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Mechanical and Physical Properties of Injection Molded Halloysite Nanotubes-Thermoplastic Polyurethane Nanocomposites

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Abstract

The high aspect ratio of nanoscale reinforcements enhances the mechanical properties of pure polymer matrix. Researchers reported the mechanical properties of thermoplastic polyurethane and halloysite nanotubes (TPU-HNTs) nanocomposites formed through casting and compression molding. Few researchers reported on TPU-HNTs formed through injection molding. Therefore, the present work described the preparation, characterization, and processing of TPU and HNT nanocomposites via injection molding. TPU and HNTs were mixed using a brabender mixer with concentration ranging from 1wt.% to 7wt.% with varying mixing parameters (mixing speed, mixing time, and mixing temperature). Injection molding was used to form tensile bars shaped with varying molding parameters (injection temperature, injection time, and injection pressure). Significant increment of tensile strength was found at 1wt.%HNT loading concentration. The tensile strength of the TPU-HNT nanocomposite exhibited 24.29 MPa at 1wt.% loading concentration, which was higher than that of pure TPU. The Young's modulus of the TPU-HNT nanocomposite was 15.45 MPa at 7wt.%. Physical properties were analyzed using Thermogravimetric Analysis (TGA) and Field emission scanning electron microscopy (FESEM). FESEM results showed that HNTs were well dispersed in TPU matrix. TGA results showed that the addition of HNTs enhanced the thermal properties. Thus, TPU-HNT has improved mechanical and physical properties compared with pure TPU due to the addition of nanofiller.

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Keywords: Halloysite Nanotubes, Nanocomposite, Injection Molding, Mechanical Properties, Physical Properties

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1. Introduction

Thermoplastic polyurethane (TPUs) is a linear segmented copolymer composed of micro-phase-separated hard and soft segments. Therefore, investigation on the microstructure development under an applied load is complicated. The microstructure development for TPU has mostly focused on its extension behavior (Li et al. 2012). Conventional TPUs are biomaterials not intended to degrade but are susceptible to hydrolytic, oxidative, and enzymatic degradation in vivo. Although the susceptibility of TPUs to such degradation is a problem for long-lasting biomedical implants, TPUs can be deliberately exploited to design biodegradable polyurethanes (PUs) (Tatai et al. 2007). TPUs are versatile materials that can display properties ranging from very soft thermoplastic elastomers to strong, rigid thermoplastics depending on their chemical compositions, backbone structures, and resultant micro-phase morphologies. During the past 40 years, numerous studies and excellent publications were published on the preparation and structural, thermal, mechanical, and morphological characterization of TPU systems. These efforts led to the development of various morphological models for segmented PUs (Yilgor et al. 2006). Halloysite nanotubes (HNTs) are a naturally occurring aluminosilicate $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}]$ with a predominantly hollow tubular structure mined from natural deposits (Joussein et al. 2005). HNTs are a new type of nanoadditive used to enhance the mechanical (Prashantha, Lacrampe, and Krawczak 2011, Du, Guo, and Jia 2010, Liu et al. 2011), thermal, crystallization (Guo et al. 2009), and fire (Marney et al. 2008) performance of thermoplastic polymers (e.g., polypropylene and polyamide-6) and thermosets (e.g., epoxy) (Deng, Zhang, and Ye 2009). The main goal of this research is to study the effects distribution and dispersion of HNT in TPU prepared by extrusion and injection molding. Furthermore, extrusion and injection molding have been applied for TPU processing and manufacturing in the biomedical industry. The conclusions of this research have answered the uncertainties of key factors affecting the design for manufacturing new parts made from nanocomposites, where feasibility and performance are very close that they fit the newest product requirements.

2. Experimental

TPU was supplied by Global Innovations-Polycarbonates Bayer Material Science AG, D-51368 Leverkusen. Halloysite nanotubes (HNTs) were supplied by Natural Nano, Inc., 832 Emerson Street Rochester, New York 14613. The typical specific surface area of this halloysite is $65 \text{ m}^2/\text{g}$ pore volume of $\sim 1.25 \text{ mL/g}$; the refractive index is 1.54; and the specific gravity is 2.54 g/cm^3 [Natural Nano, Inc., New York]. TPU and HNT were dried in a vacuum oven at a temperature of $70 \text{ }^\circ\text{C}$ for 14 h. TPU and HNT were homogenized using Brabender Machine. The mixing temperature, screw speed, and time were $200 \text{ }^\circ\text{C}$, 30 rpm, and 40 min, respectively. This experiment was performed until the injection-molded specimen was obtained.

3. Testing Equipment

Field emission scanning electron microscopy (FESEM) analysis was performed in CRIM-UKM. The morphology of the selected nanotube was investigated and viewed using the FESEM model ZEISS SUPRA 55-VP with high resolution and low charging on the sample surface. The magnification of morphology observations was in the range of 10, 25, 50, 100, and 200 k to obtain clearer images. OXFORD EDS and mapping were used for elemental analysis. Thermal gravimetric and differential thermal analyses were performed using a STA 449 F3 NETZSCH Thermogravimetric Analyzer under the helium gas condition at sample mass 5–15 mg, heating rate of $10 \text{ }^\circ\text{C}/\text{min}$, and temperature range of $30\text{--}700 \text{ }^\circ\text{C}$. The degradation temperature rate and other data were determined from the weight loss curves. The measurements of mechanical properties (tensile test) were determined with an Instron universal testing machine (INSTRON 5567) using a 200 Newton load transducer according to the standard of ASTM D-638 type V method. The crosshead speed was $50 \text{ mm}/\text{min}$, and all the tests were conducted at room temperature. Five measurements were carried out for each data point.

4. Results and discussion

4.1. Mechanical Characterization

Figure 1 shows that the tensile stress values were 24.29 MPa, 16.72 MPa, 8.95 MPa, and 6.24 MPa which corresponded to 1wt.%, 3.5wt.%, 5wt.%, and 7wt.%HNT loadings, respectively, added to the TPU. Conclusively, TPU-1wt.%HNT yielded the highest tensile stress value (i.e., 24.29 MPa) and the lowest value measured (i.e., 6.24 MPa) at TPU-7wt.%HNT compared with other compositions. At TPU-1wt.%HNT loading, the nanocomposites had better interaction between the matrix and the reinforcement HNT surface, leading to improved bond stress, which resulted in the highest tensile stress. At higher loading (e.g., above TPU-3.5wt.%HNT), the tensile stress decrease may be attributed to the agglomeration of the HNT nanotubes, which resulted in poor interaction between the matrix and the HNT surface. Similar results were also observed by other researchers (Lecouvet et al. 2011). Figure 2 shows that the TPU-7wt.%HNT composite has the highest Young's modulus value (i.e., 15.45 MPa), showing increased Young's modulus (from 0wt.% to 7wt.% of HNT loading). TPU-HNT had the highest stiffness value at 7wt.%HNT loading. The increase in the modulus may be due to the stiffness factor, where the nanosized HNT fillers were bonded to the TPU molecular chain; thus, the mobility of the molecule was arrested. For this reason, the flexibility was reduced, and stiffness was increased.

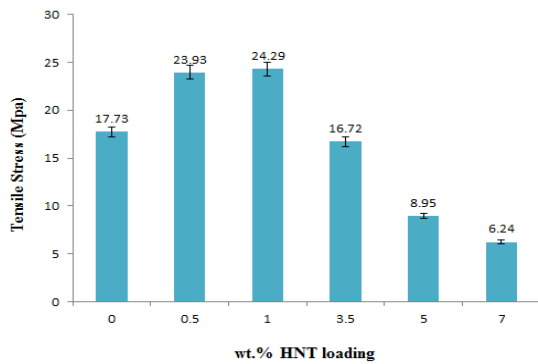


Fig. 1. Tensile Stress of TPU-HNT nanocomposites.

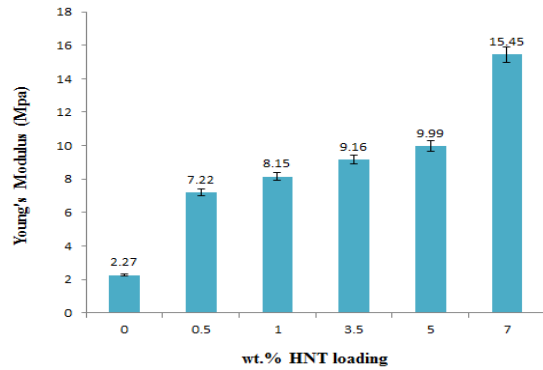


Fig. 2. Young's Modulus of TPU-HNT nanocomposites.

4.2. Morphology Characterization

Figure 3 shows the FESEM microphotographs morphology of the TPU-HNT nanocomposites to observe the dispersion and distribution of the nanotubes and their physical interaction with the TPU matrix. The HNT dispersion in the TPU matrix is clearly observed from FESEM images with low magnification that nanotubes are homogeneously dispersed throughout the TPU matrix. Also no indication of porosity and voids were observed due to the appearance of strong interfacial bonding between nanotubes and the TPU matrix. It is also observed from the micrographs that plastic deformation is prominent in the nanocomposites with higher HNT content because of the strong reinforcing effects by the HNT nanophase and a large percentage of the amorphous region in the TPU matrix.

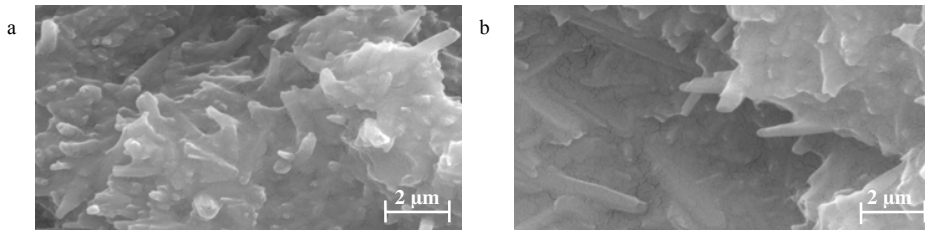


Fig. 3. FESEM microphotographs for (a) 1 wt.% HNT and (b) 7 wt.% HNT at magnification of 50.00 KX.

4.3. Thermogravimetric Analysis (TGA)

TGA curves for pure TPU and TPU-HNT nanocomposites at different loading are shown in Figure 4. For the TPU-HNT, the entire degradation step can be observed from 23 °C to 698 °C. The weight loss of TPU-HNT at 284 °C was 15%, indicating high thermal stability compared with the neat TPU. The weight reduction of about 75 wt.% at 850 °C may be caused by the decomposition of the TPU and HNT composites. However, although further heating was conducted to observe the decomposition steps of the TPU-HNT composites at higher temperatures. A double degradation step was observed for TPU-HNT, as seen in Figure 4. This finding implies that the thermal stability of TPU-HNT is superior to that of Neat TPU. For unreinforced TPU matrix, the molecular chain breaks and chars, whereas the TPU-HNT degradation requires more energy to break depending on the loading level. We can see from the curve that the thermal stability of TPU increases as the HNT loading increased from 1.0 wt.% to 7.0 wt.%. Pure TPU started to degrade at 283 °C and was completely decomposed around 810 °C. By contrast, TPU with 1.0 and 7.0 wt.% TPU-HNT started to degrade at 284 and 292 °C, respectively. A significant change was observed in the degradation temperature of TPU even at 1.0 wt.% addition of TPU-HNT at 50% wt. loss. This finding indicates that TPU-HNT is useful for obtaining a nanocomposite with high thermal stability. Nonetheless, the issues of dispersion, thermal barriers, and interfacial adhesion as the dominating parameters will be addressed in future research.

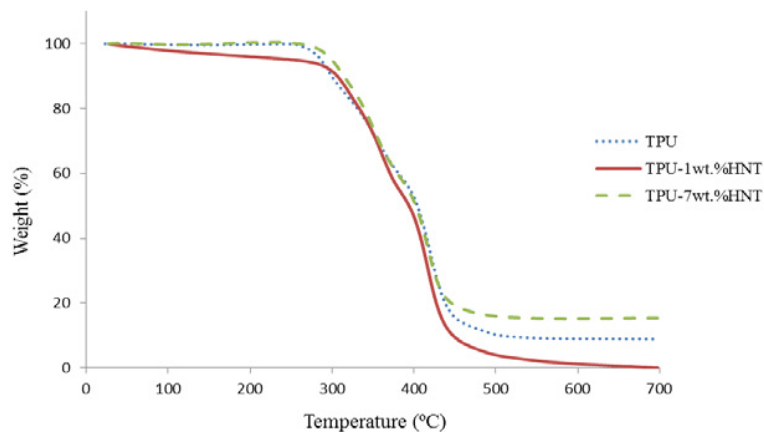


Fig.4. TGA thermograms of neat TPU and its nanocomposites containing 1.0 and 7.0 wt.% HNT loadings in nitrogen atmosphere. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

5. Conclusion

TPU-HNT nanocomposites of high modulus and strength were prepared. The nanocomposites exhibited improved properties when combined with nanoparticles in the matrix. These nanocomposites with filler loading provide traditional composite properties with advantages of nanocomposites. The HNT have high aspect ratio that is crosslinked with TPU, facilitating stress transfer from the matrix. Therefore, the matrix is less ductile than a thermoplastic via the physical crosslinks, though with continued ability to be thermoformed into various shapes. TPU-HNT nanocomposites with enhanced properties of TPU was achieved with HNT loading ranging from 1wt.% to 7wt.%.

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