A Study of the Effect of TPU and Clay Nanoparticles on the Mechanical Behavior of PBT-Based Nanocomposites

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ABSTRACT

In this research, thermoplastic polyurethane (TPU) and clay nanoparticles were incorporated into poly (butylene terephthalate) (PBT) to improve the impact and tensile properties. The PBT/TPU (90/10, 80/20 and 70/30) samples were prepared by melt mixing using a co-rotating twin-screw extruder followed by injection molding. At the next stage, clay nanoparticles of different weight fractions were added to the PBT/TPU (80/20) blend in the same way to prepare nanocomposite samples. SEM images illustrated good compatibility between TPU and PBT. To characterize the dispersion of clay layers in the polymer matrix, wide-angle X-ray diffraction (WAXD) inspections were performed. The results of the mechanical assessments showed that the addition of TPU to PBT significantly increased the impact strength but decreased the tensile strength and modulus. Incorporating clay nanoparticles into the PBT/TPU blend noticeably improved the tensile properties of PBT/TPU-based nanocomposites. A balance of the tensile and impact properties was found in the PBT/TPU/clay (80/20/3) nanocomposite system.

1. Introduction

Blending two or more polymers with different physical properties is a practical technique for enhancing the overall properties of a material by taking advantage of each component's properties [1-3]. Versatility, simplicity and low cost are some of the notable advantages of polymer blends [1]. However, most polymers are immiscible, which results in phase separation in a blend matrix [1, 4]. Incorporating nanofillers in a polymer matrix is another effective way to expand the applications of available polymers. In recent years, significant attention has been dedicated to polymer/clay nanocomposites in both the academy and industry due to their outstanding properties. Remarkable improvement in the thermal, mechanical, dimensional and barrier properties of pure polymers can be achieved by incorporating very low amounts of nanoclay into a polymer matrix (usually less than 5 wt.%) [5-8]. More recently, combining the two aforementioned polymer modification techniques have been used to form a polymer/polymer/clay ternary nanocomposite [1-3, 9-11].

Poly (butylene terephthalate) (PBT) is an important semicrystalline engineering thermoplastic with valuable properties, including a high rate of crystallization, an excellent melt-viscosity, excellent electrical properties, high rigidity, low moisture absorption, broad chemical resistance and thermal stability. In spite of these valuable attributes, PBT is intensely notch sensitive [5, 12]. Until now, several efforts have been made to enhance the impact properties of PBT [13, 14]. Thermoplastic polyurethane (TPU) displays good compatibility with PBT and can be used to improve the impact properties of PBT. Although using TPU in a PBT matrix has remarkably improved the impact strength of PBT, it leads to a reduction in the tensile strength and modulus [15, 16]. Therefore, it seems that further efforts must be made to overcome tensile drops. The use of high-aspect ratio fillers, such as nanoclay particles, in a polymer matrix can improve the mechanical properties, particularly the tensile and flexural properties of a polymer. It seems that a reduction in the tensile strength of PBT arising from adding TPU to a PBT

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matrix can be reduced by incorporating nanoclay particles in a PBT/TPU blend.

This study investigated the effects of a TPU elastomer and an organo-modified nanoclay on the morphology and mechanical properties of PBT/TPU blends and PBT/TPU/clay nanocomposites. Samples were prepared by the melt-mixing and injection-molding processes. Mechanical properties comprising tensile and notch-impact resistances were characterized. Moreover, the results of the tensile tests in terms of the modulus were compared with those of the mathematical models.

2. Experimental

2.1. Material

Poly (butylene terephthalate) with a density of 1.33 g/cm³ and MFI[1] of 19.43 g/10min (235°C, 2.16 kg), with the trade name of Tecodur ®PB 70 NL was purchased from Eurotec, Turkey. TPU (Laripur® LRP 9025) with a density of 1.22 g/cm³ and MFI of 79.2 g/10min (235 °C, 2.16 kg) was obtained from Coim, Italy. The commercial organic montmorillonite (MMT), cloisite ®15A, used as a reinforcing agent, was provided by Southern Clay Products Inc, USA. The as-received clay (cloisite ®15A) particles had a specific gravity of 1.66 g/cm³ and they were plate-like stacks of thin silicate layers.

2.2. Preparation of Nanocomposites

The polymer granules dried out before processing to avoid moisture-degradation reactions. For this purpose, PBT and TPU dehumidified at 120°C for 4 hours and at 90°C for 3 hours, respectively, in an air oven. At the first stage of sample preparation, PBT was melt blended with TPU at different weight ratios of 90/10, 80/20 and 70/30 using a co-rotating twin-screw extruder (ZSK25, Coperion, Germany) at setting temperatures of 230°C to 250°C from feed zone to die. The granules resulting from the extruder were dried at 80°C for 12 hours prior to injection molding. Then, standard specimens for mechanical tests were produced by injection molding (Imen machine paya 50/150, Iran) under a nozzle temperature of 240°C and a mold temperature of 80°C. In the second stage, samples of PBT/TPU (80/20) blends with different weight fractions of clay (1, 3 and 5 phr) were prepared in the same way as previously described. The specimens' designations and compositions are listed in Table 1.

Table 1. Samples' compositions

Specimen code	PBT (wt.%)	TPU (wt.%)	Cloisite 15A (Phr)
P100	100	0	0
PT9010	90	10	0
PT8020	80	20	0
PT7030	70	30	0
PTM1	80	20	1
PTM3	80	20	3
PTM5	80	20	5

2.3. Morphology

The fractured surfaces of different tensile specimens, which were fractured in liquid nitrogen, were studied using SEM (MIRA3 FEG-SEM, TESCAN, Czech Republic).

2.4. X-ray Analysis

Wide-angle X-ray scattering (WAXD) was conducted using D500-SIEMENS, Germany, with Cu Kα incident beam (λ= 1.54 Å). The scanning angle range was from 2 degrees to 10 degrees.

2.5. Tensile and Impact Properties

Tensile tests of blends and nanocomposites were carried out according to the ASTM D638 at room temperature using a GOTECH AI-7000M universal testing machine (Taiwan). The notch Izod Impact strengths of specimens were determined by using the SANTAM (SIT-20D) impact tester according to ASTM D256. All mechanical tests were repeated three times.

3. Mathematical Models for Predicting Mechanical Properties in Blends and Particulate Composites

3.1. A Prediction about Blend's Mechanical Properties

To date, several mathematical models have been proposed to predict the mechanical properties of two-phase blends. The two basic models representing the mechanical properties of blends include rule of mixture and series models [18]. The rule of mixture, which is also called the parallel model and serial model, are presented as equations (1) and (2), respectively.

$$K_b = K_m \emptyset_m + K_d \emptyset_d \tag{1}$$

$$\frac{1}{K_b} = \frac{\emptyset_m}{K_m} + \frac{\emptyset_d}{K_d} \tag{2}$$

where K_b, K_m and K_d are particular properties, such as the tensile strength or modulus of the blend, major phase and dispersed phase, respectively. $\emptyset_m$ and $\emptyset_d$ indicate the volume fractions of the major phase and dispersed phase, correspondingly. The other common useful model widely used to predict the mechanical properties of polymer blends, proposed

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[1] melt flow index

by Maxwell (Eq. 3). This model provides an exact solution for mechanical properties of homogeneous spheres that are randomly distributed in a homogeneous medium [19].

$$K_b = K_m \left[\frac{K_d + 2K_m + 2\emptyset_d(K_d - K_m)}{K_d + 2K_m - \emptyset_d(K_d - K_m)} \right] \tag{3}$$

Davies suggested an alternative theoretical model, which explains the tensile modulus of two-phase blends, as given below [20].

$$E_b^{1/5} = E_m^{1/5}\emptyset_m + E_d^{1/5}\emptyset_d \tag{4}$$

3.2. A Prediction About Particulate Composites' Mechanical Properties

Various mathematical models have been proposed for predicting the mechanical properties of particulate composites. The Halpin–Tsai equation estimates composite modulus as follows [21]:

$$\frac{E_c}{E_m} = \frac{1 + 2A_f \mu \emptyset_f}{1 - \mu \emptyset_f} \tag{5}$$

where E_c represents the elastic modulus of the composite and E_m denotes the elastic modulus of the polymeric matrix. A_f defines as the ratio of the lateral dimension of a nonspherical filler, such as clay, to its thickness. $\emptyset_f$ is the volume fraction of the filler and μ is the geometry factor that is established as the following equation.

$$\mu = \frac{E_f/E_m - 1}{E_f/E_m + 2A_f} \tag{6}$$

where E_f/E_m is defined as the modulus ratio of the filler to the matrix.

Additive-law predicts the modulus as follows:

$$E_c = (\eta_1 \eta_0 E_f - E_m)\emptyset_f + E_m \tag{7}$$

where the elastic modulus of composite, filler and matrix is expressed by E_c, E_f and E_m, respectively. $\emptyset_f$ denotes the filler fraction, η_0 is considered as the orientation efficiency factor, and η_1 indicates the length efficiency factor, which is described as follows.

$$\eta_1 = 1 - \frac{Tanh[a.(l/d)]}{a.(l/d)} \tag{8}$$

where l and d are length and diameter of the filler, respectively, and a is described as follows.

$$a = \sqrt{\frac{-3E_m}{2E_f \, ln(\emptyset_f)}} \tag{9}$$

Guth suggested another popular model that explains the stiffness of the filled polymer, as expressed by equation 7[22].

$$\frac{E_c}{E_m} = 1 + 0.67 \left(l/d\right)\emptyset_f + 1.62\left(l/d\right)^2 \emptyset_f^{\,2} \tag{10}$$

In this study, additive-law, the Halpin–Tsai (H-T) and Guth models were exploited, and their results were compared with those of experiments.

4. Results and Discussion

4.1. Morphological Study

To study the effect of TPU and clay nanoparticles on the morphology of PBT/TPU blends and PBT/TPU/clay nanocomposites, SEM images from the surfaces of specimens were taken. Fig. 1 demonstrates the SEM images of the fractured surface for pure PBT and blends of PBT/TPU. It is evident that the fractured surface of specimens becomes more ductile in the presence of TPU in a PBT matrix. Indeed, the relatively smooth and glossy surface of PBT turned into a rough topography with incorporation of TPU in a PBT matrix.
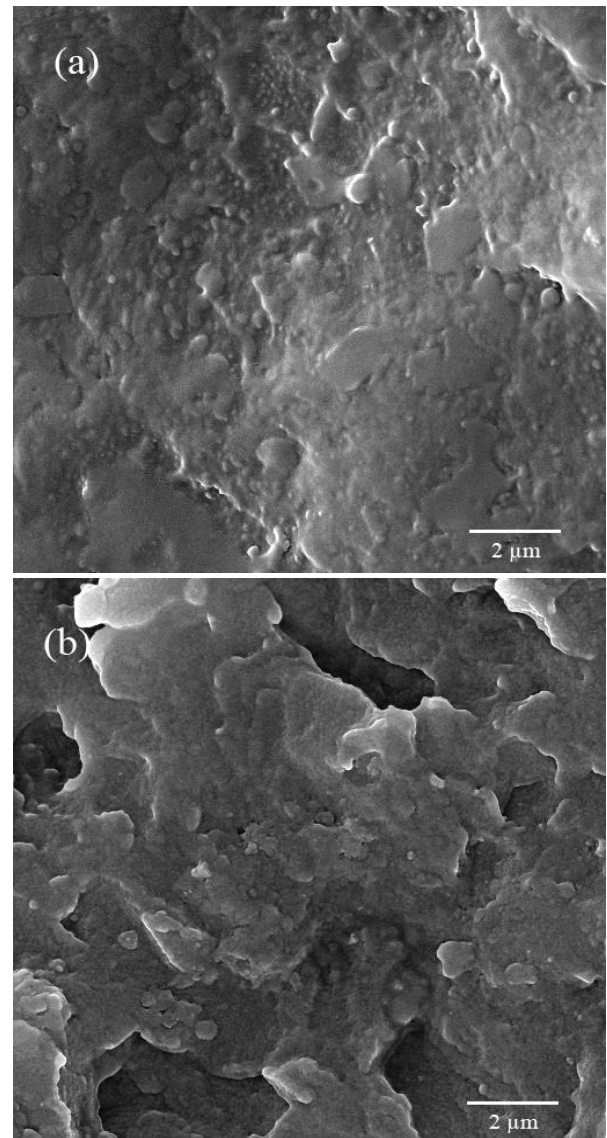

Figure 1. SEM micrographs of fractured surfaces: (a) pure PBT, (b) PBT/TPU (80/20)

Furthermore, it is clear that there is good compatibility between the two blended phases (PBT and TPU), because the minor phase (TPU) is not easily distinguishable. Otherwise, if these two phases were incompatible, the separation of the two phases was very obvious. The compatibility of PBT and TPU could be explained by the lower melt viscosity of the dispersed phase (TPU) as compared to continuous phase (PBT) [15] and the amide-ester reaction that occurs between these phases [16].
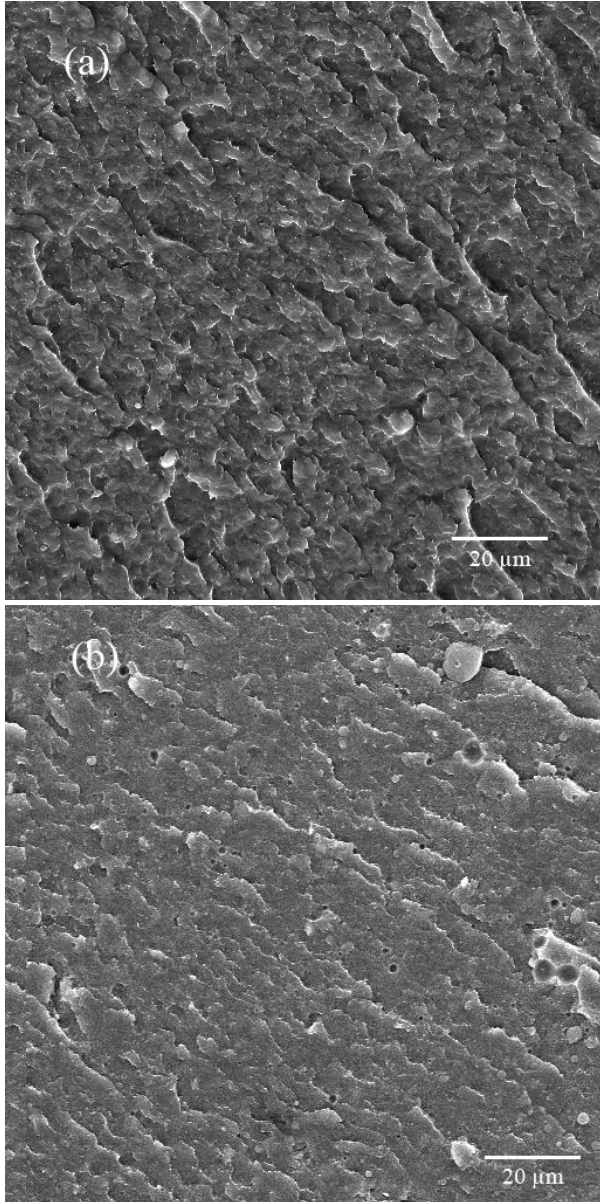

Figure 2. SEM micrographs of fractured surfaces: (a) PBT/TPU (80/20), (b) PBT/TPU/clay (80/20/5)

The effect of including 5phr clay nanoparticles on the topography of a fractured surface of a PBT/TPU (80/20) nanocomposite is illustrated in Fig. 2. It can be seen that the incorporation of nanoclay into a PBT/TPU did not interfere with the compatibility of these phases. This may be attributed to the proper dispersion of the nanoclay in the polymer matrix.

Fig. 3 (a) shows the X-ray diffraction profiles of cloisite 15A. As can be seen, clay particles have three distinct peaks at three different points (in the range of 2θ: 2 degrees to 10 degrees). The first peak from the left, which appears at $2\theta = 2.88°$ (corresponding to the d-spacing of 3.05 nm), represents the interlayer distance and basal spacing of the organically modified nanoclay particles. The second characteristic peak of the clay, which is at $2\theta = 4.91°$ (corresponding to the d-spacing of 1.8 nm), is related to a group of partially treated silicate layers. The last peak of cloisite 15A is at $2\theta=7.11°$ (corresponding to the d-spacing of 1.2 nm) is concerned with the pure montmorillonite clay bead, which has not been modified.

The X-ray diffraction patterns of PBT/TPU/clay nanocomposites are shown in Fig. 3 (b to d). The results shown in Fig. 3 demonstrate that the degree of intercalation and exfoliation of clay nanoparticles in a polymer matrix depends on the concentrations of nanoclay in the matrix. Hence, for nanocomposites containing 1 and 3 phr nanoclay, the XRD profiles are characterized by the absence of diffraction peaks. Consequently, it can be inferred that clay nanoparticles are exfoliated in a polymer matrix and have good dispersion.

For 5phr nano-clay, the indication of a slight increase in the gallery spacing of the clay from $2\theta = 2.88º$ to $2\theta = 2.56º$ suggests the possibility of a small amount of the polymer chains being intercalated into the organoclay gallery space.

4.2. Mechanical Properties

The results of mechanical assessments of the tensile and impact performances of pure PBT and PBT/TPU blends are summarized in Table 2. The incorporation of TPU in a PBT matrix enhanced the impact strength, where a 314.7% enhancement in impact resistance of a blend containing 30 wt.% TPU is perceived as compared to that of pure PBT. This improvement in the impact property is attributed to the elastomeric nature of TPU. Moreover, the compatibility of blend phases plays a vital role in improving the impact properties.

As mentioned in previous section and according to Fig. 1, the blend of PBT/TPU is compatible and such an improvement in impact resistance indicates the miscibility of the blend components. In an elastomer-toughened blend, the elastomeric phase can absorb an excessive amount of impact energy by stretching across a propagating crack. In spite of the considerable enhancement of the impact strength of the PBT/TPU blends, severe decrements in the tensile properties of blends were noted, particularly at 30 wt.% of TPU content. The stiffness and tensile strength of polymeric blends were reduced when a rubbery phase was added to a rigid matrix.

PBT/TPU (80/20) was selected as a base blend and then clay nanoparticles were incorporated in order to improve tensile properties. Fig. 4 and Fig. 5 demonstrate the effect of organoclay on the tensile strength and modulus of PBT/TPU (80/20) nanocomposites. Fig. 4 shows that incorporation of organoclay in PBT/TPU matrix leads to increment in tensile strength of nanocomposites. The maximum tensile strength was obtained by inclusion of 3 phr nanoclay that was 63% higher than pure polymer.

The greater improvement in the tensile strength of a nanocomposite containing 3 phr (as compared with 5 phr) clay was due to the better dispersion and adhesion of nano particles to a polymer matrix. This could improve the stress transfer between matrix and nanoparticles and, hence, increase the tensile strength. The results of XRD (Fig. 3) show indications of clay exfoliations in PTM1 and PTM3 nanocomposites.
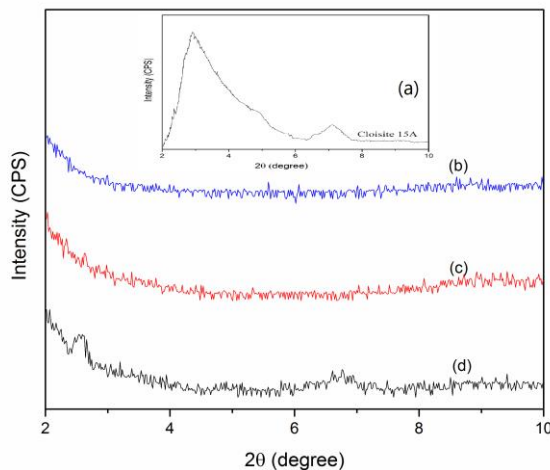

Figure 3. Wide-angle diffraction profiles of (a) 15A MMT clay, (b) PTM1, (c) PTM3 and (d)PTM5.

Table 2. The results of the tensile and impact performances of PBT/TPU blends

Material	Tensile strength (MPa)	Tensile modulus (MPa)	Izod impact strength (Kj/m²)
P100	49.61	2025.79	5.17
PT9010	39.75	1486.64	8.36
PT8020	30.13	1262.43	12.55
PT7030	21.11	883.21	21.44

As seen in Fig. 5, tensile moduli of nanocomposites are higher than a tensile modulus of a PT8020 blend. With the addition of nanoparticles to a polymer matrix, the modulus was determined via the rigidity, size and distribution of nanoparticles. The enhancement of the modulus of nanocomposites was due to the higher modulus of clay nanoparticles as compared to that of the polymer matrix. Furthermore, incorporating a nanoclay with a high aspect ratio at low content significantly increased the tensile modulus of the nanocomposite [23]. In addition, nanoparticles act as a nucleating agent in a polymer matrix and lead to an increase in crystallinity. Crystalline regions have a higher modulus as compared to the amorphous regions [23].

Fig. 6 demonstrates the effect of 20 wt.% TPU and 1, 3 and 5 phr of organoclay on the impact strength of PBT/TPU blends. Incorporating TPU dramatically raised the impact resistance. The existence of 1 phr clay nanoparticles in the polymer matrix slightly increased the impact resistance, whereas adding 3 and 5 phr clay nanoparticles reduced the impact strength. The reduction in impact strength by applying 3 and 5 phr of clay may be due to the concentration of nanoclays in the TPU flexible phase.
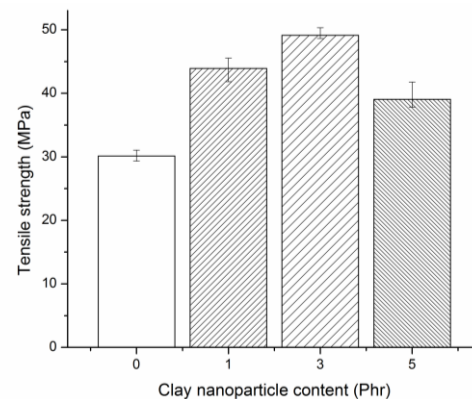

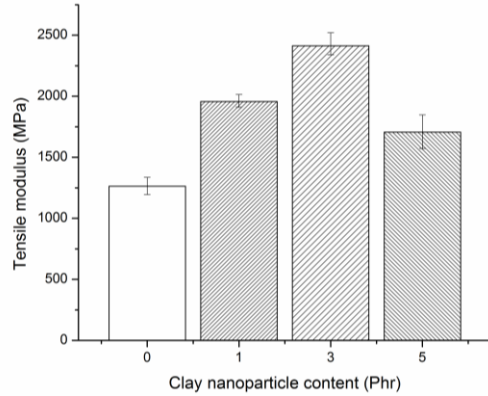**Figure 4.** The tensile strength of nanocomposites as a function of clay content

Figure 5. The tensile modulus of nanocomposites as a function of clay content

4.3. Theoretical Results

The results of experiments in terms of a tensile modulus was compared with the mathematical results for PBT/TPU blends and PBT/TPU/clay nanocomposites. The calculated values of Young's modulus for PBT/TPU blends using Eqs. (1) to (4) were compared with the experimental results as demonstrated in Fig. 7. It can be seen that the results of two simple models comprising a rule of mixture and serial models were not accurate enough to predict the elastic modulus of PBT/TPU blends. This is because these models consider the upper and lower bounds of calculated properties. In a parallel model, each phase of a blend is assumed to contribute independently to the overall modulus. Usually, the results of this model is overestimated, since it assumes perfect contact between particles in a fully percolating network [18]. However, the series model assumes that there is no contact between particles. According to Fig. 7, the Davies model displays better conformity with experimental results.
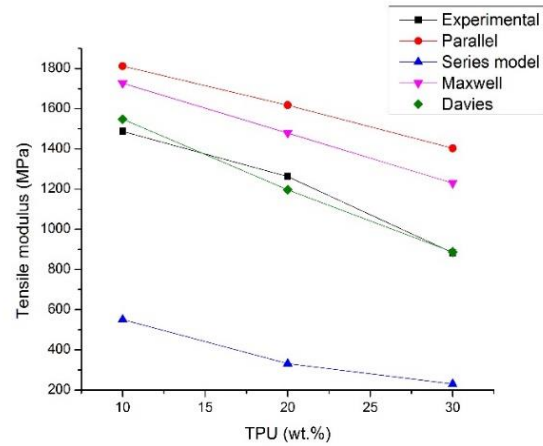

Figure 6. The notch impact resistance of PBT-based nanocomposites

Figure 7. The tensile moduli of PBT/TPU blends obtained by experiments and theoretical models

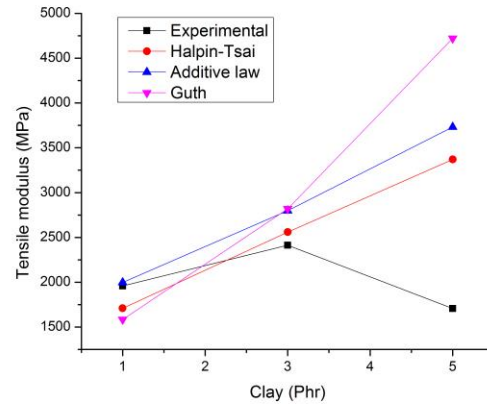**Figure 8.** The tensile moduli of PBT/TPU/clay nanocomposites obtained by experiments and theoretical models
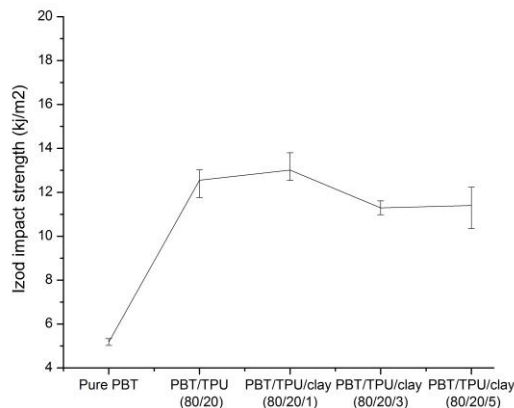
Fig. 8 compares the experimental and theoretical results for the elastic moduli of nanocomposites. In the case of PTM1 and PTM3, all selected models (Eqs. (5), (7) and (10)) almost fit with the experimental results, but the Halpin-Tsai model seems to be more accurate. However, in the case of PTM5, experimental results are lower than predicted results obtained by theoretical models. This could be explained by the lack of the appropriate dispersion of clay nanoparticles in a nanocomposite containing 5 phr nanoclay.

5. Conclusions

PBT/TPU blends and PBT/TPU/clay nanocomposites were prepared using melt compounding. SEM observations indicated proper compatibility between PBT and TPU.

The dispersion characteristics of nanoclays in a polymer matrix were studied by WAXD. Incorporating TPU and clay in the polymer matrix improved the impact and tensile properties of nanocomposites, respectively. Adding TPU into a PBT matrix had significant influence on the impact resistance and improved the notched Izod impact strength almost 150% and 300% for 20 wt.% and 30 wt.%. of TPU contents, respectively. However, applying TPU reduced the tensile strength and modulus. Including clay (3 phr) in a PBT/TPU (80/20) matrix led to the 63% enhancement of tensile strength and the 91% elevation of the modulus. The results of mathematical models in predicting Young moduli for corresponding blends and nanocomposites indicated that the Davies and Halpin-Tsai models were more consistent with experiments.

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