PREPARATION AND CHARACTERIZATION OF THERMOPLASTIC POLYURETHANE NANOCOMPOSITES AND THEIR HYBRID COMPOSITES

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ABSTRACT

PREPARATION AND CHARACTERIZATION OF THERMOPLASTIC POLYURATHENE NANOCOMPOSITES AND THEIR HYBRID COMPOSITES

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The improvement of physical properties of thermoplastic polyurethane (TPU) is still great interest of scientists due to the possible wide application areas. In this study, polyurethane matrix was reinforced with polyhedral oligomeric silsesquioxane (POSS), halloysites nanotubes (HNT) and in hybrid form. The preparation of composites were carried out using co-rotating twin-screw micro-compounder at 210 ^{o}C and the test samples were prepared by laboratory scale injection-molding device.

The weight percentages compositions of added fillers for TPU/POSS and TPU/HNT nanocomposites were 0.5%, 1.0%, 1.5%, and 2.0% respectively. As for TPU/POSS-HNT hybrid composites the weight percentages were (0.5%, 0.5%), (1.0%, 1.0%), (0.5%, 1.5%), (1.5%, 0.5%) respectively. The characterizations of obtained composites were examined via tensile test, impact test, melt flow index test, hardness test, dynamic mechanical analysis and scanning electron microscopy methods.

The obtained results showed that the best value of tensile strength was obtained for the lowest HNT content of 0.5%. For the impact test, the maximum impact strength was achieved when the POSS value was 0.5%. POSS nanoparticles are homogeneously dispersed in TPU matrix for the lowest loading (0.5%). Further additions of POSS cause formation of agglomerations. HNT and POSS nanoparticles seem to be well mixed in micro image of TPU/ 0.5% POSS 0.5%HNT hybrid composites. Homogeneity of their mixing in TPU matrix decreases as the concentrations of POSS and HNT increase, which were revealed by scanning electron microscopy.

Keywords: Polyurethane, Polyhedral Oligomeric Silsesquioxane, Halloysite, polymer composites, hybrid composites.

ÖZ

TERMOPLASTiK POLİÜRETAN NANOKOMPOZİTLER VE HİBRİT KOMPOZİTLERİN HAZIRLANMASI VE KARAKTERİZASYONU

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Termoplastik poliüretanın (TPU) fiziksel özelliklerinin geliştirilmesi uygulama alanının genişliğinden dolayı bilim adamlarının halen ilgisini çekmektedir. Bu çalışmada poliüretan matris polyhedral oligomerik silseskuioksan (POSS), halloysite nanotüp (HNT) ve hibrit formları ile karıştırılmıştır. Kompozitlarin hazırlanması çift vidalı mikrokarıştırıcı ile 210 ^{o}C'de, test numuneleri ise laboratuvar ölçekli enjeksiyonlu kalıplama cihazı ile yapılmıştır.

TPU/POSS ve TPU/HNT nanokompozitleri için yüzde kompozisyonları sırasıyla 0.5%, 1.0%, 1.5%, and 2.0% olarak hazırlanmıştır. TPU/POSS-HNT hibrit kompozitlerinin yüzdeleri sırasıyla (0.5%, 0.5%), (1.0%, 1.0%), (0.5%, 1.5%), (1.5%, 0.5%) şeklindedir. Hazırlanan kompozitlerin karakterizasyonları çekme testi, darbe testi, erime akış indeksi testi, sertlik testi, dinamik mekanik analiz ve taramalı elektron mikroskopisi yöntemleri ile gerçekleştirilmiştir.

Elde edilen sonuçlara göre en iyi çekme dayanımına en düşük oranda 0.5% HNT içeren kompozitte rastlanmıştır. En yüksek darbe dayanımı 0.5% oranında POSS içeren kompozitinde görülmüştür. POSS nanoparçacıklar TPU matrisi içinde en düşük yükleme oranında (0.5%) homojen şekilde karışmıştır. Daha fazla POSS eklenmesi aglomerasyon oluşumuna neden olmuştur. HNT ve POSS nanoparçacıklarının, TPU/ 0.5% POSS 0.5% HNT hibrit kompozitlerinin mikro-resimlerinde iyi karıştığı görülmektedir. SEM fotoğrafları incelendiğinde, bunların TPU matris içindeki homojenizasyonu, POSS ve HNT konsantrasyonu arttıkça azalmaktadır.

Anahtar Kelimeler: Poliüretan, Polihedral Oligomerik Silseskuioksan, Halloysit, polimer kompozitler, hibrit kompozitler.

Dedicated To My Husband and Family

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LIST OF ABBREVATIONS

TPU - Thermoplastic Polyurethane

PMCs - Polymer Matrix Composites

POSS - Polyhedral Oligomeric Silsesquioxane

HNT - Halloysites Nanotubes

MFI - Melt Flow Index Test

DMA - Dynamic Mechanical Analysis

SEM - Scanning Electron Microscopy

CHAPTER I

INTRODUCTION

It is an established fact that in our recent times, the whole world has witnessed the emergence of scientific explorations in the arena of polymer science and technology that have revolutionized our understanding of life and have definitely affected humankind in an amazing manner. Furthermore, such explorations and innovations have not come at a cheap price and the successful journey of making our life a lot easier than ever seems to be at start. If there were one sentence that might describe the key to these great establishments in the area of polymer science and technology, one would use the sentence "improving the features and properties of present polymers by integrating them to unlike polymers or fillers through the production process of polymer matrixes and polymer composites and nanocomposites ". Of course, the cost of such process is proven very reasonable and practical.

Furthermore, nanocomposites comprise multiphase materials as for instance metals, polymers and inorganic ceramics in which, at the minimum, one constituent phase has one dimension less than 100 nm. When nanoparticles are supplemented to a matrix for the sake of improving certain properties, then this is known as "a nanocomposite". Many researchers and academics were amazed by the properties of nanocomposites, therefore made great efforts to exploit their properties in many fields [1].

Nanocomposites are solid building blocks having a nanometer scale dimensions amongst the segments representing the structure [2]. This term, i.e., nanocomposites, is commonly used in various areas of material science: ceramics, metals and polymers. Nevertheless, polymers have been the most captivating and focused on theme in nanocomposite technology. Furthermore, there are a number of categories of nanocomposites, which are categorized through nanofillers dimensionality.

Explicitly, zero dimensional (nanoparticle), one-dimensional (nanofiber), two dimensional (nano-layer) and three-dimensional (interpenetrating network) systems can all be thought of [3]. Moreover, it is worth mentioning that the contemporary nanotechnology age has absolutely attracted enormous number of experts, engineers, trades, and industries with a very simple guarantee, which is, the utilization of building blocks having nanosize dimensions making it possible to design and improve new multifunctional materials, the so-called nanocomposite materials with excellent blending of properties unattainable with old-fashioned materials [4].

Nanocomposites are known to be the materials of the existing century in the light of retaining such uniqueness and property combinations that cannot exist in traditional composites. Newly, nanocomposites have opened the door very widely for new technologies and profitable scenarios for all areas of industry, let alone the fact that they are environmentally friendly. In other words, nanocomposites do enjoy various features that make them without a shred of a doubt, the materials of the century such as small filler size and excellent properties from mechanical point of view [5].

A hybrid composite, as the name suggests, is nothing but an amalgamation between "hybrid" and "composite". As the word hybrid suggest, an entity is made by combining two unlike components together. Consequently, this material is simply a hybridization of composite materials. The consequence of "hybrid" in hybrid composite materials is the hybridization in their structure at the microscopic level.

The concluding materials or outcome of this study is supposed to acquire higher competence and dependability as they are going to be utilized in innovative applications.

1.1 Thermoplastic Polyurethanes

TPU structure is nothing but a copolymer of interchanging soft and hard parts. The hard parts are made of groups with high polarity such as low molecular weight glycols or diamine reacted with diisocyanate. Crosslinking is the means for such groups to provide strengthening [6].

Moreover, polyester or polyether units are forming the constituents of soft parts. Due to phase separation, the hard constituents are distributed as microdomains inside the structure and an interchain hydrogen bonding are keeping them together [7]. Many chemical substances are utilized for the production of TPU. Such chemical substances are usually extracted from either petroleum resources or some kind of renewable resources. The TPU is known to be bio-based if the polyol has been manufactured from some kind of renewable resources [8]. For TPU to be bio-based, it means opening the doors very widely for researchers and academics to manufacture and create eco-friendly composites through integrating natural resources into composite structures [9].

Additionally, thermoplastic polyurethane (TPU) has many advantages, such as recyclability and practical processability by means of conventional approaches in industry. In recent times, there has been a mounting contemplation and concern about TPU in order to conclude new methodologies for their synthesis, preparation of their blends with some other polymers and the production of their composites [10].

Altering the properties of TPU through the combining of dissimilar kinds of fillers has become an established trend nowadays. That is due to the prospect of utilizing old-fashioned approaches such as extrusion, injection and compression molding. Thermoplastic polyurethane is very tempting due to its extraordinary abrasion resistance, impact strength, tensile and tear strength, low temperature flexibility and the shock absorption. However, it has definite drawbacks such as high cost, reasonable thermal stability and mechanical strength, limits in chemical resistance and processability.

Applied optimization and adaptation of these approaches from lab-scale to industrial production lines swiftly cemented the road for academics and manufacturers to produce composite parts with anticipated properties for endless applications.

1.2 Extrusion

The extrusion process is well known for the making up of both thermoplastics and elastomers.

In order to mix up polymer with some other additives such as fillers colorants, anti-oxidants and other elements, polymer is first melt up and then dissolved in such materials. The main advantage of this process is to properly manage plastic materials and to make it possible for producing shapes and forms as required such as sheets, cables, profiles, films, fibers and pellets. In the course of the extrusion process, the conveying of the polymer particles with other additives into a hopper is carried out uninterruptedly and then the whole mixture is transferred with the help of a rolling screw. Moreover, the whole combination is then pulled by means of a screw and goes through a hole that is located at the end of the barrel known as die.

Furthermore, throughout the whole process, both the extruder barrel and the rolling screw generate heat. The outside heat is generated by the extruder barrel, whereas the supplementary heat is generated by friction of the rolling screw [11].

1.3 Injection Molding

Injection molding process is very renowned for the making of thermoplastic materials. By the means of injecting molten material into a mold, injection molding is employed to produce such materials.

Ordinarily, the materials exploited for injection molding are thermoplastic polymers. A pre-heated barrel is used to heat up the material and melted plastic is then delivered into a mold by the use of appropriate pressure. The plastic material takes its final shape as per the shape of the used mold [12].

1.4 Polyhedral Oligomeric Silsesquioxane

Another constituent that was used in this work is “POSS”, or otherwise known as Polyhedral Oligomeric Silsesquioxane with the chemical formula C_{31} H_{71} N Si O_{12}. POSS is a chemical of a nanostructure feature bridging the gap between ceramic and organic materials.

One of the advantages of the POSS is that it has the ability of enhancing product competence without affecting mechanical properties; therefore, this makes it very appealing to be utilized in a wide variety of applications and manufacturing activities. Moreover, the continuous growing efforts of compounds, which are firmly connected to silicones, are behind the emergence of POSS technology via composition and terminology. To help our digital imagination perceive it, a molecule of a POSS is as smallest as silica particles. Nevertheless, when comparing POSS to both improved clays and silica, one would find that it is dissimilar to these elements. POSS molecules consist of covalently bonded receptive fittingness applicable for polymerization or otherwise ascribing POSS monomers to polymer chains [13].

Furthermore, in order for POSS sections to be compatible and harmonious with different polymer systems, every single POSS molecule consists of inactive or nonreactive organic suitability that gives POSS this unique feature. A great number of POSS monomers and polymers are available nowadays and many more are in their way to be developed and improved. This in fact expands the chemical variety of POSS technology [14]. In addition, POSS chemical technology is not problematic when it comes to using it, and obtainable in mutually liquid and solid form. POSS is utilized in a similar manner as the case for known organic additives, either in a monomer or in a polymeric form and is acknowledged to dissolve in most known solvents, resins and monomers. Moreover, POSS is added to almost all polymer kinds (glassy, elastomeric, rubbery, semi-crystalline and crystalline) and to compositions as well [15].

Furthermore, the physical properties of the polymers unified with the POSS fragments are boosted due to the POSS’s capability of managing the motions of the blocks. However, the processability of the base resin and their mechanical properties are sustained and preserved. This comes as a direct consequence of POSS’s nano-scopic size and its association to polymer dimensions. The enrichment of the physical properties of the products takes place throughout adding POSS into plastics and thermosets. A good practical example of such theoretical statement is that POSS integration intensifies modulus and hardness of the concluded products whereas the stress and strain features of the base resin are kept untouched. Moreover, since POSS is a chemical nanotechnology, processing and moldability is conserved [14].

The second physical property that benefits from the incorporation of POSS is the temperature. POSS's capability for governing chain motion usually results in its usage as temperature boosting of approximately all types of thermoplastics and thermoset polymers. Another feature which evolves as a result of POSS addition is the lightweight feature. Usage of POSS additives often decreases the need to employ common fillers such as silica. Based on loading level, bulk density decreases of up to 10% have been observed with viscosity drops of up to 24% relative to silica [14].

As for enhancing "Fire Retardation" connected to common fire retarded plastics, polymers containing POSS prove delayed combustion and major decreases in heat evolution [16].

Furthermore, when it comes to variety of usage and whether POSS can be custom-made to suit many real applications, then the answer is very inspiring. POSS technology has the capability to be alterable because of its chemical nature, and this feature enables POSS from meeting both resin and consumer compatibility necessities [17].

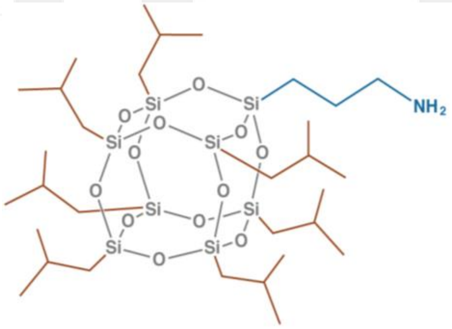

Figure 1 Molecular structure of POSS

1.5 Halloysite Nanotubes

Moreover, another indispensable component, which has been employed in this work, is Halloysite Nanotubes, i.e., HNT with the chemical formula ($Al_2Si_2O_5(OH)_4 .2H_{20}$). It is an acknowledged proclamation that several productive outcomes of nanotechnology like carbon nanotubes, nanofluids, nanoparticles, nanoemulsions, nanocapsules and so on are not perceived to be safe for individuals and humans as well as for the environment owing to their toxicology potencies.

Halloysite nanotubes are unsurprisingly occurring eco-friendly nanotubes with low price, which are harmless to human beings [18].

It is worth mentioning that “Halloysite Nanotubes” (HNTs) are both exceptional and multipurpose nanomaterials. HNT consists of double-layered aluminosilicate minerals with a primarily deep tube-shaped structure in submicron range.

They are not hazardous and enjoy adaptable release rates and fast rates of adsorption. These nanotubes are employed in a wide range of applications, for instance, in anticancer treatment, sustained delivery agents, act as template or nano-reactor for biocatalyst, and have been utilized in personal care and cosmetics and even employed in environment protection [18].

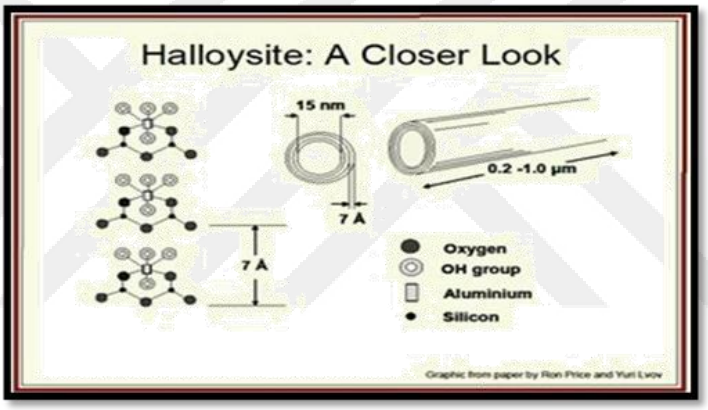

Figure 2 Chemical representation of HNT

Halloysite nanotubes are known to be magnificent nanomaterials, which consist of double layer of aluminum, silicon, hydrogen and oxygen. Thus, being small, HNTs does not display any harmfulness even at high concentrations and cytotoxicity will not be a problem in forthcoming applications.

Owing to features such as nano-sized lumens, high L/D ratio, low hydroxyl group density on the surface, more and more thrilling applications have been exposed for these exclusive, inexpensive and plentifully deposited clays. Therefore, it can be said that HNTs enjoy encouraging prospects in the preparation of new structural and practical materials [18].

1.6 Hybrid Composites

Hybrid materials are composites comprising two ingredients, which are at the nanometer or molecular level, one of them is inorganic in nature whereas the other is organic. Therefore, they differ from old-style composites where the ingredients are at the macroscopic level. In very simple terms, hybrid composites are materials, which are prepared through merging two or more dissimilar kinds of fibers in common matrix. They usually have the aptitude to deliver a wide range of properties, which cannot be acquired with a single type of reinforcement [19].

1.7 Fundamentals of Polymer Composites

Due to their great suitability to easy manufacturing, polymer matrix composites are considered the most advanced type within composite materials. Either thermosets or thermoplastics are used in order to accomplish the aim of being a matrix for polymer composites. Furthermore, it is known that thermoplastics possess various benefits compared to thermosets, including their facility to be processed and reshaped with great degree of easiness throughout the utilization of old-fashioned processing practices and methods [20]. In order to participate to lowering the cost of polymers' production, improving properties and perfecting polymers processing, additives known as fillers are commonly supplemented to polymers [21]. The properties of polymer composites are affected by numerous factors. Among them are interfacial adhesion, shape and the orientation of fillers and the properties of polymer matrix. Moreover, the interface of reinforcement/polymer has a pronounced influence on the mechanical strength of the composite material. Strength and stiffness can be accommodated by the reinforcement material throughout conveying load from the matrix due to the fact that the interfacial adhesion is strong [22, 23].

Many characteristics of polymer composition can be influenced such as the interfacial interactions between polymer and filler, in addition to mechanical properties.

The polymer composite properties, which can be influenced, include rheological behavior, resistance to environmental circumstances and processing restrictions [21].

Furthermore, estimating the role of interfaces, which exist as a result of the mechanism and strength of interaction developing between two phases in composites, is proven to be a bit of a challenge [24].

1.8 Aim of this Study

In this work TPU was used as a polymer matrix, POSS and HNT were both added separately, and together to obtain single and hybrid reinforced composites, respectively. Our aim was to investigate any synergistic effect of POSS and HNT fillers in TPU matrix. The composites were prepared via extrusion. Injection molding was employed to attain our test samples. Because of the fact that these processing methods are extensively exploited in industrial applications, this study can be effortlessly enhanced into large-scale production. The characterization process was carried out to clarify mechanical, thermal, and morphological properties of the composites.

CHAPTER II

MATERIALS AND METHODS

2.1 Production Methods of Polymer Composites

There have been numerous approaches employed for the production of polymer composites namely solution mixing, in-situ polymerization and melt blending. Extrusion, i.e., melt mixing, is considered the most applied process and is regarded as the most convenient approach for producing polymeric composite materials in large capacity [25].

2.2 Materials and Processing

Before compounding, TPU was usually dried up at a temperature of 80˚C for a period of 12 hours. Typically, TPU composites were prepared through the use of melt mixing process by means of a counter rotating twin screw micro-extruder (15 ml micro-compounder, DSM Xplore, Netherlands) while the screw was speeding at100 rpm at 200˚C for a period of time of as long as 5 minutes.

The fillers were integrated at four dissimilar compositions in TPU matrix. The samples were typically prepared through an injection molding instrument (Microinjector, Daca Instruments) at a barrel and mold temperature of 200˚C and 40˚C, respectively. Moreover, an injection pressure of 5 bar was applied at this stage. Finally, specimens of injection molded dog-bone shape were prepared with dimensions of 7.4×2.1×80 mm^3.

Table 1 The materials used in the study

Materials	***Trade Name***	***Supplier***
Polyurethane	Ravathane 130 A85	Ravago Turkey
POSS	AM0265	Hybrid Plastics
Halloysite	EH 01	Eczacıbaşı ESAN

Figure 3 The lab-scale twin screw extruder

Figure 4 The micro-injection molding machine

2.3 Characterization Methods

The word “characterization” in the English dictionary means a description of qualities or assists that someone or something holds. Characterization guarantees that innovative composite materials meet application performance necessities for proposed usage in industry. Composites material characterization is a vital piece of the product progress and manufacturing process. Physical and chemical characterization aids creators to further their understanding of products and materials, consequently safeguarding quality control.

2.3.1 Tensile Test

All tensile properties measurements were executed by means of Lloyd LR 30 K universal tensile testing machine. In accordance with the ASTM D-638 standard, the load cell was (5 kN) at crosshead speed of 5 cm/min. ASTM D-638 standard handle tensile properties of unreinforced and reinforced plastics. Developers and designers of such materials have profited so much from the ASTM and other institutes to create baselines. Moreover, tension tests were implemented on dog-bone shaped samples (7.4×2.1×80 mm^3). Recording results are carried out for tensile strength, percentage elongation at break and tensile modulus.

Figure 5 Tensile strenght machine

2.3.2 Impact Test

The most common impact tests, Izod and Charpy, are specified in ASTM D256-92 [27]. In this work, Charpy impact tests were done by Ceast Resil Impactor for TPU composites in order to determine their impact strengths. They are an ASTM method to specify the material’s impact resistance. A notched specimen was utilized in order to define the impact energy and the notch sensitivity.

Figure 6 The impact test machine

2.3.3 Melt Flow Index Test (MFI)

MFI values were determined by using Meltfixer LT, Coesfield Material Test (Figure 9). The measurements were done under specified load of 2.16 kg at process temperature of 220 ^{o}C. The results for TPU and its composites were reported through the average of ten measurements.

Figure 7 The melt flow indexer

2.3.4 Hardness Test

Shore hardness is a practical measurement used to investigate a TPU’s resistance to indentation or penetration under a well-defined force [27]. Zwick R5LB041 digital Shore hardness tester (Figure 8) according to ISO 7619-1 standard has been utilized in order to obtain the Shore hardness measurements.

Figure 8 Hardness tester

2.3.5 Dynamic Mechanical Analysis (DMA)

The purpose of carrying out the DMA test was to reveal mechanical properties of the new products, i.e., composites; the dynamic mechanical thermal analyzer (DMA 8000, Perkin Elmer) has been employed. The temperatures according to the procedures were ranging from -70°C to 150°C in dual cantilever bending mode. The frequency, which was 1 Hz, had to be constant. The heating rate was 10°C/min. The test samples were obtained by injection molding.

2.3.6 Scanning Electron Microscopy (SEM)

The POSS and HNT reinforced TPU and TPU itself was inspected by a field emission scanning electron microscope (JSM-6400 Electron Microscope). Before SEM photographs were taken, fractured sample surfaces were made conductive via coating with a thin layer of gold and the photographs were taken at x10,000 magnification.

Because of its significant deepness in focusing, reasonably modest image clarification and simplicity of sample preparation, SEM is the favored technique for observing sample features at a resolution well beyond that of the light microscope. The SEM images richly exhibits the three-dimensional features of the item surface under inspection [28].

CHAPTER III

RESULTS AND DISCUSSION

3.1 Tensile Test

The aim of the tensile test is to obtain the force required to fracture a specimen and the extent to which the specimen elongates. Standard test method for tensile properties (ISO 527-2-5a) employs samples of a specified shape, typically a dog-bone. The sample is clamped at one end and pulled at a constant rate of elongation (10 cm/min) until the center of the specimen fails. The stress–strain curves of TPU/POSS, TPU/HNT composites and TPU/POSS-HNT hybrid nanocomposites are represented in Figure 7, Figure 8, and Figure 9, respectively and the relevant tensile test data are listed in Table 2.

Table 2 Summary of tensile properties of composites

Samples	**Tensile Strength (MPa)**	**Elongation at break (%)**	**Young's modulus (MPa)**
TPU	32.9±2.2	856.2±22.3	14.9±3.4
TPU/0.5% POSS	36.7±1.8	878.1±6.1	12.6±5.4
TPU/1.0% POSS	34.8±2.4	780.1±5.7	15.3±4.5
TPU/1.5% POSS	33.8±1.7	823.0±8.4	16.9±6.1
TPU/2.0% POSS	32.9±1.8	865.1±6.1	16.6±5.4
TPU/0.5% HNT	39.2±1.7	823.5±8.4	18.0±6.1
TPU/1.0% HNT	34.5±1.7	782.6±4.9	14.4±4.9
TPU/1.5% HNT	31.1±1.7	882.9±4.9	15.2±4.9
TPU/2.0% HNT	26.8±1.7	857.6±4.9	16.6±4.9
TPU/0.5% POSS+0.5% HNT	38.3±1.7	855.4±8.4	16.2±6.1
TPU/1.0% POSS+1.0% HNT	36.3±2.4	833.1±5.7	17.5±4.5
TPU/0.5% POSS+1.5% HNT	33.7±1.8	865.2±6.1	19.5±5.4
TPU/1.5% POSS+0.5 HNT	37.8±1.7	816.4±8.4	18.7±6.1

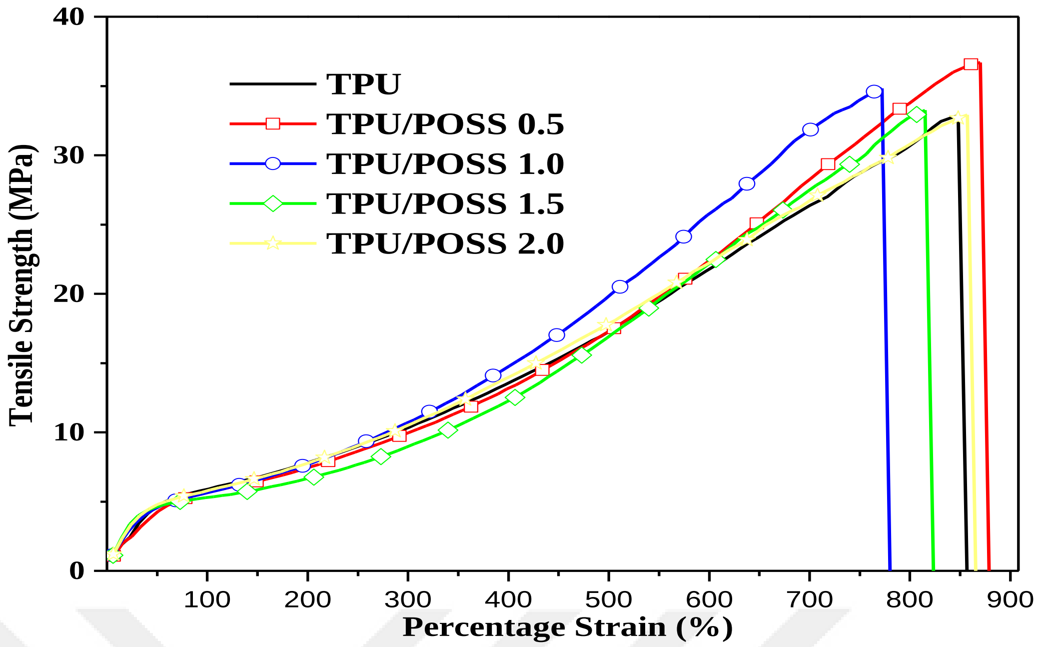

Figure 9 Stress-strain curves of TPU/POSS composites

According to Figure 9 and Table 2, the addition of 0.5% POSS has increased tensile strength of TPU about 4% which is the highest value obtained. As POSS content increased, tensile strength decreased. An increase in the elongation at break values for TPU was observed with POSS content 0.5%. As the POSS content increased, elongation at break values decreased irregularly.

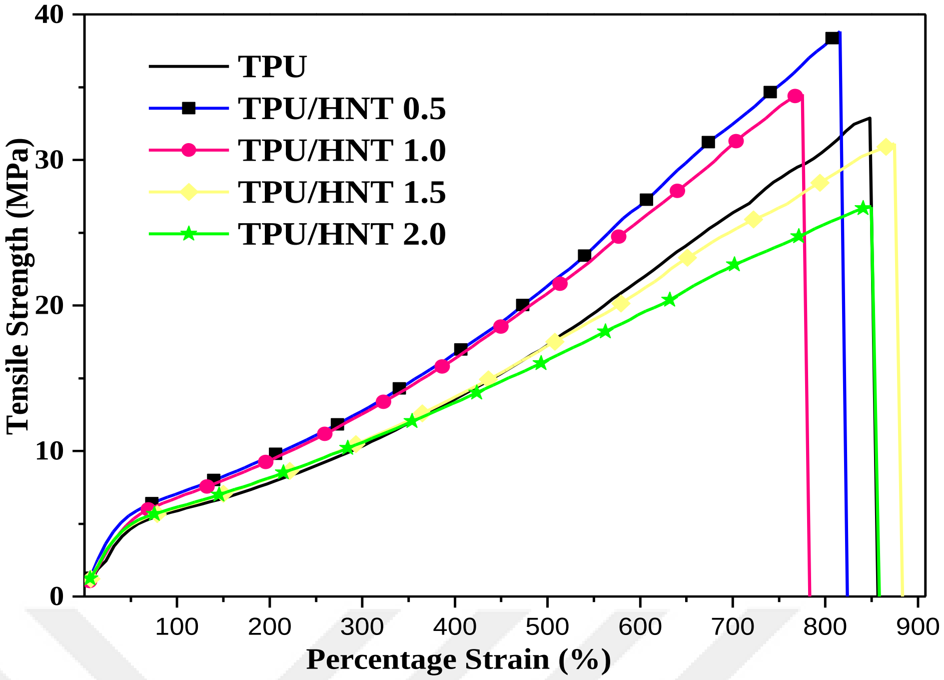

Figure 10 Stress-strain curves of TPU/HNT composites

According to Figure 10 and Table 2, addition of HNT content has resulted in the decrease of tensile strength. In other words, as the HNT content increases, tensile strength decreases. The maximum tensile strength was obtained when the percentage of HNT was 0.5%, and it was about 6% increase. Furthermore, the maximum elongation at break values for TPU was observed when the HNT content was 1.5%.

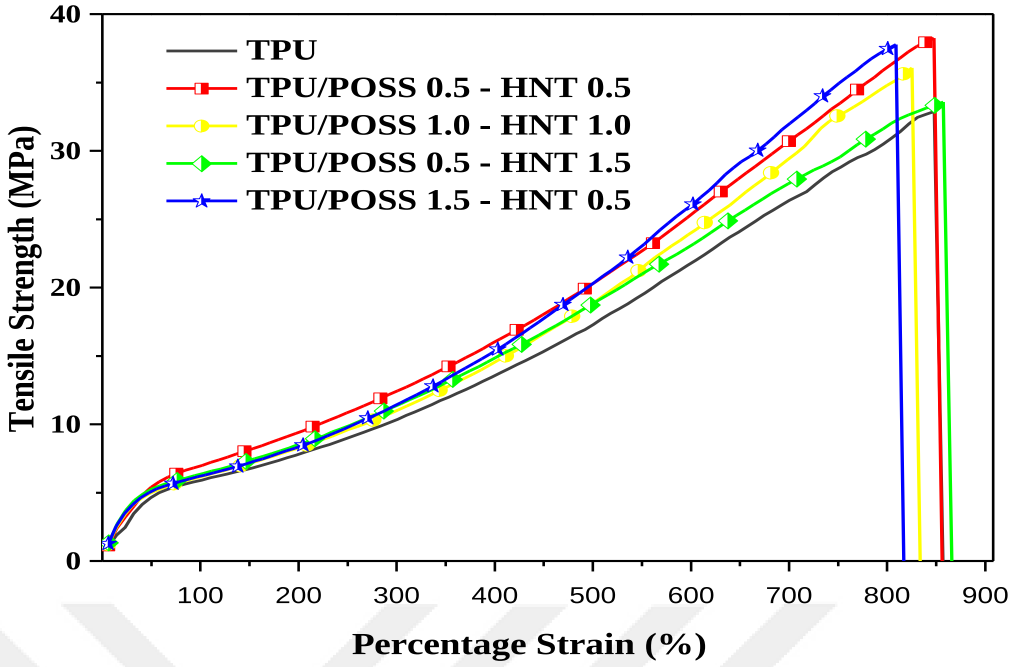

Figure 11 Stress-strain curves of TPU/POSS-HNT composites

According to Figure 11 and Table 2, the maximum value of tensile strength for hybrid composites was obtained for minimum POSS and minimum HNT content, i.e., (POSS 0.5% -HNT 0.5%). Moreover, for hybrid composites the higher modulus was observed for low POSS – HNT content (0.5-0.5).

3.2 Impact Test

It is a test, which establishes the quantity of energy absorbed by means of certain material during the course of its fracture. Impact test for that reason is a high strain rate test. In order to measure the toughness of a material, quantifying the absorbed energy becomes an essential process. The absorbed energy is then utilized to investigate the temperature dependent ductile / brittle transition.

Table 3 Impact test results

Samples	**Impact Strength (kJ/m^2)**
TPU	10.1±0.1
TPU/POSS 0.5	11.3±0.3
TPU/POSS 1.0	10.8±0.2
TPU/POSS 1.5	10.6±0.1
TPU/POSS 2.0	10.0±0.3
TPU/HNT 0.5	11.7±0.2
TPU/HNT 1.0	12.2±0.2
TPU/HNT 1.5	12.7±0.3
TPU/HNT 2.0	13.4±0.4
TPU/POSS 0.5+HNT 0.5	11.0±0.2
TPU/POSS 1.0+HNT 1.0	11.5±0.1
TPU/POSS 0.5+HNT 1.5	11.8±0.2
TPU/POSS 1.5+HNT 0.5	10.8±0.2

Impact test results of TPU composites and their hybrid nanocomposites are shown in Table 3. It is obvious from the table that the maximum impact strength was obtained when the POSS value was 0.5%. Moreover, as the POSS content increased, impact strength exhibited a reduction. In addition, the increase in the HNT content has resulted in an increase in the impact strength as well. As regards hybrid nanocomposites, it can be seen from the Table 3 that there was no significant increase in the impact strength.

3.3 MFI Test

For the sake of measuring the ease of flow of the thermoplastic melt, MFI test, otherwise known as melt flow index, was utilized for that purpose. It can be defined as the mass of material in grams flowing in 10 minutes through a capillary of specific diameter and length.

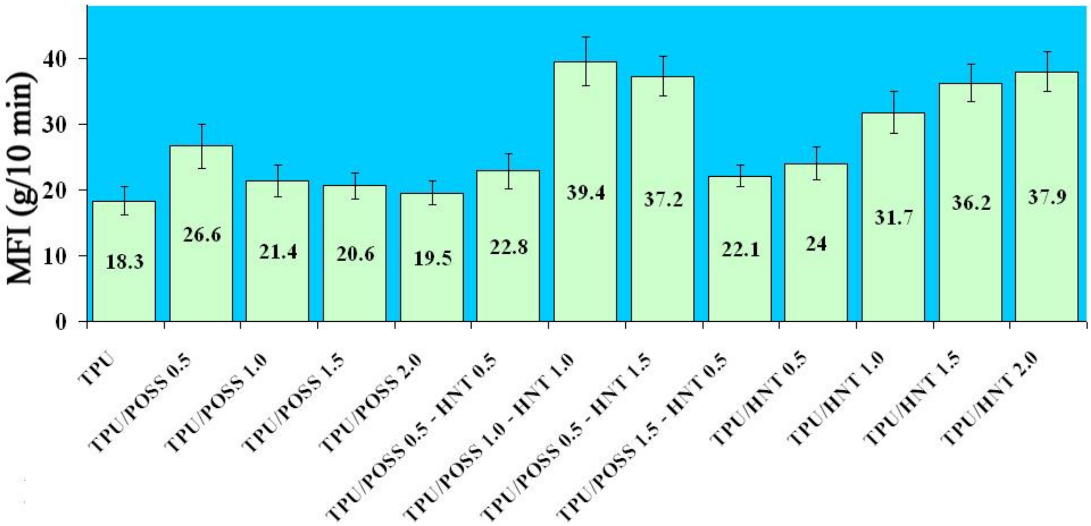

Figure 12 Melt flow index of TPU and composites

As shown in Figure 12, MFI results reveal clearly that the maximum MFI value for TPU composites was acquired when the POSS content was 0.5%. Moreover, as the POSS content increased to 1.0%, there was an obvious decrease in the MFI value. Furthermore, the increase in the POSS content had a very small effect on the MFI values. As a final point for hybrids, the maximum MFI value was obtained when the POSS-HNT content was 1.0-1.0 %.

3.4 Hardness Test

It is worth mentioning that for elastomers and their composites shore hardness is considered as a distinguishing factor. Table 4 lists the values of hardness for TPU and fillers added TPU composites. Hardness of TPU slightly increases with the incorporation of the fillers. In general, there is no significant increase in the hardness after adding the fillers to the TPU.

Table 4 Shore hardness values of composites

Samples	**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

3.5 DMA Test

DMA analysis provides information about thermo-mechanical and damping properties of polymeric materials. Figure 13 displays the values of storage modulus versus temperature graphs of TPU and its composites.

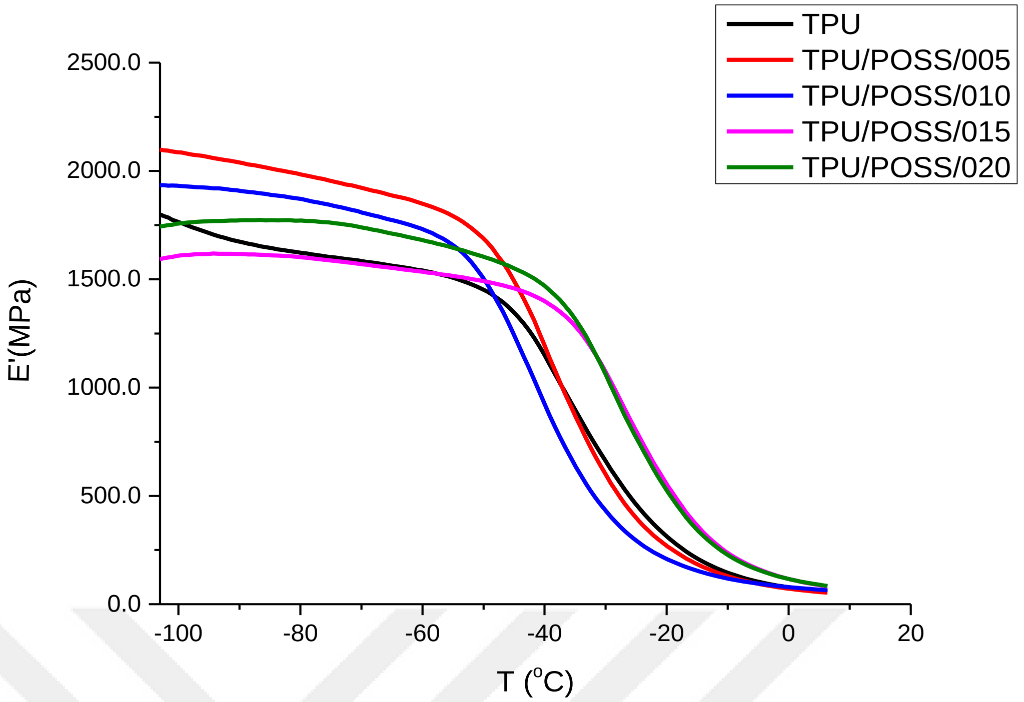

Figure 13 The dynamic storage modulus of TPU/POSS composites as a function of temperature

It can be seen from the curves in Figure 13 that storage modulus of TPU and its composites display the sharp reduction around -40 ^{o}C that indicates glass transition temperature (T_g) of TPU. 0.5% and 1.0% POSS containing composites gave higher storage modulus than that of unfilled TPU and other concentrations. The improvements of storage modulus values at low loadings may be due to their higher load bearing capacity at the interfaces between POSS and TPU matrix [29,30]. The higher storage modulus of these composites also means that they have more stiffness compared to TPU.

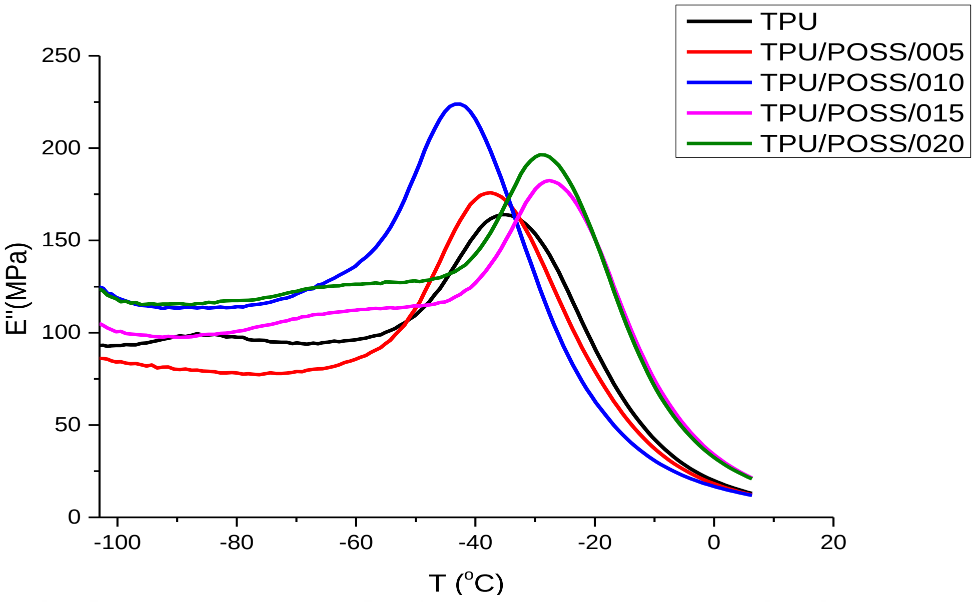

Figure 14 Loss modulus E'' versus temperature data for TPU/POSS

According to Figure 14, all composites give higher loss modulus as compared to pristine TPU. The highest lost modulus is observed in 1.0% POSS loaded composite that may be due to better dispersion in TPU matrix with respect to other POSS containing composites.

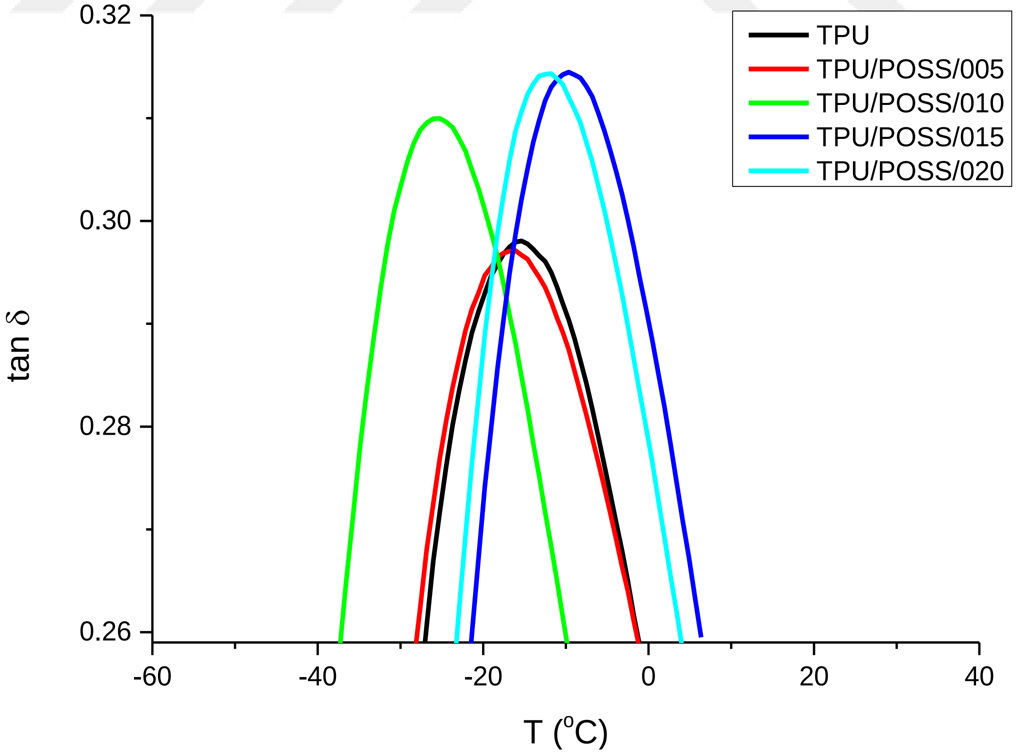

Figure 15 Tan δ of TPU/POSS composites as a function of temperature

The peak of tan δ curve is related to the glass transition temperature (T_g) of TPU and as seen in Figure 15, T_g shifts to higher temperatures with the additions of POSS nanoparticles. The one exception is observed that 1.0% POSS containing composite gives lower tan δ peak value and tan δ curve of 0.5% POSS filled composite is observed as almost identical with that of TPU. T_g of TPU increases with increase in concentration of POSS.

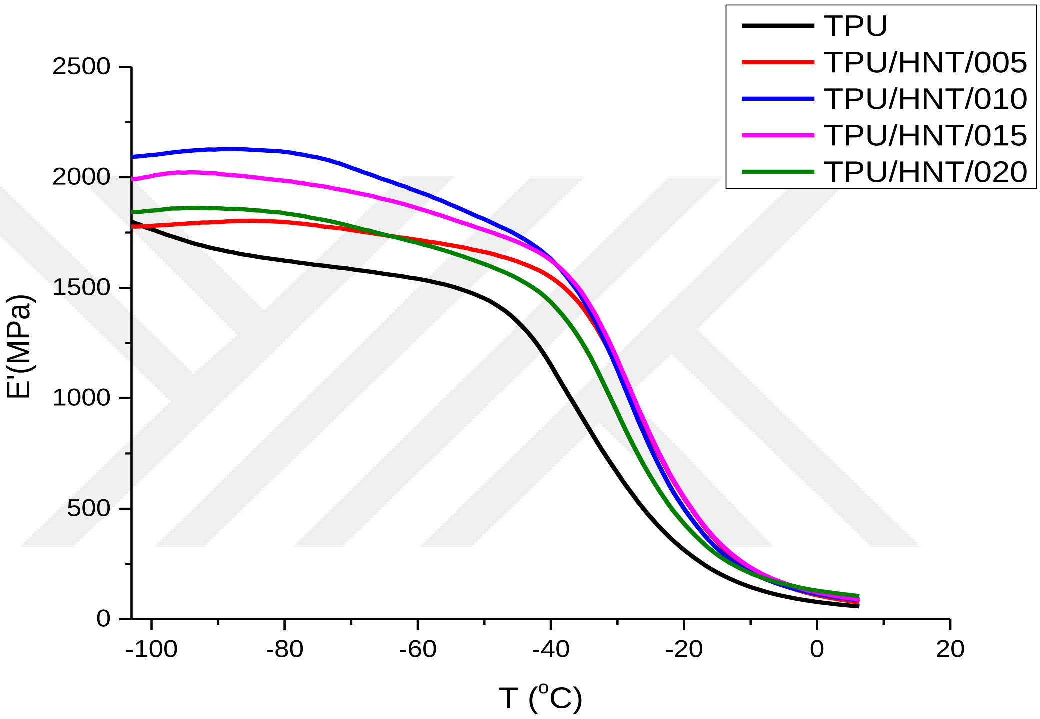

Figure 16 The dynamic storage modulus of TPU/HNT composites as a function of temperature

As can be seen from Figure 16, HNT additions cause enhancements in storage modulus of TPU as similar with POSS additions. TPU becomes stiffer with HNT loadings.

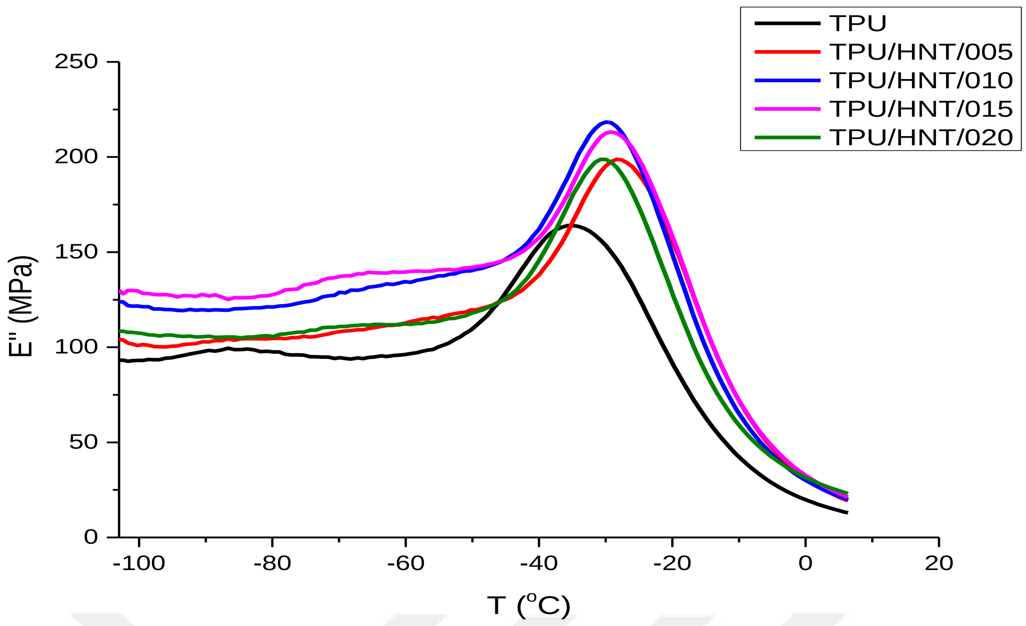

Figure 17 Loss modulus E'' versus temperature data for TPU/HNT

All composites show almost identical and higher loss modulus values as compared to pristine TPU according to Figure 17. The highest lost modulus is observed in 1.0% HNT containing composite. This result may due to increase in stress transfer between halloysite nanotubes and TPU matrix [31].

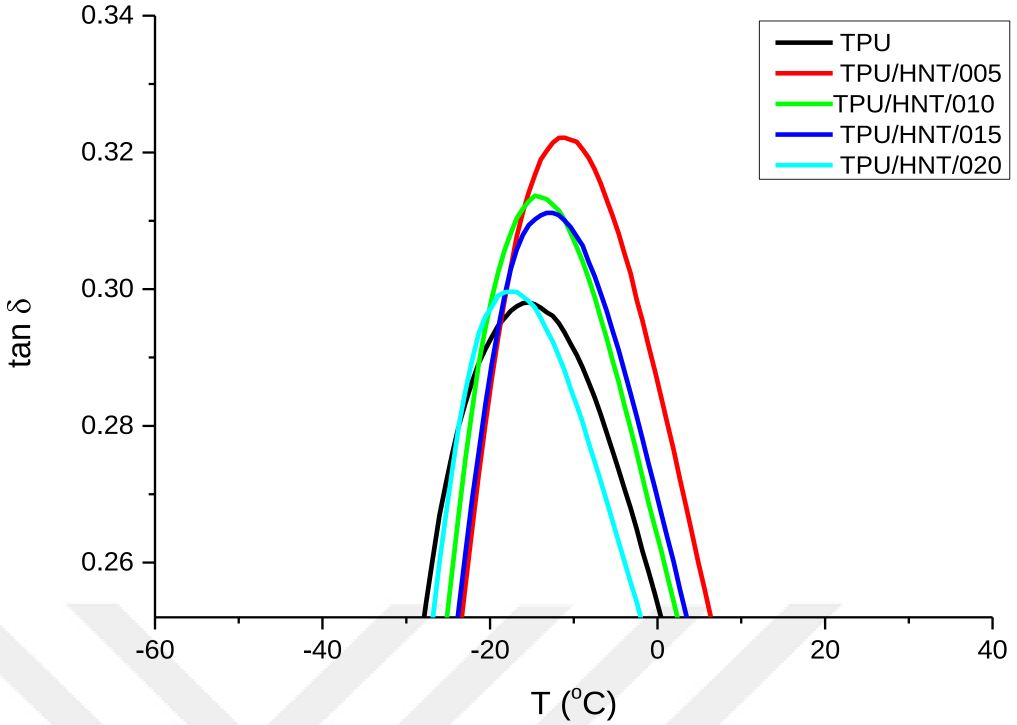

Figure 18 Tan δ of TPU/HNT composites as a function of temperature

As seen in Figure 18, all composites give higher tan δ values than that of TPU. It is also seen that peak values of tan δ shifts higher temperatures with the additions of HNT into TPU matrix. The highest T_g is observed in the lowest HNT concentration (0.5%).

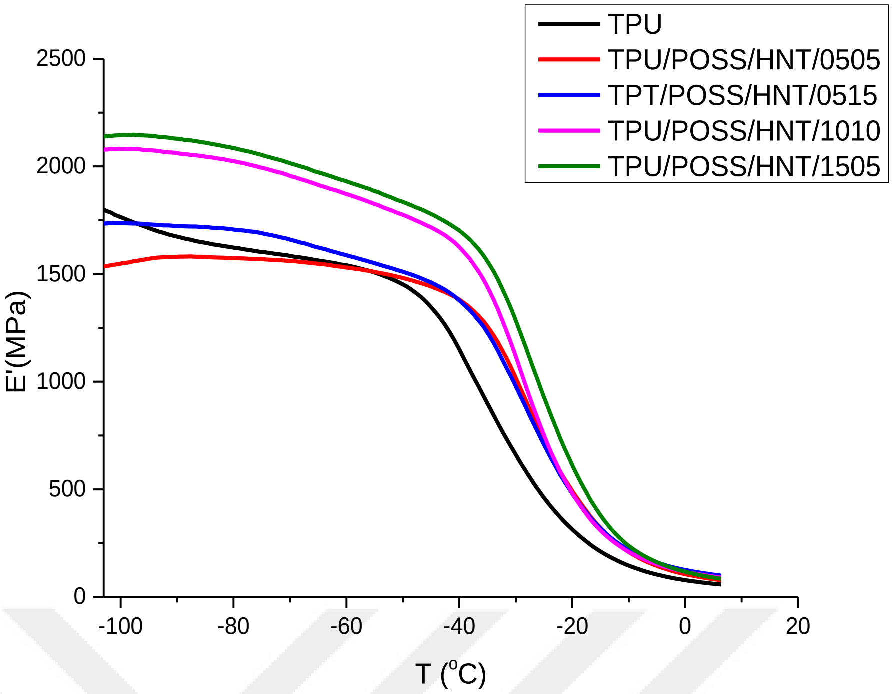

Figure 19 The dynamic storage modulus of TPU/POSS/HNT hybrid composites as a function of temperature

Figure 19 shows that storage modulus of hybrid composites are higher than that of TPU. Storage modulus curves of hybrid composites display the sharp displacement to higher temperatures according to T_g of TPU. Storage modulus values and temperature shifting are getting higher with increase in POSS concentration in hybrid composites. Possible physical interactions such as hydrogen bonding between POSS nanoparticles and TPU matrix may be the reason of these improvements in storage modulus [32].

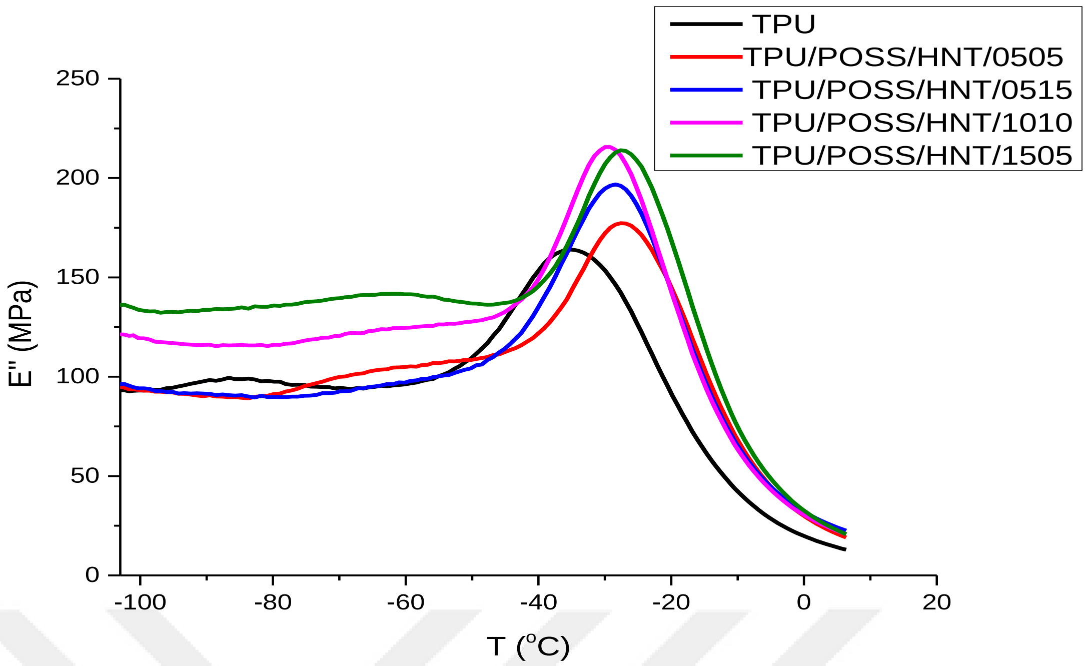

Figure 20 Loss modulus E'' versus temperature data for TPU/POSS/HNT

It is seen from the Figure 20 that all of the hybrid composites give higher loss modulus values as compared to unfilled TPU. The higher loss modulus values are observed in higher loadings of POSS nanoparticles. This result is similar with previous result of storage modulus.

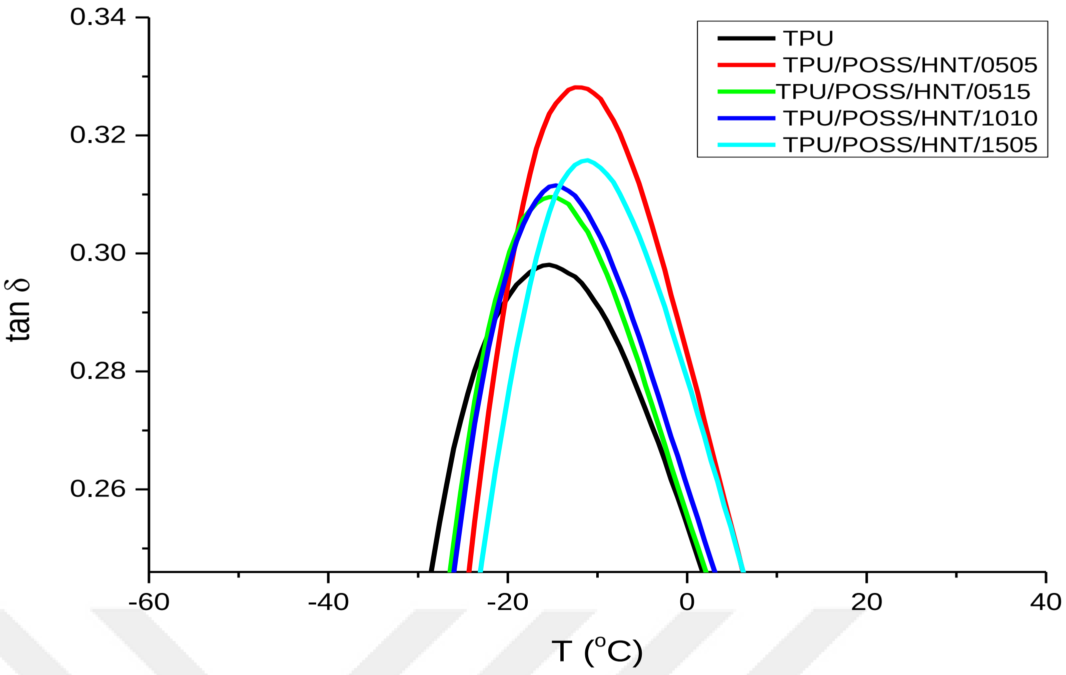

Figure 21 Tan δ of TPU/POSS/HNT hybrid composites as a function of temperature

All of the hybrid composites exhibit improvements in tan δ values and peak tan δ values as seen in Figure 21. The highest increment in tan δ is observed in the lowest HNT and POSS containing composite that may due to more homogeneous dispersion as compared to other hybrid ones.

3.6 SEM Analysis

To investigate the scattering of morphological structures like fillers in polymer nanocomposites, image-processing method on 3D scanning electron microscopy image of the polymer nanocomposites was utilized. In other words, the impacts of surface treatments on the composites morphology are established by SEM. By means of accurate analysis of SEM images, one can quantify shape and size of the morphological structures more accurately.

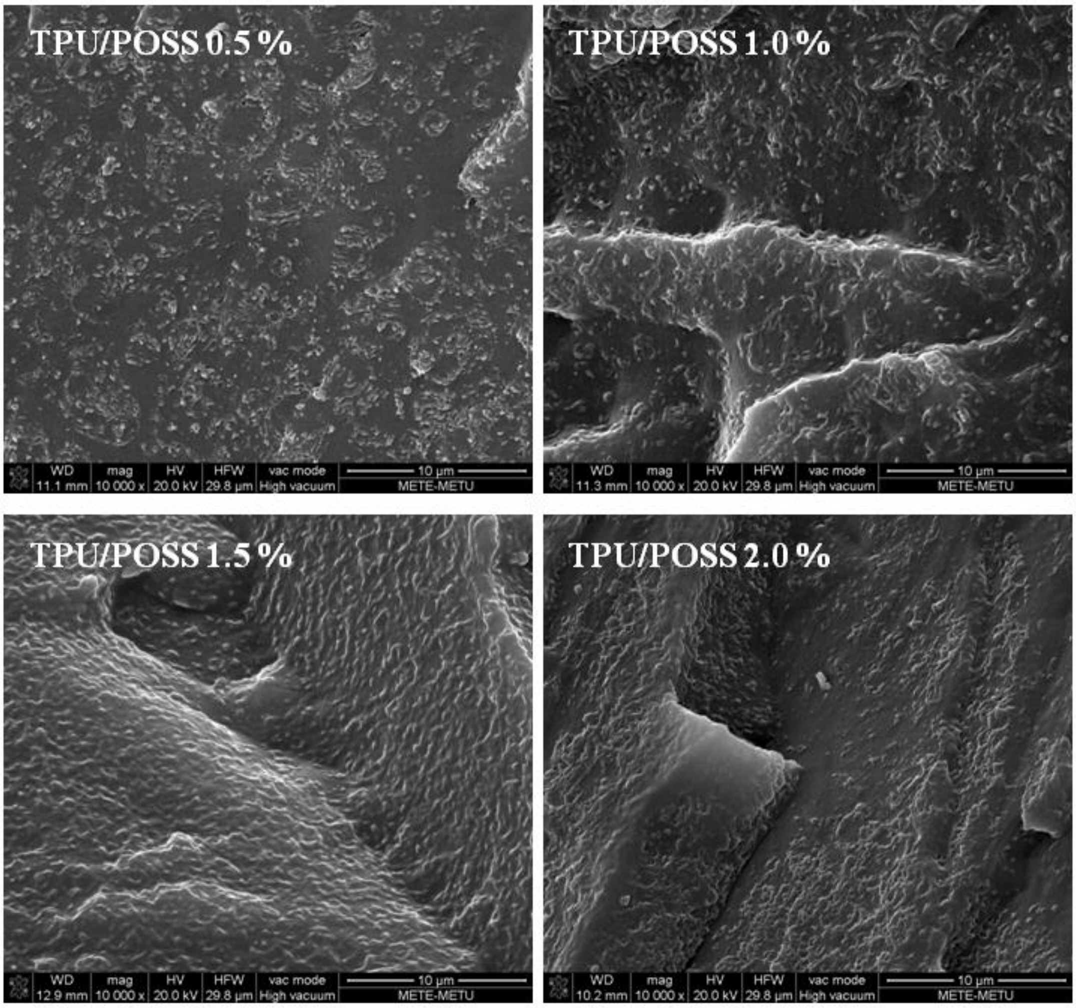

Figure 22 SEM images of TPU/POSS composites with 10,000 magnifications

As represented in Figure 22, POSS nanoparticles are homogeneously dispersed in TPU matrix for the lowest loading (0.5%). Further additions of POSS cause formation of agglomerations. Agglomerates can be clearly identified in micro images of 1.5% and 2.0% POSS containing TPU composites. These observations are consistent with the mechanical test data discussed earlier sections.

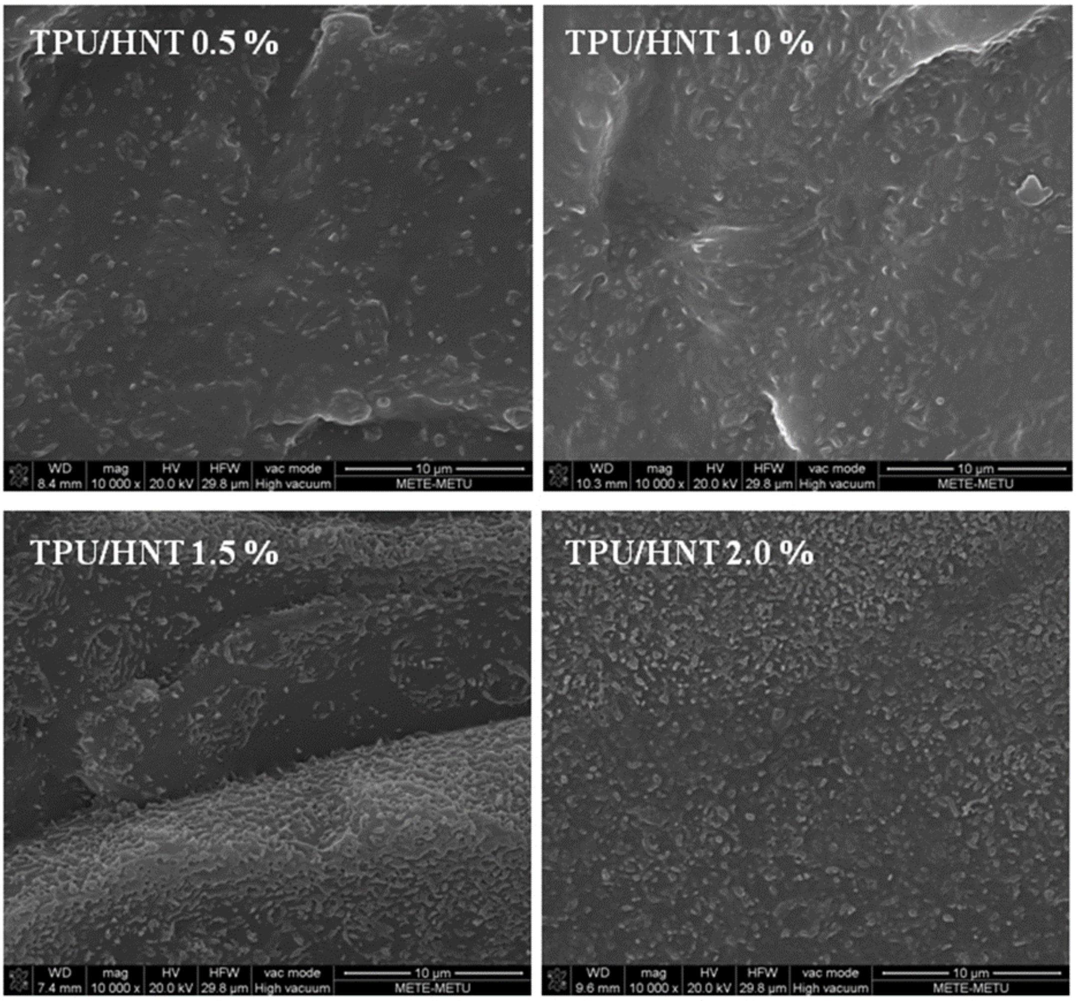

Figure 23 SEM images of TPU/HNT composites with 10,000 magnifications

HNT fibers display homogeneous dispersion in TPU matrix for their 0.5% concentration as seen in Figure 23. Nanotubes tend to interact themselves after that loading level. Formation of bundles can be clearly observed in 1.5% and 2.0% concentrations of HNT containing TPU composites from their micro images given in Figure 21. Observation of well-dispersion of HNT in the lowest loading level is in accordance with mechanical test and DMA analysis data which mentioned in earlier sections.

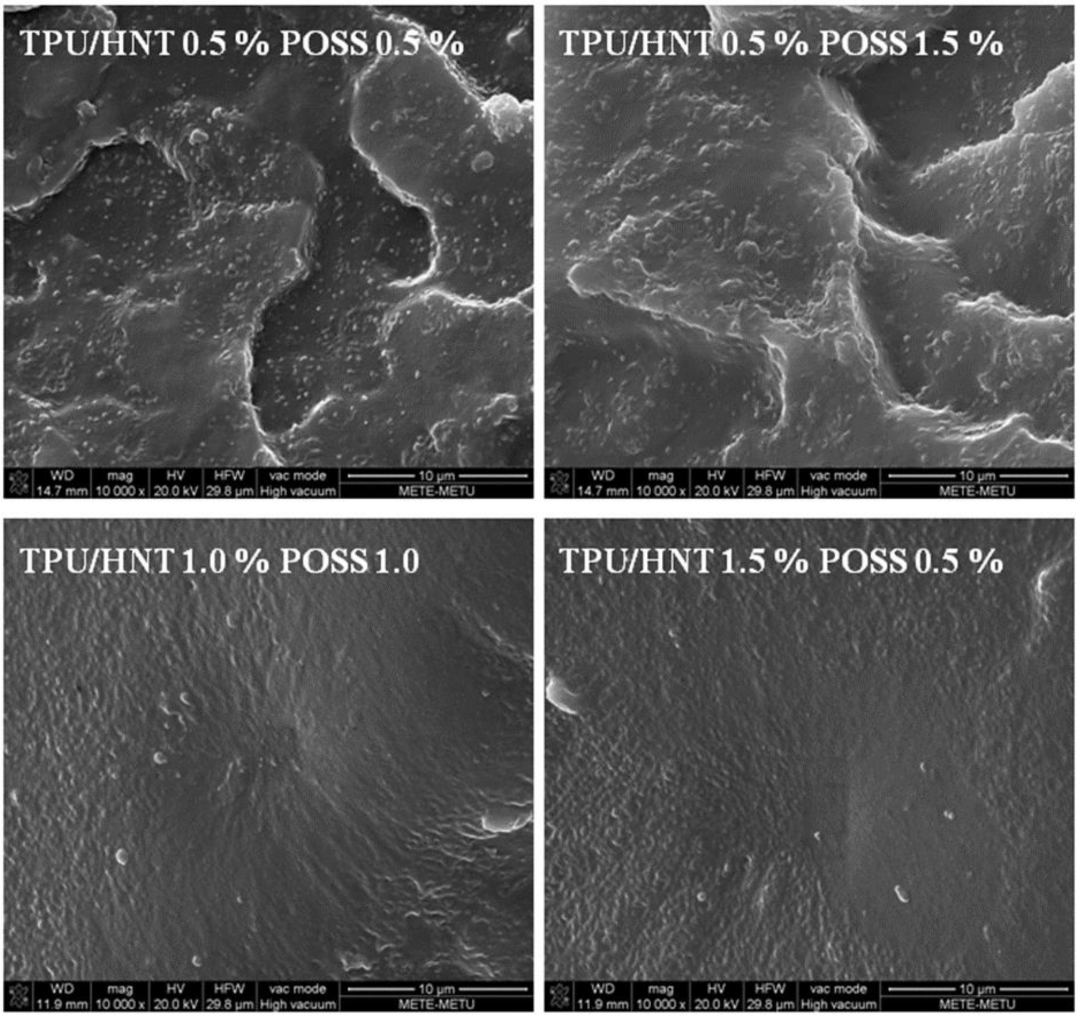

Figure 24 SEM images of hybrid composites with 10,000 magnifications

SEM images of fractured surfaces of hybrid composites are given in Figure 24. HNT and POSS nanoparticles seem to be well-mixed in image of TPU/0.5% POSS 0.5%HNT hybrid composite. Homogeneity of their mixing in TPU matrix decreases as the concentrations of POSS and HNT increase.

CHAPTER IV

CONCLUSION

In this study, both polyhedral oligomeric silsesquioxane (POSS) and halloysite nanotubes (HNT) were added to thermoplastic polyurethane (TPU) matrix, individually and together in hybrid form. Processing methods were chosen as melt mixing and injection molding for the purpose of practical adaptation to large-scale composite applications. The mechanical, flow, thermomechanical, and morphological characterization of produced composites were examined via tensile and hardness tests, impact test, melt flow index test, DMA analysis and scanning electron microscopy (SEM) techniques respectively.

The over-all results revealed that the optimum values for POSS, HNT and hybrid form were found as 0.5%, 0.5% and 0.5% HNT- 0.5% POSS, respectively. The maximum tensile test values were obtained at 0.5% POSS, and 0.5% POSS -0.5% HNT filling ratios as impact strength and glass transition temperatures estimated were obtained in this optimum compositions of composites. Further additions of these fillers have resulted in agglomerations for both POSS and HNT particles and bundle formations according to SEM micrographs. Such reformation has led to restriction of their homogenous distribution in the TPU matrix. MFI test results displayed that POSS 1.5% -HNT 0.5 % filled hybrid composites gave lower MFI values, attributing to higher surface area of hybrid composites at these percentages.

Even though, the main target was to obtain better overall properties in the case of hybrid forms of HNT and POSS, additions of these fillers resulted in generally lower mechanical properties.

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