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EFFECT OF NONISOCYANATE POLYURETHANE AND NANOCLAY ON THE MECHANICAL PROPERTIES OF AN EPOXY RESIN

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The effect of condensation nonisocyanate polyurethane (NIPU) addition on the mechanical properties, chemical structure, and morphology of an epoxy resin (EP) modified with nanoparticles (Nanobent) was investigated. The impact strenght (IS), flexural strength, and critical stress intensity factor (K_C) of the epoxy resin was determined as functions of NIPU and Nanobent content. The highest values of IS and K_C were found for the hybrid composition containing 10% NIPU and 1% Nanobent. SEM micrographs suggested that the enhancement of mechanical properties might be due to the extensive yielding of EP associated with the formation of stratified elongated structures. Based on an IR analysis, the characteristic bands for both the epoxy matrix and the condensation NIPU were identified, indicating that the polymers formed the NIPU network without a grafting reaction.

Introduction

In the last few decades, a good deal of effort has been devoted to the preparation of environmentally friendly nonisocyanate polyurethanes (NIPUs) with improved mechanical properties, instead of the conventional polyaddition polyurethanes, which are based on the toxic and expensive diisocyanates. The majority of studies dealt with the preparation and evaluation of the mechanical properties of NIPUs using carbon dioxide and diamines [1-5].

Diakoumakos and Kotzev [6] analyzed the DMA of NIPUs prepared from cyclocarbonate and amine. The analysis confirmed that the NIPUs obtained had a very low glass-transition temperature (–1°C), a short gel time (390 min) at room

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temperature, and a relatively high elongation at break (approximately 70%). Zhao et al. [7] used a simple nonisocyanate route to synthesize crystallizable aliphatic segmented thermoplastic poly(ether urethane)s (PEIUs) and elastomers exhibiting good mechanical properties. The PEIUs obtained had a high melting temperature (about 140°C) and a tensile strength of about 50 MPa.

Soybean and other vegetable oils were used as alternatives by several researchers to produce environmentally friendly nonisocyanate polyurethanes [8-10]. Javni et al. [8] found that the NIPUs based on diamines with a rigid aromatic or cyclic structure had a high strength and rigidity. Their tensile strength was higher than that of aliphatic diamine-based polyurethanes. The highest tensile strength was obtained with p-xylylene diamine and the lowest with m-xylylene diamine. DSC results confirmed that all amines produced elastomeric polyurethanes with glass-transition temperatures between –6 and 26°C. Wilkes et al. [9] evaluated the mechanical and dynamic properties of NIPUs prepared using different amines. Bähr and Mülhaupt [10] prepared NIPUs, using carbonated soybean and linseed oils with different diamines, with improved glass-transition temperatures and stifness.

It has to be mentioned that nanoclays were already succesfully used as toughening agents for epoxy resins [11-15]. Almost all the studies attributed the improvement in the mechanical properties of polymers to the exfoliation and/or intercalation processes of clay nanoparticles. The possible specific interactions between nanoclays and the polymeric matrix may could enhance their properties still further.

However, only few studies have considered the toughening of epoxy resin with NIPUs. Ke et al. [16] studied the properties of NIPU/epoxy blends and showed that a NIPU based on amines with more functional groups led to an improved tensile strength and elongation at break than diamine-based blends. He et al. [17] investigated the properties and structure of hybrid nonisocyanate polyurethanes (HNIPUs). Their results showed that the HNIPUs based on a Bisphenol-A epoxy resin having a mean epoxy value of 0.51 exhibited the best mechanical and thermal properties because of its high cross-linking density. Wazarkar e al. [18] investigated the properties of epoxy-urethane hybrid composites prepared by the nonisocyanate route. The composites exhibited improved mechanical and corrosion resistances as compared with those of epoxy resin.

The purpose of the present work was to toughen an epoxy resin by using a combination of nanoparticles and condensation nonisocyanate polyurethane.

1. Experimental

1.1. Materials

The following chemicals were used in the present study.

- Polymeir matrix: epoxy resin (ER) — diglycidyl ether of bisphenol A (trade name Epidian 5) from Organika Sarzyna (Poland), with a molecular weight of about 380 g/mol and epoxy number 0.49-0.52 mol/100g;

- Curing agent: triethylene tetramine (trade name Z1), purchased from Organika (Sarzyna, Poland);

- Modifiers:

- nonisocyanate polyurethanes with different content of hard segments;
- Nanobent nanoclay ZR1 modified with dimethylbenzyl (C12-18) alkyl ammonium chloride (product of ZGM “Zębiec” S.A. Poland).

1.2. Preparation of epoxy/Nanobent and epoxy/polyurethane compositions

Epoxy nanocomposites containing different amounts of Nanobent (1, 2, and 3 wt.%) were prepared according to the following procedure. First, a 15% dispersion of organomodified Nanobent was mixed with acetone using a Hielscher UP 200H ultrasonic stirrer with an amplitude of 260 μm during 15 min. Then, Nanobent was mixed with epoxy resin during 30 min under the same conditions. The air bubbles and solvent were removed by leaving the systems under vacuum in an air-circulating oven for 3 h at 40°C. Finally, a stoichiometric amount of curing agent (12 g per 100 g of resin) was added, and the mechanical mixing continued for 5 min. The epoxy samples prepared were poured into clean aluminum molds with adequate geometries suitable for mechanical testing. Curing of the nanocomposites occurred at room temperature for 24 h, followed by postcuring for 5 h at 60°C.

An epoxy resin containing different amounts of polyurethane (5, 10, 15 wt.%) and a reference virgin epoxy composition were prepared under the same conditions. The nonisocyanate polyurethanes, having different amounts of hard and flexible segments, were prepared according to the procedure described in [19].

1.3. Preparation of epoxy nanocomposites modified with NIPU

The NIPUs obtained were incorporated into an epoxy resin containing dispersed organomodified layered aluminosilicate (Nanobent). Epoxy compositions containing 1% nanofiller and different amounts of NIPU were prepared. Nanobent was added as a 15% dispersion in acetone and homogenized ultrasonically with Hielscher UP200H. Each composition contained 1wt.% Nanobent and different amounts (5, 10, and 15 wt.%) of synthesized oligomeric liquid urethane. They were first cured with triethylene tetramine (Z1) at room temperature for 24 h and then postcured during 5 h at 60°C. These procedures were selected based on the results of previous experiments, where composites were postcured for 1-7 h at different temperatures. Samples of the unmodified epoxy resin were prepared and cured in the same manner using 12 g triethylene tetramine per 100 g epoxy resin.

1.4. Evaluation of the properties, structure and morphology of epoxy nanocomposites

The nanocomposite samples obtained were subjected to mechanical tests to determine their resistance to slow (the critical stress intensity factor K_C) and fast crack propagations (the impact strength — IS) and the flexural strength in three-point bending.

- The impact strength was measured according to the Charpy method using a Zwick/Roell Z012 apparatus, according to PN-EN ISO 179:2001, on 10 × 10 × 4-mm samples with a 1-mm notch.
- The critical stress intensity factor K_C was evaluated in three-point bending on 80 × 10 × 4-mm samples with a 1-mm notch. The measurements were carried out, using Zwick/Roell Z010, at room temperature with a deformation rate of 5 mm/min and a span $L = 60$ mm [20]. K_C was found as

$$K_C = \frac{3PL\sqrt{a}}{2Bw^2} Y\left(\frac{a}{w}\right),$$

where P is the load at break, a is the notch length, w is sample width, B is sample thickness, and Y is a geometrical factor, which was calculated from the equation [20]

$$Y\left(\frac{a}{w}\right) = 1.93 - 3.07\left(\frac{a}{w}\right) + 14.53\left(\frac{a}{w}\right)^2 - 25.11\left(\frac{a}{w}\right)^3 + 25.80\left(\frac{a}{w}\right)^4 .$$

The flexural properties (the stress and strain at break) were estimated, according to PN-EN ISO 178:2011, at room temperature on specimens of the same dimensions as for impact tests by using Zwick/Roell Z010 at a deformation rate of 5 mm/min and $L = 60$ mm.

The Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet iS10 spectrophotometer (Thermo Scientific), recording the infrared spectra from 400 to 4000 cm^{-1}, with KBr pastilles containing 1.2 ± 0.1 mg of tested composition. A Hitachi SU8010 scanning electron microscope was used to perform a morphology analysis of fracture surfaces of the samples obtained from impact tests.

TABLE 1. Composition of NIPUs and Their Mechanical Properties

Designation of oligomers with HS	Base components, mole				Molar ratio HS : FS in NIPU	Tensile strength, MPa	Tensile strain at break, %
	PSA	F	U	HNSA			
MNF 10	0.09	0.20	0.10	0.01	0.8:1	10.3	120
					1.0:1	11.4	110
					1.5:1	11.2	110
MNF 20	0.08	0.20	0.10	0.02	0.8:1	11.2	85
					1.0:1	11.9	110
					1.5:1	12.5	100
MNF 30	0.07	0.20	0.10	0.03	0.8:1	11.8	100
					1.0:1	12.7	110
					1.5:1	12.9	95

*PSA: Phenol Sulfonic Acid, F: Formaldehyde, U: Urea, HNSA- Hydroxy Naphtalene Sulfonic Acid, HS: Hard Segments, FS: Flexible Segments.

TABLE 2. Some Mechanical Properties of Epoxy Resin Modified with Different Amounts of Nanobent

Amount of Nanobent ZR1, %	Impact strength, kJ/m^2	K_C, MPa · m$^{1/2}$	Flexural strength, MPa	Strain at break, %
0	1.0	1.0	40	2.0
1	1.6	1.7	45	4.7
2	1.4	1.6	48	4.2
3	1.2	1.3	44	4.0

2. Results and Discussion

2.1. Mechanical properties of nonisocyanate polyurethanes

Some mechanical properties of NIPUs containing different amounts of 2-hydroxy –6 naphthalene sulfonic acid are shown in Table 1.

The tensile strength and elongation at break of the NIPUs prepared were evaluated on oligomers subjected to a thermal treatment at 60°C during 2h. The highest tensile strength (12.7 MPa) and a satisfactory elongation at break (110%) were obtained from an MNF 30 oligomer with an equimolar ratio of hard to flexible segments in NIPU, and this polyurethane was selected as the modifier for the epoxy resin modified with 1 wt.% nanofiller.

2.2. Mechanical properties, structure, and morphology of epoxy nanocomposites and epoxy/NIPU/Nanobent ternary composites

Table 2 shows the mechanical properties of epoxy resin containing different amount of Nanobent. It is seen that the impact strength, the critical stress intensity factor K_C, and the flexural strain at break reached their maxima at only 1 wt.% of Nanobent, which by about 60 and 70%, and more than 130%, respectively, exceeded those of neat epoxy samples. However, the nanocomposite showed only a 13% increase in the flexural strength. In the studies on epoxy nanocomposites, their improved

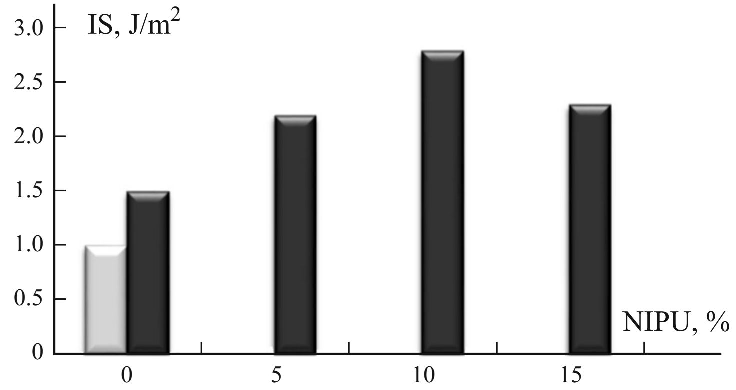

Fig. 1. Effect of polyurethane content on the impact strength of the ER modified with 1% Nanobent (■). □ — pure epoxy resin (designations for Figs. 1-4).

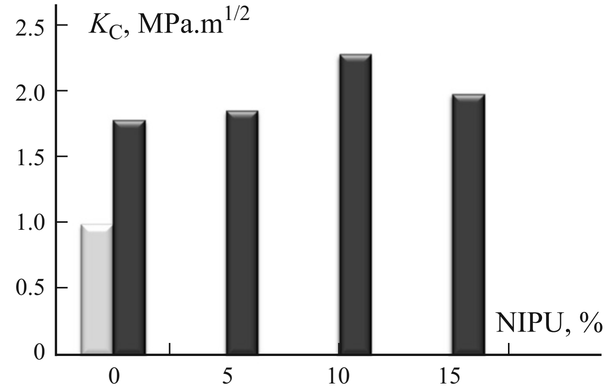

Fig. 2. Effect of polyurethane content on the critical stress factor K_C of the ER modified with 1% Nanobent.

resistance to the slow crack propagation, expressed by K_C, and the impact strength, representing the fast crack propagation, was attributed to the exfoliation/intercalation processes of nanoparticles [21-23].

The increase in the strain at break of epoxy resin due to the presence of Nanobent might be explained by the plasticizing effect of crosslinked epoxy chains. This is further confirmed by the high aspect ratio of contact surface of the organomodified nanoclay. Park and Jana [24] showed that the plasticization of epoxy networks could be achieved by hydrocarbon chains of quaternary ammonium ions of nanoclays, which resulted in a significant reduction in the glass-transition temperature and in lowering of the storage modulus of cured epoxy networks. Indeed, it is well known that the addition of a plasticizing agent increases the free volume, which facilitates the motion of polymer chains and thus increases the elongation at break and, consequently, the energy needed to fracture the samples.

Figure 1 shows the effect of nonisocyanate polyurethanes (NIPU) based on MNF30 (i.e., polyurethane prepared with 30% moles of 2-hydroxy –6 naphthalene sulfonic acid) and 1 wt.% Nanobent content on the impact strength (IS) of epoxy resin (ER). It can be seen that the impact strength first increased and then decreased with increasing amount of the polymeric modifier. Moreover, all epoxy hybrid composites (i.e., epoxy compositions containing both nanoparticles and polyurethane) had a significantly higher IS in comparison with that of the neat epoxy sample and the ER modified with 1 wt.% Nanobent. The maximum value of IS, corresponding to about a 180% increase in relation to that of the unmodified ER and 85% vs ER containing 1% Nanobent, was obtained for the hybrid composition containing 10% NIPU and 1% Nanobent.

Figure 2 represents the effect of NIPU addition on the critical stress intensity factor K_C of epoxy nanocomposites. As is seen, the addition of nanoparticles and the polymeric modifier increased the factor K_C of the virgin ER. As in the case

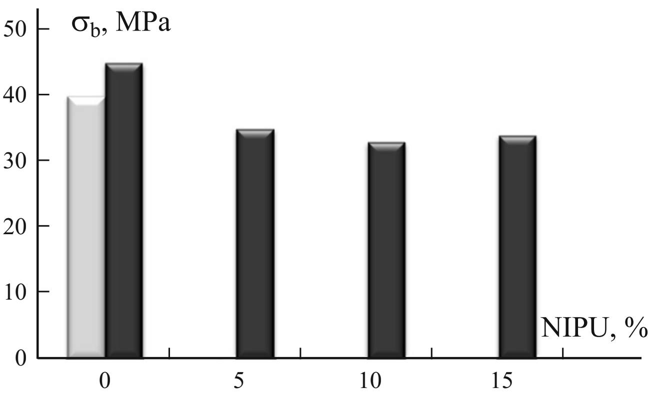

Fig. 3. Effect of polyurethane content on the stress at break σ_b of the ER modified with 1% Nanobent.

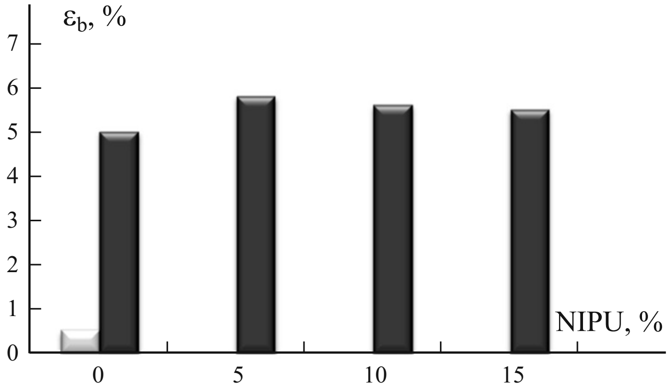

Fig. 4. Effect of NIPU content on the strain at break ε_b of the ER modified with 1% Nanobent.

of impact strength, whose values are shown in Fig. 1, K_C increased for all ER samples containing NIPU and nanoparticles. However, the maximum value of K_C was obtained for the hybrid epoxy composite containing 10% NIPU and 1% Nanobent. The resistance to slow crack propagation increased by 80 and 25% in comparison with that for neat epoxy samples and the ER modified with 1% Nanobent, respectively. The growth in the impact strength and K_C can be explained by the penetration of polyurethane chains between nanoclays platelets and the exfoliation/intercalation of nanoclay [25]. A good dispersion of nanoparticles, combined with specific interactions between the modifier and the polymeric matrix, may contribute to a further increase in the resistance to crack propagation.

The flexural stress at break as a function of nonisocyanate polyurethane (NIPU) content is shown in Fig. 3. A slight decrease in the flexural strength (about 10% in relation to that of the neat epoxy sample or the epoxy nanocomposite based on 1% Nanobent) upon incorporation of NIPU can be seen. It should be mentioned that the addition of 1% Nanobent increased the flexural strength by approximately 12.5% in relation to that of the unmodified epoxy matrix.

The strain at break ε_b of epoxy resin containing 1wt.% Nanobent as a function of content of the polyurethane-based MNF30 is shown in Fig. 4. A very significant increase in ε_b is seen for epoxy composites based on 1% Nanobent and hybrid epoxy composites with nonisocyanate polyurethanes, but the maximum one exhibited the hybrid composite based on 1wt.% Nanobent and 5% NIPU.

Table 3 shows the effect of nonisocyanate polyurethane (NIPU) content on the flexural energy (FE) to break and the brittle fracture energy (BFE) of the epoxy resin modified with 1 wt.% Nanobent. The energy to break of samples in flexure and the brittle fracture energy were evaluated from the areas under the flexural strain–strain curve and the curve obtained during estimation of the critical stress intensity factor, respectively. It can be noted that the maximum value of FE was exhibited

TABLE 3. Fracture Energies of the ER Modified with 1% Nanobent as a Function of NIPU Content

NIPU content, %	Flexure energy to break, kJ/m^2	Brittle flexure energy, kJ/m^2
0	3.9	0.9
5	4.4	1.4
10	4.2	1.6
15	3.3	1.3

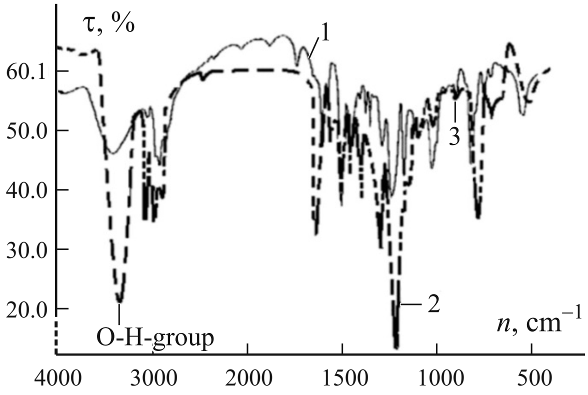

Fig. 5. FTIR spectra (transmittance τ vs. wave number n) of the virgin ER and ER modified with 10% polyurethane and 1% Nanobent.

by the hybrid epoxy nanocomposite containing 5% NIPU. The enhancement of FE can be explained by the maximum value of strain at break of the hybrid nanocomposite with 5% NIPU, as shown in Fig. 4. However, the maximum value of BFE was obtained for the hybrid nanocomposite containing 10% NIPU, as in the case of K_C (Fig. 2). The growth in fracture energies clearly confirm the increase in ductility of the epoxy matrix with addition of modifier, in agreement with the growing strain at break.

In Fig. 5, FTIR spectra of the unmodified EP and the composition containing 1% Nanobent and 10% NIPU are shown. Since the spectra of epoxy nanocomposites with different amounts of polyurethane did not show noticeable differences, only the spectrum for the pure ER and the composite containing 10% NIPU are presented.

From Fig. 5, it is seen that the ER modified with NIPU showed and increased intensity peak of hydroxyl group, appearing at 3300 cm^{-1}. This might be related to the stretching of O–H groups from the epoxy matrix and polyurethane, as well as stretching of NH. The absorption band at 1640-1650 cm^{-1} is associated with the C=0 group in polyurethane, while other modes of -CH$_2$ are seen in the bands appearing at 1460 and 1360 cm^{-1}. In addition, the NH vibrations are identified by the bands at 1540 cm^{-1}.

There is a small peak, characteristic of urethane groups, at 2160 cm^{-1}. The characteristics peaks of base polyurethane ingredients (urea, urethane, phenolic group, and the epoxy resin group O–H) are also identified. Other peaks are specific to NIPU and EP.

The presence of distinct characteristic bands of both the epoxy matrix and the condensation segmented polyurethane allows us to assume that these polymers formed an interpenetrating polymer network.

In order to explain the effect of NIPU and nanoclay addition on the mechanical properties of the polymeric matrix, SEM micrographs of sample surface after impact tests were obtained and analyzed. Figure 6 shows SEM micrographs of the pristine epoxy resin and hybrid epoxy nanocomposites with NIPU.

The micrograph of the unmodified epoxy resin shows a flat surface (Fig. 6a), which is characteristic of glassy and brittle polymers. Figures 6b, c, and d show the micrographs of epoxy nanocomposites modified with 5, 10, and 15% NIPU.

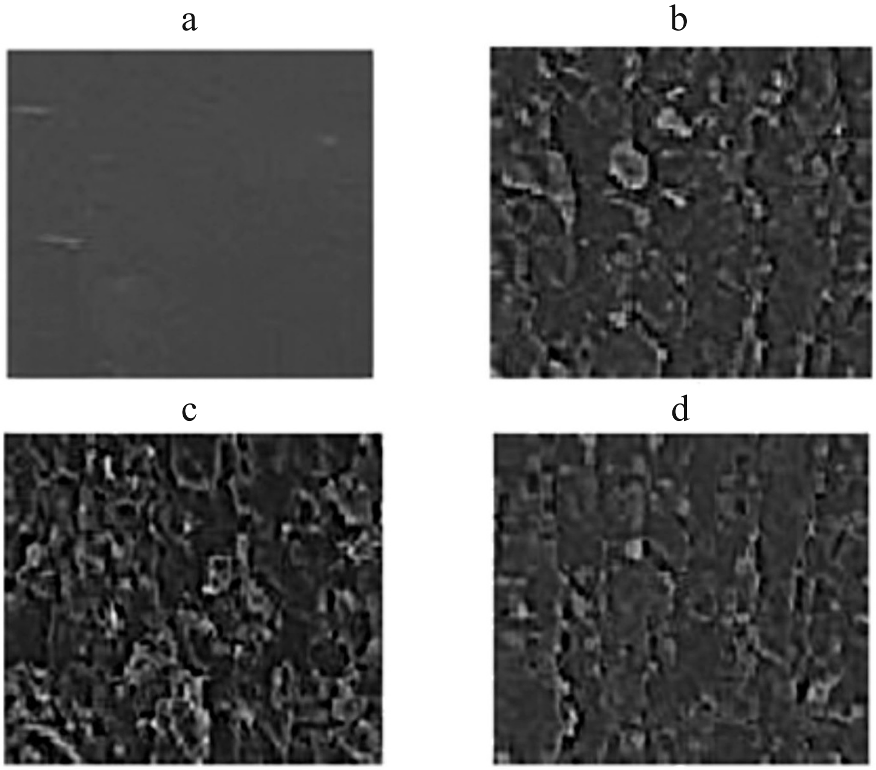

Fig. 6. SEM micrographs (magnification 1500×) of fracture surfaces of samples containing the unmodified epoxy resin (a), 5% NIPU and 1% Nanobent (b), 10% NIPU and 1% Nanobent (c), and 15% NIPU and 1% Nanobent.

As seen, these fracture surfaces are rough, stratified structures with embedded Nanobent nanoparticles. The most important plastic yield zones and a rough surface can be observed for the sample containing 10% NIPU and 1% Nanobent. However, as reported earlier [26], the micrograph of ER (Epidian 5) modified with 1% Nanobent ZR1 show stratified and more elongated structures and nanoparticles uniformly embedded in the polymeric matrix. The existence of these specific features explains the increased impact strength, critical stress intensity factor, and fracture energies of the polymeric matrix.

Conclusions

Hybrid epoxy composites with improved mechanical properties were prepared by using nonisocyanate polyurethane (NIPU) and Nanobent. All epoxy composites containing 10% NIPU and 1% Nanobent showed a higher impact strength (IS) and critical stress intensity factor K_{C} than the neat epoxy and the EP modified with 1% Nanobent. The increase in IS and K_{C} attained 180 and 80%, respectively, in comparison with those of the unmodified EP. The hybrid epoxy composites were more ductile, with a higher flexural strain at break and a higher flexural energy to break and brittle fracture energy.

A FTIR analysis revealed the characteristic bands of both the epoxy matrix and the condensation NIPU and confirmed the formation of an interpenetrating polymer network structure without grafting reactions, explaining further the increase in ductility and fracture toughness of the polymeric matrix. The SEM micrographs of hybrid epoxy composites based on 1 wt.% Nanobent and NIPU showed rough and stratified fracture surfaces with a significant plastic yielding, explaining the increase in the resistance to slow and fast crack propagations. The SEM micrograph of the virgin epoxy sample showed a flat surface, typical of brittle polymers, without plastic yielding or an elongated structure.

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