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Impact modified epoxy/montmorillonite nanocomposites: synthesis and characterization

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Abstract

Diglycidyl ether of bisphenol A type epoxy resin-polyether polyol-organically treated montmorillonite ternary nanocomposites were synthesized in this study. The effects of addition of polyether polyol as an impact modifier on morphological, thermal and mechanical properties of nanocomposites were investigated by X-ray diffraction, scanning electron microscopy (SEM), differential scanning calorimetry, impact and tensile testing. The results showed that organically treated montmorillonite is intercalated by epoxy, since the interlayer spacing expanded from 1.83 to 3.82 nm upon nanocomposite synthesis. The addition of polyether polyol impact modifier had no effect on the interlayer spacing. SEM examination showed that polyol forms an immiscible phase in the epoxy matrix. Thermal characterization of nanocomposites indicated an increase in T_g with respect to both polyether polyol and montmorillonite contents. The impact strength of the samples with no clay was improved approximately 160% upon adding 7 wt% polyether polyol. In polyether polyol modified nanocomposites, the impact and tensile strengths decreased with respect to increasing amount of montmorillonite and showed a maximum with respect to the polyether polyol content at constant clay loading. The Young's modulus of the nanocomposites exhibited an increase with respect to the montmorillonite loading and showed a maximum with respect to the polyol content at each clay loading.

Keywords: Nanocomposites; Impact modification; Montmorillonite

1. Introduction

Polymer–clay nanocomposites are particulate-filled composites in which the reinforcement material is in the form of sheets with thickness of one to few nanometers and length of hundreds to thousands of nanometers. Owing to the high aspect ratio of the reinforcement, they show several advantages over typical composites in terms of mechanical, thermal, physical and barrier properties. Investigations on nanocomposite materials were started by Toyota researchers in which nylon 6-clay nanocomposites were obtained by the polymerization of ε-caprolactam in the interlayer gallery region of organoclays [1,2].

Epoxy resins find many industrial applications in adhesives, construction materials, composites, laminates, coatings and aircraft and spacecraft industries owing to their high strength, low viscosity, low volatility and low shrinkage during cure, low creep and good adhesion to many substrates [3]. Thus, epoxy–clay nanocomposites have also been studied [4–9]. Kornmann et al. [8], synthesized diglycidyl ether of bisphenol A (DGEBA) epoxy resin–organophilic montmorillonite nanocomposites in which the epoxy was cured with different curing agents. They concluded that the choice of the curing agent and curing conditions controlled the extent of exfoliation of the clay. The largest extent of exfoliation was observed in the aliphatic diamine cured epoxy system. Zerda and Lesser [6] examined the synthesis of intercalated nanocomposites prepared by modified montmorillonite and glassy epoxy which was cured with an aliphatic diamine curing agent. Pinnavaia et al. [9] synthesized epoxy–clay nanocomposites and obtained exfoliation of organoclays.

Epoxy resins are usually brittle materials in their cured state and exhibit poor resistance to crack growth. Thus, they are usually combined with a wide range of modifiers to attain greater impact resistance and flexibility [10–13]. For this purpose, Shih et al. [10] investigated polydimethylsiloxane containing isocyanate group-modified epoxy resin. Pearson and Yee [11] studied the influence of particle size

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and particle size distribution on toughening mechanisms in rubber modified epoxies. Franco et al. [12] blended DGEBA epoxy resin with various proportions of amine-terminated polyoxypropylene (POPTA) elastomer and cured it by using an aliphatic diamine hardener. Harani et al. [13] used a polyol, hydroxyl-terminated polyester as a toughening agent for epoxy resins.

The objectives of this work are to synthesize nanocomposite materials with an impact modified epoxy resin and study the effects of polyether polyol and montmorillonite contents on the morphological, thermal and mechanical properties of the ternary systems obtained, by X-ray diffraction (XRD), scanning electron microscopy (SEM), differential scanning calorimetry (DSC) and impact and tensile tests.

2. Materials and experimental

2.1. Materials

The epoxy resin was diglycidyl ether of bisphenol A (DGEBA), Araldite M. It was cured with an aliphatic amine curing agent, triethylenetetramine, HY 956. The epoxy resin and hardener were both purchased from Ciba Specialty Chemicals. Polyether polyol impact modifier (Voranol 3322) with a functionality of 3 and molecular weight of 3500 g/mol was obtained from Dow Chemicals. It can be represented by the following formula: $R\text{-}[(OCH_2\text{-}CH_2\text{-})_n\text{-}OH]_3$. Owing to the hydroxyl groups it has the potential to react with DGEBA. The clay used in this study was montmorillonite (Cloisite® 30B) from Southern Clay Products that was modified by methyl, tallow, bis-2-hydroxyethyl quaternary ammonium chloride. The average dry particle size of the organically modified clay is 13 μm, and the concentration of the modifier in the clay is 90 mequiv./100 g as reported by the manufacturer.

2.2. Nanocomposite preparation

Organically treated montmorillonite and DGEBA were mechanically stirred for 2 h at 35 °C, followed by ultrasonic mixing for 30 min with a Bransonic B2200 ultrasonic bath having a frequency of 47 kHz. Predetermined amounts of polyether polyol were added to the mixture and mechanically stirred for one more hour. The DGEBA–montmorillonite–polyol mixture was degassed, cooled to room temperature and the triethylenetetramine curing agent was added at a ratio of 100:20 (DGEBA/hardener) by weight. The slurry mixtures were poured into aluminum molds and cured at 75 °C for 16 h followed by postcuring at 130 °C for three more hours. All of the weight percentages mentioned in the text are based on the final weight of the nanocomposite.

2.3. Characterization experiments

XRD patterns were obtained by a Rigaku Miniflex diffractometer equipped with Cu Kα X-ray radiation, operating at 40 kV and 30 mA. The diffraction patterns were collected between angles (2θ) of 1–10° at a scanning rate and step size of 5°/min and 0.02°, respectively. The fracture surfaces of the materials obtained by impact testing were examined by a low voltage Scanning Electron Microscope (JEOL JSM-6400). The glass transition temperature of the nanocomposites was determined with a 910 S Dupont TA Differential Scanning Calorimeter. The samples were heated from 20 to 220 °C at a heating rate of 20 °C/min under nitrogen atmosphere. The samples were then cooled to room temperature and the heating cycle was repeated. The second heating run results are reported. Tensile tests were performed using a computer controlled testing machine (Lloyd 30K), according to ASTM 638-M 91a. Charpy impact tests were performed according to ASTM D 256, by using a Pendulum Impact Tester manufactured by Coesfeld Material Testing. All mechanical tests were performed at 23 °C. Impact strength and tensile properties reported represent the average of the results on 10 samples.

3. Results and discussion

3.1. X-ray analysis

In Fig. 1, curve (a) represents the XRD pattern of Cloisite® 30B powder. It can be seen that the [001] diffraction peak of this organically modified clay appears at

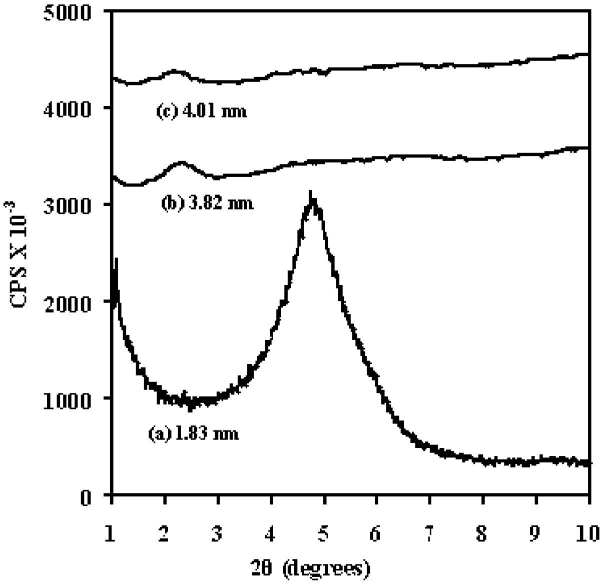

Fig. 1. XRD patterns of (a) Cloisite 30B powder, (b) Nanocomposite with 3% Cloisite 30B, (c) Nanocomposite with 3% Cloisite 30B and 7% polyether polyol.

$2\theta = 4.81°$. The characteristic basal spacing d is 1.83 nm as calculated from Bragg's Law given in Eq. (1):

$$n\lambda = 2d \sin \theta \quad (1)$$

where n, an integer, λ, the wavelength, θ, the glancing angle of incidence and d, the interplanar spacing of the clay layers.

In Fig. 1, curve (b) shows the XRD pattern of epoxy-hardener/Cloisite® 30B system with 3% montmorillonite and no impact modifier. The diffraction peak is shifted to $2\theta = 2.31°$ and the d-spacing is increased to 3.82 nm, since montmorillonite particles are intercalated in the DGEBA–hardener matrix. The diffractogram in curve (c) of Fig. 1 belongs to a nanocomposite with 7% polyol impact modifier and 3% montmorillonite. It shows nearly the same basal spacing and 2θ value as in (b). Thus, it may be concluded that polyol domains do not enter into the clay galleries and the interlayer spacing does not change with the addition of polyol impact modifier. The molecular weight of the polyol is 3500 g/mol, whereas the molecular weight of the hardener is 146 g/mol and the reported epoxy equivalent weight of the DGEBA is 232–250 g/mol. Since the polyol has a much greater molecular weight, it is expected to diffuse less in between the clay layers. SEM data discussed later confirm this interpretation.

3.2. SEM analysis

In Figs. 2 and 3, micrographs of the specimens having no clay but 1 and 7 wt% polyether polyol, respectively, can be seen. Spherical polyether polyol rich domains form an immiscible phase in the epoxy resin. The polyol has the potential of reacting with the epoxy group. Based on the volume fraction of polyol rich domains observed in the SEM, it can be said that most of the polyol is cured and solidified by the epoxy and formed a rubbery phase that is immiscible with the DGEBA–hardener matrix. The polyol rich domains are uniformly distributed throughout the matrix. Uniform distribution of domains is very important as it allows the yielding process to take place throughout the matrix [14]. Generation of voids due to cavitation of the rubbery domains is the most important energy-dissipating mechanism in the case of rubber toughened epoxy [11]. The voids generated act as crack stoppers and improve the impact strength. As the impact modifier content is increased, in general, the number and average diameter of domains also increase as observed from Figs. 2 and 3. The average diameters of the domains are reported in Table 1.

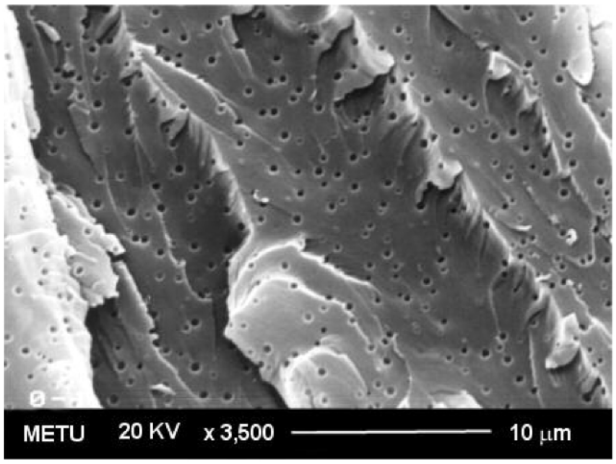

Fig. 2. SEM micrograph of the specimen having no clay, but 1 wt% polyether polyol (× 3500).

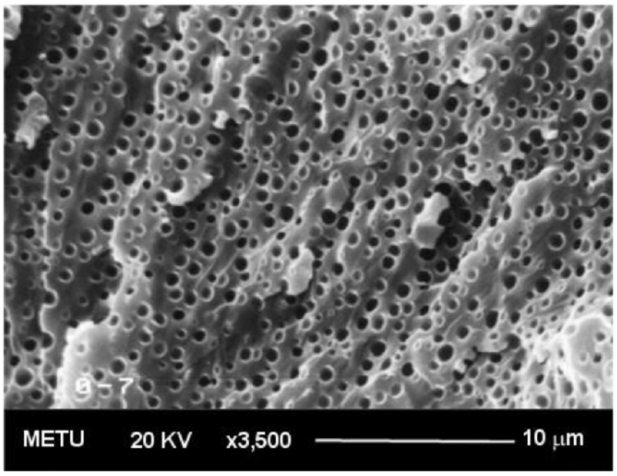

Fig. 3. SEM micrograph of the specimen having no clay, but 7 wt% polyether polyol (× 3500).

Figs. 4 and 5 are SEM photographs of toughened nanocomposites containing 1 wt% clay–1 wt% polyether polyol and 1 wt% clay–7 wt% polyether polyol, respectively. Three distinct phases of epoxy–hardener matrix, montmorillonite and polyether polyol-rich domains are seen. Comparison of Figs. 2 and 3 with Figs. 4 and 5, respectively, indicates that the presence of clay in the materials results in the formation of larger polyol-rich domains. The average diameters of the polyol-rich domains reported in Table 1 support this observation. Figs. 6 and 7 are SEM photographs of nanocomposites having 3 wt% clay–1 wt% polyether polyol and 3 wt% clay–7 wt% polyether polyol, respectively. Comparison of Figs. 6 and 7 with Figs. 4 and 5 in which the clay content is only 1%, indicates that as the clay concentration increases, the clay particles form larger agglomerates and the polyol-rich domains also become larger. The presence of clay in the material prevents uniform dispersion of polyether

Table 1
Average diameter of the polyether polyol domains from SEM analysis

Montmorillonite (wt%)	Domain size (μm)	
	1 wt% polyether polyol	7 wt% polyether polyol
0	0.33	0.57
1	0.47	0.90
3	0.48	0.95
5	0.47	1.03

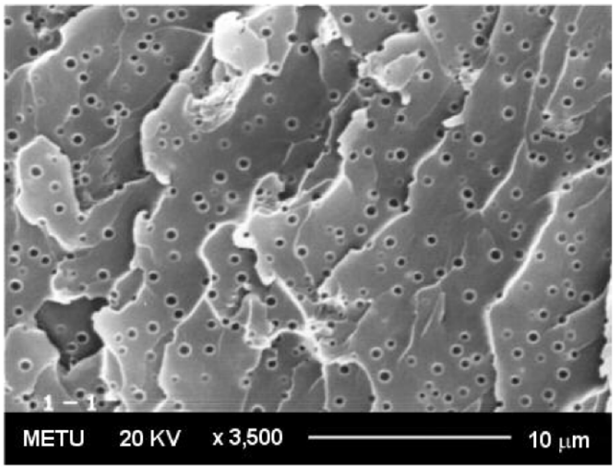

Fig. 4. SEM micrograph of the nanocomposite containing 1 wt% clay and 1 wt% polyether polyol (× 3500).

polyol-rich domains, especially at high polyether polyol concentrations. At high clay contents, the polyol-rich domains join together, and these large domains may act as defects and initiate failure. Figs. 8 and 9 are SEM photographs of samples with 5 wt% clay–1 wt% polyether polyol respectively and 5 wt% clay–7 wt% polyether polyol. Comparison of Figs. 8 and 9 with SEM of specimens containing 3 wt% clay and same amounts of polyether polyol (Figs. 6 and 7) support the previous discussion on the effects of clay content on clay agglomeration and polyol-rich domain size. As seen from Table 1, in samples with 7 wt% polyether polyol, and 0, 1, 3, and 5 wt% clay, the average diameter of the polyol-rich domains is 0.57, 0.90, 0.95, and 1.03 μm, respectively.

3.3. DSC analysis

Table 2 shows the effects of clay and polyether polyol content on the glass transition temperature of the nanocomposites. In general, nanocomposites having 3 wt% Cloisite® 30B display higher glass transition temperatures than the counterparts with no clay. The mobility of the polymer chains falls due to the interaction between the clay and polymer molecules resulting in higher T_g. Considering the variation of T_g with the polyol content, at low polyol contents, the increase in T_g with increasing amount of polyol may be attributed to the possible crosslinking reaction between the OH groups on the polyether polyol-rich domain surface and the surrounding epoxy groups, resulting in lower chain mobility. However, at high polyol contents, the T_g may decrease even if a small portion of the polyol mixes and reacts in the epoxy-rich matrix, thereby increasing the chain mobility of the epoxy-rich matrix.

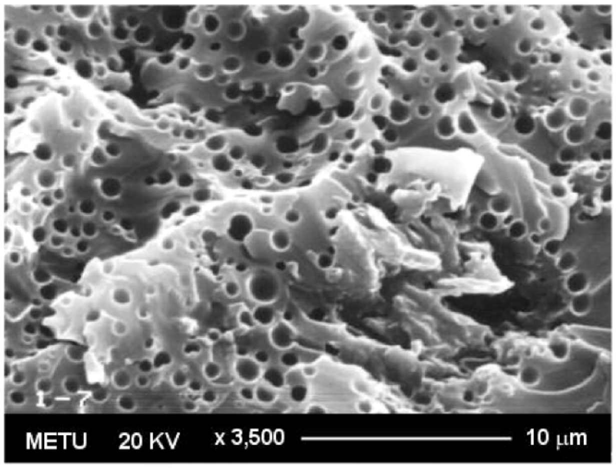

Fig. 5. SEM micrograph of the nanocomposite containing 1 wt% clay and 7 wt% polyether polyol (× 3500).

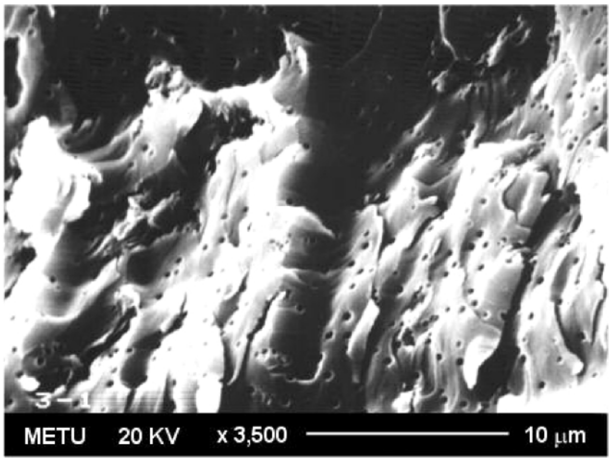

Fig. 6. SEM micrograph of the nanocomposite having 3 wt% clay and 1 wt% polyether polyol (× 3500).

3.4. Mechanical properties

The impact strength of the materials is shown in Fig. 10. The error bars indicate the standard deviation in Figs. 10–13. In general, the impact strength of materials with no clay increases with increasing polyol content. With respect to the impact strength of the neat epoxy, approximately

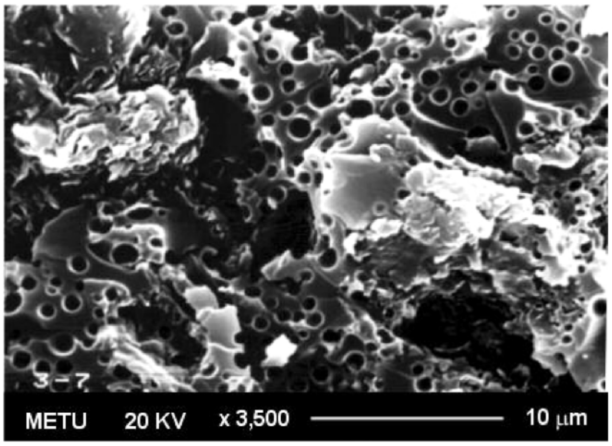

Fig. 7. SEM micrograph of the nanocomposite having 3 wt% clay and 7 wt% polyether polyol (× 3500).

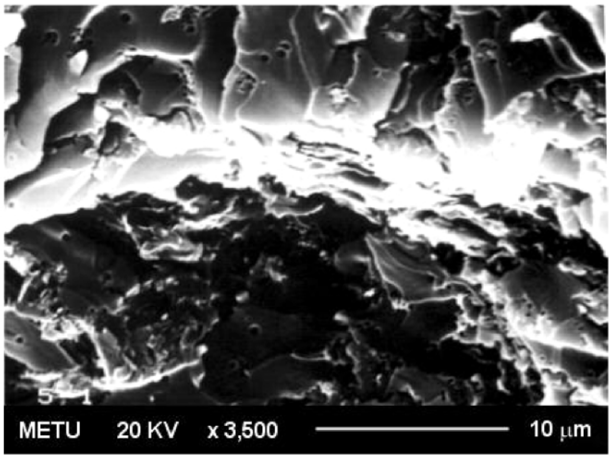

Fig. 8. SEM micrograph of the nanocomposite having 5 wt% clay and 1 wt% polyether polyol (× 3500).

160% increase in impact strength is achieved with the addition of 7% polyether polyol to the DGEBA–hardener system. The immiscible polyol-rich domains observed by SEM would increase the impact resistance by cavitation. It is observed from Fig. 10 that, in general, the impact strength decreases with respect to the clay content. Especially at high clay contents, clay particles agglomerate and act as stress concentrators decreasing the impact strength. In samples with both clay and polyether polyol, the impact strength shows approximately 130% increase in the material containing 1 wt% montmorillonite and 1 wt% polyether polyol in comparison to the impact strength of neat epoxy resin. Beyond an optimum polyether polyol concentration a reduction in impact strength is observed, since large polyol domains with irregular spacing form at high polyol contents.

In Fig. 11, the tensile strength, in general, is observed to decrease with increasing amount of montmorillonite at constant polyol content. This is attributed to higher stress concentration effect of clay agglomerates at high clay contents. Nonexfoliated clay particles form larger agglomerates, and thus clay–polymer surface interactions decrease as the clay content increases resulting in lower tensile strength. Tensile strength of the nanocomposites modified with polyether polyol, generally tends to show a maximum with respect to the polyol content. As discussed in the DSC analysis, upon addition of polyol, crosslinking of the system at the polyol-rich domain interface may increase the tensile strength. Also, at low polyol contents, the polyol-rich domains may act as crack stoppers and increase the tensile strength. However, at higher polyol contents, the rubbery effect of the polyol domains may become dominant and the tensile strength may exhibit a tendency to decrease. Morphology of the system also plays a major role. At high polyol contents, the polyol-rich domains are larger, and thus the stress concentration effect of these domains could be higher resulting in lower tensile strength.

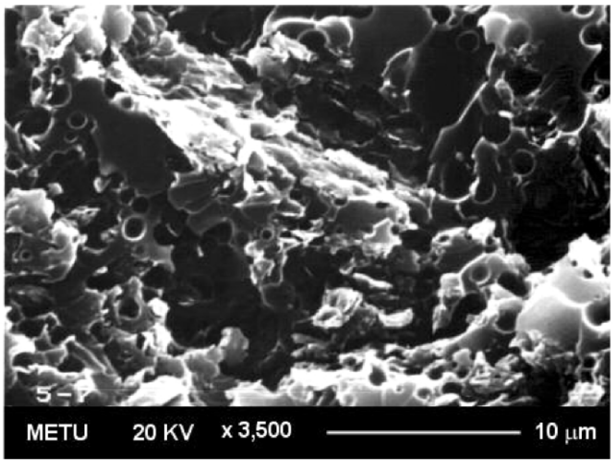

Fig. 9. SEM micrograph of the nanocomposite having 5 wt% clay and 7 wt% polyether polyol (× 3500).

Table 2
Glass transition temperature (T_g) of the nanocomposites

Polyether polyol (wt%)	T_g (°C)	
	Clay (0%)	Clay (3%)
0	72	71
1	76	85
3	82	84
5	83	85
7	81	85

In Fig. 12, the tensile modulus of the nanocomposites are shown. In general, the tensile modulus increases with increasing amount of montmorillonite at constant polyol

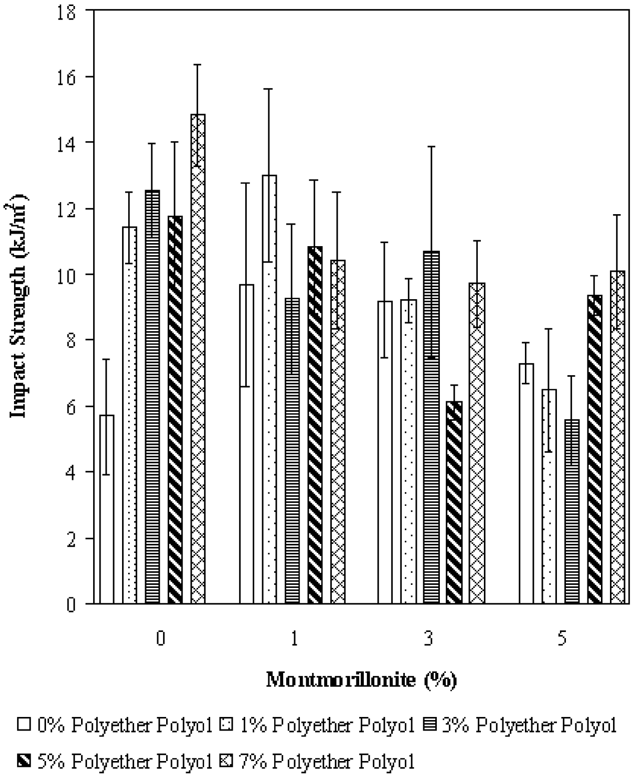

Fig. 10. Impact strength versus wt% of Cloisite® 30B and polyether polyol.

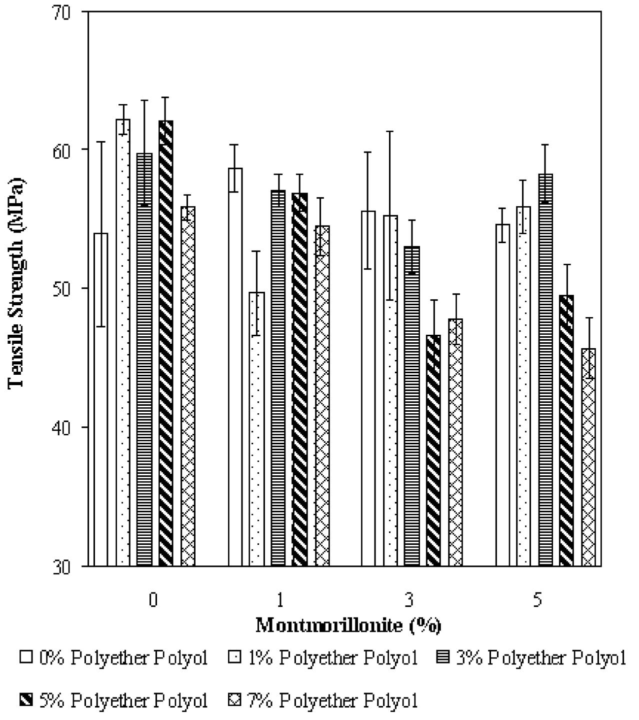

Fig. 11. Tensile strength versus wt% of Cloisite® 30B and polyether polyol.

content. The modulus of a composite depends on the ratio of filler modulus to matrix material modulus [15]. Since montmorillonite has a higher modulus than the polymeric matrix, the modulus increases with the clay content. However, in general, the tensile modulus shows a maximum with respect to the polyether polyol content at constant clay loading. As the polyol content increases, the number of crosslink points at the polyol-rich domain surface increases as discussed earlier. Thus the tensile modulus at first increases with the polyol content. However, at high polyol contents, the tensile modulus gradually decreases as the amount of the low modulus, rubbery phase increases.

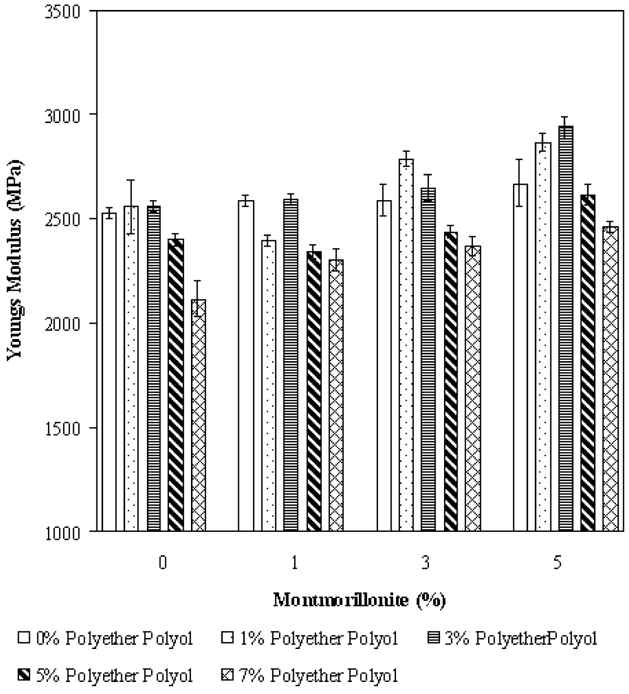

Fig. 12. Young's modulus versus wt% of Cloisite® 30B and polyether polyol.

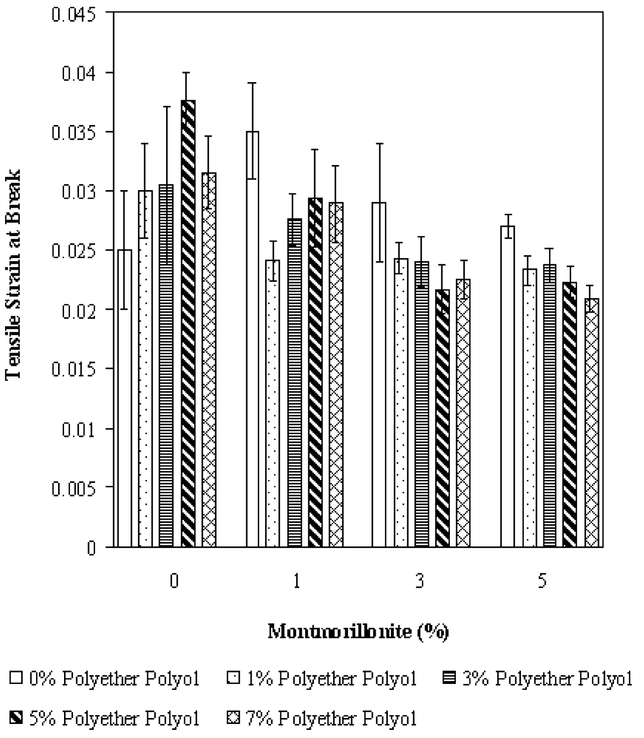

Fig. 13. Tensile strain at break versus wt% of Cloisite® 30B and polyether polyol.

Tensile strain at break results are shown in Fig. 13. The strain at break of polyol modified epoxy with no montmorillonite increases with the polyol content, up to 5% polyol, owing to the high extensibility of the rubbery polyol-rich domains. However, at 7% polyol content, the existence of large polyol-rich domains results in lower strain at break. Also, the effectiveness of polyol in increasing the tensile strain at break diminishes as montmorillonite is added in larger quantities. In ternary nanocomposites, the strain at break decreases as the montmorillonite content in the nanocomposites increases. Since montmorillonite is rigid, almost all of the elongation comes from the polymer matrix and the measured elongation of the nanocomposites is lower than the actual elongation of the polymer matrix. It can be concluded that the effect of montmorillonite is in general more dominant in the elongation at break behavior.

4. Conclusions

Partially intercalated nanocomposites were synthesized, since the basal spacing of organically modified montmorillonite powder increases from 1.83 to 3.82 nm upon mixing into the DGEBA–hardener system. The addition of polyether polyol impact modifier does not significantly change the basal spacing. Thus, it can be concluded that polyether polyol domains do not enter into galleries between the clay layers.

SEM micrographs show that polyol forms an immiscible phase in epoxy matrix. The rubbery domains are distributed more nonuniformly and the diameter of the domains increases as the polyether polyol content increases. It is also observed that the clay particles form agglomerates especially at high polyol and montmorillonite contents.

DSC analyses indicate that T_g increases with the addition of montmorillonite, and exhibits a maximum with respect to the polyether polyol content.

In polyol modified epoxy (with no montmorillonite) the impact strength increases as the polyether polyol content increases. However, in the epoxy–montmorillonite binary systems (with no polyol), impact strength shows a maximum at 1 wt% montmorillonite content. In epoxy–montmorillonite–polyether polyol ternary systems, the impact strength, in general, decreases with respect to increasing amount of montmorillonite.

Tensile strength and strain at break show a maximum at 1 wt% montmorillonite content in epoxy–montmorillonite binary systems. In polyol modified nanocomposites, the tensile strength and strain at break decrease, in general, as the montmorillonite content increases.

Young's modulus of the samples increases with increasing amount of montmorillonite. However, it shows a maximum with respect to the polyether polyol content.

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