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Makale / Research Paper

Mechanical Properties and Damage Behavior of MWCNT Reinforced Polyurethane Nanocomposites

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Abstract: Nanomaterials have been developed as an alternative to composites due to their superior mechanical properties, thermal stability and lightweight. In this study, tensile and hardness tests on different proportions of multi-walled carbon nanotube (MWCNT) reinforced/unreinforced polyurethane nanocomposite materials under static loading were investigated. They were prepared according to ASTM D638 standard and reinforced with MWCNT with the mass ratio of 0.25%, 0.35% and 0.45%. Their modulus of elasticity, tensile strength, toughness, elongation and hardness values were compared with those of pure polyurethane. The hardness measurements were carried out according to the Shore D scale. While the tensile strength and modulus of elasticity of the pure polyurethane materials were 20.94 MPa and 0.601 GPa, the values of the polyurethane nanocomposite materials reinforced with 0.35% MWCNT was 23.21 MPa and 1.077 GPa. The reinforced MWCNTs increased these values by 11.0% and 0.79, respectively. In addition, fractured surfaces were examined using a scanning electron microscope (SEM) to determine the damage mechanisms.

Keywords: MWCNT, Polyurethane, nanocomposite, mechanical properties, damage mechanisms

MWCNT Takviyeli Poliüretan Nanokompozitlerin Mekanik Özellikleri ve Hasar Davranışları

Öz: Nanomalzemeler sahip oldukları üstün mekanik özellikler, ısıl kararlılık ve hafiflik gibi özelliklerinden dolayı kompozit malzemelere alternatif olarak geliştirilmiştir. Bu çalışmamızda, ağırlıkça farklı oranlarda çok cidarlı karbon nanotüp (MWCNT) takviyeli/takviyesiz poliüretan nanokompozit malzemelerin statik yük altında çekme ve sertlik testleri yapılarak sonuçları incelendi. Ağırlıkça % 0.25 ,% 0.35 ve % 0.45 oranlarında MWCNT takviyeli poliüretan nanokompozit malzemeler ASTM D638 standardına göre hazırlanarak, elastiklik modülü, çekme dayanımı, tokluk, birim şekil değişimi ve sertlik değerleri saf poliüretan ile karşılaştırılmıştır. Sertlik ölçüm testleri Shore D skalasına göre yapılmıştır. Saf poliüretan malzemenin çekme dayanımı ve elastiklik modülü sırasıyla 20.94 MPa ve 0.601 GPa iken ağırlıkça % 0.45 oranında MWCNT ilave edilmiş poliüretan nanokompozit malzemelerde % 11.0 ve % 79.0 artış oranıyla çekme dayanımı 26.80 MPA ve elastiklik modülü 1.077 GPa elde edilmiştir. Ayrıca hasar mekanizmalarını belirlemek için kırık yüzeyler Taramalı Elektron Mikroskobu (SEM) ile incelenmiştir.

Anahtar Kelimeler: MWCNT, poliüretan, nanokompozit, mekanik özellikler, hasar mekanizmaları

1. Introduction

Polyurethane (PU), which is one of a variety of polymer derivatives used to make polymer-based nanocomposite materials with carbon nanotubes (CNTs), has properties such as chemical resistance, abrasion, hardness, elastic modulus, tensile strength, and high resistance to maximum elongation at break, among others. They are characterized [1, 2]. These properties are used in many industries such

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as electronics, medicine, aerospace, automotive, and marine [3-6]. PU structure is generally the molecular weight, crosslinking ability, hard and soft segments i are determined by. Hydrogen bonding in polyurethane improves the physical bonding between polymer chains to improve overall performance and properties. Segments of hard and soft polyurethane segments can cause phase separation. In recent studies, nanoparticles, nanowires and nanofibers have been added to PU polymers to improve their mechanical properties [7-9]. It can also add polymers such as PU, polymethyl methacrylate (PMMA), epoxy, boron nitride nanoplatelets, nano silica, carbon nanotubes, etc. The addition of nanoparticles has enhanced the electrical, acoustic, abrasion resistance and other characteristic properties and studies on polymer nanocomposite materials have been widely published [10-12]. The main reasons for using CNTs as reinforcement in the polymer matrix are: low density, high flexibility, high aspect ratio, high strength to weight ratio, excellent thermal and electrical properties [13]. To produce an effective nanocomposite, good dispersion and distribution of CNTs in the polymer is necessary to ensure damage mechanisms such as stress transfer and to stop crack propagation [14, 15].

Numerous methods have been developed in the scientific community for the preparation of CNT-based polymer nanocomposites. These methods include in situ polymerization of monomers in the presence of CNTs, direct mixing, electrospinning, melt mixing, and solution mixing. It is very difficult to mix CNTs directly into the polymer matrix, to establish a strong interfacial bond between the CNTs and the polymer, and to achieve homogeneous distribution [16]. Otherwise, agglomeration occurs in carbon nanotubes, poor wettability, etc. weak interactions have negative effects on the charge transfer of the polymer used [17].

In this study, multi-walled carbon nanotube (MWCNT) reinforced/non-reinforced polyurethane nanocomposite materials were produced at 0.25, 0.35 and 0.45 wt% were prepared and their mechanical properties were investigated. The samples were prepared in accordance with ASTM D638 standard. The tensile strength, elastic modulus, toughness, strain and hardness values of the polyurethane nanocomposites were compared with those of pure polyurethane. After the test, Scanning Electron Microscopy (SEM) was used to examine the damage mechanisms of the fracture surfaces such as bridging, pull out, crack branching and deflection of nanoparticles.

2. Material and Method

2.1. Material

In this study, a solvent-free, two-component polyurethane-based adhesive with a viscosity of 2 100 mPa, coded KLB 75, was used as the polyurethane hardener. The mixing ratio of polyol urethane and isocyanate hardener is 80/20 by weight. MWCNTs were produced by NANOCYL company by a chemical vapor deposition method. They have a diameter of 5-50 nm and a length of 10 to 30 µm.

2.2. Method

As shown in Figure 1, the preparation of MWCNT-reinforced polyurethane-based nanocomposites with different weights is schematically illustrated. First, the polyurethane was weighed out to 40 g in a beaker on a precision balance. Then, 0.25 and 0.35 wt% of the polyurethane polymer MWCNTs were placed on the aluminum foil, weighed on a precision balance and carefully added to the polyurethane beaker. Acetone was added to this prepared mixture in an amount of 1/100 g/ml, based on the weight of MWCNTs in the beaker, to reduce the viscosity and ensure a more homogeneous dispersion. 10 min with the probe homogenizer. Mixing was done 3 times for a total of 30 min. This is done at intervals so that the nanoparticles and polymer are not damaged by heat. To remove air bubbles and acetone from the mixture, it was then kept in a vacuum oven at 60 °C and a pressure of 10 incHg for 12 hours. With the acetone evaporating, the vacuum was increased back to the same pressure in pressure drops. Polyurethane/hardener was added in the ratio of 80/20 determined by the manufacturer and mixed mechanically for at least 10 minutes without air bubbles. Finally, this mixture was ready for use by vacuuming again for 15 minutes at a pressure of 10 inchHg to remove the air bubbles created by mechanical mixing.

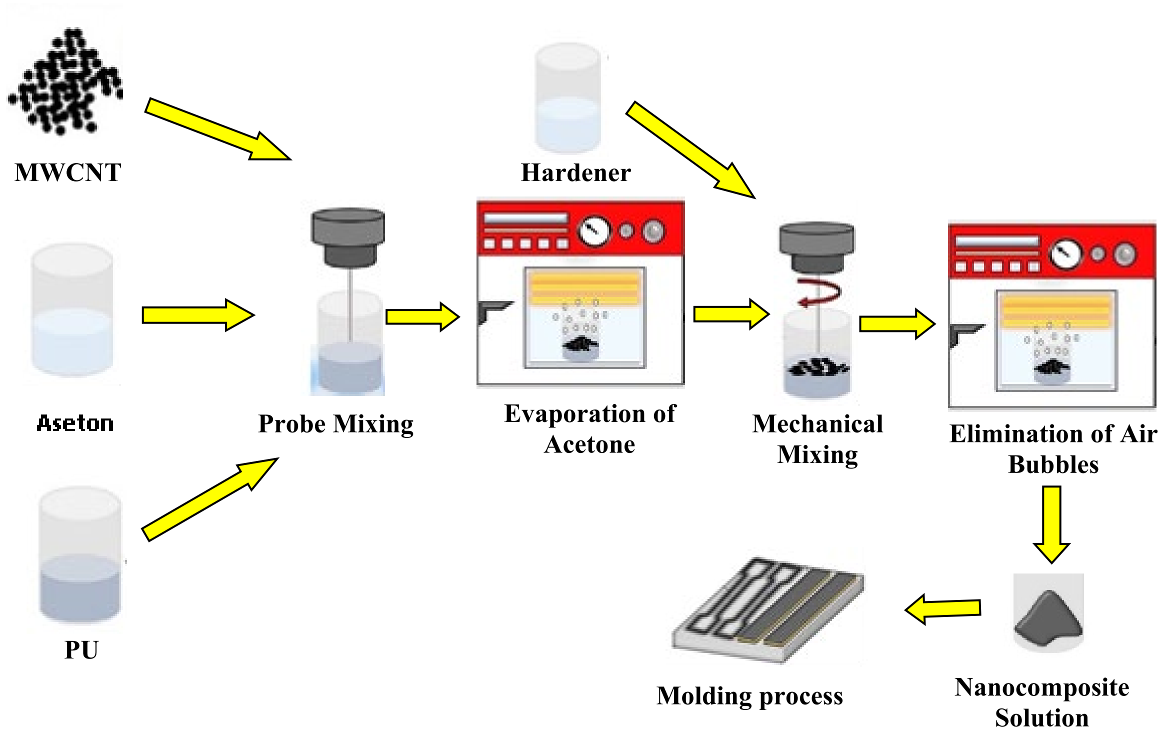

Figure 1. Production scheme of MWCNT reinforced PU nanocomposite materials

For tensile testing, it was applied to prepared steel molds measuring 4x6x115 mm according to ASTM D638-10 standard, using wax to form a thin film to prevent the polyurethane polymer from sticking. The mixture of polyurethane nanocomposite with/without additives prepared in these composite molds was poured slowly (Figure 1). After casting, the mold was kept at room temperature for 168 hours for tensile testing, according to the manufacturer's recommendation for curing. To ensure the reliability of the test results, 5 specimens with the same properties were prepared. After curing, the top surface of the tensile specimen was sanded with 360 grit silicon carbide sandpaper in the tensile direction to eliminate the size differences on the top surface.

2.3. Characterization

The tensile test on the specimens was carried out using Shimadzu AGS-X universal tensile tester at a tensile speed of 2 mm/min in accordance with ASTM D638-10 standard. All tests were conducted at room temperature. Measure the length of the load applied to the specimen up to the strain at break in the Epliso Model 3560 biaxial dynamic extensometer to determine the Poisson's ratio and modulus of elasticity.

The hardness measurements of the fabricated composite panels were carried out with Shore Durometer hardness tester TH 210 using a measuring tip with a diameter of 1.40 mm, a taper angle of 30° and a radius of 0.1 mm according to ASTM D2240 standard. The hardness values are expressed in Shore values (Shore D) by taking the arithmetic mean of the measurements of at least 5 points for each sample.

3. Results and Discussion

3.1. Hardness Tests of Nanocomposite Materials

As a result of the researches in the literature in determining the ratios of multi-walled carbon nanotubes, it appears that it is difficult to distribute them homogeneously in the polyurethane, so ratios between 0.5 and 1 are generally preferred for infiltration threshold values [15, 16]. The mechanical properties of both composites and nanocomposites materials improve infiltration threshold values. Hardness measures how resistant a material is to deformation when compressive loads are applied. The increase in hardness is attributed to the good dispersion of MWCNTs in the polyurethane matrix. Homogeneously dispersed MWCNTs can shorten the distance between crosslinking points, which increases the crosslinking density of the matrix and plays a positive role in improving the mechanical properties [17].

The Shore hardness of MWCNT reinforced polyurethane nanocomposites is shown in Figure 2. While the hardness value of polyurethane resin was 78 Shore D, the hardness value of 0.25 wt.% MWCNT reinforced polyurethane nanocomposite material was 81 Shore D, which is an increase of 3.85%. The increase in the hardness of the nanocomposites with the increase of MWCNT addition results from the (i) superior mechanical properties of the carbon nanotubes; their tensile strength is 10-60 GPa, elasticity is 1 TPa, and (ii) their high surface-to-volume ratio is attributed. However, as the nanoparticles agglomerated after the infiltration threshold, a decrease in the hardness value of 0.35% and 0.45% MWCNT-reinforced polyurethane nanocomposites by weight was observed.

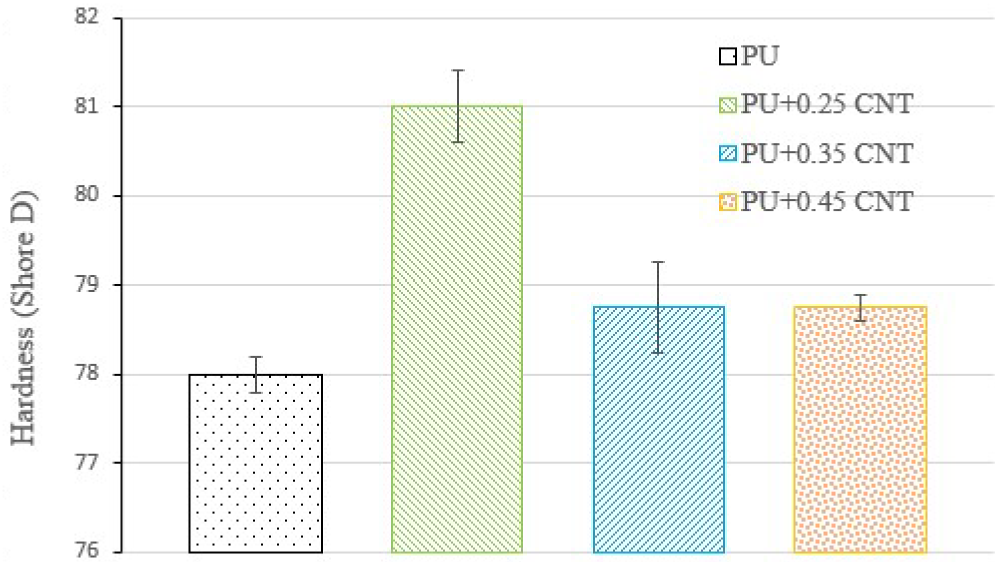

Figure 2. Hardness values of nanocomposites

The addition of nano additives can effectively increase the bonding strength between the polyurethane matrix and the additives. Homogeneous dispersion of the additives increases the stiffness of the polymer composite. The improvement in stiffness is mainly due to the formation of a three-dimensional network with a homogeneous and gradual distribution of carbon nanotubes in the polymer matrix [18].

The polyurethane matrix, which is a thermosetting polymer, bridges the MWCNT defects during crosslinking, charge transfer takes place from the matrix to the carbon nanotubes, and the hardness value of the polyurethane increases. The reason for the decrease in hardness values at higher additive levels is that the agglomerations that occur cause an increase in voids that occur during production [19, 20].

3.2. Tensile Tests of Nanocomposite Materials

Figure 3. the stress-strain diagram obtained as a result of tensile tests of MWCNT reinforced polyurethane-based nanocomposites under constant load is shown. The tensile strength of the polyurethane resin is 20.93 MPa. The tensile strength of 0.45% MWCNT reinforced polyurethane nanocomposite by weight was 26.63 MPa with an increase of 27.23%. The tensile strength of the polyurethane nanocomposite materials increased with the increase of MWCNT addition. However, the strain of the polyurethane sample is 0.0 73 mm/mm, while 0 wt% 35 MWCNT reinforced nanocomposite was obtained 0.024 mm/mm. It was found that the polyurethane nanocomposite materials exhibited brittle behavior by decreasing the strain by increasing the MWCNT addition. However, it was found that the strain of 0.45% MWCNT reinforced polyurethane nanocomposites increased by 0.063 mm\mm.

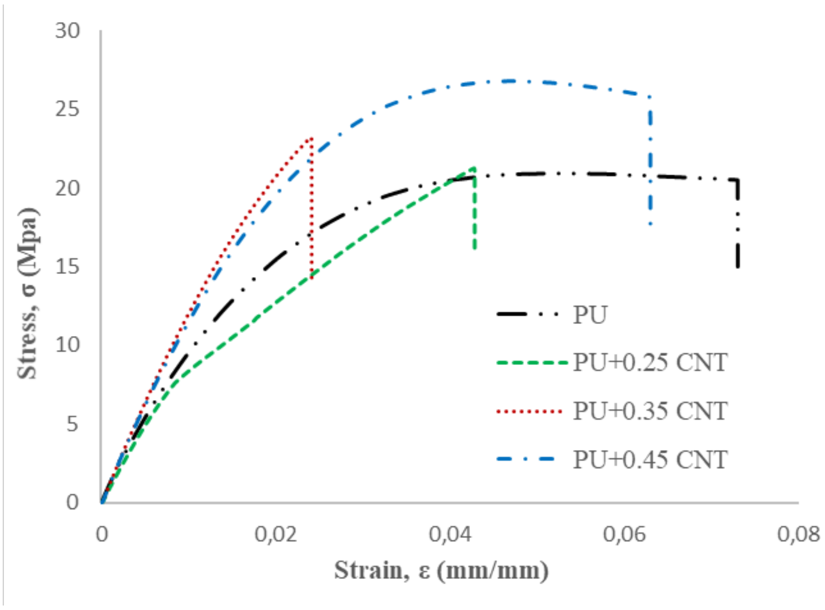

Figure 3. Nanocomposites stress-strain graph of change

Table 1. Mechanical properties of MWCNT reinforced PU nanocomposite materials

Sample	Max load (N)	Tensile stress (MPa)	Modulus of elasticity (GPa)	Toughness (kJ/m^3)	Poisson's ratio
PU	565.18	20.93±0.21	0.849	1236	0.16
PU+0.25 CNT	1492.03	21.25±0.16	0.431	545	0.22
PU+0.35 CNT	571.08	23.21±0.12	1.149	320	0.36
PU+0.45 CNT	643.19	26.80±0.20	0.995	1306	0.40

Maximum loading, tensile stress, modulus of elasticity, toughness and Poisson’s ratios of MWCNT reinforced PU nanocomposite materials are given in Table 1. When the Poisson’s ratios were examined, it was found that while the PU polymer was 0.16, it was 0.40 for the MWCNT reinforced PU nanocomposite at a rate of 0.45% by weight. Poisson's ratio, modulus of elasticity and tensile stress increased with the addition of MWCNT.

The maximum tensile strength of the PU+0.45 MWCNTs modified nanocomposite sample was 26.80 MPa, increasing by 28% compared to the Polyurethane polymer. In addition, adding 0.45% by weight of MWCTs to the polyurethane polymer improved both the modulus of elasticity and the toughness.

3.3. Damage Mechanisms of Polyurethane Nanocomposites

As reported in the literature, the mechanical strength of the composite depends on the homogeneous distribution of MWCNTs in the polymer matrix. Therefore, it becomes quite important to study the distribution of MWCNTs across the matrix. In Figure 4, SEM images of the fractured surfaces after the tensile test of MWCNT reinforced PU nanocomposites are given at 20 KX magnification. As a result of the observations, it was observed that the uniform distribution throughout the matrix was successfully achieved. The mechanical properties of nanocomposites, and especially tensile strength, are affected by the presence of defects, voids, often agglomerations and other residues that help initiate fracture [18].

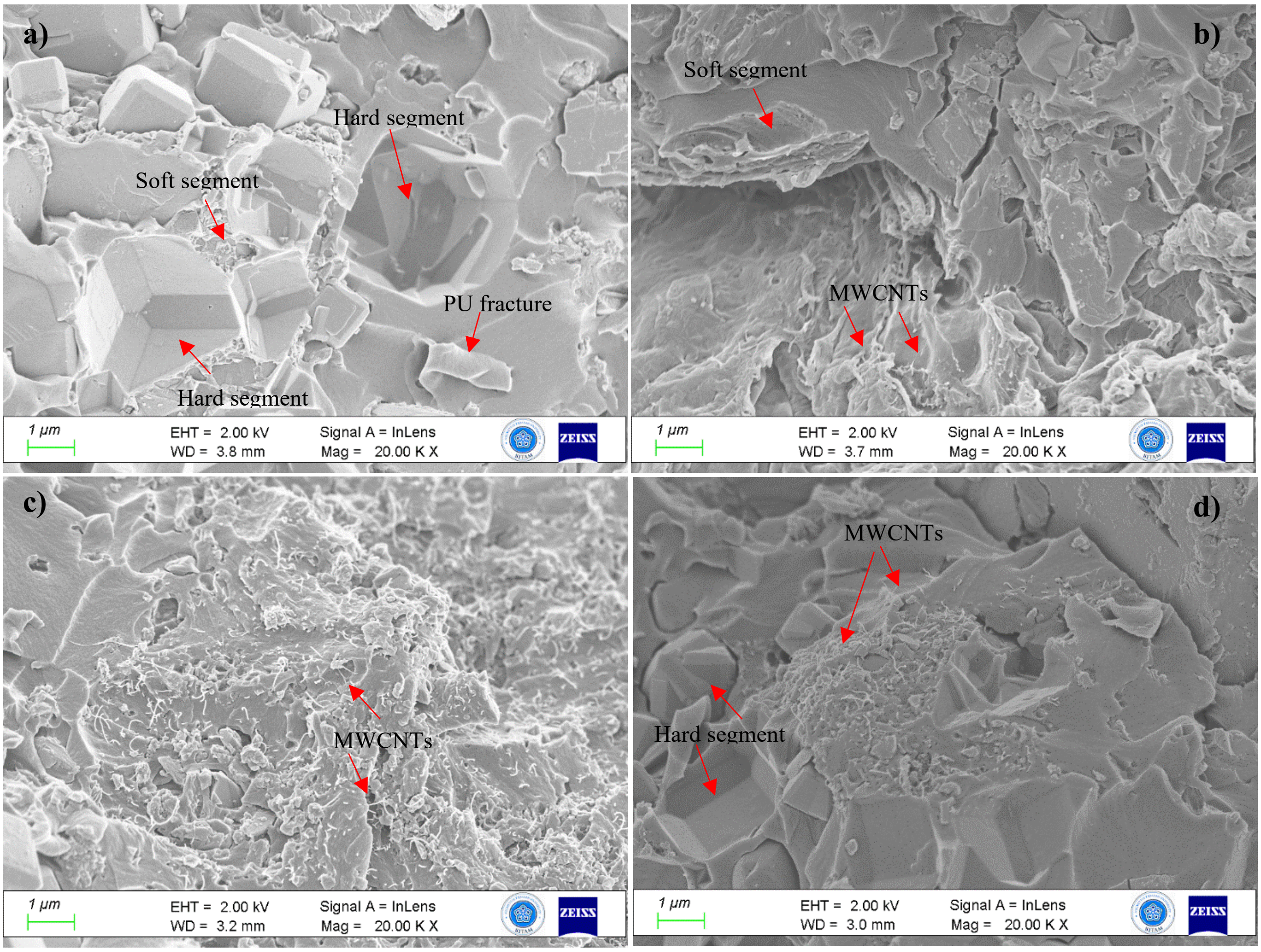

Figure 4. SEM images of nanocomposites; a) PU, b) PU+0.25 CNT, c) PU+0.3 5 CNT and d) PU+0.45 CNT

PU samples' damage mechanisms' soft and hard segments that originated from the structure of PU are seen in Figure 4.a. In addition, hard segments are seen more intense than soft segments. For this reason, plastic frature occurred as the dense hard segments created a pin effect as the damage mechanism in the PU specimen.

The addition of MWCNTs has the effect of increasing the fracture toughness and tensile strength of PU. As can be seen, the toughness and modulus of elasticity of the polyurethane were improved by about 6 and %18, respectively, by the addition of %0.45 by weight CNTs. Investigating these behaviors requires a comprehensive understanding of the damage mechanisms associated with these nanocomposite materials. It has been reported that the dominant damage mechanisms identified in polyurethane/CNT nanocomposites are bridging, pull out, fracture of MWCNT and crack deflection [19]. Figure 4 b, c and d, by weight of %0.25, 0.35 and 0.45 CNT of the fracture surface when viewed CNTs bridging, CNTs are pulled out and the crack deflection thermoset polyurethane / multi-walled carbon nanotube nanocomposite damage the mechanism behaves conclusion can be reached.

As a result, crack deflection was observed by examining transversely growing cracks, in which the CNTs changed the crack propagation direction in the tensile direction. The bridging mechanism is observed perpendicular to the pull direction, which prevents crack opening and increases the energy for crack propagation in the matrix. The pull-out of both CNTs and hard segment at the fracture surface indicates that the bridging CNTs eventually separate from the crack plane.

4. Conclusions

In this study, we proposed a method to improve the mechanical properties of MWCNT nanoparticles by adding different ratios of MWCNT nanoparticles into the polyurethane polymer using the solution mixing method. In the production of nanocomposites, the use of nano-sized MWCNT reinforcements with excellent properties enabled us to obtain polyurethane-based nanocomposites with better mechanical properties.

The tensile strength of the polyurethane nanocomposite improved by 27% with 0.45% wt. MWCNTS. It was concluded that nanoparticle reinforcement can be used to increase strength. However, the addition of MWCNTs changed both the type of fracture (Poisson's ratio) and decreased the strain. The Shore hardness value of 0.25 wt% MWCNT reinforced polyurethane nanocomposite showed an increase of 3.85% compared to the hardness value of polyurethane resin.

When the SEM images of the nanocomposites were examined, it was seen that the MWCNTs improved the damage mechanisms. The pull-out of both CNTs and hard segment at the fracture surface indicates that the bridging CNTs eventually separate from the crack plane.

Authors' Contributions

Manuscript preparation is done by MRK. MRK prepared the first draft of the article. NY visualized and collected data for the article. ME is the inventor of the original device and the overall supervisor of the project. All the authors read and approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

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