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Article

Hybrid nanocomposites of elastomeric polyurethane containing halloysite nanotubes and POSS nanoparticles: tensile, hardness, damping and abrasion performance

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Abstract

Thermoplastic polyurethane (TPU) matrix was reinforced with polyhedral oligomeric silsesquioxane (POSS) and halloysite nanotubes (HNT), both separately and combined. Composite samples were fabricated using a melt-compounding method. Characterization of the composites obtained was performed via tensile and hardness tests, melt-flow index measurements (MFI), abrasion tests, dynamic mechanical analysis (DMA) and scanning electron microscopy (SEM) to investigate the mechanical performance, flow behaviour, tribological characteristics, thermo-mechanical response and morphological properties. The greatest tensile strength value was obtained for the smallest HNT content. Further addition of HNT resulted in agglomerations for both POSS and HNT particles. The shore hardness of TPU was enhanced by filler inclusions. The TPU/POSS composites displayed significant improvement in terms of abrasion resistance compared to TPU at lower loading levels. The DMA study showed that composites containing 0.5% POSS and 1.0% HNT displayed the greatest storage modulus. The glass-transition temperature of TPU shifted to smaller values with the addition of both nanoparticles. The HNT inclusions increased the MFI value of TPU because of their large aspect ratio. Homogeneous mixing of nanoparticles in the TPU matrix was confirmed by a SEM study of the composites. Their dispersion decreased as the concentrations of POSS and HNT increased. An adjuvant effect of POSS with HNT was achieved in their hybrid composites.

Keywords: Extrusion, halloysite nanotube, hybrid composites, POSS, polymer-clay composites, thermoplastic polyurethane

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Nanocomposites are multiphase compounds where one of the phases, which is usually referred to as the filler, has at least one dimension which is <100 μm. They are used in ceramics, metals and polymers where they usually form the matrix in which nanoscale fillers are added. Polymers have been used extensively in nanocomposite technology because they offer advantages in numerous application areas (Ajayan *et al.*, 2003; Grimsdale & Müllen, 2005; Rao *et al.*, 2006; Dzenis, 2008). Polymeric nanocomposites are materials that retain uniqueness and performance combinations, unlike traditional composites. Recently, polymer nanocomposites have been used in new technologies and offered profitable scenarios in several industrial sectors (Manocha *et al.*, 2006; Mollo & Bernal, 2015; Silvestre *et al.*, 2016; Dubey *et al.*, 2017; Fu *et al.*, 2019). Hybrid composites are made by combining two dissimilar components together. The basic aim of hybrid composites is to obtain various properties through combination of the characteristics of each additive. Hybrid polymer composite materials are designed to integrate multifunctional materials thanks to synergy between the filler phases (Sanchez *et al.*, 2005; Gerasin *et al.*, 2013; Szeluga *et al.*, 2015; Nguyen *et al.*, 2017; Ravishankar *et al.*, 2019; Sadjadi, 2020; Sanusi *et al.*, 2020).

Polyhedral oligomeric silsesquioxane (POSS) is a nanostructured material bridging the gap between ceramic and organic materials. The best property of POSS is its ability to enhance product competence without affecting mechanical properties, rendering it suitable for a wide variety of applications and manufacturing activities (Baney *et al.*, 1995; Lickiss & Rataboul, 2008). The ever-growing interest in compounds is the driving force for POSS technology via composition and terminology. The POSS molecule is as small as silica nanoparticles but is different from modified nano-clays and nano-silica because it has a covalently bonded structure suitable for polymerization (Li *et al.*, 2001; Phillips *et al.*, 2004; Cordes *et al.*, 2010). Furthermore, POSS is compatible with various polymer systems thanks to its inactive or non-reactive organic suitability. The ability of POSS to control chain motion usually results in its use in 'temperature boosting' for nearly all types of thermoplastics (Joshi & Butola, 2004; Kuo & Chang, 2011). In addition to rigidity, dyeability and weight reduction, polymers containing POSS display delayed combustion characteristics, i.e. decrease the heat-release rate thus demonstrating fire resistance (Zhao *et al.*, 2008; Gnanasekaran *et al.*, 2009; Qian *et al.*, 2013; Zhang & Muller, 2013; Baykus *et al.*, 2017; Zhang *et al.*, 2017; Turgut *et al.*, 2018).

Halloysite nanotubes are natural nanomaterials which consist of rolled alumosilicate layers containing tetrahedral SiO_4 and

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octahedral $AlO_2(OH)_4$ sheets with intercalated water molecules between adjacent layers. The countries with the most abundant HNT reserves are USA, New Zealand, China and Turkey. Because of unique properties such as nano-sized lumens, a large length/diameter (L/D) ratio, cation exchange capacity (CEC) and low hydroxyl group density on the surface, HNT is employed in various applications as structural and multifunctional materials (Joussein *et al.*, 2005; Rawtani & Agrawal, 2012; Hillier *et al.*, 2016). Despite its nano-scale dimensions, HNT is harmless even at high concentrations and cytotoxicity causes no problem in production steps (Kamble *et al.*, 2012; Yuan *et al.*, 2015; Churchman *et al.*, 2016). Recently emerging applications of HNT-reinforced polymer nanocomposites have been used in anti-cancer treatment (Du *et al.*, 2010; Liu *et al.*, 2016) with sustained drug-delivery systems (Liu *et al.*, 2014; Lvov *et al.*, 2016), as catalysts (Idumah *et al.*, 2019), as fire-resistant coatings (Huang *et al.*, 2016; Goda *et al.*, 2018;) and as anti-corrosive structures (Erpek *et al.*, 2017; Kausar, 2018).

The structure of thermoplastic polyurethane (TPU) involves interchanging soft and hard parts. Polyester or polyether units constitute the soft parts. The characteristic flexibility of TPU derives from this soft segment which corresponds to an elastomeric polyurethane term. The hard parts are made of groups with high polarity such as low-molecular-weight diisocyanate constituents (Hepburn, 1992; Bhowmick & Stephens, 2001; Drobny, 2013). TPU has many advantages, such as recyclability and practical processing by means of conventional industrial approaches. Recently, there has been interest in developing new methodologies for TPU synthesis, preparation of its blends with other polymers and production of its composites (Atiqah, 2017; Kuang & Mather, 2018; Almahmoud *et al.*, 2020). Tuning the properties of TPU by combining several types of fillers is done because of the high cost of alternatives compared to that of fillers, modest mechanical strength, and limits in terms of chemical and abrasion resistance (Petrovic & Ferguson, 1991; Biron, 2018).

Polyurethane nanocomposites displayed remarkable behaviour after the inclusion of POSS nanoparticles. In previous studies, POSS was used effectively as a chain extender for the replacement of partial diol monomer at the polymerization stage of polyurethane (Liu & Zheng, 2005; Zhang *et al.*, 2006, Zhang *et al.*, 2011; Lopes *et al.*, 2012; Markovic *et al.*, 2013; Mahapatra *et al.*, 2012; Lewicki *et al.*, 2014; Zhao *et al.*, 2019). Moreover, POSS promotes flame retardancy (Bourbigot *et al.*, 2009; Kim *et al.*, 2014; Michalowski & Pielichowski, 2018; Kavuncuoglu *et al.*, 2019;), self-healing (Diao *et al.*, 2015; Behera *et al.*, 2018), scratch protection (Lai *et al.*, 2009; Ghermezcheshme *et al.*, 2015; Hebda & Pielichowski, 2018), thermal shielding (Kannana *et al.*, 2006; Janowski & Pielichowski, 2008; Spoljaric & Shanks, 2012; Carmo *et al.*, 2014; Liu *et al.*, 2015; Pagacz *et al.*, 2018; Szolyga *et al.*, 2018; Zaharescu *et al.*, 2018), hydrogel formation (Mather *et al.*, 2006; Wu *et al.*, 2010), drug-releasing stent coatings (Guo *et al.*, 2009; Huitron-Rattinger *et al.*, 2013) and thin-film applications (Oaten & Choudhury, 2005; Madbouly & Otaigbe, 2009; Blattmann & Mulhaupt, 2016) as it was incorporated in polyurethane networks. Recent advancements in HNT-polyurethane systems have also been postulated in several studies and reviews in which the polyurethane matrix was given specific properties including: shape memory (Bouaziz *et al.*, 2019), corrosion resistance in protective coatings (Zahidah *et al.*, 2017; Zeng *et al.*, 2019), drug delivery (Hanif *et al.*, 2016; Fizir *et al.*, 2018), removal of pollutants from water (Anastopoulos *et al.*, 2018; Papoulis, 2019) and thermal stability + fire-proofing (Tang *et al.*, 2008; Smith *et al.*, 2018).

The novelty of this research study lies in addressing the effect of POSS and HNT inclusions, in hybrid form, on the basic properties of elastomeric polyurethane; no previous reports have been published about TPU/POSS-HNT composite systems. The preparation of binary (TPU/POSS and TPU/HNT) and hybrid (TPU/HNT-POSS) composites was conducted by melt-blending. Characterization of unfilled TPU and composite samples was performed mainly using mechanical, melt-flow, tribological, thermo-mechanical and morphological approaches. Dynamic mechanical analysis (DMA), scanning electron microscopy (SEM) analysis, tensile, shore hardness, abrasion and melt-flow index (MFI) tests were integrated to investigate related properties. Comparisons of test results based on individual and hybrid additions of nanostructures with two different geometries to polyurethane elastomer were reported. The results reflect the potential use of TPU-based nanocomposites in varied areas from shape-memory to abrasion-protection applications.

Materials

Commercially available TPU was supplied by Ravago Petrochemicals, Izmir, Turkey, under the trade name Ravathane 130 A85. This saturated polyester-grade TPU has a density of 1.19 g cm^{-3} according to the supplier. Aminopropylisobutyl-terminated POSS was purchased from Hybrid Plastics, Hattiesburg, USA, under the commercial name AM0265. Aminopropylisobutyl POSS was used due to the enhancement of compatibility and interfacial adhesion between the POSS additive and polyurethane phases. The tubular HNT clay was obtained from Esan Eczacıbaşı Industrial Raw Materials Co., Istanbul, Turkey. The trade name of this unmodified naturally occurring aluminosilicate clay is ESH HNT 5. The hollow tubes have diameters, lengths and wall thicknesses of 20–40 nm, 0.5–3.0 μm and 0.7–1.0 nm, respectively.

Experimental methods

Preparation of composites

Before compounding, TPU, aminopropylisobutyl-terminated POSS and HNT were dried at 80°C for 12 h using a vacuum oven (FN 055/120, Nuve AS, Ankara, Turkey). Typically, unfilled TPU and composite samples were prepared via melt mixing using a counter-rotating, twin screw micro-compounder (MC 15 HT, Xplore Instruments, Sittard, Holland). The screw speed, mixing time and process temperature were established as 100 rpm, 5 min and 200°C, respectively. The unfilled TPU was subjected to melt-mixing under the same processing conditions as the composite samples. Fillers in hybrid systems were mixed prior to introducing them in the extruder. POSS and HNT were incorporated separately in the TPU matrix at four different compositions: 0.5, 1.0, 1.5 and 2.0 wt.% and they were labeled accordingly as TPU/POSS 0.5, TPU/HNT 0.5, TPU/POSS 1.0, TPU/HNT 1.0, TPU/POSS 1.5, TPU/HNT 1.5, TPU/POSS 2.0 and TPU/HNT 2.0, respectively. The amounts of POSS/HNT in hybrid composites were 0.5/0.5,1.0/1.0, 0.5/1.5 and 1.5/0.5 wt.% and were labelled as TPU/POSS 0.5-HNT 0.5, TPU/POSS 1.0-HNT 1.0, TPU/POSS 0.5-HNT 1.5 and TPU/POSS 1.5-HNT 0.5, respectively. The dog-bone shaped test samples were typically prepared by an injection molding instrument (Micro-injector, Daca Instruments, California, USA). During injection molding, the injection pressure and the barrel and mold temperatures applied

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were 5 bar, 200°C and 30°C, respectively. Finally, test specimens with dimensions of 7.4 mm × 2.1 mm × 80 mm were obtained for each composite sample.

Characterization techniques

The tensile properties of composites were investigated using a Lloyd LR 30 K universal tensile testing machine (West Sussex, England). The cell load of 5 kN and crosshead speed of 5 cm min^{-1} were applied during tests. Tensile strength, percentage strain and tensile modulus values were recorded as an average of at least five samples in accordance with the ASTM D-638 standard (ASTM D-638, 2014). A-type Shore hardness parameters were estimated using a Zwick R5LB041 digital hardness tester (Zwick Roell Group, Ulm, Germany) according to the ISO 868 standard (ASTM-868, 2020).

Abrasion tests of samples were performed using a TF215 abrasion tester (Testex Instruments, Guangdong, China) according to the ISO 4649 standard (ISO 4649, 2017). Recorded results represent an average value of at least five samples with standard deviations.

The DMA study was conducted using a DMA 8000 analyzer (Perkin Elmer, Massachusetts, USA). Tests were carried out in the temperature range 70–150°C in dual cantilever bending mode at a constant frequency of 1 Hz and a heating rate of 10°C/min.

The MFI values were determined using a Meltfixer LT device (Coesfeld GmbH, Dortmund, Germany). The measurements were performed under a specified load of 2.16 kg at a process temperature of 200°C. The reported MFI parameters represent an average of 10 measurements.

A JEOL JSM-6400 field emission scanning electron microscope (JEOL Ltd, Tokyo, Japan) was used to examine the morphology of the composites. Before SEM analysis, cyro-fractured surfaces of samples were made conductive via coating with a thin layer of gold.

Results and discussion

Tensile performance of the composites

The characteristic stress–strain curves of TPU and its nanocomposites are shown in Fig. 1. The relevant tensile test data for these samples including tensile strength, elongation at break, and tensile modulus are listed in Table 1. Addition of 0.5% POSS caused a ~12% increase in tensile strength of the TPU (Fig. 1). With further increase in the amount of POSS, the tensile strength values decreased gradually. Similarly, a 2.5% increase in the elongation at break value for TPU was observed with a POSS content of 0.5%. Further addition of POSS led to a deterioration in the tensile strain values for the composites. The POSS inclusions also improved the tensile modulus of the TPU slightly. These results might be attributed to the formation of micro-phase separation into the TPU matrix after addition of POSS nanoparticles (Qi & Boyce, 2005; Efrat *et al.*, 2006; Pan *et al.*, 2019; Szefer *et al.*, 2019; Zhao *et al.*, 2019).

The smallest proportion of HNT (0.5%) led to a 19% enhancement in terms of tensile strength for TPU (Table 1). Further addition of HNT resulted in a sharp decrease in the tensile strength of the composites, in accord with previous work in which the tensile strength of the polyurethane matrix shifted to higher values following the addition of HNT with 0.5 and 1.0% filling ratios (Jiang *et al.*, 2014; Gong *et al.*, 2016; Gaaz *et al.*, 2017, 2018).

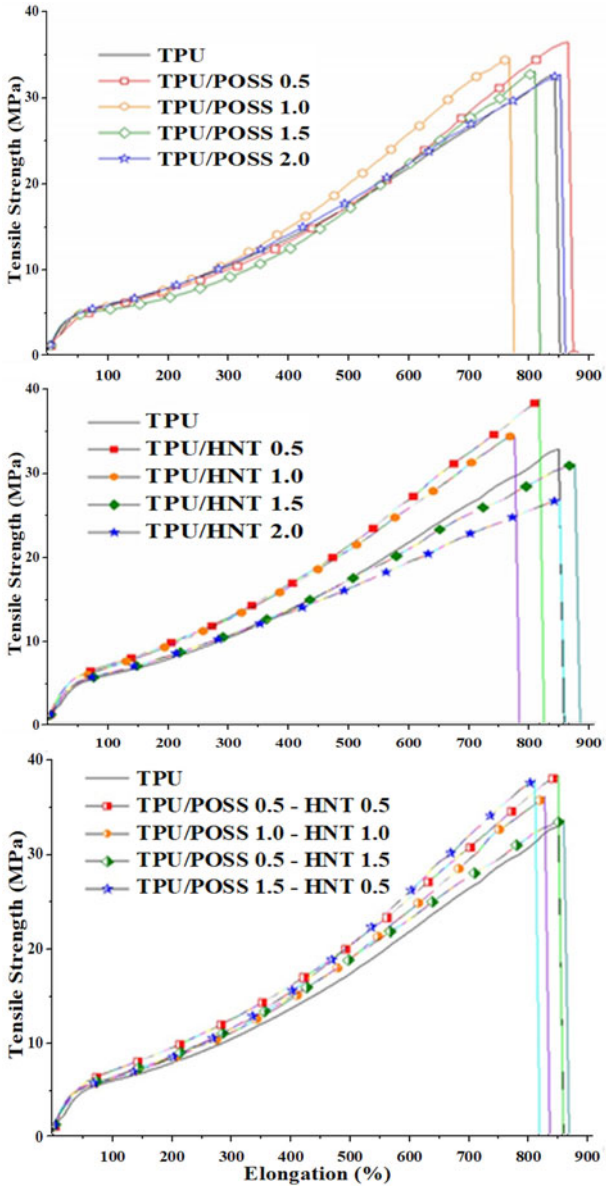

Fig. 1. Strain–strain curves of TPU and composites.

Composites with smaller loadings of HNT showed reduction in elongation at break of TPU, whereas, 1.5 and 2.0% concentrations of HNT led to greater elongation with respect to the unfilled TPU. The maximum tensile modulus value was obtained for the TPU/0.5% HNT sample among the binary composites.

The maximum value of tensile strength for hybrid composites was obtained for the TPU/0.5% POSS-0.5% HNT composite. Similar to binary composites, the smallest amount of both additives yielded greater strength parameters in hybrid composites. The tensile strength of hybrids was reduced with an increase in HNT concentration. In other words, further additions of HNT and POSS had a negative effect on the tensile strength. The TPU/0.5% POSS-1.5% HNT composite yielded nearly identical elongation values with the unfilled TPU, and significant reductions were recorded for other hybrid composites. Similarly, the greatest tensile modulus among all samples was recorded for TPU/0.5% POSS-1.5% HNT.

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Table 1. Tensile test data for TPU and composites.

Samples	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
TPU	32.9 ± 1.2	856.2 ± 12.3	14.9 ± 1.4
TPU/0.5% POSS	36.7 ± 1.0	878.1 ± 16.0	12.6 ± 2.1
TPU/1.0% POSS	34.8 ± 0.9	780.1 ± 15.1	15.3 ± 1.5
TPU/1.5% POSS	33.8 ± 0.7	823.0 ± 8.5	16.9 ± 1.6
TPU/2.0% POSS	32.9 ± 0.8	865.1 ± 9.4	16.6 ± 1.3
TPU/0.5% HNT	39.2 ± 1.1	823.5 ± 10.7	18.0 ± 2.0
TPU/1.0% HNT	34.5 ± 0.7	782.6 ± 9.9	14.4 ± 1.8
TPU/1.5% HNT	31.1 ± 0.5	882.9 ± 8.2	15.2 ± 1.3
TPU/2.0% HNT	26.8 ± 0.8	857.6 ± 11.1	16.6 ± 1.7
TPU/0.5% POSS + 0.5% HNT	38.3 ± 1.0	855.4 ± 8.5	16.2 ± 1.6
TPU/1.0% POSS + 1.0% HNT	36.3 ± 0.5	833.1 ± 7.9	17.5 ± 1.9
TPU/0.5% POSS + 1.5% HNT	33.7 ± 0.8	865.2 ± 9.8	19.5 ± 1.4
TPU/1.5% POSS + 0.5% HNT	37.8 ± 0.7	816.4 ± 8.1	18.7 ± 1.9

Table 2. Shore hardness values for TPU and composites.

Samples	Hardness (Shore A)
TPU	85.0 ± 0.1
TPU/0.5% POSS	85.3 ± 0.1
TPU/1.0% POSS	85.6 ± 0.1
TPU/1.5% POSS	87.0 ± 0.1
TPU/2.0% POSS	87.2 ± 0.1
TPU/0.5% HNT	86.0 ± 0.2
TPU/1.0% HNT	86.7 ± 0.1
TPU/1.5% HNT	86.8 ± 0.2
TPU/2.0% HNT	87.0 ± 0.1
TPU/0.5% POSS + 0.5% HNT	86.4 ± 0.1
TPU/1.0% POSS + 1.0% HNT	87.0 ± 0.1
TPU/0.5% POSS + 1.5% HNT	86.8 ± 0.2
TPU/1.5% POSS + 0.5% HNT	87.5 ± 0.1

Hardness measurements

The Shore A hardness test data of TPU and its composites are listed in Table 2. The Shore hardness of unfilled TPU improved after the inclusion of additives regardless of their type. The positive effect of nanosized additives for TPU matrix at their minimum loading level was also observed in previous studies (Taheri & Sadeghi, 2015). The enhancement of hardness values was more pronounced for smaller amounts of HNT. The hardness of the composites was affected to a lesser degree than was HNT by the inclusion of POSS at low concentrations; this may be due to the formation of POSS aggregates in the hard segment of TPU (Fu *et al.*, 2001; Lach *et al.*, 2010; Bain *et al.*, 2017; Sui *et al.*, 2017). This observation was valid for hybrid composites where the greatest hardness was achieved by the TPU/1.5% POSS-0.5% HNT sample with a ∼3% improvement compared to TPU. Large amounts of POSS enhanced the hardnesses of hybrid composites.

Table 3. Abrasion test data for TPU and composites.

Samples	Abrasion loss (mm^3)
TPU	50 ± 1
TPU/0.5% POSS	33 ± 2
TPU/1.0% POSS	40 ± 1
TPU/1.5% POSS	51 ± 1
TPU/2.0% POSS	66 ± 2
TPU/0.5% HNT	64 ± 1
TPU/1.0% HNT	80 ± 2
TPU/1.5% HNT	93 ± 1
TPU/2.0% HNT	98 ± 2
TPU/0.5% POSS + 0.5% HNT	46 ± 2
TPU/1.0% POSS + 1.0% HNT	65 ± 2
TPU/0.5% POSS + 1.5% HNT	100 ± 2
TPU/1.5% POSS + 0.5% HNT	68 ± 2

Abrasion resistance

The 'abrasion resistance' of a material is defined as its resistance to wear deformation. Smaller abrasion loss values equals better abrasion durability performance (Ozdil *et al.*, 2012). The composites containing POSS displayed greater abrasion resistance than HNT-filled composites (Table 3), probably due to the well-known corrosion and scratch stability behaviour of POSS (Lai *et al.*, 2009; Hebda & Pielichowski, 2018). The increase in abrasion-loss values with increase in concentration of POSS indicated that the abrasion resistance of POSS was more effective at lower loading levels. HNT-filled composites displayed less favourable results compared to pristine TPU. The 2% HNT-loaded composite showed the lowest abrasion resistance behaviour in which twice the abrasion loss value was achieved compared to TPU. In the case of hybrid composites, the abrasion loss increased with an increasing amount of HNT. The greatest abrasion durability was observed for composites reinforced with 0.5% POSS and 0.5% HNT. The smaller abrasion-loss value was obtained for this sample compared to the abrasion-loss value of unfilled TPU. Similar findings were reported in recent studies where POSS nanoparticle addition promoted the abrasion resistance of the polyurethane-based composites (Mihelčič *et al.*, 2019; Wei *et al.*, 2019). In those studies, slightly greater abrasion efficiencies were reported compared to the present study, which may be attributed to a better distribution of the POSS nanoparticles using a solution-mixing rather than a melt-mixing technique.

Thermo-mechanical response

The representative storage modulus and Tan δ curves of TPU and relevant composites as a function of temperature are shown in Figs 2 and 3, respectively. The sharp decline in storage modulus curve centered at −30°C indicates that the characteristic temperature of glass transition (T_g) belongs to soft segment of TPU (Savas *et al.*, 2019). The storage modulus of pristine TPU was improved with the inclusion of nanosized additives (Fig. 2). Similar to previous work, the presence of small amounts of HNT and POSS increased the storage modulus values. In contrast, hybrid composites displayed greater storage modulus values with greater (1.5%) concentrations for both the POSS and HNT. TPU/1.5% POSS-0.5% HNT and TPU/0.5% POSS-1.5% HNT hybrids gave higher values compared to TPU/0.5% POSS-0.5% HNT and TPU/1.0% POSS-1.0% HNT samples. The presence of POSS and HNT nanoparticles caused phase-separation in the hard portion of TPU chains which resulted in hindrance of their segmental motions (Chattopadhyay & Webster, 2009; Barick & Tripathy, 2011; Raftopoulos & Pielichowski, 2016). For this reason, large amounts of nanoparticles added led to increases in the storage modulus of the polymer.

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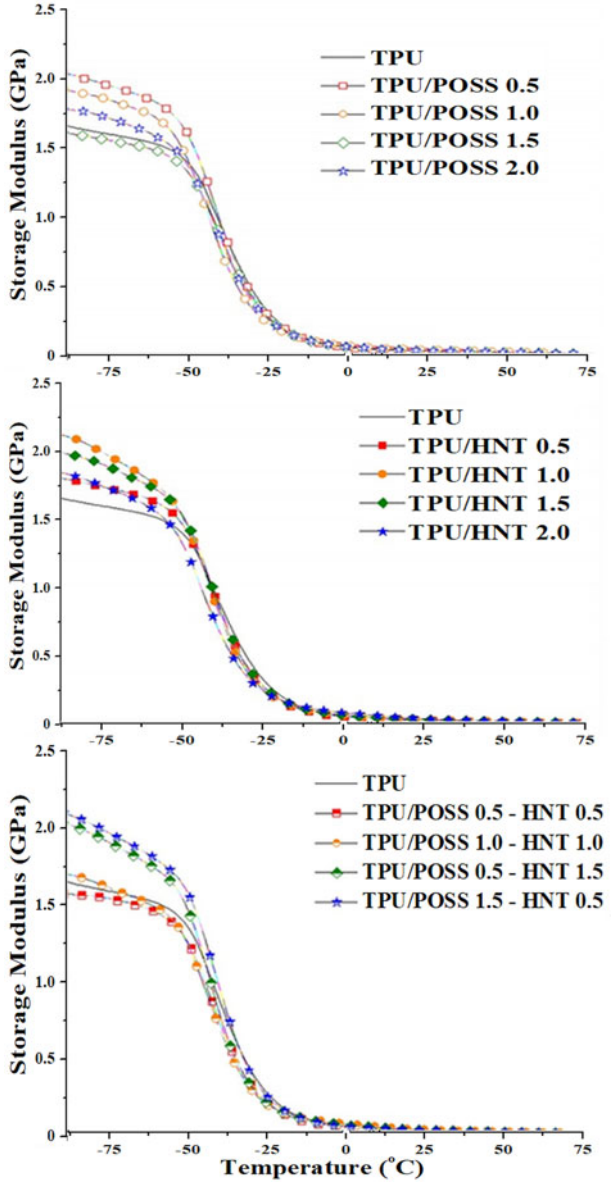

Fig. 2. Storage modulus curves of TPU and composites.

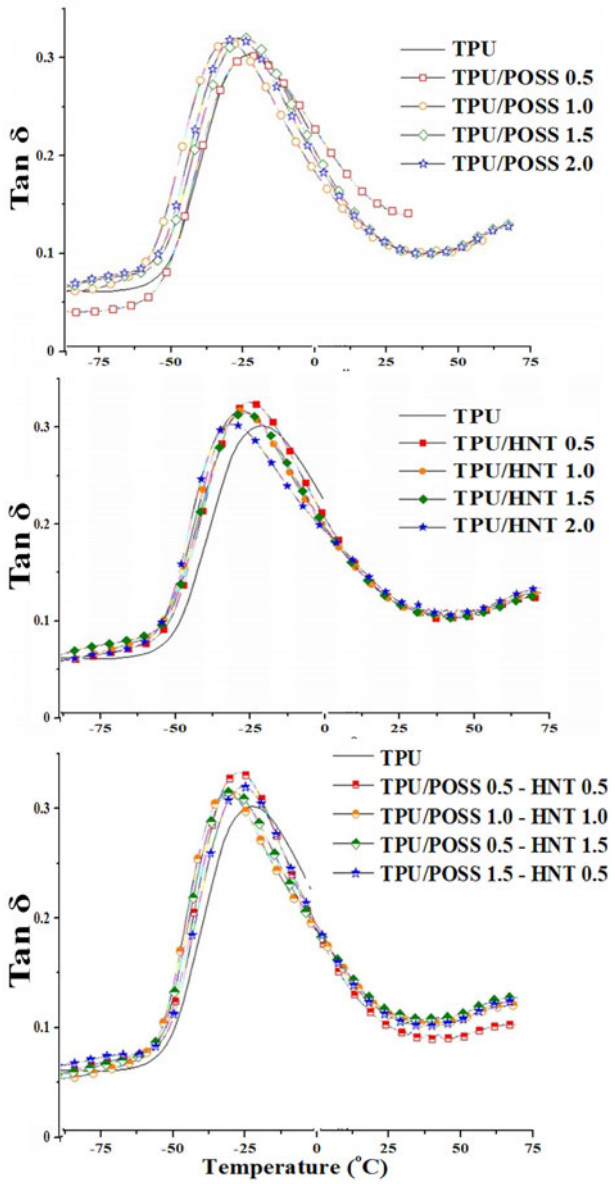

Fig. 3. Tan δ curves of TPU and composites.

All of the composites yielded greater Tan δ maxima relative to pristine TPU, regardless of their compositions (Fig. 3). On the other hand, composites containing POSS showed broadenings compared to the Tan δ curve of TPU. The broadened Tan δ curve was linked to vibration damping behavior of the polymeric material (Sung & Kim, 2017; Kanbur & Tayfun, 2019). The peak value of Tan δ indicates the characteristic T_g value of the polymer. The T_g value of unfilled TPU moved to lower temperatures following the addition of POSS and HNT (Fig. 3). The smallest value was observed for 1.0% HNT-loaded sample *vs*. binary composites. Similarly, the smallest value for T_g among hybrid composites was obtained for the TPU/1.0% POSS-1.0% HNT sample. The reduction in T_g may be related to the plasticizing effect of nanoparticles as their addition caused expansion of the free volume in the TPU matrix (Oh & Green, 2009). HNT imparted this plasticizing behaviour to TPU more than was evident with POSS.

MFI measurements

The MFI parameters of unfilled TPU and composites are shown in Fig. 4. The HNT and POSS displayed completely different melt-flow behaviour as they were compounded with TPU matrix. Incorporation of POSS gradually reduced the MFI of TPU thanks to its viscosity-promoting property in accordance with similar studies related to rheology of the polyurethane/POSS system (Nanda *et al.*, 2006; Madbouly *et al.*, 2007). In contrast, HNT additions improved significantly the MFI of TPU. Composites containing 2.0% HNT had MFI values which were twice as high as pristine TPU.

Hybrid composites containing small amounts of HNT exhibited intermediate performance compared to the values for individual additions of both nanoparticles. The MFI values increased swiftly following increase in HNT concentration in hybrid composites, however. Because HNT has a fibrous structure with a large aspect ratio, a reduction in the viscosity and an

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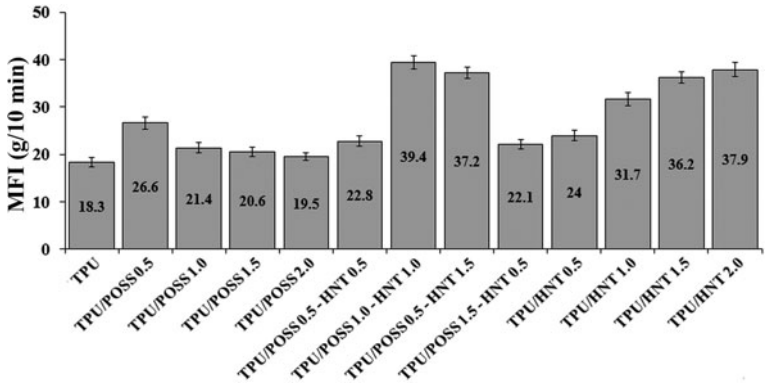

Fig. 4. MFI results of TPU and composites.

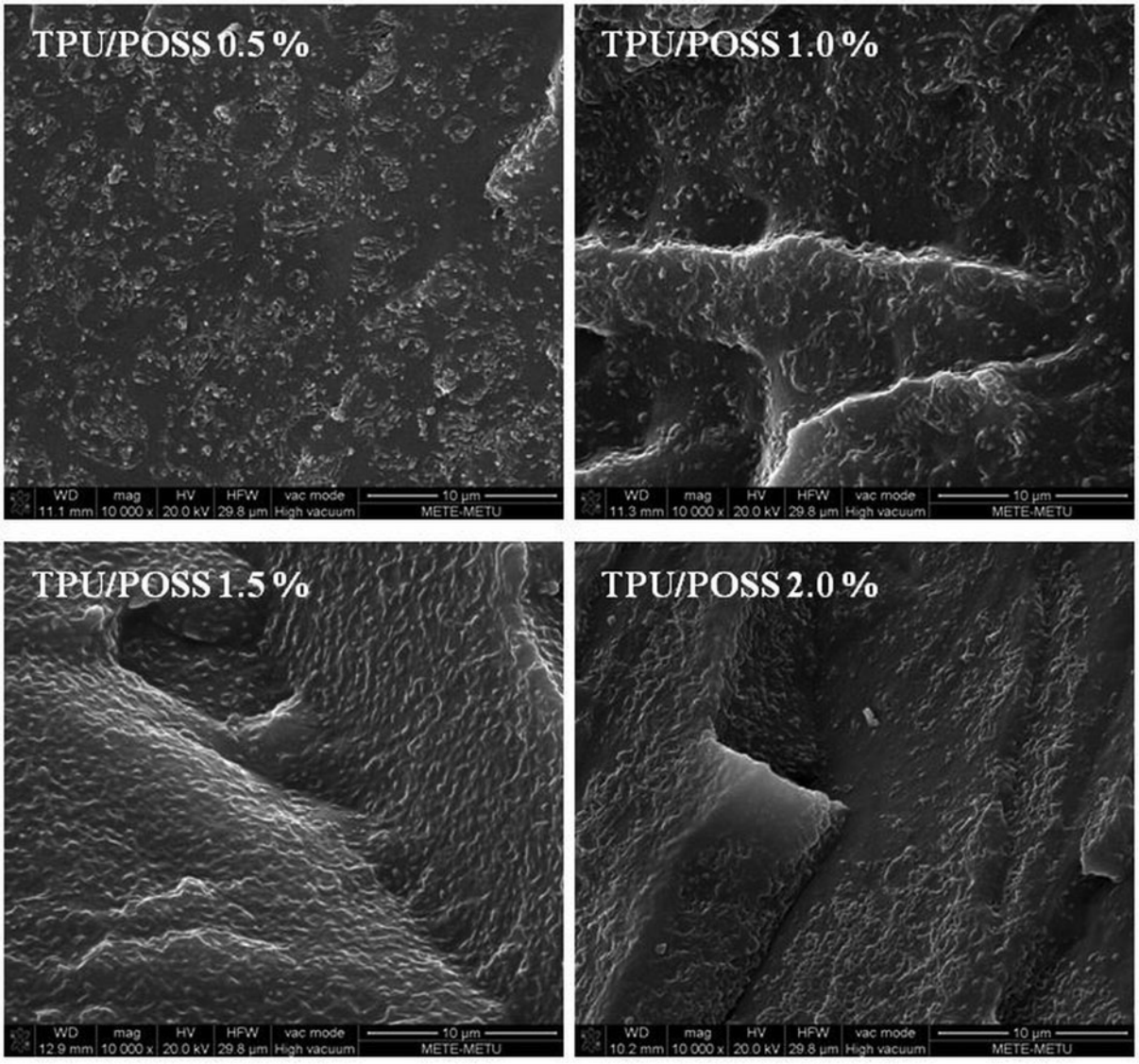

Fig. 5. SEM images of TPU/POSS composites.

increase in the shear of the polymeric phase was achieved (Arbelaiz *et al.*, 2005; Pandey *et al.*, 2017; Tayfun *et al.*, 2017; Eselini *et al.*, 2020). The formation of oriented HNT fibres into the flow direction of polymer chains might also have increased the MFI values.

Morphology of the composites

The SEM images of TPU/POSS, TPU/HNT and hybrid composites are shown in Figs 5, 6 and 7, respectively. The POSS nanoparticles were dispersed homogeneously in the TPU phase at the

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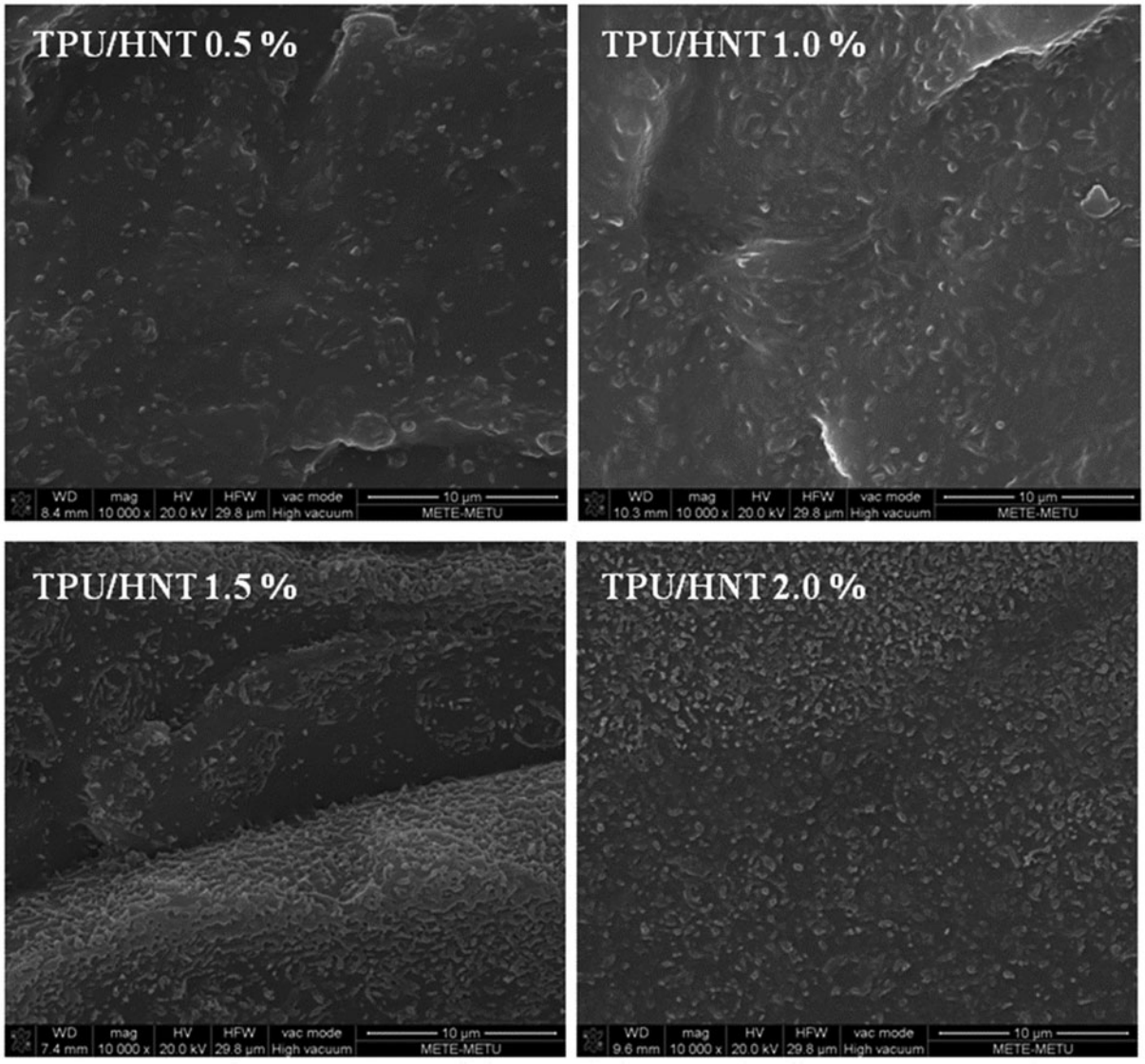

Fig. 6. SEM images of TPU/HNT composites.

lowest loading ratio (0.5%) (Fig. 5) Further additions of POSS caused the formation of agglomerates. Indeed, agglomerates were identified in micrographs of TPU composites containing 1.5% and 2.0% POSS. These observations are consistent with the mechanical test data discussed above.

The fibrous HNT showed homogeneous dispersion in the TPU matrix for a concentration of 0.5%, similar to POSS nanoparticles (Fig. 6). Nanotubes tend to interact with themselves after that loading level. The formation of bundles was observed in TPU composites containing 1.5% and 2.0% HNT (Fig. 6). The good dispersion of HNT particles for smaller amounts was in accordance with the results described above.

In the case of hybrid composites, the HNT and POSS nanoparticles which seem to be best mixed (Fig. 7) are in the TPU/0.5% POSS 0.5%HNT sample. Homogeneous mixing in the TPU phase was reduced as the concentrations of POSS and HNT increased. The POSS particles tended to form agglomerates and HNT portions remained as bundles in the matrix at high concentrations. These observations are in accordance with the results presented in earlier sections in which favorable performances were achieved at low loading levels of POSS and HNT nano-additives.

The improvement in mechanical performance of TPU following the inclusion of HNT and modified POSS in smaller amounts resulted from the enhanced compatibility between the polymer matrix and surfaces of the additives. Previous work has shown that surface free energies of TPU, aminopropylisobutyl-POSS and HNT are ~40 mJ/m^2 (Pötschke *et al.*, 2002; Król & Król, 2012; Primel *et al.*, 2017; Díez-García *et al.*, 2020), 60 mJ/m^2 (Turri & Levi, 2005; Misra *et al.*, 2007; Song *et al.*, 2019; Zhang *et al.*, 2019), and 50 mJ/m^2 (Hope & Kittrick, 1964; Owoseni *et al.*, 2015; Cheng *et al.*, 2018), respectively. The narrow range of surface-energy values between phases creates strong adhesion of fillers to the TPU matrix. In addition, interfacial adhesion of POSS nanoparticles to the polyurethane chain was extended because of the presence of the aminopropylisobutyl tail. The interaction between the amino group of modified POSS and the hard isocyanate segment of TPU promotes the compatibility of these two phases. The ability to recover the mechanical deformation of the composite material is due to the establishment of

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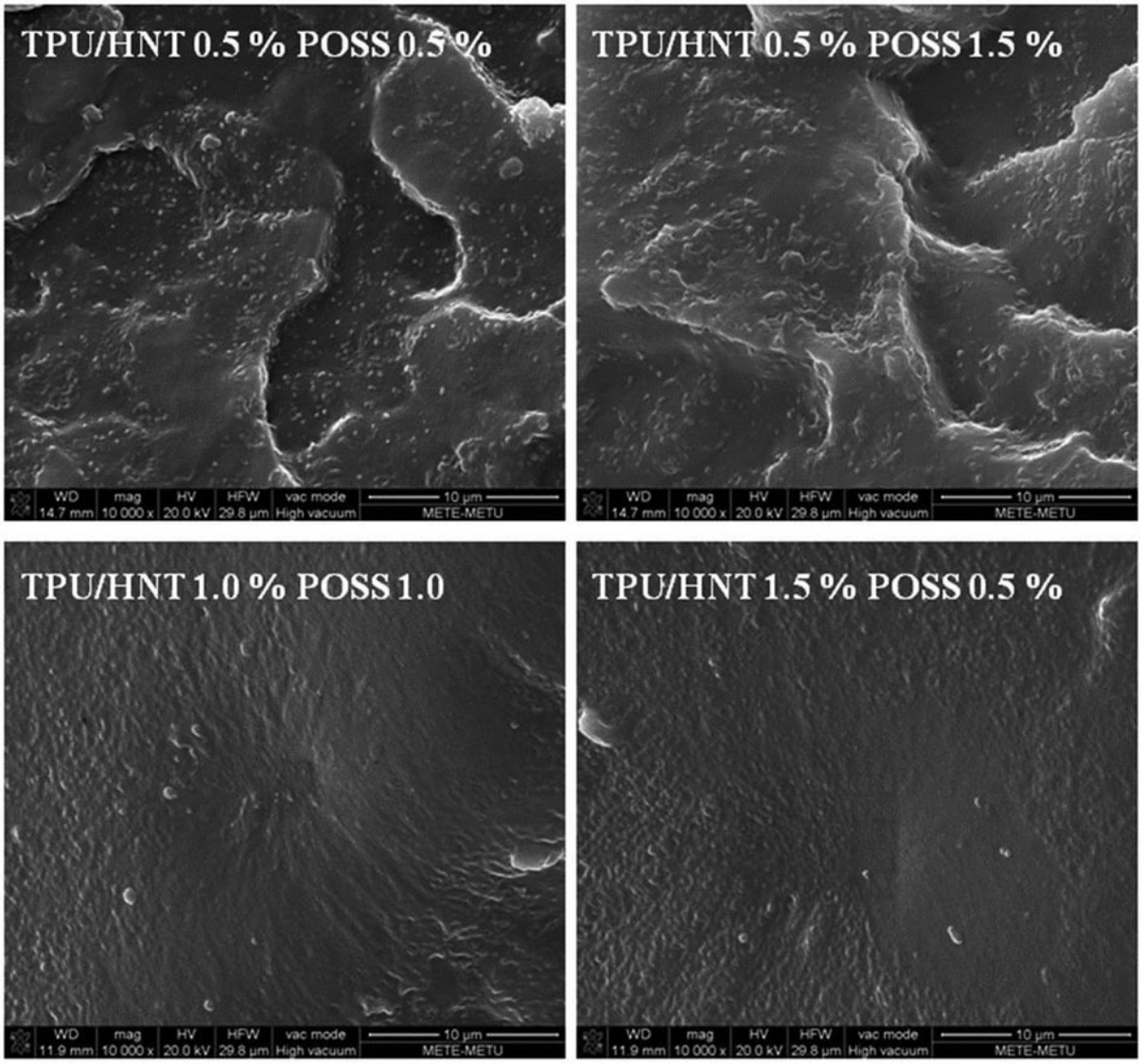

Fig. 7. SEM images of hybrid composites.

the strong adhesion of the additive to the polymer phase. For this reason, the greatest mechanical response was achieved for composites filled with the smallest amount of nano-additives.

Summary and conclusions

In the present study, elastomeric polyurethane was reinforced with POSS and HNT nano-additives, as individual and hybrid forms, by extrusion followed by injection molding processes. The maximum tensile stress strength was obtained for composites containing 0.5% POSS, 0.5% HNT and their hybrid form of 0.5% POSS-0.5% HNT. Further additions of these fillers formed agglomerates of POSS particles in addition to bundle formations of HNT fibres. Tensile-strength reduction was more significant for HNT-filled composites. HNT gave better strength values at the smallest (0.5%) loading ratio. Abrasion resistance of TPU increased after the addition of POSS. A negative effect of HNT was observed for the abrasion performance of composites. Shore hardness of TPU improved with both POSS and HNT inclusions. All composites displayed greater storage modulus values than did unfilled TPU. The addition of POSS yielded remarkable enhancement in terms of the damping behaviour of TPU. Addition of POSS and HNT gave smaller values for T_g than those measured for unfilled TPU because of the plasticizing effect of nanoparticles. The addition of HNT increased the MFI value due to its high aspect ratio and tubular structure. By comparison, the POSS nanoparticles contributed to a greater reinforcing effect with respect to HNT. HNT exhibited better results in some cases at lower concentrations because it has a larger aspect ratio than POSS. The adjuvant effect of POSS with HNT inclusions was achieved for hybrid composites in which intermediate values were obtained compared to composites added individually. The smallest filling ratios (0.5%) of POSS and HNT displayed optimum results for hybrid composites. Further additions of these additives resulted in the formation of bundles and agglomerates.

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