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Influence of Sulfuric Acid on the Tensile Properties of Halloysite Reinforced Polyurethane Composite

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ABSTRACT

In this study, the mechanical properties of injection molded of HNTs-TPU composites were investigated. The composites were first made by adding halloysite nanotubes (HNTs) at weight percentages of 1, 2, and 3 wt.% to thermoplastic polyurethane (TPU). Then, HNTs were sulfuric acid-treated before adding to TPU at same weight percentage to create sulfuric acid HNTs-TPU composites. The samples were fabricated using injection molding. The HNTs-TPU composites were characterized according to the mechanical properties, including tensile strength, tensile strain and Young's modulus. The highest mechanical values obtained at 2 wt.% HNTs loading, and similar findings are shown at the samples treated with sulfuric acid. The tensile strength increased until reach 23.78 MPa compare with the 17.7 MPa of the neat TPU, which showing about 25% improvement. For the acid-treated composites, the improvement has reached 34.4% compared to the neat sample. Regarding the tensile stain, the improvement was about 82% at 2 wt.% HNTs loading. The Young's modulus results obtained in this study have shown that it is linearly improved with increment of loading content and sulfuric acid treated of HNTs. Where it achieving the highest values of Young's modulus at 3 wt.% HNTs of 13.3 MPa and 15.2 MPa for untreated and treated, respectively.

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Introduction

Injection molding is not a new technology; it is a rather very conventional technique that had used for many centuries at a very low creativity. Recently, injection molding has become one of the fastest technique due to its importance in many fields such as automotive, screens, and roller systems and films [1]. In plastic processing technology, particularly injection molding is considered as the mass production technique due to automation, precision, material utilization, and good flexibility on the complex geometry [2]. TPU, as one of the most used plastic, has been employed extensively due to its excellent physical properties such as low flexibility, high tensile strength, tear and abrasion resistance, solvent resistance, and high versatility in chemical structure [3]. The main world's polyurethane market is used for the applications of coatings, adhesives, sealants, and elastomers [4]. TPU can be an improving factor in many services such as thermal stability, fire redundancy and mechanical properties where TPU plays an important role in chemical properties [5]. In addition to TPU, HNTs, whose structure is $Al_2Si_2O_5(OH)_4.2H_2O$, have become a very important mined natural product in nanotechnology [6]-[8]. HNTs, treated or untreated with acids, are additive products at very low ratios to TPU to create composite whose physical and chemical properties may drastically improve. Nanotechnology has evolved in the last three decades and since then numerous areas of production were benefited with new and more reliable products as in the medical fields [9] and in the production of high-quality porcelain [10]. The HNTs are nanoadditive that has been used to enhanced the mechanical, thermal, crystallization, and fire performance of thermoplastic polymers (example polypropylene and polyamide-6) [11].

This main objectives of this study is to study the effect of two parameters (the percentage additive ratio and sulfuric acid treatment) on the mechanical properties enhancement.

Experimental

Materials

TPU semi-round-Ester type of about 5 mm in diameter was purchased from Global Innovations-polycarbonates Bayer Material Science AG, D-51368 Leverkusen. The properties of TPU and its physical shapes are shown in Table 1 and Figure 1 (a), respectively. HNTs, in powder form with an average size of 20 nm, were purchased from Natural Nano, Inc., 832 Emerson Street, Rochester, New York, as shown in Figure 1 (b). The chemical composition and the physical properties of HNTs are summarizing in Table 2 and Table 3, respectively.

Table 1: Physical properties of TPU

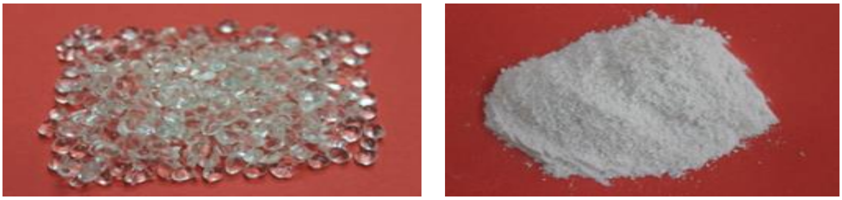
Hardness	**Tensile strength**	**Density**	**Melting temperature**	**Specific gravity**
55D	20 MPa	1224 Kg/m^3	200 °C	1.21

Table 2: Chemical composition of HNTs

Chemical compositions	**SiO_2**	**Al_2O_3**	**TiO_2**	**Impurities**
Weight %	61.19	18.11	20.11	≤ 0.5 %

Table 3: Physical properties of HNTs

Chemical formula	**Surface area (m^2/g)**	**Pore volume (mL/g)**	**Density (Kg/m^3)**	**Refractive index**
$Al_2Si_2O_5(OH)_4.nH_2O$	65	~1.25	2540	1.54



(a) (b)

Figure 1: (a) TPU of about 5 mm size, and (b) HNTs of 20 nm size

Preparation of HNTs-TPU composites

Reprenstative samples for investigation are shown in Figure 2. The first sample, the neat TPU, is shown in Figure 2 (a). All other six samples are formed with TPU and different HNTs loading. HNTs and TPU were dried in an oven at 80 °C for 12 h to reduce the amount of absorbed water due to storage effect [12]. The HNTs were dispersed in TPU matrix using Brabender mixer was performed with a Brabender mixer (Model W 50 EHT) Corder PL 2000 compounder equipped with a 50 cm^3 kneader chamber at mixing temperature (200 °C), screw speed (30 rpm), and mixing time (40 min) [13]. For the preparation of specimens for testing, the injection apparatus DSM Xplore moulding injection machine was used. The chamber of 10 cm^3 can be heated up to 350 °C. The three samples were labelled with 1, 2, 3 wt.%

untreated HNTs-TPU composites. The other three samples are prepared by using treated HNT's with sulfuric acid. The procedure of creating these three samples started by dissolving 15 g HNTs in 100 ml 3M-sulfuric acid at 90 °C rate and mixed at a rate of 200 rpm for 8 h, followed by drying in vone procedure [14]. The second samples was prepared by taking same ratios as in the first sample with treated HNTs. The three samples were labelled with 1, 2, and 3 wt.% acid treated HNTs-TPU composites. Figure 2 (b-g) shows the treated and untreated samples.

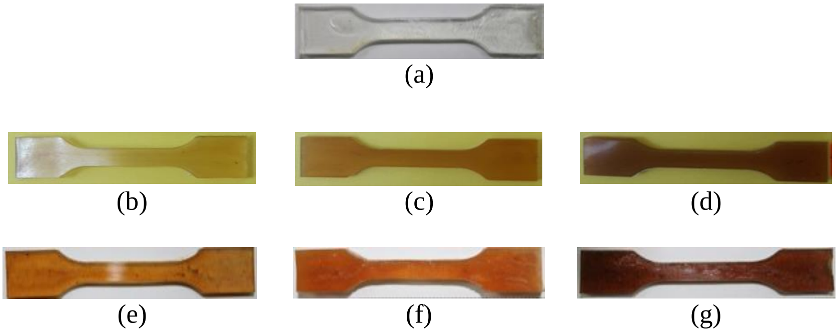

(a)
(b) (c) (d)
(e) (f) (g)

Figure 2: Samples of HNTs-TPU composites (a) neat TPU, (b, c, d) 1, 2, 3 wt.% untreated HNTs-TPU, (e, f, g) 1, 2, 3 wt.% acid treated HNTs-TPU

Testing equipment

Tensile properties were experimentally measured using an Instron 5567 machine, according to ASTM D-638 type V [1]. Three specimens were tested with a crosshead speed of 50 mm/min [1]. FESEM, model ZEISS SUPRA 55-VP (Manufacturer, Konigsallee, Deutschland) with a magnification up to 25Kx, was used to investigate and view small structures on the surface of the HNTs-TPU composites.

Results and Discussion

Effect of HNTs loading on the mechanical properties of HNTs-TPU

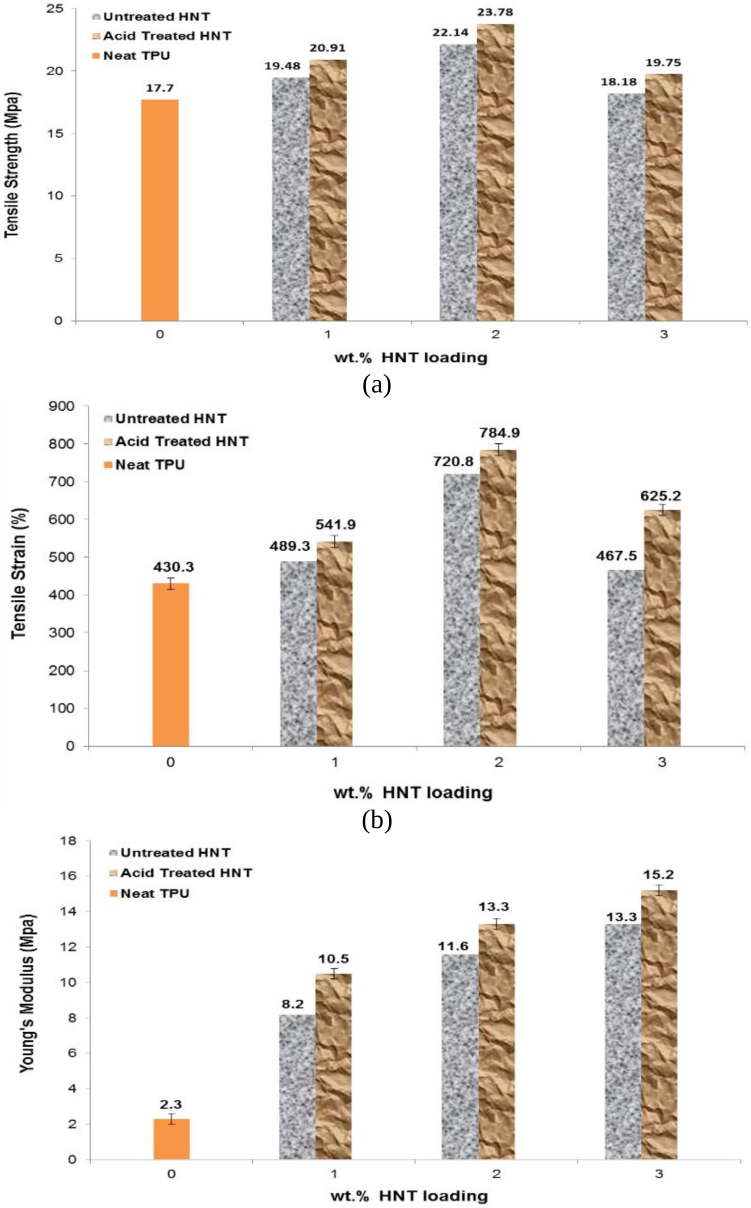
The mechanical properties under investigation include the tensile strength, tensile strain, and Young's modulus. Each composition was made at three samples and each sample was experimentally treated. The average results of the tensile strength, tensile strain, and Young's modulus of the seven samples are listed in Table 4. The highest values of the tensile strength were obtained at 2 wt.% untreated HNTs-TPU composites and 2 wt. % sulfuric acid treated HNTs-TPU composites at 22.14 MPa and 23.78 MPa, respectively. The results suggest that the improvement in the tensile strength were 25% and

34.4% for the two samples, respectively. The improvement of both samples can be attributed to the additive HNTs while for the acid-treated sample, the improvement was attributed to both HNTs and the better dispersion of HNTs in the bulk. The dispersion occurred between the layered silicate of HNTs and the TPU chains [5].

Table 4: Tensile properties of HNTs-TPU composites

Sample	**Tensile strength MPa**	**Tensile strain %**	**Young's modulus MPa**
Neat TPU	17.7	430.3	2.3
1 wt.% untreated HNTs-TPU	19.48	489.3	8.2
2 wt.% untreated HNTs-TPU	22.14	720.8	11.6
3 wt.% untreated HNTs-TPU	18.18	467.5	13.3
1 wt.% acid treated HNTs-TPU	20.91	541.9	10.5
2 wt.% acid treated HNTs-TPU	23.78	784.9	13.3
3 wt.% acid treated HNTs-TPU	19.75	625.2	15.2

The results of tensile strength, tensile strain, and Young's modulus for neat TPU sample, untreated HNTs, and acid-treated HNTs composites in Table 4 are documented in Figure 3 (a), Figure 3 (b), and Figure 3 (c), respectively. As shown in Figure 3 (a), the highest treated of 3 wt.%, the tensile strength of the untreated and treated declined compared to the 2 wt.% samples from 22.14 to 18.18 MPa and from 23.78 to 19.75 MPa, respectively. At higher loading above 3 wt.% HNTs-TPU composites, the tensile strength decreases which could be attributed to the agglomeration of the HNTs which naturally leads to poor interaction between HNTs and TPU. Similarly, the tensile strength, the tensile strain of untreated and treated has its highest values at 2 wt.% samples has shown improvement by 720.8% and 784.9%, respectively as shown in Figure 3 (b). These results show that the tensile strain has improved by about 9% which is very close to the improvement of the tensile strength. The Young's modulus results shown in Table 4 for the same sequence are shown in Figure 3 (c). Firstly, the results show that Young's modulus of the untreated samples increases linearly with wt.% HNTs loading achieving the highest Young's modulus at 13.3 MPa while Young's modulus of the treated samples was recorded at 15.2 MPa at the 3 wt.% acid treated HNTs-TPU loading. Secondly, Young's modulus of 2 wt.% acid treated HNTs-TPU composites and 3 wt.% untreated HNTs-TPU composites do not show any difference.



(a)

(b)

(c)

Figure 3: Effect acid treated HNTs on the tensile properties of HNTs-TPU composites; (a) Tensile strength, (b) Tensile strain and (c) Young's modulus

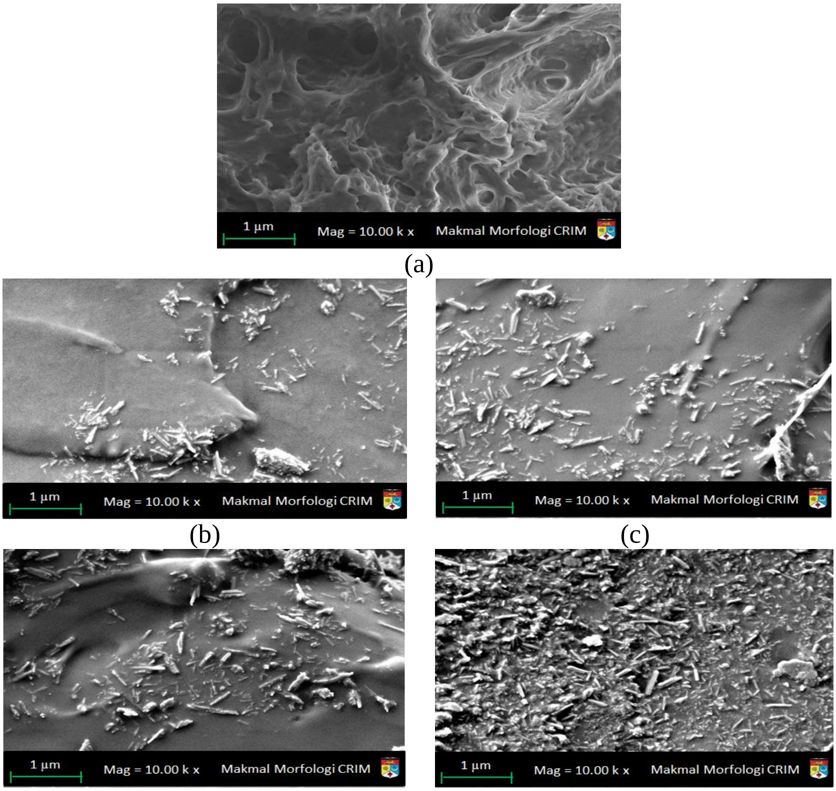
Surface characterization

Five samples were selected including TPU matrix for FESEM investigation as shown in Figure 4. The fractured surface of the TPU matrix is shown in Figure 4 (a). The surface does not show irregularities and seemingly TPU still behaves as a bulk material. When TPU is enforced by 1 and 3 wt.% untreated HNTs, the images of the fractured surfaces show the presence of untreated HNTs distributed in the matrix as depicted in Figure 4 (b and c). The amount of untreated HNTs on the fractured surface of 3 wt.% untreated HNTs-TPU composites is clearly about three times that on the surface of 1 wt.% untreated HNTs-TPU composites as shown in Figure 4 (b and c), respectively. A close investigation of Figure 4 (b and c) reveals that surface morphology improved for 3 wt.% untreated HNTs-TPU as the cavities are much less in both the size and number. For the 3 wt.% untreated HNTs-TPU composites, the surface looks smoother than that of 1 wt.% untreated HNTs-TPU composites.

The HNTs shown on the fractured surface of the TPU matrix disappeared or their sizes were reduced significantly. Disappearing of HNTs suggests that the tensile strength becomes better than that of neat TPU. The second modification for HNTs-TPU composites was conducted by treating HNTs with acid treated HNTs at 1, 2, and 3 wt.% to create three samples of untreated HNTs-TPU composites as explained earlier. FESEM images of 1 wt.% acid treated HNTs-TPU composites and 3 wt.% acid treated HNTs-TPU composites are shown in Figure 4 (d and e). The fractured surface becomes more smoother as the acid treated HNTs distribution becomes clearly seen. When acid treated HNTs reached 3 wt.%, the composites, surface becomes rougher and some amount of acid treatment HNTs are broken cause changes on the properties of the composites.

Conclusion

The increased demands for light weight and high performance materials was initiate with the invention of very strong and light composites materials. This work goes along that line by creating an HNTs-TPU composites where a 25%-improvement was achieved in tensile strength compared to the neat TPU. Moreover, when HNTs are treated with sulfuric acid, the tensile strength was improved by 34.4% compared to the neat TPU for 2 wt.% HNTs-TPU nanocomposite. Sulfuric acid treated HNTs resulted in better characteristics for HNTs dispersion in the composites. The tensile strain and Young’s modulus have shown improvement of 84% and 564%, respectively. Possible applications for this work is needed for wider industrial applications as in the medical fields.



(a)

(b) (c)

(d) (e)

Figure 4: FESEM (10 k x) of (a) TPU matrix, (b) 1 wt.% untreated HNTs-TPU composites, (c) 3 wt.% untreated HNTs-TPU composites, (d) 1 wt.% acid treated HNTs-TPU composites, (e) 3 wt.% acid treated HNTs-TPU composites

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