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Effect of HNTs Addition in the Injection Moulded Thermoplastic Polyurethane Matrix on the Mechanical and Thermal Properties

(Kesan Penambahan HNTs dalam Pengacuan Suntikan Matriks Termoplastik Poliuretana ke atas Sifat Mekanik dan Terma)

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ABSTRACT

The additions of nanofillers are able to enhance the mechanical properties of neat polymer matrix. There were few researchers reported on the mechanical properties of halloysite nanotubes reinforced thermoplastic polyurethane (HNTs-TPU) nanocomposites formed through casting and compression moulding. However, fewer researchers also reported study on HNTs-TPU formed through injection molding. The main objective of this paper was to study the effect of HNTs addition of TPU matrix on mechanical and physical properties. HNTs were mixed in TPU matrix using a brabender mixer with concentration ranging from 0.5 to 7 wt. % HNT loading (at specific mixing speed, mixing time and mixing temperature). Injection moulding was carried out to form tensile bar shaped specimens with specific moulding parameters (injection temperature, injection time and injection pressure). Increment around 35% of tensile strength of the specimen was found at 1 wt. % HNT loading concentration which exhibited the value of 24.3 MPa, compared to neat TPU; the best mixing. The Young's modulus was increased with increasing HNTs loading. The elongation decreased with increasing HNTs loading. The FESEM results showed that HNTs were dispersed in TPU matrix. The TGA results showed that the addition of 1 wt. % HNTs enhanced the thermal properties. It can be concluded that HNTs-TPU has improved tensile and physical properties compared with neat TPU due to the addition of nanofiller.

Keywords: Halloysite nanotubes; mechanical properties; nanocomposites; physical properties; thermoplastic polyurethane

ABSTRAK

Penambahan nano pengisi dapat meningkatkan sifat mekanik matriks polimer tulen. Terdapat beberapa penyelidik telah melaporkan mengenai sifat mekanik tiub nano haloisit diperkuat nanokomposit termoplastik poliuretana (HNTs-TPU) yang dibentuk melalui pengacuan tuangan dan mampatan. Walau bagaimanapun, hanya sedikit penyelidik yang mengkaji tentang HNTs-TPU yang dibentuk melalui pengacuan suntikan. Objektif utama penyelidikan ini ialah mengkaji kesan penambahan HNTs matriks TPU ke atas sifat mekanik dan fizikal. HNTs telah dicampurkan dalam matriks TPU menggunakan pembancuh brabender dengan kepekatan antara 0.5 hingga 7 % bt. Pembebanan HNT (pada kelajuan, masa dan suhu pencampuran yang telah ditetapkan). Pengacuan suntikan telah dijalankan untuk membentuk spesimen berbentuk bar tegangan dengan parameter pengacuan tertentu (suhu, masa dan suntikan pengacuan). Pertambahan nilai kekuatan tegangan spesimen sebanyak 35% diperoleh pada 1 % bt. kepekatan pembebanan HNT dengan mengeluarkan nilai 24.3 MPa berbanding TPU tulen; campuran terbaik. Nilai modulus Young meningkat apabila pembebanan HNTs meningkat. Pemanjangan menyusut dengan peningkatkan pembebanan HNTs. Keputusan FESEM menunjukkan bahawa HNTs meresap ke dalam matriks TPU. Keputusan analisis TGA menunjukkan bahawa penambahan 1 % bt. HNTs telah meningkatkan sifat terma. Oleh itu, dapat disimpulkan bahawa HNTs-TPU telah menambah baik sifat tegangan dan fizikal berbanding dengan TPU tulen berdasarkan kesan penambahan nano pengisi.

Kata kunci: Nano komposit; sifat fizikal; sifat mekanik; termoplastik poliuretana; tiub nano haloisit

INTRODUCTION

TPUs are linear segmented copolymers, composed of microphase separated hard and soft segments. Therefore, the investigation of the microstructure development under an applied load is complicated. The susceptibility of TPUs to such degradation is a problem for long lasting biomedical implants, which can be deliberately exploited to design biodegradable polyurethanes (PUs) (Li et al. 2012). For the past 40 years, there have been numerous studies and excellent publications on the preparation and structural,

thermal, mechanical and morphological characterization of TPU systems by various research groups. These efforts led to the development of various morphological models for segmented polyurethanes (Yilgor et al. 2006).

TPU is one of the most attractive engineering thermoplastics with elastomeric properties. This interest was caused by the necessity of handling the problems resulted from specific structures of TPU macromolecules, interphase interactions and microphase transformations in blending systems based on TPU (Wang & Luo 2004). TPU is

a unique polymeric material with special physical-chemical properties (Bian et al. 2013). It is used in products in the group of engineering thermoplastics with elastomeric properties. TPUs possess higher tensile modulus in comparison to rubber. Many polymers may be blended with TPUs to enhance their physical properties and toughness (Ha et al. 1998). TPU may be subjected to different environmental conditions that affect its mechanical properties (Boubakri et al. 2010). Several studies showed that TPU materials, exposed to aggressive conditions, undergo significant structural changes which have been found to depend on their structure and morphology. These changes lead to a deterioration of the physical properties of the polymer (Boubakri et al. 2009).

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 have recently recognised as a new type of nanoadditive for enhancing the mechanical (Du et al. 2010; Liu et al. 2011; Prashantha et al. 2011a), thermal, crystallization (Guo et al. 2009; Lecouvet et al. 2011a) and fire (Marney et al. 2008) performance of thermoplastic polymers, such as polypropylene and polyamide-6 (Prashantha et al. 2011b) and thermosets, such as epoxy (Deng et al. 2009). During recent years, the assembly of ordered metal nanoparticles on one-dimensional nanotubes to synthesis nanocomposites is attracting much attention in electro-analytical chemistry and in particular, electrochemical sensors (Cheng et al. 2002).

Halloysite was found to be a viable and inexpensive nanoscale container for encapsulation of drugs that was first demonstrated by several researchers (Kelly et al. 2004; Price et al. 2001; Shchukin et al. 2005). Polymer-halloysite composites are prospective materials for medical implants, for example, bone repairing (Zhou et al. 2010). The main goal of this research was to study the effects of concentration of HNTs on the TPU matrix on the mechanical and thermal properties of injection moulded HNTs-TPU nanocomposites.

EXPERIMENTAL DETAILS

TPU was purchased from Global Innovations-Polycarbonates Bayer Material Science AG, D-51368 Leverkusen. HNTs were purchased from 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 (Reported by Natural Nano, Inc., New York). HNT and TPU were dried at a temperature of 70°C for 14 h. HNTs were mixed in TPU matrix using Brabender Mixer at mixing temperature (200°C), screw speed (30 rpm), and mixing time (40 min). Figure 1 shows the flow chart of experimental which consist of mixing, injection and characterized. Figure 2 shows the digital images fabricated TPU nanocomposites samples at different HNT loading percentages, namely (0.5, 1, 3.5, 5, 7 wt. % HNT).

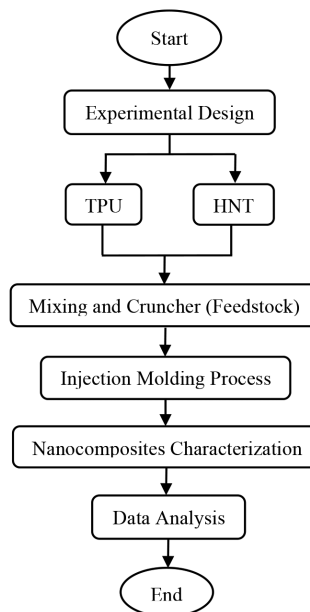


FIGURE 1. Experimental flow chart

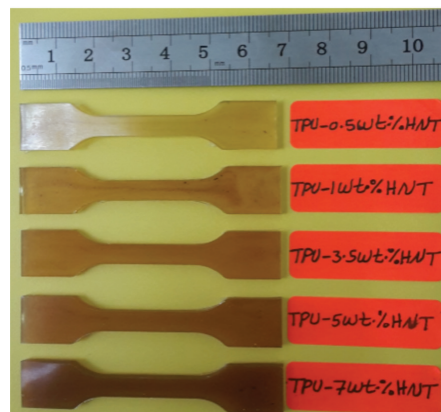


FIGURE 2. Samples of HNT-TPU nanocomposite

The measurement of tensile properties was determined with an Instron universal testing machine (Instron 5567) using a 200 N load transducer according to the standard of ASTM D-638 type V method (ASTM 1998). The crosshead speed was 50 mm/min and all the tests were conducted at room temperature. Five measurements were carried out for each data point. The field emission scanning electron microscopy (FESEM) observation was performed at UKM CRIM Lab. 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 of $500\times$ to obtain clearer images. The thermogravimetric analysis (TGA) was performed using a STA 449 F3 NETZSCH thermogravimetric analyzer under the helium gas condition at sample mass 5-15 mg, heating rate of $10^\circ\text{C}/\text{min}$ and temperature range of $30\text{-}700^\circ\text{C}$.

The degradation temperature rate and other data were determined from the weight loss curves.

RESULTS AND DISCUSSION

TENSILE TEST

Figure 3 shows the variation tensile strength in term of increasing HNTs content. The values tensile strength were 17.7, 23.9, 24.3, 16.7, 9.0 and 6.2 MPa which corresponded to 0, 0.5, 1, 3.5, 5 and 7 wt. % HNT loadings, respectively. It can be seen that TPU-1 wt. % HNT yielded the highest tensile strength value (i.e. 24.3 Mpa) and the lowest strength is 6.2 MPa at 7 wt. % HNT-TPU nanocomposite. At 1 wt. % HNT-TPU loading, it was assumed that the nanocomposites had better interaction between TPU and HNT than 7 wt. % HNT nanocomposite. The reinforcement HNT surface, leading was improved bond stress, which resulted in the highest tensile stress. At higher loading above 3.5 wt. % HNT-TPU, the tensile stress decrease which 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. 2011b).

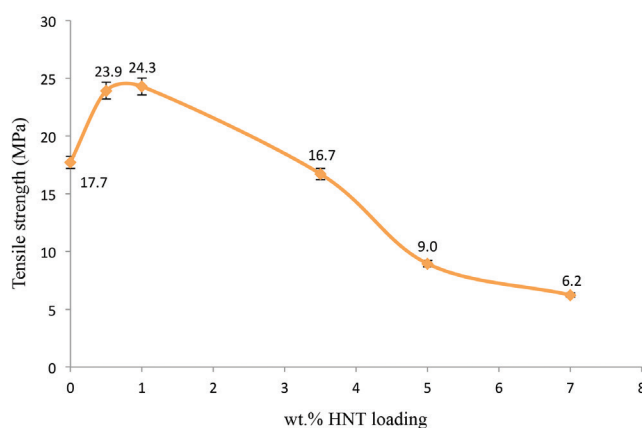


FIGURE 3. Variation of tensile strength of HNT-TPU nanocomposite against HNT concentration

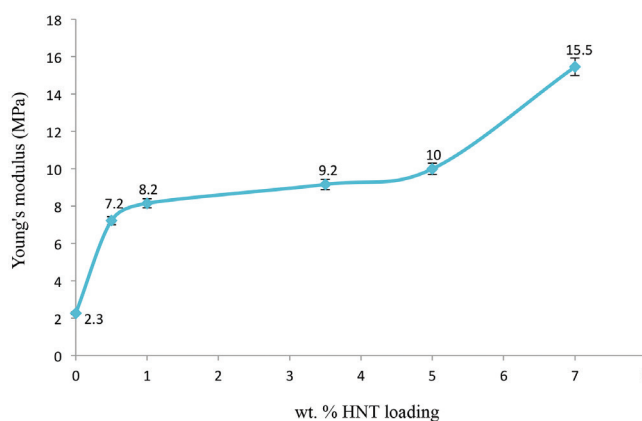


FIGURE 4. Variation of Young's modulus of HNT-TPU nanocomposite against HNT concentration

Figure 4 shows the variation of Young's modulus against HNT concentration. Figure 4 indicates that Young's modulus increased with the increase of HNT content. The value of Young's modulus at 7 wt. % HNT-TPU nanocomposites has the highest Young's modulus value (i.e. 15.5 MPa), showing increased Young's modulus (from 0 to 7 wt. % of HNT loading). HNT-TPU had the highest Young's modulus at 7 wt. % 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 (Ismail et al. 2008). For this reason, the flexibility was reduced and stiffness was increased.

Figure 5 shows the variation of elongation against HNT concentration. Figure 5 indicated elongation is decreased with increasing HNTs loading. Figure 5 shows the highest elongation at break for neat TPU the value of 353.7% (from 0 wt. % of HNT loading). It was also observed from this Figure 5, that the elongation at break value decreases with the loading of HNT. For 0.5 wt. % HNT-TPU, the value is 335.4%, 1 wt. % HNT-TPU the value is 320%. The decreasing trend continues with the increase of the nanofiller loading where the value reaches 134.7% at 7 wt. % HNT loading. The monotonic was decreased of

the elongation at break with the increased of HNT loading means that the value of stiffness increases with the increase of HNT loading. Neat TPU showed the smallest stiffness among the others that decreased the elongation at break when the wt. % HNT loading increased at other values of HNT-TPU. Finally, the highest value for stiffness of all the samples recorded was at elongation at break value of 134.7% for the 7 wt. % HNT-TPU nanocomposite.

Figure 6 shows the maximum load in term of HNT concentration. Figure 6 shows the maximum load value of 408.4 N was observed for 1 wt. % HNT-TPU. Whereas, at 3.5 wt. % HNT loading results in lower value for maximum load which is 273.6 N as presented in Figure 6. The values of maximum load decreased with the increase of HNT loading to 129.8 N and 100.9 N, which corresponds to 5 and 7 wt. % HNT, respectively. The highest value of 408.4 N for 1 wt. % HNT-TPU and the lowest value of 100.9 N for 7 wt. % HNT-TPU. The typical stress-strain curves for the samples containing 0, 0.5, 1, 3.5, 5 and 7 wt. % HNT nanocomposite are presented in Figure 7. The results showed a non-monotonic trend of mechanical properties with the filler loading.

FRACTURED SURFACES OF TENSILE SPECIMEN

Figure 8(a) shows FESEM micrographs (500 × mag.) of the fracture surfaces of neat TPU sample. Figure 8(b) to 8(f) shows the resultant nanocomposites with different wt. % HNT loading. It can be seen on the fracture surface of the neat TPU specimen in Figure 8(a) give smooth surface. However, increased in the wt. % HNT loading, it fractured surface become rougher. Figure 8(b) and 8(c) indicates the tough surface of the nanocomposites with 0.5 wt. % and 1 wt. % HNT loading. When the HNT loading reached 3.5, 5 and 7 wt. % HNT loading Figure 8(d)-8(f) shows that the alignment becomes more irregular but still can be distinguished. In Figure 8(d)-8(f), the fracture surface of the nanocomposites with 3.5, 5 and 7 wt. % HNT loading are full of bumps and hollows with many crystallites randomly distributed inside the TPU matrix.

The dispersion of HNT particle in the TPU matrix is uniformly dispersed. It is of particle clusters at different sizes of shown in Figure 8(d)-8(f). There are also some isolated particle clusters at relatively large size up to several microns, particularly for the nanocomposites containing more than 3.5 wt. % HNT loading. Although

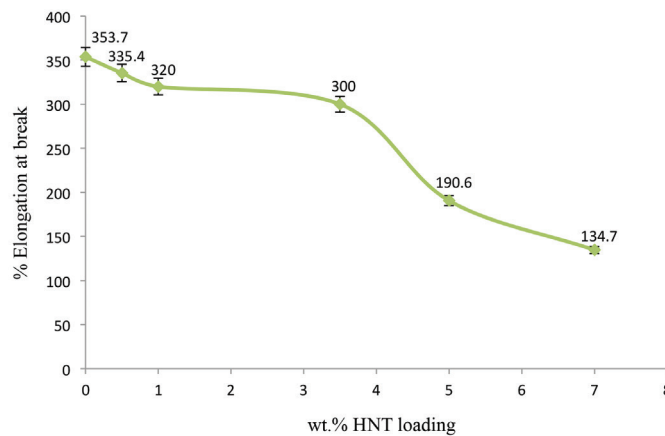


FIGURE 5. Variation of elongation at break of HNT-TPU nanocomposite against HNT concentration

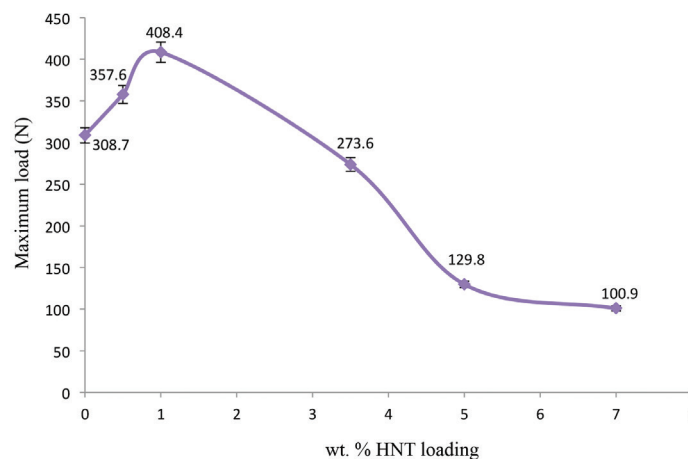


FIGURE 6. Variation of maximum load of HNT-TPU nanocomposite against HNT concentration

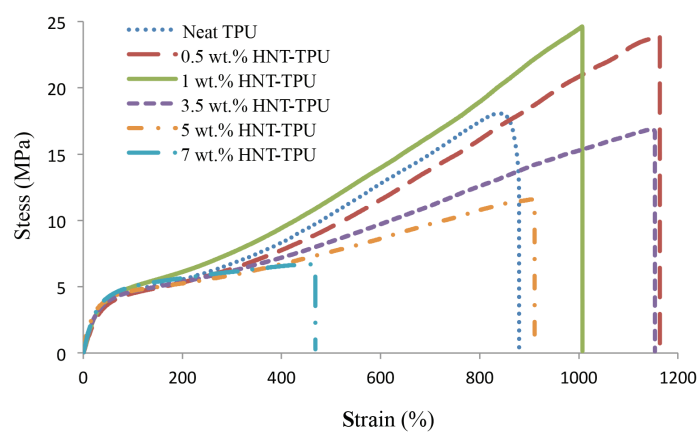


FIGURE 7. Stress-strain curves of HNT-TPU nanocomposite

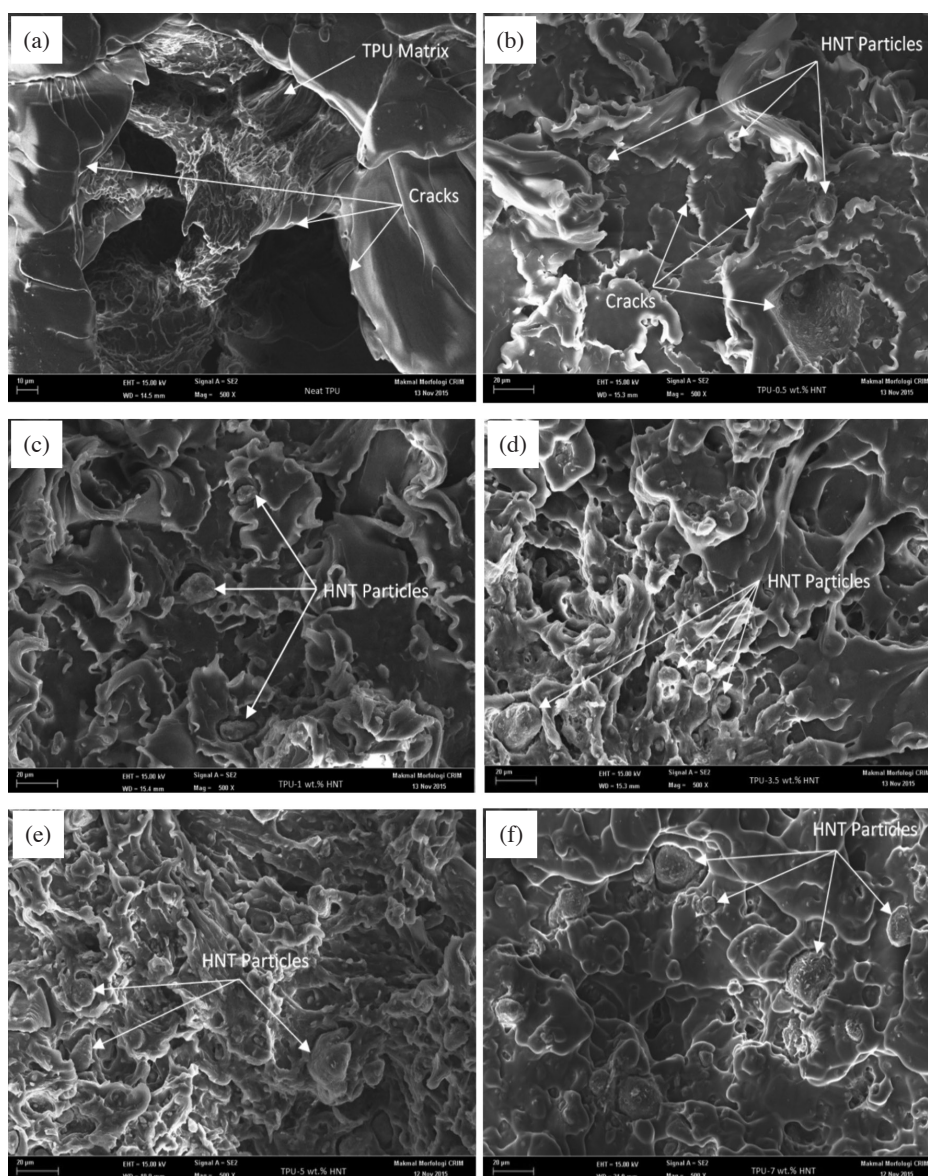


FIGURE 8. FESEM microphotographs of fracture surface for (a) Neat TPU, (b) 0.5 wt. % HNT, (c) 1 wt. % HNT, (d) 3.5 wt. % HNT, (e) 5 wt. % HNT and (f) 7 wt. % HNT

the HNT particle clusters are not in nanoscale, they consist of numerous nanosized particles, mainly nanotubes. The matrix resin has fully penetrated into a large HNT particle cluster and formed a HNT-rich region. This phenomenon was also identified by Barick and Tripathy (2011). The dispersion of HNT particles in the TPU matrix is not sufficiently homogeneous in nanoscale, because of the presence of HNT particle clusters, in spite of the fact that the HNT particles in the clusters are fully surrounded by the matrix resin. Most importantly, if the HNT clusters are oversized they tend to sink to the bottom, leading to significant cross-thickness inhomogeneity which may cause a significant deterioration in mechanical properties, particularly strength and failure strain.

THERMOGRAVIMETRIC ANALYSIS (TGA)

The thermogravimetric analyses of the TPU and HNT-TPU nanocomposites are shown in Figure 9(a)-9(d). The

decomposition of TPU occurs at 200 to 350°C with 36% weight loss due to decomposition of urethane matrix. The second step is a 62% of weight loss between 350 to 535°C (Marini et al. 2014). It can be seen from the curve that the thermal stability of TPU raises as the HNT loading increased from 0.5 to 7 wt. %. Neat TPU starts to degrade at 283°C and was completely decomposed around 700°C, while TPU with 0.5 wt. % HNT-TPU and 1 wt. % HNT-TPU starts to degrade at 284°C and 292°C, respectively. There was a significant change in the degradation temperature of TPU even at 1 wt. % addition of HNT-TPU at 50% weight loss.

This indicates that HNT-TPU is useful for obtaining a nanocomposite with high thermal stability but the issues of dispersion, thermal barriers and interfacial adhesion as the dominating parameters will be addressed in the further research. This retarding effect is attributed to the strong interfacial interaction between HNTs and TPU matrix as well as restricted molecular mobility imparted by the

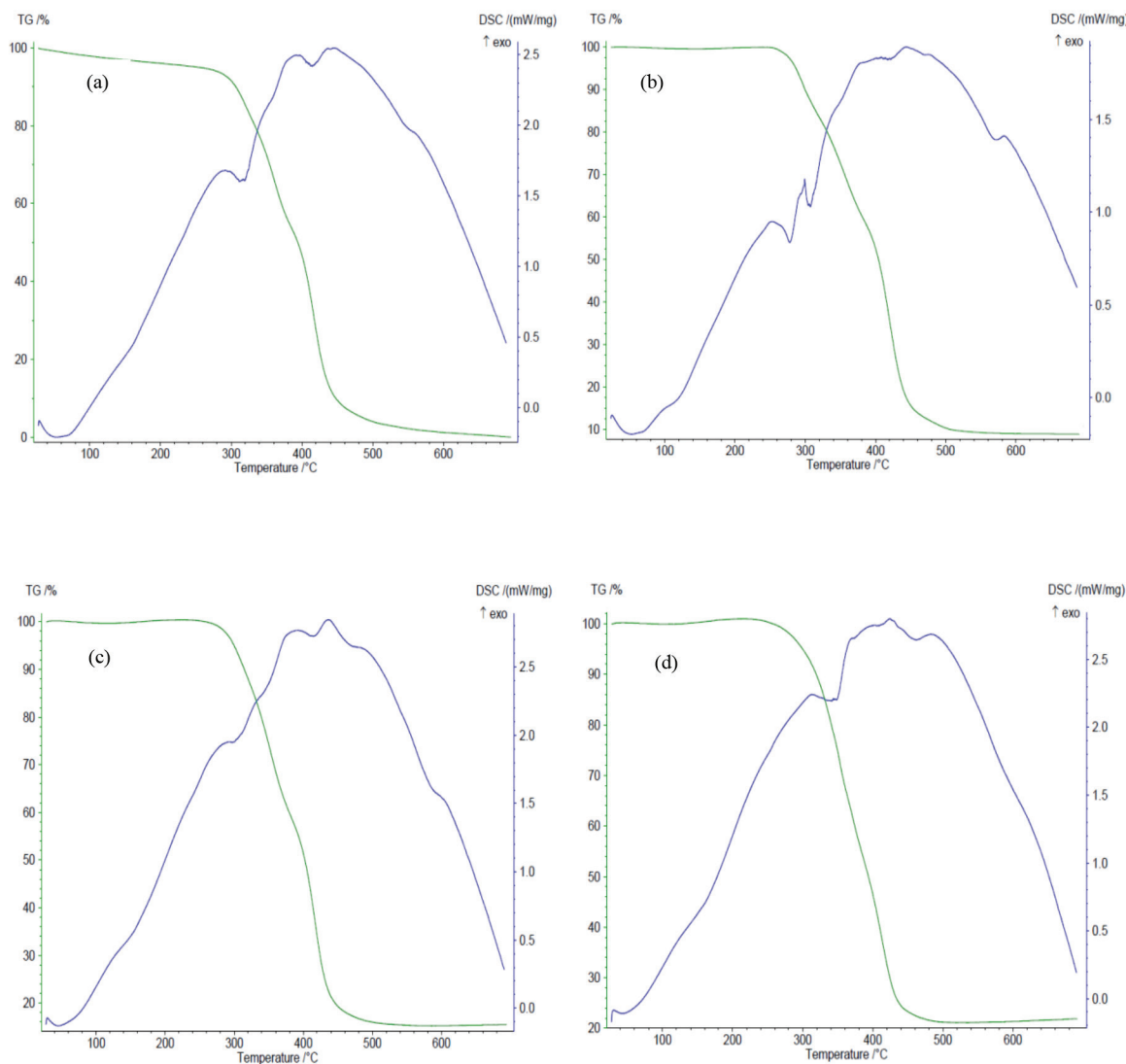


FIGURE 9. TGA thermograms of (a) Neat TPU, (b) 0.5 wt. %, (c) 1 wt. % and (d) 7 wt. % HNT loadings nanocomposites in nitrogen atmosphere

HNTs also plays a vital role in this thermal decomposition phenomenon. Furthermore, it is likely to be a result of absorption and adsorption of free radicals generated during TPU degradation process on the active halloysite particle surface of nanotubes (Gholami & Mir Mohamad Sadeghi 2015).

CONCLUSION

HNTs-TPU 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 has 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. HNTs-TPU nanocomposites with enhanced properties of TPU was achieved with HNT loading ranging from 0.5 to 7 wt. %. It was found the best mixing at 1 wt. % HNT loading concentration which exhibited the value of 24.3 MPa, which was higher than that of neat TPU. Also it was found the Young's modulus values of the HNTs-TPU nanocomposites at 7 wt. % was 15.5 MPa. The thermal analysis technique such as TGA was enhanced the data accuracy and reliability when studying the thermal properties of nanocomposites.

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