Effect of Alumina Nanoparticles on the Enhancement of Shape Memory, Mechanical and Impact Properties of TPU/ABS blend

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Abstract
In this paper, the shape memory, mechanical and Izod impact properties of a new shape memory nanocomposite based on thermoplastic polyurethane (TPU), acrylonitrile butadiene styrene (ABS) and alumina nanoparticles were investigated. The morphological results showed that the presence of 1% alumina nanoparticles made a reduction in diameter of ABS domains and caused a uniform distribution of the ABS phase into the TPU matrix. Surprisingly, the addition of 2 and 3% alumina made the ABS domain larger. We found that this increment in size of droplets can be attributed to the nanoparticle migration into ABS phase in more concentration and agglomeration of nanoparticles which can worsen the compatibility of the blend. In all samples, the tensile strength and impact resistance first increased and then decreased significantly when the content of alumina was more than 1 wt%. Furthermore, the shape memory investigation showed that the shape recovery and fixity of neat TPU/ABS blend improve significantly by presence of alumina nanoparticles. The shape recovery ratio increased from 93.88% for the neat TPU/ABS to 98.99% by loading only 1 wt% nano alumina and, the shape fixity changes from 92.98% to 99.8% by loading 3% alumina nanoparticles.

Keywords: Thermoplastic polyurethane; Acrylonitrile butadiene styrene; Alumina nanoparticles; shape memory

1.Introduction

Shape memory polymers (SMPs) are one classification of smart and adaptive materials which can response to different stimuli, such as, temperature, electric, light, chemical or magnetic fields, and recover from a deformed shape to their original shape [1]. Since SMPs have significant advantages like, low density, low cost, high deformation, and controllability of recovery temperature compared to shape memory alloys and ceramics, they have attracted significant attention from academia and industries during the past two decades [2]. SMPs can be employed in diverse applications like medical equipment, mechanical actuators [2], car accessories and morphing wings in aerospace industry [3], self-folding machines [4], self-assembly robots [5], crawling robots [6] and shape memory hybrids [7]. Despite SMPs have a lot of advantages they also have some important shortcomings which can seriously limit their applications in broader fields. The important shortcomings of SMPs are their low strength and stiffness. To improve the mechanical properties of shape memory polymers and also to achieve polymers with the new functionality, which will respond to different stimuli, two general solutions is considered. One simple method is to add high modulus organic or inorganic fillers in micro and nano-scales and the other solution is blending two or more polymers. Generally the composite manufacturing as well as polymer blending targets are: improving the mechanical

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properties and recovery stress, reducing the recovery time by increasing thermal conductivity, producing a new polymer blend with shape memory properties, controlling the transmission temperature and mechanical properties, and also producing a new SMP which can respond to other stimuli such as humidity, electricity, magnetism or light [8].

One of the most popular thermo-responsive SMPs is thermoplastic polyurethane (TPU) which is known due to good elongation, high abrasion resistance and excellent low-temperature properties [3, 9-13]. TPU like the other polymers has low strength and stiffness. In terms of polymer blending TPU is blended with various polymers in order to make a new SMP with improved mechanical properties. The main reported studies showed that TPU is blended with Phenoxy resin [14], Polyvinylidene fluoride (PVDF) [15], Poly (ε -Caprolactone) (PCL) [16], Polybenzoxazine (PB) [17, 18], Polypyrrole (PPy) [19], poly butylene terephthalate (PBT) [20], poly vinyl chloride (PVC) [21, 22] ,poly lactic acid (PLA) [9, 23-25], and Acrylonitrile butadiene styrene (ABS) [26].

In terms of using fillers, nanofillers due to their large surface area can improve the mechanical properties of composites significantly. It means that because of high surface-to-volume ratio of nanofillers, the interfacial area between phases in nanocomposite is larger than traditional composites. So more physical and chemical bonding between the nanofiller surface and polymer matrix magnify the interfacial interaction and as a result, improve the mechanical performance of nanocomposite [27]. As we know the shape (spherical, cylindrical, platelet) and size of particles and also their aspect ratio plays an important role in the mechanical performance of the nanocomposites. Reports have shown that the spherical nanoparticles such as alumina, silica, silicon carbide can increase the toughness and fracture toughness of polymers [28]. Research in the early 92's indicated that mineral nanoparticles which have silicon in their structures, reduce the shape memory effect even in low weight percentage [29]. GAL et al.[29] reported that shape memory effect of epoxy polymer which is reinforced with silicon carbide decreased significantly, while It's mechanical properties and recovery stress increased. In another study, polyurethane co-polymer with Tetraethoxysilane (TEOS) is produced using sol-gel method [30]. In this nanocomposite, mechanical properties and recovery force increased without the negative impact on the shape memory effect [30]. Also, the other report indicated the negative impact of silicon carbide nanoparticles on the polyurethane shape memory effect [29]. Silicon carbide nanoparticles have a negative influence on the shape memory effect of polyurethane due to decreasing soft segment of polyurethane[31, 32]. Celite is a spherical nanoparticle which is made from the combination of silica and alumina [33]. This material has the hydroxyl chain which probably has a reaction with polyurethane chains [3, 29]. Celite/ polyurethane nanocomposite is made using in situ polymerization. The incredible mechanical and shape memory properties were obtained by only 0.2% wt% of celite [33]. Also in another report, alumina and silica spherical particles were utilized in order to reinforce the crosslinking polystyrene co-polymer. This nanocomposite which is reinforced with alumina showed higher young's modulus and yield stress due to the inherent higher stiffness of these Particles while its failure strain is lower than nanocomposite which is reinforced with silica [1].

The main objective of this study was to construct a new SMP with the compounding of thermoplastic polyurethane and acrylonitrile butadiene styrene. Alumina nanoparticles are used as spherical fillers in this polymer blend. The effect of this nanoparticle on mechanical, shape memory and morphological properties of this new SMP are investigated.

2. Material and Methods

Thermoplastic polyurethane (TPU), (grade Desmopan 385S) was supplied by BAYER company. Acrylonitrile Butadiene Styrene (ABS), (grade SD0150) was purchased from Tabriz petrochemical company (Iran). The density of TPU and ABS are 1.2 and 1.06 g/cm³. Also, the NANO-ALUMINUM OXIDE (crystal phase Gamma) was purchased from neutrino company (average particle size 10 to 20nm, specific surface area 90-160 m^2/g and density 3.65$g/_{cm^3}$).

1.2 Nanocomposite preparation

In the present study, a new composition of TPU and ABS (80:20 wt%) were melt blended with a different amount of alumina (0.5 to 3 wt%), a kind of spherical nanoparticle, as a reinforcement. All the above materials were dried in the oven at 100°C for at least 6 hours in order to remove any possible moisture.

Brabender internal mixer model W50 is chosen for nanocomposite preparation. To start the mixing process, first TPU was pre-mixed with alumina about 5 minutes. Then ABS granules were added and finally they were mixed together for about 10 minutes. The mixer temperature and the rotor speed were set up at 195°C and 60 rpm, respectively. Then the obtained polymer blend was compression molded under the pressure of 30 MPa and at 195°C for 5 min into the plates with a thickness of 1 and 3 mm.

1.3 Morphological characterizations
The fractography study of this hybrid nanocomposite was carried out through the Scanning electron microscopy (SEM, VEGA-TESCAN Company) to investigate the morphology of nanocomposite and the dispersion of nano-Alumina in the matrix. First, the samples were fractured in liquid nitrogen, then in order to remove the ABS phase, the fractured surfaces were etched in butyl acetate solvents at room temperature for 4hours. In the next step, the etched samples were kept in an oven at 80°C for about 6 hours and finally the surface of samples was covered by a layer of gold.

Besides, the dispersion of nanoparticles in the matrix was analyzed using the mapping analysis of SEM/EDAX by INCA, Oxford instruments, England according to the ASTM Standard Guide for Quantitative Analysis by Energy-Dispersive Spectroscopy1 (E 1508 – 98). Also, samples for EDAX analysis (JXA 840, Japanese) were coated with thin Gold film in order to avoid influence of charge effect during the SEM operation.

1.4 Mechanical characterizations
In this study, the HIWA200 universal tensile machine was employed for measuring the mechanical properties of TPU/ABS/Alumina nanocomposites according to the ASTM D638 standard (Type IV) with a thickness of 1 mm. The tensile tests were done at room temperature with a cross-head speed of 150 mm/min on at least three individual specimens. Some important mechanical properties such as Young's modulus, tensile strength, and elongation at break were obtained in this section.

1.5 Impact test
According to ASTM D526 specimen with a size of $63.5 \times 12.7 \times 3.2 \ mm$ was prepared for Izod Impact test. Since the glass transition temperature (T_g) of the prepared polymer blend nanocomposites are very low (about $-30 \ °C$), the samples do not break at room temperature, so the impact test should be done at a temperature below T_g of polymer blend system (-50°C). In order to reach to -50°C, samples were put into a chamber for about 2 hours before the test.

1.6 Dynamic mechanical thermal analysis
Dynamic mechanical thermal analysis (DMTA) test is used to evaluate the thermal and dynamic mechanical behavior of a polymer. This test was carried out in a tensile mode by Tritec 2000 DMA (Triton Technology). The tests were conducted at a frequency of 1HZ, in a temperature range of -100 to 180 °C with a heating rate of 5°C/min on a rectangular sample with a dimension of $30 \times 10 \times 1 \ mm$. Finally, the Storage modulus (E'), Loss modulus (E'') and tan δ were obtained as a function of temperature.

1.7 Shape memory test
The cyclic thermo-mechanical test is a standard method for determining shape memory properties of SMPs. The SANTAM universal tensile machine model STM-50 was used for measuring shape recovery and shape fixity ratio. In this method, the initial gauge length at the room temperature is considered as ε_0. Then the sample is stretched to the strain of 100% at a constant crosshead speed of $5 \ mm/min$ and the measured gauge length in this stage is ε_m. Next, the sample is cooled by liquid nitrogen to temperatures of -50°C and holding for about 5 min, then unloading the stress to zero, the gauge length at this stage is ε_f. Eventually, the unloaded specimen is reheated up to room temperature and after 5 minutes the final length is measured (ε_i). This process is repeated three times (N) for each specimen and both shape recovery and fixity ratio are obtained from the following relations [34]:

$$R_r = \frac{\varepsilon_m(N) - \varepsilon_i(N)}{\varepsilon_m(N) - \varepsilon_i(N - 1)} \times 100$$
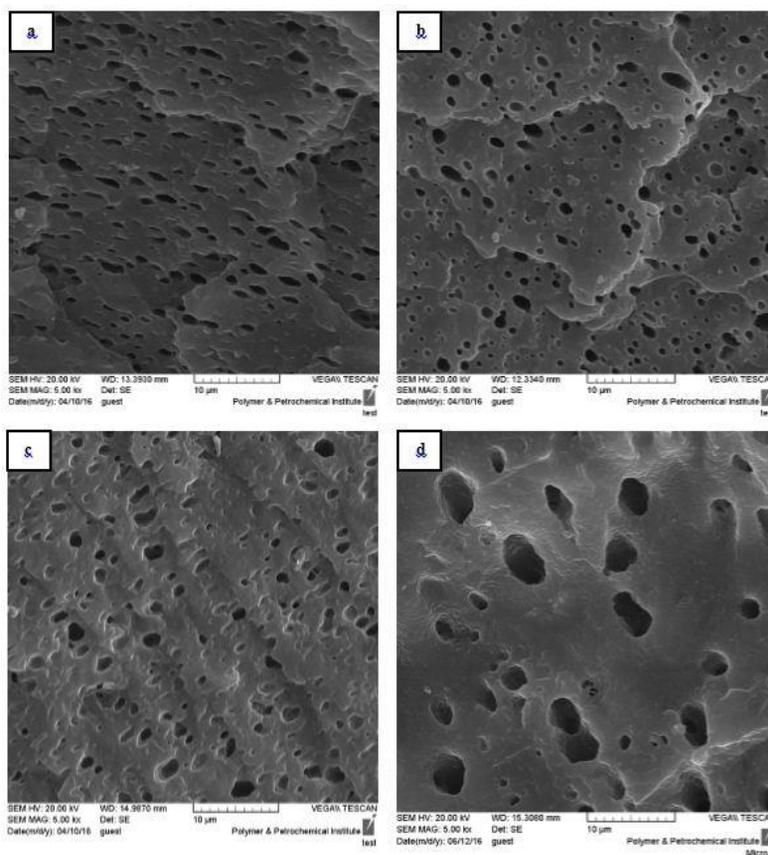
Figure 1. SEM images of TPU/ABS/Alumina blends (a) 79.5/20/0.5 (b) 79/20/1 (c) 78/20/2 (d) 77/20/3 ratios etched in butylacetate.

$$R_f = \frac{\varepsilon_f(N)}{\varepsilon_m(N)} \times 100$$

where ε_m and ε_f are the maximum strain and the fixed strain of the sample, respectively, unloaded at -50 °C, ε_i is the final strain after the shape recovery at room temperature and N is the number of cycles.

3. Results and discussion

3.1 Morphological characterizations

Since the most important factors in making a nanocomposite with high mechanical properties are the uniform dispersion of the nanoparticles in the matrix [35], the dispersion of alumina nanoparticles in the matrix should be considered. So in order to investigate the morphological characterizations of the nanocomposites, all the cryogenically fractured samples were etched in butyl acetate. The SEM and EDAX images were used to check the dispersion of nanoparticles in the matrix, also SEM was utilized to measure the size of ABS droplets. Figure 1 represents the SEM images of TPU/ABS/Alumina blends. The dark zones in the images belonged to ABS phase and it were shown that the chosen solvent finely extracted the ABS phase. According to these images and using ImageJ Software we found that the size of ABS droplets varied for different content of Alumina (Table 2). As shown in Table 2, the size of the ABS droplets obviously depends on the amount of alumina in the matrix. As the amount of alumina increased to 1 wt%, the number of droplets increased, and the diameter of the droplets decreased significantly. This phenomenon happens due to the addition of alumina to the TPU matrix in the first stage. Since TPU has a lower viscosity than the ABS [36-38], by adding alumina to the TPU matrix the viscosity of TPU increase significantly [39, 40] and as a result, the covalent interaction between the alumina and the polymer matrix improve the interfacial

interactions; therefore, they considerably influence the mechanical properties.

Table 3. Tensile properties of TPU/ABS/Alumina nanocomposites.

Samples	Tensile strength (MPa)	Elongation (%)	Tensile Modulus (MPa)
TPU/ABS	26.19	452.7045	36.93
TPU/ABS/0.5Alumina	30.953	383.8837	43.712
TPU/ABS/1Alumina	33.356	349.012	48.558
TPU/ABS/2Alumina	17.79	293.3117	55.25
TPU/ABS/3Alumina	14.73	238.1971	62.85
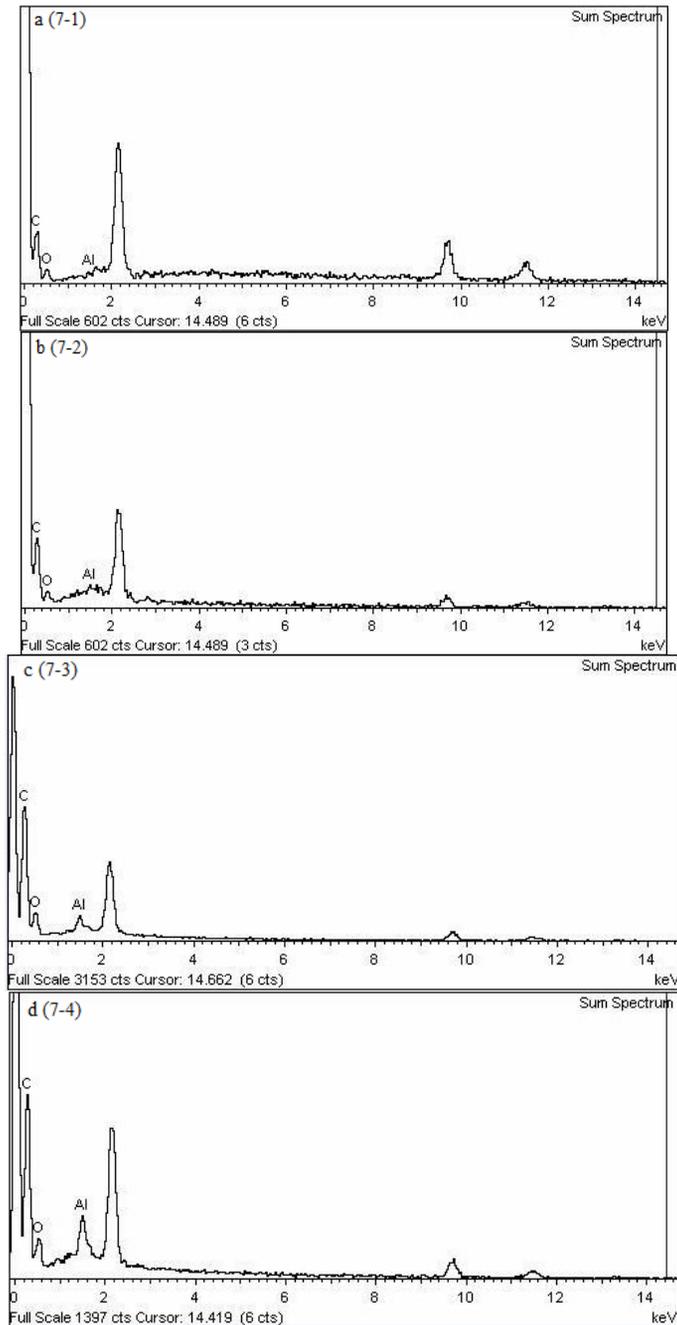
Figure 2. EDX spectrum of TPU/ABS/Alumina blends (a) 79.5/20/0.5 (b) 79/20/1 (c) 78/20/2 (d) 77/20/3 ratios.
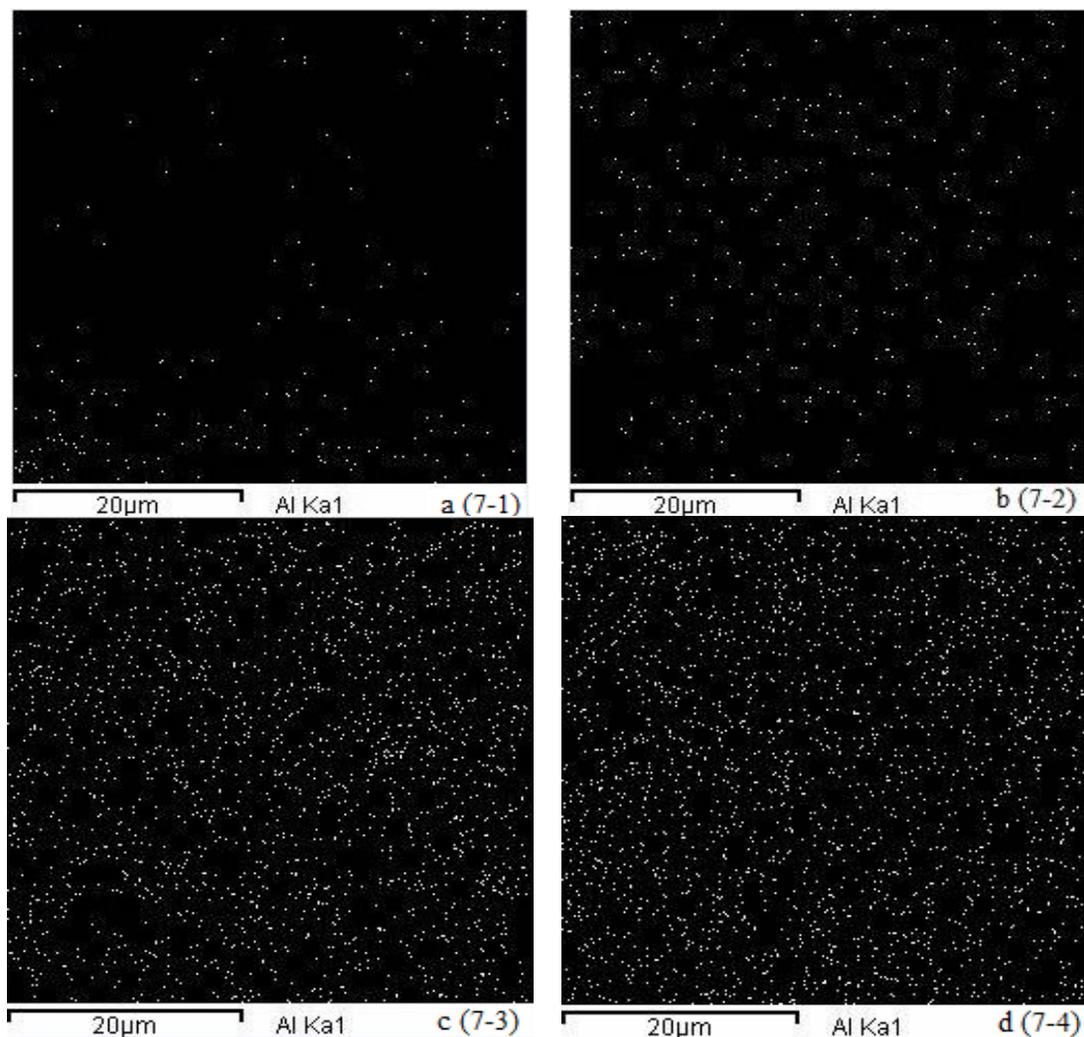
Figure 3. EDAX mapping analysis of TPU/ABS/Alumina blends (a) 79.5/20/0.5 (b) 79/20/1 (c) 78/20/2 (d) 77/20/3 ratios**.**

Then by increasing the amount of alumina to 2 and 3 wt% the size of droplets increased meaningfully. The increment in size of droplets can be attributed to the nanoparticle migration into ABS phase and agglomeration of nanoparticles which can worsen the compatibility of the blend. As we know, TPU/ABS is an immiscible polymer blend, and the dispersion of alumina in such polymer blends is interesting [41]. Conductive fillers prefer to localize in one of the phases because of the differences in polarities and surface energies [42]. Additionally, due to the different chemical nature of the nano-fillers, different polymers show different interfacial interactions with the fillers [43].

The following two major localizations are possible for alumina nanoparticles: (1) the particles localize in a specific phase (one of the two phases) or (2) the particles localize at the interface of the two polymers [44]. If both polymers have a similar polarity and interfacial interaction with the filler, the procedure of melt blending becomes important in the selective localization of fillers [61]. If alumina nanoparticles are pre-compounded in an unfavorable polymer, it is possible that they migrate into a more desirable condition. In the mechanical properties section, we will observe that the growing in size of droplets lead to a drastic drop in tensile strength. So the variation in the size of ABS droplet, can directly affect the mechanical properties. The EDAX spectrum for all of the samples is presented in Figure 2. Only Al, O and C signals can be observed in Figure 2 (a-d) which have been known as the principal elements of the nanocomposite. Carbon signals are related to ABS and TPU polymer and Al and O signals are subjected to Al_2O_3.
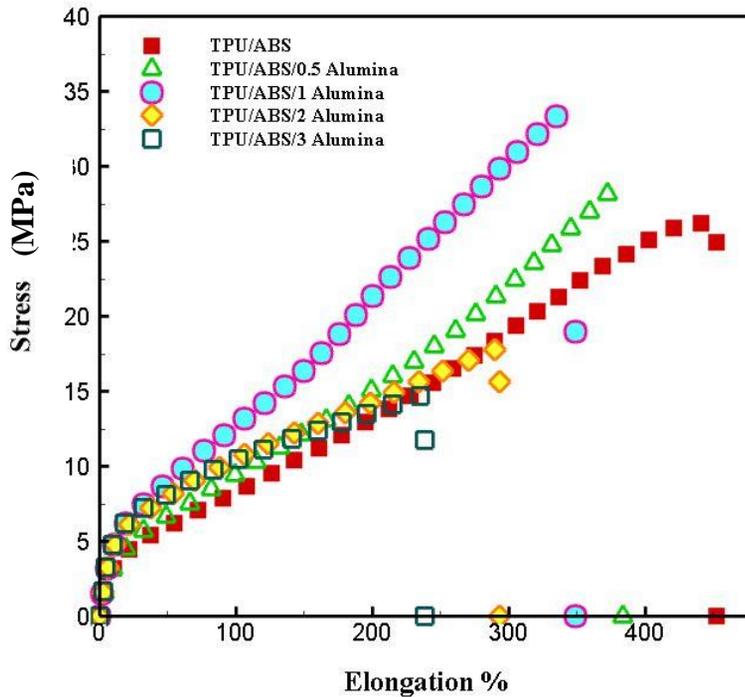
Figure 4. Stress–Elongation curves of TPU/ABS/ Alumina blends at room temperature with a cross head speed of 150 mm/min**.**
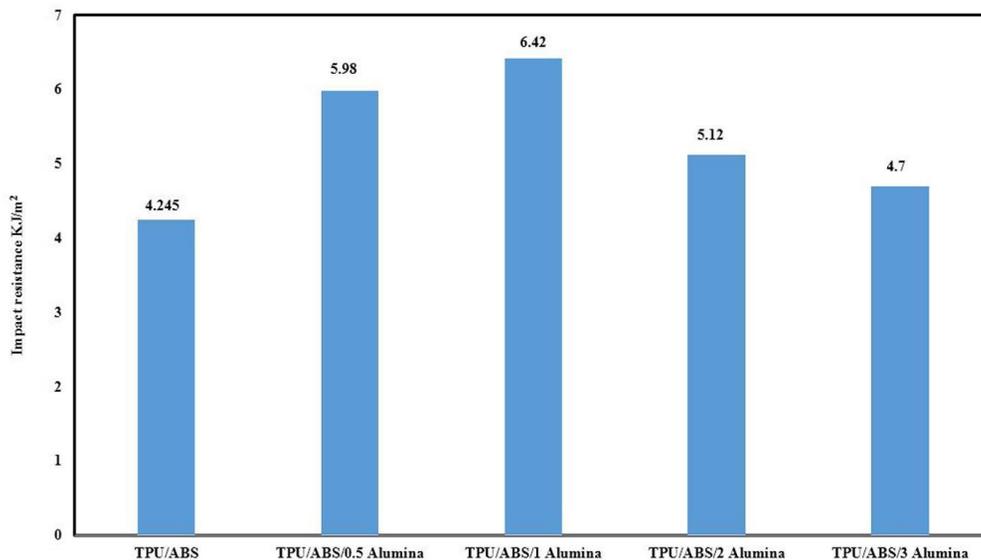
Figure 5. impact resistance of TPU/ABS/ Alumina blends.

Moreover, the nanoparticle distribution in nanocomposite can be analyzed using the mapping analysis of SEM/EDAX. EDAX can map the elemental distribution of feasible elements in samples. The EDAX spectral mapping for all samples is illustrated in Figure 3in which the bright dots represented the alumina (Al_2O_3) nanoparticles in the polymeric matrix. This can clearly identify the dispersion of the alumina in the TPU matrix. EDAX maps show homogeneous and uniformly dispersion of nanoparticles (Al_2O_3) in the TPU matrix.
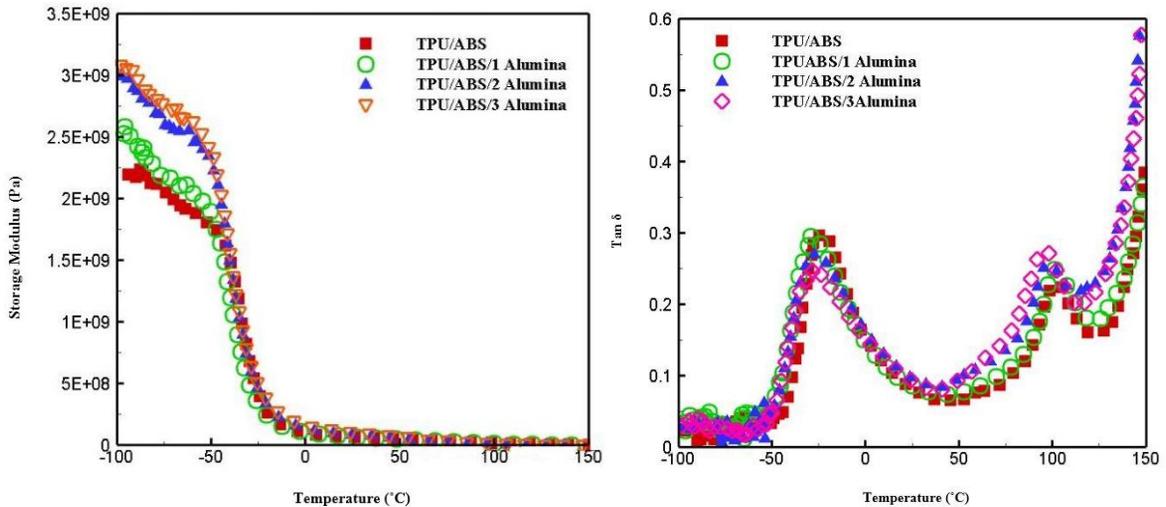
Figure 6. (a) Storage modulus as a function of temperature (b) Tan δ as a function of temperature.

3.2 Mechanical properties

The effect of alumina nanoparticles on the mechanical properties, such as Young's modulus, tensile strength, and elongation at break of the TPU/ABS/Alumina nanocomposites, is investigated. Stress–Elongation curves of TPU/ABS/Alumina blends are shown in Figure. 4. The results obviously indicate that the TPU/ABS blends act as an elastomer. They show rubbery behavior without necking, yield or stress hardening because all of the tests were performed at a temperature greater than the glass transition temperature. Since in the neat TPU/ABS blend the interfacial interactions are weak, the ABS phase is large and easily peels off the TPU phase. After the addition of alumina, as shown in Figure 1, the morphology changes a little and the domain of the ABS phase becomes smaller. Therefore, in the fracture process, the ABS and TPU phase break together because of the stronger interfacial interactions [45]. As we know the addition of alumina nanoparticles made a significant improvement in Young's modulus of the samples due to reducing the chain mobility of matrix and strengthen the matrix, and also reduced the elongation at break. Alumina at a lower content (less than 1 wt%) improve tensile strength; however, after further loading of alumina nanoparticle, the tensile strength decreased. As we know due to interaction forces between alumina particles, a tendency for agglomeration between them is so high. When the specific surface area increase, the area between particles and matrix which is interactive become larger and as a result particles tend to agglomerate [46-48]. Especially at higher concentration of alumina nanoparticles the possibility of agglomeration is increased and so the stress concentration increased too. The increment in stress concentration leads to crack propagation and so tensile stress reduce. Also, when nanoparticles agglomerate the chemical bonding between these inorganic particles and organic matrix decrease. So these two reasons are prominent in reduction of tensile strength at higher weight percentage of alumina nanoparticles. The obtained mechanical properties are summarized in tables 3.

Table 4. Storage modulus of TPU/ABS/Alumina at glass transition temperature of TPU (Tg1), ABS (Tg2) and room temperature.

SAMPLES	T_{g1}	T_{room}	T_{g2}
TPU/ABS	338.31	61.78	11.16
TPU/ABS/1Alumina	462.31	64.64	12.07
TPU/ABS/2Alumina	548.34	81.62	12.71
TPU/ABS/3Alumina	599.51	98.73	14.52
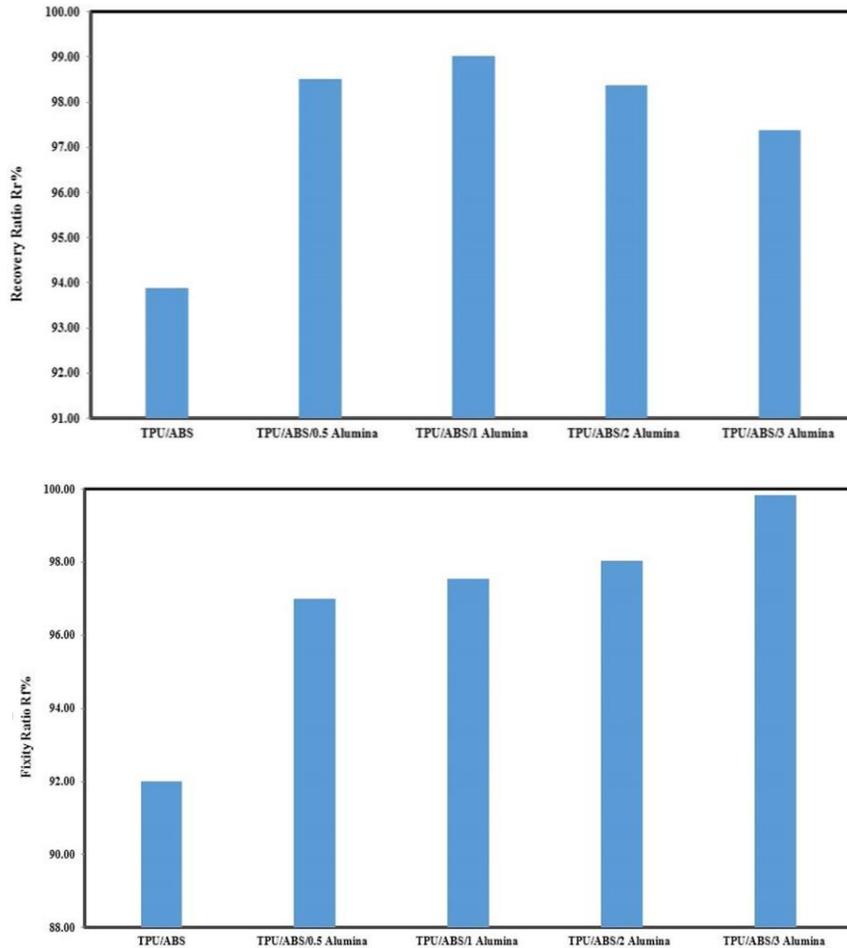
Figure 7. (a) shape recovery of TPU/ABS/Alumina blends (b) shape fixity of TPU/ABS/Alumina blends (first cycle).

The effect of alumina nanoparticles on impact resistance of TPU/ABS blend is reported in this section. As mentioned before the Izod impact tests were done at the temperature of -50°C. With an increase in weight percentage of alumina nanoparticles in TPU/ABS blend, the impact energy increases up to a critical concentration and after that decreases gradually. The impact energy of the nanocomposite attains its optimum value at critical concentration of 1 wt% alumina.

The results showed that the impact resistance of TPU/ABS/1Alumina improved about 52% in comparison with the neat blend. When the concentration of alumina nanoparticles increases up to 1 wt% the impact energy reduced gradually and at TPU/ABS/3Alumina nanocomposite a drastic reduction in the impact energy was observed. Previous reports showed that nanoparticles made several mechanisms in relation with energy absorbing at low concentration of nanoparticles which cause the strong increase in impact energy [49]. But at higher filler content, the agglomeration of nanoparticles induced stress concentration effect and as a result, a dramatic decrease in impact energy is observed. Also, inhomogeneous dispersion of nanoparticles in the matrix can reduce the impact resistance [49]. At lower concentrations of alumina nanoparticles because of the better dispersion of alumina particles, the interfacial area between matrix and nanoparticles increase meaningfully. So the strong interfacial interactions strengthen the nanocomposite significantly while the aggregated nanoparticles tend to make defects and these defects weaken the nanocomposite.

Also another reason for a reduction of impact resistance is attributed to the size of ABS droplets which at high concentration of nano alumina become larger. When holes become larger stress concentration increase around them and thereafter cracks extend into the body.
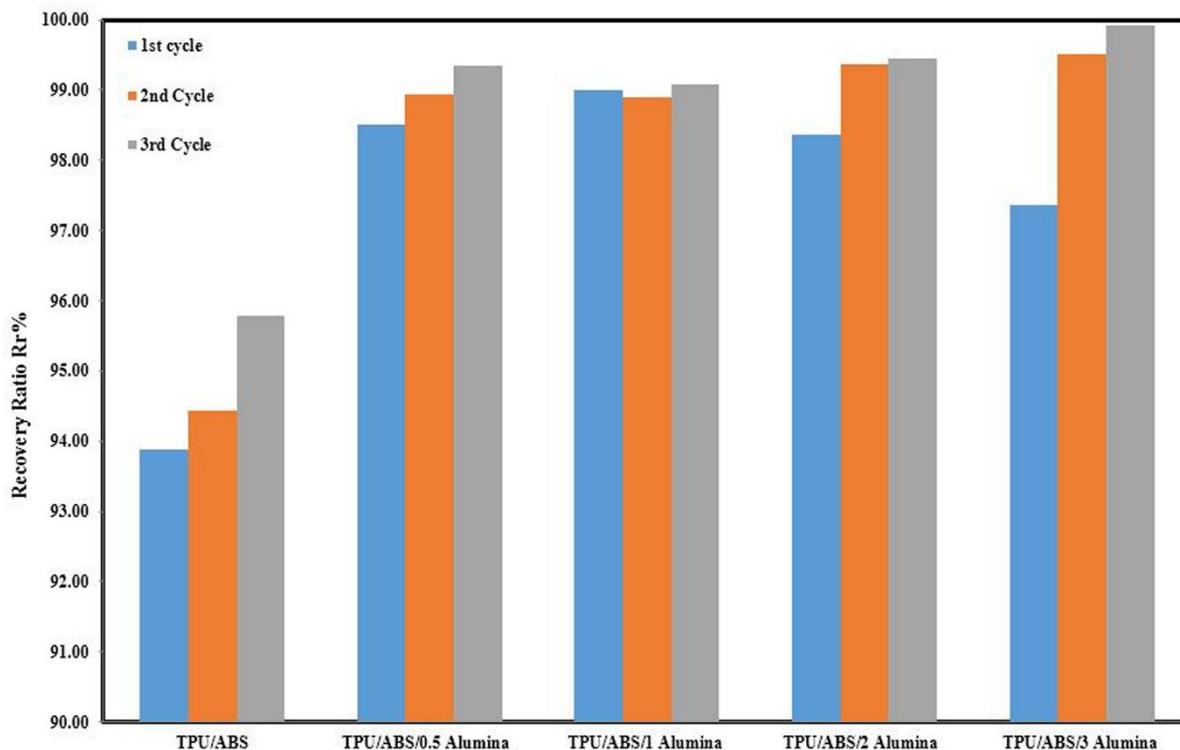
Figure 8. Shape recovery of TPU/ABS/Alumina blends in three cyclic tests.

3.3 Dynamic mechanical thermal analysis

The viscoelastic properties of the materials were studied using dynamic mechanical thermal analysis (DMTA). DMTA is a valuable tool for characterization of the viscoelasticity of composites and provides additional insight into their mechanical behavior. The Young's storage modulus (E') is the quantity of energy stored elastically, and the Young's loss modulus (E") is the quantity of energy lost as heat during cyclic deformation. The ratio of the loss and storage moduli (i.e., tangent delta (E"/E'= tan δ)) is the ratio of the energy lost to the energy stored. The storage modulus (E') describes the relative stiffness or rigidity of a material. The maximum E" and tan δ are also used to determine the glass transition temperature (Tg). The glass transition temperature is one of the most important characteristics of polymeric materials. This temperature represents the boundary between glassy and rubbery behavior. In polymer blends, Tg has been used as a parameter for the discussion of component miscibility. Figures 6 shows plots of E' and tan δ as a function of the temperature for the five different samples. According to Figure 6(a), the significant increase in E' of the nanocomposite was due to the inherent stiffness of alumina nanoparticles, and this result is consistent with previously reported tensile results. For example, the dynamic modulus of neat TPU/ABS at room temperature at a frequency of 1 Hz is equal to 61.78 MPa, and upon addition of 3 wt% of alumina nanoparticle to TPU/ABS (80/20 blend), the dynamic modulus of this sample increased to 98.73 MPa. Furthermore, the TPU/ABS/alumina nanocomposites exhibited two peaks, as shown in Figure 6(b). These peaks correspond to the Tg_1 and Tg_2 values of pure TPU and pure ABS, respectively. This result reflects the existence of two immiscible phases in the TPU/ABS blends. The Storage modulus of TPU/ABS/Alumina nanocomposites at glass transition temperature of TPU (Tg_1), ABS (Tg_2) and room temperature are summarized at Table 4. As shown in Figure 6(a), a sharp drop in modulus is observed above Tg_1 within a narrow temperature range due to the softening effect of polymer nanocomposites.

Also Figure 6 (b) shown that, as the alumina content is increased from 0 to 3 wt%, the peak height of tan δ at Tg_1 gets smaller, whereas the peak height at Tg_2 gets higher.

3.4 Shape memory test

Finally, the shape memory properties of the TPU/ABS/alumina nanocomposites were investigated. The

good shape memory property depends on both a good shape fixing ratio and a good shape recovery ratio. As we know, TPU has an elastomeric network consisting of the following two important parts: (i) hydrogen bonded urethane linkages, which are a hard segment and act as a fixed phase, and (ii) ester -COO- groups related to the polyol segment, which act as a reversible phase [50]. Thus, in a semi-crystalline TPU, the micro-crystals can memorize the original shape, and the glassy state can maintain the temporary shape [51]. Therefore, the necessary factors for TPU with shape memory effects are crystallinity of the soft segments at room temperature. The ABS in the TPU/ABS blend acts as a fixed phase that can improve the shape fixity of the blend but has a negative effect on the shape recovery ratio. The effect of the addition of alumina nanoparticles on the shape fixity and shape recovery ratio is measured. A cyclic thermal mechanical test was performed to extract the shape memory properties of samples. To examine the repeatability, three cycles were performed, and both factors are characterized in all three cycles. The obtained R_r and R_f values for the TPU/ABS/alumina nanocomposites with various concentration of alumina are plotted in Figures 7a and 7b, respectively. As we know, the shape recoveries of all the shape memory polymers are in the range of 70 to 98% [52]. Our results showed that the addition of alumina nanoparticles improves the shape recovery, but this improvement is better in small amounts of alumina. The presence of only 1 wt% alumina nanoparticles increased the shape recovery of the first cycle from 93.88 to 98.99. Furthermore, with increasing alumina content, the shape recovery ratio slightly decreased due to the aggregation of the nanoparticles and the localization of alumina in the ABS phase which make the ABS droplets larger. Figure 7 (b) shows the shape fixity of the samples in the presence of Al_2O_3. The addition of alumina significantly changes the shape fixity of the neat TPU/ABS, and, by loading 3 wt%, the shape fixity reaches 99.8%. One probable reason of this phenomenon is attributed to the migration of the added nanoparticles (in this percentages) into ABS phase.

Figure 8 demonstrates the shape recovery of TPU/ABS/Alumina blends in three cyclic test. In all of the examined samples, the stress–strain behavior, shape fixity and recovery ratio of the first cycle were substantially different from the other cycles [53]. This fact, which is commonly observed in thermoplastic elastomers, is attributed to the thermo-mechanical history of the chains and the distribution of the crystalline phase [53].

3. Conclusion

A new shape memory polymer blend nanocomposite, based on TPU and ABS, is prepared via the melt mixing process in the presence of alumina nanoparticles. The mechanical, shape memory, morphological and Izod impact properties of TPU/ABS/Alumina nanocomposite were investigated. The obtained results showed that presence of only 1 wt% alumina nanoparticles can meaningfully increase the Young's modulus, tensile strength and impact resistance due to the homogenous dispersion and interfacial interactions between alumina and polyurethane polymer. The Young's modulus, tensile strength and impact resistance of TPU/ABS/1Alumina improved about 32%, 27% and 52% respectively, in comparison with the neat blend. At higher concentration of alumina nanoparticles, the possibility of agglomeration is increased and so the stress concentration increased too and as a result tensile strength and the impact energy reduced gradually. In terms of shape memory properties, the result showed that the presence of only 1 wt% alumina nanoparticles increased the shape recovery of samples from 93.88 to 98.99. Furthermore, with increasing alumina content, the shape recovery ratio slightly decreased due to the aggregation of the nanoparticles and the localization of alumina in the ABS phase which make the ABS droplets larger. Also, the addition of alumina significantly changes the shape fixity of the neat TPU/ABS, and, by loading 3 wt%, the shape fixity reaches 99.8%. Finally, the SEM observations and size distributions data indicate that the mean diameter of the ABS droplets decreased with increasing alumina content to 1% and then by increasing the amount of alumina to 2 and 3 wt% the size of droplets increased meaningfully. The increment in size of droplets can be attributed to the nanoparticle migration into ABS phase and agglomeration of nanoparticles which can worsen the compatibility of the blend.

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