = \frac{1 + \xi \eta V_p}{1 - \eta V_p}
\]  

[Equ. 3.12]

where the parameter \( \eta \) is given by:

\[
\eta = \frac{\frac{Y_p}{Y_m}}{\frac{Y_p}{Y_m} + \xi}
\]  

[Equ. 3.13]

\( Y_c, Y_m, Y_p \) are the Young’s modulus of the nanocomposites, polymer matrix and particles, respectively. \( V_p \) is the volume fraction of the particles. \( \xi \) is a measure of
reinforcement geometry and can be taken as $\frac{2l}{l}$, where $l$ is the length of a ribbon with thickness of $t$. In our case, $Y_p = 0.39$TPa$^{25}$. Graphene has diameter of 10 µm and thickness of 1.0 nm.

The following equation shows the relationship between graphene volume fraction ($V_f$) and weight fraction ($M_f$):

$$V_f = \left[1 + \left(\frac{\rho_f}{\rho_m}\right)\left(1 - \frac{M_f}{M_r}\right)^{-1}\right]^{-1}$$

Where $\rho_f$ is the density of graphene (2 g/cm$^3$), while $\rho_m$ is the density of TPU (1.2 g/cm$^3$). The calculated Young’s modulus of nanocomposites based on Halpin-Thomas model are shown in Table 3.2.

In the Halpin –Thomas model, graphene platelets are aligned, which is not possible to achieve experimentally, since melt mixing cannot orient graphene in the TPU matrix$^{26}$. Highly oriented fillers have better reinforcing effect comparing with randomly oriented samples. This is one reason why experimental moduli are much lower than those calculated from Halpin –Thomas model. Another issue is the strong van der Waals attractions that can cause the aggregation of graphene platelets, which leads to a consistent decrease in surface area, leading to reduced filler-matrix interface, which in turn reduces the load transfer effects and make mechanical properties decrease.

**Fig 3.4.1** shows the mechanical properties of the Neat TPU and TPU composite as a function of graphene content. Young’s modulus of nanocomposites keeps increasing with increasing loading of graphene, reaching 24MPa at 1.0 wt%
filler, which is about 55% improvement with respect to the neat polymer. However, tensile strength and elongation at break only increase at 0.1 wt%, while they decrease at 0.7 and 1.0 wt% reaching values below that of the neat TPU. The decrease in tensile strength and elongation at break is mainly attributed to aggregation, as filler aggregates represent potential points of stress concentration so that the sample breaks more easily at low loadings.

3.4.2 Dynamic Mechanical Analysis

Fig 3.4.2 shows the DMA measurements of TPU-graphene nanocomposites. By adding graphene into the TPU matrix, the storage modulus increased at high temperatures (100–200°C). Moreover, nanocomposites containing 0.1 to 0.5 wt% filler showed higher breaking temperature comparing with that of the neat polymer. For example, the 0.3 wt% composite fails at 215°C, while the neat one fails at 195°C. However, when considering composites filled with 0.7 and 1.0 wt%, a lower storage modulus and lower breaking temperature are observed, which is caused by the aggregation of graphene platelets that makes the sample easier to break at high temperatures.

The glass transition temperature (Tg), determined from the Tangent delta (tan δ) curve, is higher in the case of the nanocomposite at 0.1 wt% but decreases at greater filler loadings, indicating good graphene dispersion at low concentration and aggregation in the other samples. In fact, well-dispersed graphene can prevent the movement of TPU chains, thus shifting the glass transition at higher temperatures.
3.5 CNT-Surfactant/TPU Nanocomposites

Based on previous morphological observations, CNTs were shown to be easily entangled with each, leading to a non-uniform filler dispersion and distribution within the matrix. In order to help the dispersion of CNTs in the TPU matrix, a surfactant was used to modify the surface of CNTs, therefore limiting filler aggregation and change the way CNTs disperse and interact with the matrix. Noteworthy, the surfactant/filler ratio was set to 3:1.

Surfactants are amphiphilic molecules with both polar and apolar groups and have the capability to interact with CNTs surfaces in order to promote stable dispersions\textsuperscript{27}. Although there are lots of surfactants suitable for CNTs, the final choice should take into account the thermal stability of the surfactant at the processing temperature.

3.5.1 Thermal Stability of Surfactant

The thermal stability of the surfactant was investigated by TGA. Fig 3.5.1 shows the TGA curve of surfactant BYK333 (polyether-modified polydimethylsiloxane, provided by ALTANA chemical company), evidencing that 5% weight loss was recorded at 320\degree, which is higher than the processing temperature (i.e. 230\degree C). Thus, it is proved that the surfactant BYK333 is stable and there is no decomposition occurring during processing.

3.5.2 Influence of surfactant on mixing torque
The torque is recorded as a function of time during melt mixing (Fig. 3.5.2). The curve shows the thermo-mechanical history that the polymer experienced during mixing. The first increase of the torque comes from the resistance offered by the solid granules when they first impact the rotating blade in the mixing chamber. After the granules are progressively fragmented, the torque decreases and reaches a steady state for around one minute. Then the torque increases again when the surfaces of the granules start to melt and finally decreases upon complete melting.

**Fig 3.5.2** shows the change of torque during melt mixing. CNT/TPU sample shows a significantly higher first peak when compared to that of the neat sample, since CNTs have strong mechanical properties. Therefore, CNTs added into the chamber with TPU granules can generate higher resistance to the rotating blade. Interestingly, the CNT-S sample shows a significant delay of the second peak, probably because the surfactant itself is highly viscous and acts like a lubricant agent, thus decreasing the friction between the solid granules and the chamber walls, hence delaying the melting of the TPUs.

3.5.3 Dispersion of CNTs in nanocomposites

**Fig 3.5.3** represents the image of CNTs after freeze-drying. It shows that CNTs with surfactant dispersed in water after freeze-drying have a volume almost twice that of CNTs without surfactant. The increase in volume indicates less entanglement of CNTs, attributed to the effect of surfactant which is able to wrap on the CNTs surfaces.
Fig 3.5.4 shows the SEM images of CNT/TPU nanocomposites and CNT-S/TPU nanocomposites. Unfortunately, because of the very low filler concentration, it appears difficult to observe the presence of CNTs aggregates within the matrix. On the other hand, CNT-S/TPU nanocomposites is supposed to present a better CNTs dispersion, but further characterizations will be necessary to validate this hypothesis.

3.5.4 Tensile Mechanical Properties

In order to prove that the surfactant is effectively able to improve the CNTs dispersion, three control samples have been prepared: 1) TPU-CNTs with the filler directly mixed with TPU (CNT-0.1), 2) TPU-CNTs with the filler sonicated in DI-water after freeze-dry and subsequently mixed with TPU (CNT-sonicated-0.1) and 3) TPU-Surfactant considering the surfactant directly mixed with TPU (Neat-surfactant).

Fig 3.5.5 shows the mechanical properties of the Neat TPU and TPU composites. CNT-S/TPU nanocomposites exhibit the highest elastic modulus, tensile strength and elongation at break. However, strength and elongation at break drastically decrease when considering the sample based on TPU and surfactant. Moreover, sonications seems not to affect the mechanical properties (CNT-sonicated-0.1). Therefore, the properties comparison indicated that surfactant and sonication are not effective alone, but their combination might results in significant properties improvement.

3.5.5 Dynamic Mechanical Analysis
Fig 3.5.6 shows the DMA measurements of CNT-S/TPU nanocomposites. As observed in these curves, Neat TPU and CNT/TPU nanocomposites show almost the same storage modulus at high temperature, which indicates poor dispersion of CNTs. However, CNT-S/TPU nanocomposites show excellent high temperature performance due to the fine dispersion of CNTs in the TPU matrix, since homogeneous dispersion can help maximize the reinforcing effects.

Tangent delta (tan δ) curve shows almost the same Tg for neat TPU, CNT/TPU and CNT-S/TPUtant nanocomposites, probably because of the very low loading (i.e. 0.1 wt%) which limits the effects on the Tg even in the case of good filler dispersion.

3.5.6 Creep-Recovery Behavior

For thermoplastic polymers, creep behaviour is an important property because it indicates the material dimension stability under a constant stress applied over a long time\(^2^8\). From an experimental point of view, investigation of the creep behavior can give important insights into the dimensional stability under different stress and temperature conditions.

Fig 3.5.7 shows that CNT-S/TPU nanocomposites exhibit the highest creep resistance comparing with neat TPU and CNT/TPU nanocomposites. The improvement in creep resistance comes from the presence of CNTs which can significantly restrain the creep deformation of the polymer matrix. Moreover, the
reason why CNT-S/TPU nanocomposites show even higher creep resistance is attributed to the better CNT dispersion.

Creep is typically characterized by three stages: 1) instantaneous elastic deformation (i.e. the elastic deformation of polymer segments which happens immediately when the stress is applied, and will totally recover when the stress is removed), 2) primary creep (i.e. the viscoelastic deformation of the polymer chains which will recover after the stress is removed over a longer time) and 3) secondary creep (i.e. the viscous deformation of the whole polymer chains, which is a permanent deformation\(^\text{29}\)). The well-dispersed CNTs can reinforce TPU by improving the elastic modulus, so decreasing the first instantaneous deformation. Moreover, CNTs also play a role to prevent the movement of TPU chains which will increase the viscosity of TPU system. More energy needs to be applied to make the viscoelastic and viscous deformation, thus the last two stages of creep are also reduced\(^\text{30}\).

3.5.7 Thermal Stability

**Fig 3.5.8** shows the TGA curve of Neat TPU, CNT/TPU and CNT-S/TPU nanocomposites, evidencing that the use of surfactant effectively improves the thermal stability of TPU nanocomposites. As mentioned before, there are two stages of decomposition of TPU, which come from the degradation of hard and soft segments, respectively. Neat TPU shows one decomposition peak on the derivative curve, which indicates the phase mixing structure. However, the TGA derivative curve of CNT-S/TPU nanocomposites shows two separated decomposition peaks, evidencing a more
phase-separated structure. It is shown in literature that CNTs can influence the microstructure of TPUs\textsuperscript{31}, further increasing their properties.

### 3.6 CNT-Surfactant/Graphene Hybrid TPU Nanocomposites

To further improve the properties of TPUs with using a lower filler amount, CNT/graphene hybrid TPU hybrid nanocomposites were also prepared and tested. In particular, the combination of 1D-CNT with 2D-graphene is supposed to favor the formation of a more efficient network, characterized by a greater contact area between filler and matrix. Therefore, synergistic effects on some properties\textsuperscript{32} might be observed and significant improvements might be achieved at lower filler loading. From an industrial point of view, using less filler would result in a reduction in density and final cost of the component.

#### 3.6.1 Tensile Mechanical Properties

**Fig 3.6.1** shows the mechanical properties of the Neat TPU and TPU composites with different ratio of hybrid filler: a) Young’s modulus b) Tensile strength and c) Elongation at break. Hybrid nanocomposites with ratio 6:4 (Graphene:CNT-S) show the highest Young’s modulus and tensile strength among all hybrid composites and individual CNT and graphene composites. Hybrid (6:4) exhibits more than 20% improvement in Young’s modulus comparing with neat TPU, and 10% improvement in tensile strength. The improvement in mechanical properties of the hybrid (6:4) are even higher than those predicted by the mixing rule (dotted line), evidencing significant synergistic effects.
The long and tortuous CNTs prevent the aggregation of graphene platelets by bridging adjacent graphene plates to form an efficient network. The similar chemical structure makes CNTs and graphene compatible with each other instead of repulsive, which prevent the entanglement between CNTs and aggregation between graphene. The increase of contact area between fillers and matrix can enhance the load transfer effects, thus improving the mechanical properties.

3.6.2 Dynamic Mechanical Analysis

Since some hybrid systems showed synergistic effect on the tensile properties, the other properties might be also of interest to be investigated. In particular, Fig 3.6.2 shows the measurements of TPU-hybrid nanocomposites, evidencing that the hybrid (6:4) composites have the highest storage modulus at high temperature comparing with neat TPU and individual CNT or graphene composites, which is another indication of synergistic effects. Tangent delta (tan δ) curve shows almost the same Tg of neat TPU and TPU composites; given the very low filler loading it might be difficult to observe significant changes in Tg.

3.6.3 Creep –Recovery Behavior

Fig 3.6.3 shows the creep -recovery curve of TPU-hybrid nanocomposites, which indicate that the hybrid (6:4) composites have the highest creep resistance among neat TPU and individual CNT or graphene composites. The well-dispersed
CNTs and graphene prevent the viscoelastic movement of TPU chains thus increasing the creep resistance.

The recovery behavior is also highly improved when introducing nanofillers in TPU system. In particular, the hybrid (6:4) system shows the highest recovery rate due to the more efficient network formed by CNT and graphene which can increase the viscosity of the TPU system and limit the viscous deformation. Thus the permanent deformation decreases resulting in a faster recovery of the original dimensions.

3.6.4 Thermal Stability

**Fig 3.6.4** shows the TGA curve of TPU-hybrid nanocomposites. The derivative curve shows two decomposition peaks in the hybrid (6:4) composites, however only one peak is visible in the case of neat TPU and individual CNT or graphene composites. The transition from one peak to two peaks is a clear indication of more substantial phase separation in the TPU system, and is consistent with the improvements in mechanical properties, as reported in the current literature.
<table>
<thead>
<tr>
<th>CNTs loading (wt%)</th>
<th>Experimental (MPa)</th>
<th>Halpin–Tsai model (MPa)</th>
<th>Rule of mixtures (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>26 ± 1.30</td>
<td>27.00</td>
<td>56.00</td>
</tr>
<tr>
<td>0.20</td>
<td>28 ± 1.40</td>
<td>31.00</td>
<td>120.00</td>
</tr>
<tr>
<td>0.50</td>
<td>29 ± 1.50</td>
<td>34.00</td>
<td>180.00</td>
</tr>
<tr>
<td>0.70</td>
<td>27 ± 1.40</td>
<td>38.00</td>
<td>240.00</td>
</tr>
<tr>
<td>1.00</td>
<td>22 ± 1.10</td>
<td>43.00</td>
<td>330.00</td>
</tr>
</tbody>
</table>

Table 3.1 Experimental Young’s modulus compared to the modulus determined according to the Halpin–Tsai model and the Rule of Mixtures.
<table>
<thead>
<tr>
<th>Graphene loading (wt%)</th>
<th>Experimental (MPa)</th>
<th>Halpin-Thomas model (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10</td>
<td>17±0.85</td>
<td>120.00</td>
</tr>
<tr>
<td>0.20</td>
<td>19±0.95</td>
<td>330.00</td>
</tr>
<tr>
<td>0.50</td>
<td>19±0.95</td>
<td>540.00</td>
</tr>
<tr>
<td>0.70</td>
<td>23±1.20</td>
<td>740.00</td>
</tr>
<tr>
<td>1.00</td>
<td>24±1.20</td>
<td>1100.00</td>
</tr>
</tbody>
</table>

Table 3.2 Experimental Young’s modulus compared to the modulus determined according to the Halpin–Thomas model
Fig 3.1 a) TGA curve of Neat TPU. Temperature ramp of 3.00 °C/min from room temperature to 600 °C

Fig 3.1 b) TGA curve of Neat TPU - isothermal at 230 °C for 45 min
Fig 3.2.1 A) AFM image of the GO sheet on the surface of silicon substrate B)
Height profile of the GO sheet
Fig 3.2.2 FTIR spectrum of GO synthesized by Hummers method and Graphite
Fig 3.2.3 TGA curves and derivative of Neat TPU and TPU-0.2wt%GO nanocomposites
Fig 3.2.4 FTIR spectrum of GO, Neat TPU and TPU-GO nanocomposites
Fig 3.3.1 Mechanical properties of the Neat TPU and TPU composite as a function of CNT content: a) Young’s modulus b) Tensile strength c) Elongation at break
Fig 3.3.2 DMA measurements of TPU-CNT nanocomposites as a function of temperature: a) Storage modulus and b) Storage modulus at high temperature c) Tangent delta
Fig 3.3.3 Electrical conductance of TPU-CNT nanocomposites
Fig 3.4.1 Mechanical properties of the Neat TPU and TPU composite as a function of graphene content: a) Young’s modulus b) Tensile strength c) Elongation at break
Fig 3.4.2 DMA measurements of TPU-graphene nanocomposites: a) Storage modulus and b) Storage modulus at high temperature c) Tangent delta
Fig 3.5.1 TGA curve of surfactant BYK333
Fig 3.5.2 Rotor torque recorded during melt mixing
Fig 3.5.3 Image of CNTs after freeze dry: (left) without surfactant and (right) with surfactant.
Fig 3.5.4 SEM images of CNT/TPU nanocomposites (a-b) and CNT-S/TPU-nanocomposites (c-d)
Fig 3.5.5 Mechanical properties of the Neat TPU and TPU composite a) Young’s modulus b) Tensile strength c) Elongation at break
Fig 3.5.6 DMA measurements of CNT-S/TPU nanocomposites: a) Storage modulus b) Tangent delta
Fig 3.5.7 Creep-recovery curve of CNT-S/TPU nanocomposites
Fig 3.5.8 TGA curve of CNT-S/TPU nanocomposites
Fig 3.6.1 Mechanical properties of the Neat TPU and TPU composite with different ratio of hybrid filler: a) Young’s modulus b) Tensile strength c) Elongation at break. Dotted line shows the mixing rule.
Fig 3.6.2 DMA measurements of TPU-hybrid nanocomposites: a) Storage modulus and b) Storage modulus at high temperature c) Tangent delta
Fig 3.6.3 Creep-recovery curve of TPU-hybrid nanocomposites
Fig 3.6.4 TGA curve of TPU-hybrid nanocomposites
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Chapter 4

Conclusions and Future Work

4.1 Conclusions

It was assumed that oxygen functional groups on the surface of GO can form hydrogen bonding with the TPUs urethane groups, and the hydroxyl groups can react with –NCO groups on the ends of TPU chains to form urethane groups. The beneficial combination of physical and chemical bonding formed between GO and TPUs can thus maximize their interactions. However, the mixing procedure at high temperature was shown to cause GO reduction, with removal of functional groups located on its surface, as indicated by FTIR. Although reduced GO improves the thermal stability of TPUs, degradation occurring during mixing indicates that melt mixing is inappropriate to prepare TPU-GO nanocomposites.

TPUs incorporating nanofillers (CNTs or graphene) as directly mixed via melt blending exhibited extensive filler agglomeration, since shear mixing is not effective enough to exfoliate entangled CNTs and aggregated graphene platelets in the highly viscous mixing conditions. Agglomeration resulted in a significant decrease in strength and ductility in TPU nanocomposites, accompanied by an increase in electrical percolation threshold when comparing with model calculated values.

CNT-surfactant samples pre-prepared via sonication showed that surfactant can effectively prevent the entanglement of CNTs and improve its stability in water. CNT-S/TPU nanocomposites exhibited higher tensile mechanical and dynamic
mechanical properties comparing with same filler loading of nanocomposites without surfactant. The property improvement was attributed to better filler dispersion, as shown by SEM morphological studies. TGA analyses shed some light on a second mechanism of improvement in the mechanical properties: the well-dispersed CNTs can also increase the phase separation in TPUs, leading to a better microstructure which is able to enhance the load transfer effects and maximize the mechanical properties of the material.

Synergistic effects were observed in TPU-Graphene/CNT hybrid composites, especially when combining graphene and CNTs at a ratio of 6:4, showing higher tensile mechanical and dynamic mechanical properties with respect to the systems incorporating individual CNTs and graphene in nanocomposites. This improvement was attributed to a synergetic combination of CNTs and graphene, hypothesizing that the long tortuous CNTs limit graphene aggregation and bridge adjacent graphene platelets in order to form a more efficient network that has better reinforcing effects in the TPU matrix. Moreover, hybrid (6:4) nanocomposites also showed the highest creep resistance and recovery ability since the network formed by 1D CNT and 2D graphene can prevent the movement of TPU chains, leading to a decrease in viscoelastic and viscous deformation.

The TPUs used in this study are mainly applied to produce sealing components that undergo long-time loads, thus high dimensional stability is mainly required. Therefore, the improved creep stability and recovery capability are greatly beneficial to maximize the target properties demanded for this type of TPUs.
4.2 Future work

Interactions between surfactant and TPU matrix should be further investigated to have better insights in how the surfactant affects the physical and mechanical properties of the material.

The procedure of preparation of the CNT-surfactant sample via sonication should be optimized to maximize the surfactant effect on the CNTs (i.e. surfactant wrapped on the surfaces of CNTs).

The multifunctional properties of the TPU nanocomposites should be extensively investigated, in particular the thermal conductivity, self-healing mechanisms and shape-memory form effects. The dependency of such properties on the nanofiller type and content should be studied, including potential synergistic effects among different fillers. TPUs nanocomposites presenting advanced functional properties will open the possibility to extend their use to many other technological applications.
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