

Preparation and Characterization of an Epoxy Resin Modified by a Combination of MDI-Based Polyurethane and Montmorillonite

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ABSTRACT: The present work investigates the modification of epoxy resin by using a combination of nanoclay (montmorillonite—Cloisite 30B) and a liquid polymeric modifier (polyurethane). Polyurethane was obtained from 4,4'-diphenylmethane diisocyanate and polydiols with different molecular weight: polyethylene glycol (PEG 400) and polyoxypropylene diols with molecular weight 1000 g/mol and 2000 g/mol. The impact strength, the critical stress intensity factor as well as the flexural strength were evaluated as functions of modifiers content. The obtained results showed that hybrid composites exhibit enhanced mechanical properties without significant changes of the

glass transition temperature. FTIR analysis showed that chemical reactions took place between the hydroxyl groups of epoxy resin and the isocyanate groups of polyurethane, explaining an improvement of the mechanical properties of epoxy resin. However, XRD results demonstrated the formation of an exfoliated structure for the hybrid compositions with both polyurethane and montmorillonite. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3237–3247, 2011

Key words: epoxy resin; polyurethane; MDI; montmorillonite; nanocomposites; mechanical properties

INTRODUCTION

Several methods have been used to overcome brittleness and enhance toughness of cured epoxy resins (EP) having fracture toughness about two orders of magnitude lower than engineering thermoplastics.^{1–5}

Due to their high flexibility and versatile structure, polyurethanes (PUR) have extensively been used to improve the mechanical properties of epoxy resins.^{6–8}

Recently, the effect of polyurethanes differing in their isocyanate index on the mechanical and thermal properties of diglycidyl ether of Bisphenol A was investigated, and the positive effect of the reactive groups was confirmed.⁹ Moreover, it was shown that polyurethane can be linked to the epoxy network through physical entanglements as well as chemical bonding resulting in graft IPN structures with enhanced mechanical properties.^{10–14} The surface free energy and its components were also measured as function of polyurethanes isocyanate index,¹⁵ and the increase of the critical stress inten-

sity factor (K_{IC}) and impact strength (IS) at low temperatures was related to the polar components of the surface free energy. The enhancement of the mechanical properties was explained as a result of improvement of hydrogen bonding between hydroxyl groups of EP and isocyanate groups of PUR.

In the last few decades, hybrid epoxy compositions containing two different modifiers (one in a liquid state and another in a solid state) were prepared with the aim to improve mechanical and thermal properties of brittle epoxy resin via synergism mechanism. The use of both stiff and soft modifiers may promote, under optimal conditions, the simultaneous occurrence of two toughening mechanisms providing the synergistic effect on the fracture toughness.

Fröhlich et al.¹⁶ used both inorganic nanofiller and compatibilized polyether liquid rubbers to modify an epoxy resin. They found enhanced toughness of epoxy resin due to the presence of compatibilizer which induced phase separation of the rubber.

Furthermore, Ramos et al.¹⁷ reported improvement of the mechanical properties (impact strength) of epoxy resin modified with carboxyl-terminated butadiene acrylonitrile copolymer (CTBN). For the hybrid compositions containing fly ash microspheres, an improvement of the impact strength was noticed only when CTBN was added.

Shetty and Rai^{18,19} toughened diglycidyl ether of Bisphenol A based epoxy resin with thermoplastic

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hydroxyl-terminated polyurethane elastomer and fly ash as well as hydroxyl-terminated polyurethane elastomer and silane coupling agent treated granite powder. In both cases, the results demonstrated that toughened composites exhibited enhanced properties in comparison to the neat matrix.

The effect of modified montmorillonite and carboxyl-terminated butadiene acrylonitrile on the mechanical properties and morphology of epoxy resin cured with polyetheramine was investigated by Lee and his research group.²⁰ It was noted that nanoclay can be well dispersed in the ternary epoxy based nanocomposite and the curing agent contributed to the intercalation of montmorillonite resulting in improved properties of the polymer matrix.

Very recently, Mirmohseni and Zavareh²¹ evaluated the impact strength and tensile properties and analyzed the structure of diglycidyl ether of bisphenol A reinforced with a thermoplastic (acrylonitrile-butadiene-styrene) and organically modified clay (Cloisite 30B). Their results showed that impact strength of epoxy matrix increased significantly upon the addition of 2.5% clay and 4 phr ABS. Moreover, impact and tensile strengths of ternary nanocomposites were higher than those of binary systems. New morphologies were achieved for epoxy/ABS and epoxy/ABS/clay hybrid materials. Exfoliated clay structure was obtained for a ternary nanocomposite.

Jia et al.²² used nanosized silicon dioxide particles to modify interpenetrating polymer networks (IPN) of polyurethane and epoxy resin. They showed that an addition of nanoparticles improves the compatibility between the components as well as the damping and phase structure of IPN matrices.

Polyurethane based on polyether and toluene diisocyanate was also combined with glass beads to toughen diglycidyl ether of bisphenol A.²³ The obtained results showed that hybrid compositions containing 10 phr PUR and 15 phr of glass beads exhibited the maximum tensile energy to break in relation to neat epoxy resin as well as composition containing only 10 phr PUR.

Zeng et al.²⁴ modified epoxy resin by using a combination of SiO₂ nanoparticles and carboxyl-randomized liquid butadiene-acrylonitrile rubber (CRBN) nanocomposites. They found that nanocomposite containing 2% SiO₂ and 5% CRBN showed improved impact strength and modulus. Moreover, the nanocomposites morphology analysis by means of scanning electron microscopy and transmission electron microscopy showed a three-phase system as well as uniform dispersion of both the rubber and the SiO₂ nanoparticles in the epoxy matrix.

In our previous work,²⁵ we have evaluated the properties and analyzed the morphology of an ep-

oxy resin modified with montmorillonite nanoclay and polyurethanes obtained from polyethylene glycol (PUR 400) and polyoxypropylene diol (PUR 1002). It was found that the composition containing 2% nanoclay and 10% PUR 400 as well as compound with 1% nanoclay and 15% PUR 400 exhibited maximum improvement of impact strength in comparison with unmodified epoxy resin. Moreover, the flexural strain at break of the composition containing 15% PUR 1002 and 2% nanoclay was significantly increased. The improvement of the mechanical properties of epoxy resin was associated with increased yielding of the polymer matrix as well as the occurrence of chemical reactions which have taken place between the hydroxyl groups of epoxy resin and the isocyanate groups of polyurethane.

The aim of the present work is to investigate the mechanical properties and morphology of an epoxy resin modified with polyurethane and reinforced with an organomodified montmorillonite. The occurrence of interactions between the isocyanate groups of PUR and the hydroxyl groups of the quaternary ammonium salt in the nanoclay on one side, and the amine groups of the curing agent on the other side is expected. This is supposed to lead into enhancement of the stability of the nanoclay dispersion after exfoliation.

EXPERIMENTAL

Materials

For nanocomposites preparation the following components were used:

1. Epoxy resin—diglycidyl ether of bisphenol A (Epidian 5, Organika Sarzyna, Poland) with a molecular weight of 400 g/mol, viscosity at 25°C around 30 Pa.s and epoxy number equal to 0.49 to 0.52 mol/100 g;
2. Triethylenetetramine hardener (trade name Z1, Organika Sarzyna, Poland);
3. Polyethylene glycol with molecular weight of 400 g/mol (PEG 400) and 277 mg/g hydroxyl number (Merck, Germany);
4. Polyoxypropylene diol with 1000 g/mol molecular weight (POPD 1002) and hydroxyl number of 180 mg/g (Rokita, Poland);
5. Polyoxypropylene diol with 2000 g/mol molecular weight (POPD 2002) and 46 mg/g hydroxyl number obtained from Rokita, Poland;
6. 4,4'-diphenylmethane diisocyanate (MDI) produced by Merck, Germany; pure for synthesis
7. Dibutyltin dilaurate catalyst (Merck, Germany);
8. Montmorillonite nanoclay modified with tallo-quaternary ammonium salt (Cloisite 30B, Southern Clay Products Inc.);

9. Toluene and acetone solvents (Lahner, Czech Republic).

Samples preparation

Synthesis of polyurethane

Three types of polyurethanes were prepared from 4,4'-diphenylmethane diisocyanate (MDI) and polyols: PUR based on PEG 400 (abbreviated PUR 400M) and polyoxypropylene diols POPD 1002 (PUR 1002M) and POPD 2002 (PUR 2002M). The appropriate amounts of MDI were calculated as follows: 27 g for PUR 400M, 13.5 g for PUR 1002M, and 6.6 g for PUR 2002M. Polyols were purified by means of azeotropic and vacuum distillation with toluene to eliminate water. First, 50 g of polyol and 0.25 cm³ of dibutyltin dilaurate were stirred for 5 min under vacuum and cooled to below 10°C to slow down exothermic reaction between isocyanate and hydroxyl groups and after that an appropriate amount of MDI was added rapidly. The reaction was carried out under nitrogen atmosphere with intensive mixing for 10 min and temperature maintained below 15°C. All prepared polyurethanes had the isocyanate index equal to 1.05.

Preparation of polyurethane modified epoxy resins and epoxy-montmorillonite composites

Polyurethane was mixed with epoxy resin in amounts of 5, 10, and 15 wt % at room temperature using a homogenizer for 10 min at a rotational speed of 2400 rpm. The mixtures were then placed in a vacuum oven to remove air bubbles. The curing agent was then added and mixing continued for 5 min before pouring the obtained compositions into the cavities of a mold to produce specimens for mechanical tests. The curing reactions were carried out at room temperature for 48 h followed by post curing for 3 h at 80°C.

The epoxy/MMT composites were prepared using 1 and 2 wt % of Cloisite 30B (MMT). Ten grams of MMT were added to 40 cm³ of acetone to disperse the nanoclay and then poured in a preheated epoxy resin (40°C), followed by mechanical stirring for 15 min at 2400 rpm. After homogenization, the epoxy based mixtures were placed in a vacuum oven to remove air bubbles and the residual solvent. Finally, the curing agent was admixed and the mixtures were poured into the cavities of the mold. Curing and postcuring were carried out under the same conditions as for epoxy/PUR compositions.

Preparation of epoxy nanocomposites modified with polyurethane

Compositions containing 1 and 2 wt % Cloisite 30B and different amount of PUR were prepared. First, a

specific amount of MMT with solvent was mixed with epoxy resin for 10 min before the PUR incorporation and mixture homogenization. After degassing in vacuum oven, the curing agent was added and the compositions were placed in the teflon coated mold with appropriate geometry. Curing and postcuring processes were carried out as described previously.

Mechanical properties measurements

Impact strength was measured according to Charpy method (ISO 179) using Zwick 5012 apparatus, on rectangular shaped samples having 80 mm in length, 10 mm in width, 4 mm in thickness, and 1 mm in notch length.

Three point bending tests (ISO 178) were carried out at room temperature on Instron 5566 with the samples of the same dimensions as for impact tests and deformation rate of 5 mm/min with 60 mm of distance between the spans.

The same testing mode was applied on the notched samples to obtain data for critical stress intensity factor K_C calculation according to the following equation²⁶:

$$K_C = \frac{3 \cdot P \cdot L \cdot a^{1/2}}{2B \cdot w^2} Y \left(\frac{a}{w} \right) \quad (1)$$

where P stands for load at break, L represents spans distance equals to 60 mm, a is notch length (1 mm), w stands for sample width, B is sample thickness, and Y means a geometry factor.

The geometry factor was calculated using the following equation²⁶:

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

Structure characterization

Infrared spectroscopy (FTIR) was performed on a Perkin-Elmer spectrophotometer (1000 PC) recording the IR spectra from 400 to 4000 cm⁻¹ with KBr pastilles containing 1.0 ± 0.1 mg of tested composition for precise characterization of peak intensity.

Scanning electron microscope SEM was performed with TESCAN VEGA/LMU instrument produced by Czech Republic to examine the fracture surfaces of specimens obtained from the impact tests.

X-ray diffraction (XRD) tests were performed using X'PERT PRO Analytical X-ray diffractometer with a CuK_{α1} = 1,54 Å radiation source operating at 40 kV and 30 mA.

Differential scanning calorimetry (DSC) tests were carried out using PYRIS 1 instrument produced by

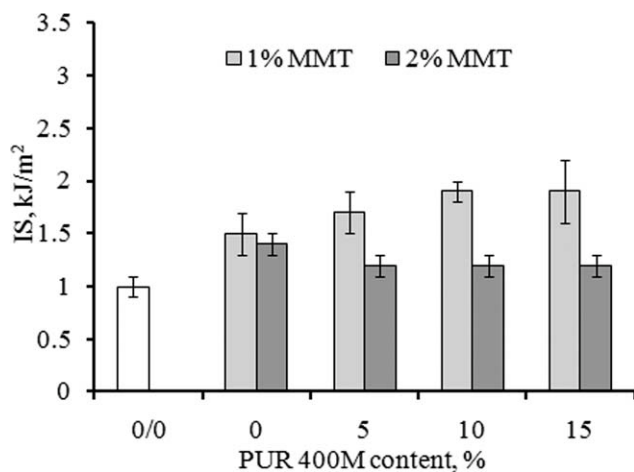


Figure 1 Effect of polyurethane (PUR 400M) content on impact strength (IS) of nanocomposites containing 1 and 2% montmorillonite (MMT).

Perkin–Elmer with heating rate 10°C/min and temperature range from –25 to 200°C and 10 ± 0.1 mg of samples weight. The nitrogen flow 20 ml/min was applied as a purge gas. The glass transition points were detected at the median point in the range of glass transition.

RESULTS AND DISCUSSION

Mechanical properties

Based on the obtained results from the mechanical tests two concentrations of montmorillonite (MMT) 1 and 2% were selected for hybrid compositions preparation. Our previous investigation²⁷ also confirmed that the addition of polyurethanes based on TDI in amount not exceeding 20% resulted in a large increase in impact strength (IS) and critical stress intensity factor (K_C) values as well as improved flexural properties.

In the light of these results three concentrations of polyurethane (5, 10, and 15%) were chosen to prepare the modified epoxy nanocomposites using 4,4'-diphenylmethane diisocyanate (MDI) and PEG 400, POPD 1002, and POPD 2002 for the polyurethanes synthesis.

Figure 1 shows the effect of polyurethane based on MDI and PEG 400 (PUR 400M) content on IS for compositions containing 1 and 2% nanoclay. From these data it can be noted that IS of nanocomposite containing 1% MMT increases with increasing amount of incorporated PUR 400M. Maximum IS enhancement, representing approximately 90 and 30% in comparison to the neat epoxy resin and 1% MMT nanocomposite, respectively, is obtained for nanocomposite containing 1% MMT and 10% PUR 400M.

However, it was observed that IS of nanocomposite containing 2% MMT and PUR is slightly decreased in comparison with nanocomposite with only 2% MMT (without PUR), but higher than IS of virgin epoxy resin.

The impact strength values of nanocomposites based on 1 and 2% MMT are shown in Figure 2 as function of PUR 1002M content. One can observe that the nanocomposite containing 15% PUR 1002M and 1% MMT exhibits the highest impact strength in comparison with neat epoxy resin as well as nanocomposite containing only 1% MMT without polymeric modifier. The IS value of this composite (3 kJ/m²) is three times higher than that obtained for unmodified epoxy resin and twice a composition modified with 1% MMT.

Such significant improvement might be attributed to the formation of an interpenetrating polymer network structure between PUR and polymer matrix. The incorporated flexible polyurethane chains provide more free volume to the system, and hence increase the flexibility and energy to break of the obtained blends.

However, the modification of epoxy resins with polyurethane PUR 1002M and 2% MMT leads to a slight decrease of the impact strength in comparison with nanocomposite containing only 2% MMT.

Figure 3 depicts the influence of PUR 2002M on the impact strength of epoxy nanocomposites containing 1 and 2% MMT. It can be seen that IS increases with increasing PUR 2002M amount, and reaches maximum value of 3 kJ/m² for composition containing 1% MMT and 10% polyurethane. However, upon further increase of polyurethane content a decay of IS is measured. Similarly to IS data of material containing PUR 1002M (Fig. 2), maximum IS enhancement is three and two times higher than that

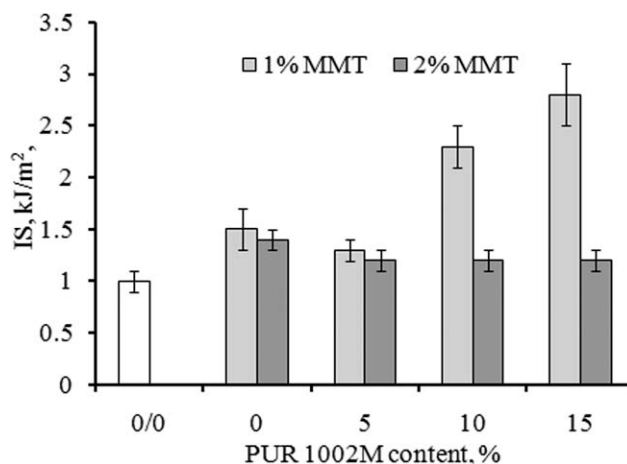


Figure 2 Impact strength (IS) of nanocomposites containing 1 and 2% montmorillonite (MMT) as function of polyurethane (PUR 1002M) content.

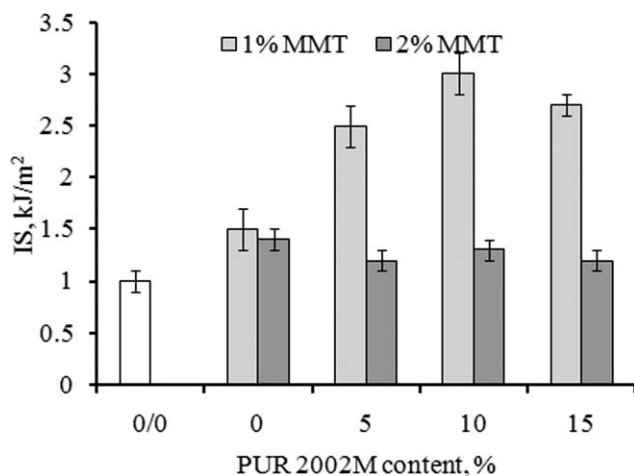


Figure 3 Impact strength of epoxy compositions containing montmorillonite (MMT) as a function of PUR 2002M content.

of neat epoxy resin and epoxy resin modified only with 1% of MMT, respectively. Furthermore, also it can be concluded that modification of epoxy resin with 2% MMT and polyurethanes gives composites with lower values of impact strength.

The critical stress intensity factor K_C values under three point bending mode is shown in Figure 4 as function of montmorillonite and polyurethane contents. As one can observe, K_C values of epoxy nanocomposite containing 1% MMT remains, within an experimental error, almost unchanged upon PUR 400M addition; the same observation applies for nanocomposites with 2% MMT content.

Moreover, it has to be emphasized that in all cases hybrid nanocomposites containing PUR 400M exhibit higher resistance to crack propagation expressed by higher K_C values than those of neat epoxy resin.

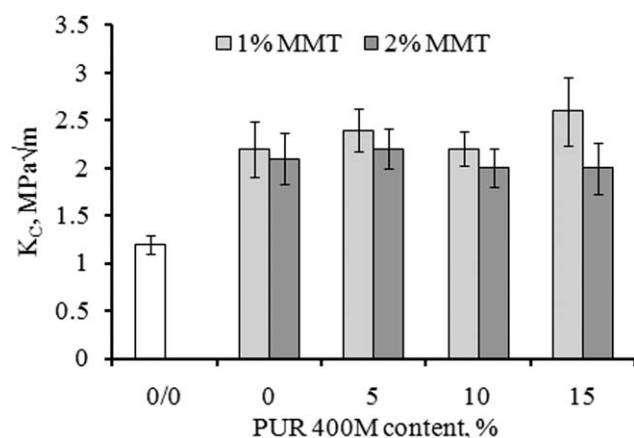


Figure 4 Effect of polyurethane (PUR 400M) and montmorillonite (MMT) contents on the critical stress intensity factor (K_C).

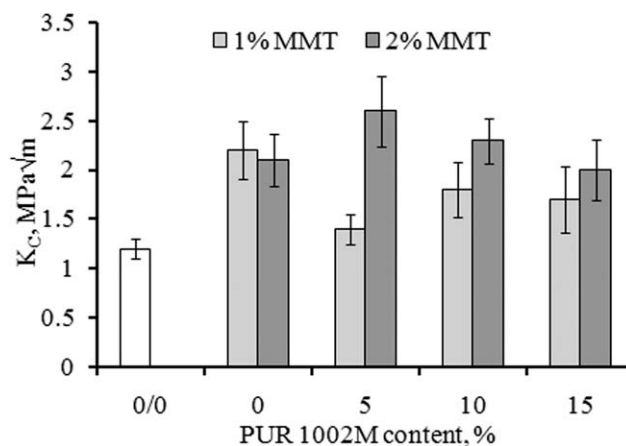


Figure 5 Critical stress intensity factor (K_C) values of epoxy nanocomposites modified with polyurethane (PUR 1002M).

As shown in Figure 5, the incorporation of polyurethane based on polyoxypropylene diol (POPD 1002M) and diphenylmethane diisocyanate (MDI) as a second modifier for hybrid nanocomposites results in different trends when compared to hybrid nanocomposites based on PUR 400M (Fig. 4).

It can be noted that the addition of polyurethane with longer flexible segments to epoxy nanocomposite containing 1% MMT rather unexpectedly decreases the critical stress intensity factor values. However, K_C of nanocomposites containing 2% MMT and 5% PUR 1002M reaches maximum value of $2.6 \text{ MPa}\cdot\text{m}^{1/2}$.

The results of K_C for nanocomposites modified with polyurethane based on POPD 2002 (PUR 2002M) are presented in Figure 6. The K_C parameter of the nanocomposite based on 2% MMT and 5% PUR 2002M reaches maximum value representing about 25 and 120% enhancement in comparison to the nanocomposite containing only 2% MMT (without PUR) and pristine epoxy resin, respectively.

The strong interactions between the well distributed chains of the polymeric modifier and the matrix, through the formation of the grafted interpenetrating polymer networks systems, could be the other reason for the improvement of the resistance to both fast and slow crack propagation as expressed with obtained impact strength and critical stress intensity factor values, respectively.

The analysis of the above presented results indicates that composites containing 1% MMT and 10 to 15% polyurethane with longer flexible segments (PUR 1002M and PUR 2002M) exhibit improved impact strength, while epoxy/polyurethanes composites with 2% MMT are more resistant to low speed crack propagation as represented by K_C parameter.

Table I summarizes the results of flexural tests of epoxy compositions containing different amounts of

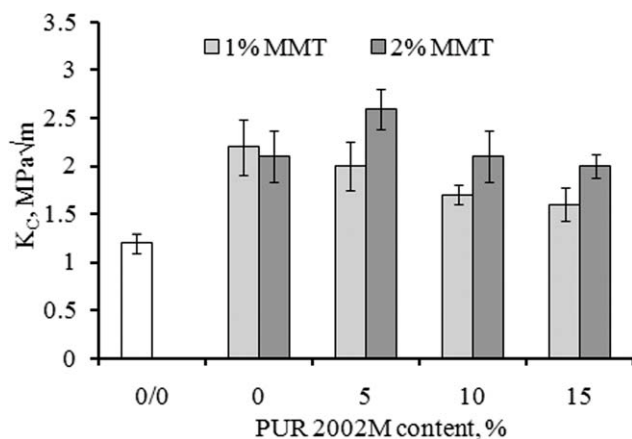


Figure 6 Effect of PUR 2002M and MMT content on critical stress intensity factor K_C values.

polyurethanes and montmorillonite. As it can be seen, the compositions modified with PUR 400M have the highest values of stress at break suggesting that polyurethane based on MDI and PEG 400 creates strong crosslinked rigid material with significantly (two times and more) improved flexural resistance as well as relatively high values of strain at break in comparison to a virgin epoxy resin.

The energy at break values calculated from the load/displacement curve also confirm that the use of PUR 400M results in a tougher material in comparison to neat epoxy resin and epoxy resin modified only with montmorillonite. It can be further observed that the simultaneous incorporation of 2% MMT and 5% PUR 400M gives the toughest composite. However, the strain at break and energy at break

are maximally enhanced with 2% MMT and 15% PUR. In the case of epoxy resin modification using PUR 1002M and PUR 2002M, the strain increases with increasing PUR content most probably due to an increase of free volume induced by longer flexible segments of these polyurethanes, and also via the formation of interchains bonds between epoxy resin and polyurethane. Moreover, we can highlight that the addition of 5% POPD based polyurethane is sufficient to improve the toughness of epoxy resin, flexural strength and strain at break. However, the hybrid composites with 2% MMT exhibit significant rigidity, although epoxy resin modified with 2% MMT has all values of strength parameters lower than composition containing 1% MMT. This can be explained by the compatibilization effect of polyurethane or/and polyurethane's promoted exfoliation process.

Fracture surface analysis

SEM micrographs, which were obtained from fractured surfaces of samples after impact tests near the crack tip, are employed to explain the toughening mechanism induced by MMT and PUR incorporation. The micrograph of the unmodified epoxy composition fracture surface is flat and glassy [Fig. 7(a)], indicating the occurrence of regular crack propagation path and low fracture energies of the tested samples.

The micrograph of epoxy resin containing 1% MMT and 10% PUR 400M [Fig. 7(b)] shows a regular and rough fracture surface, with larger elongated domains which are well dispersed in the polymer

TABLE I
Flexural Test Results for Modified Epoxy Resin Compositions

Composition	Polyurethane content (%)	Flexural stress at break (MPa)	Flexural strain at break ($\times 10^{-2}$)	Energy at break (kJ/m^2)
EP (virgin)	–	41 ± 3	0.5 ± 0.1	4.3 ± 0.2
EP + 1 % MMT	–	54 ± 5	1.9 ± 0.3	3.7 ± 0.4
EP + 2 % MMT	–	77 ± 7	2.0 ± 0.3	5.9 ± 0.3
1 % MMT + PUR 400M	5	80 ± 5	2.7 ± 0.3	10.2 ± 1.4
	10	84 ± 6	3.5 ± 0.3	10.5 ± 1.2
	15	91 ± 5	4.0 ± 0.4	12.3 ± 1.2
2 % MMT + PUR 400M	5	99 ± 3	3.4 ± 0.2	11.2 ± 1.2
	10	94 ± 3	3.6 ± 0.4	11.8 ± 1.1
	15	91 ± 5	3.7 ± 0.1	11.9 ± 0.8
1 % MMT + PUR1002M	5	82 ± 5	2.8 ± 0.3	8.5 ± 0.9
	10	70 ± 5	3.4 ± 0.2	7.9 ± 0.8
	15	73 ± 5	3.7 ± 0.4	8.0 ± 1.0
2 % MMT + PUR1002M	5	74 ± 5	2.8 ± 0.2	7.4 ± 0.7
	10	70 ± 5	3.9 ± 0.4	9.2 ± 1.0
	15	62 ± 3	4.0 ± 0.3	9.3 ± 1.0
1 % MMT + PUR2002M	5	74 ± 4	3.2 ± 0.3	8.6 ± 0.8
	10	74 ± 5	3.4 ± 0.4	8.9 ± 0.9
	15	73 ± 5	3.7 ± 0.4	10.1 ± 1.2
2 % MMT + PUR2002M	5	84 ± 4	3.4 ± 0.6	12.2 ± 1.3
	10	69 ± 6	3.4 ± 0.2	8.8 ± 0.9
	15	67 ± 5	3.5 ± 0.2	8.5 ± 0.8

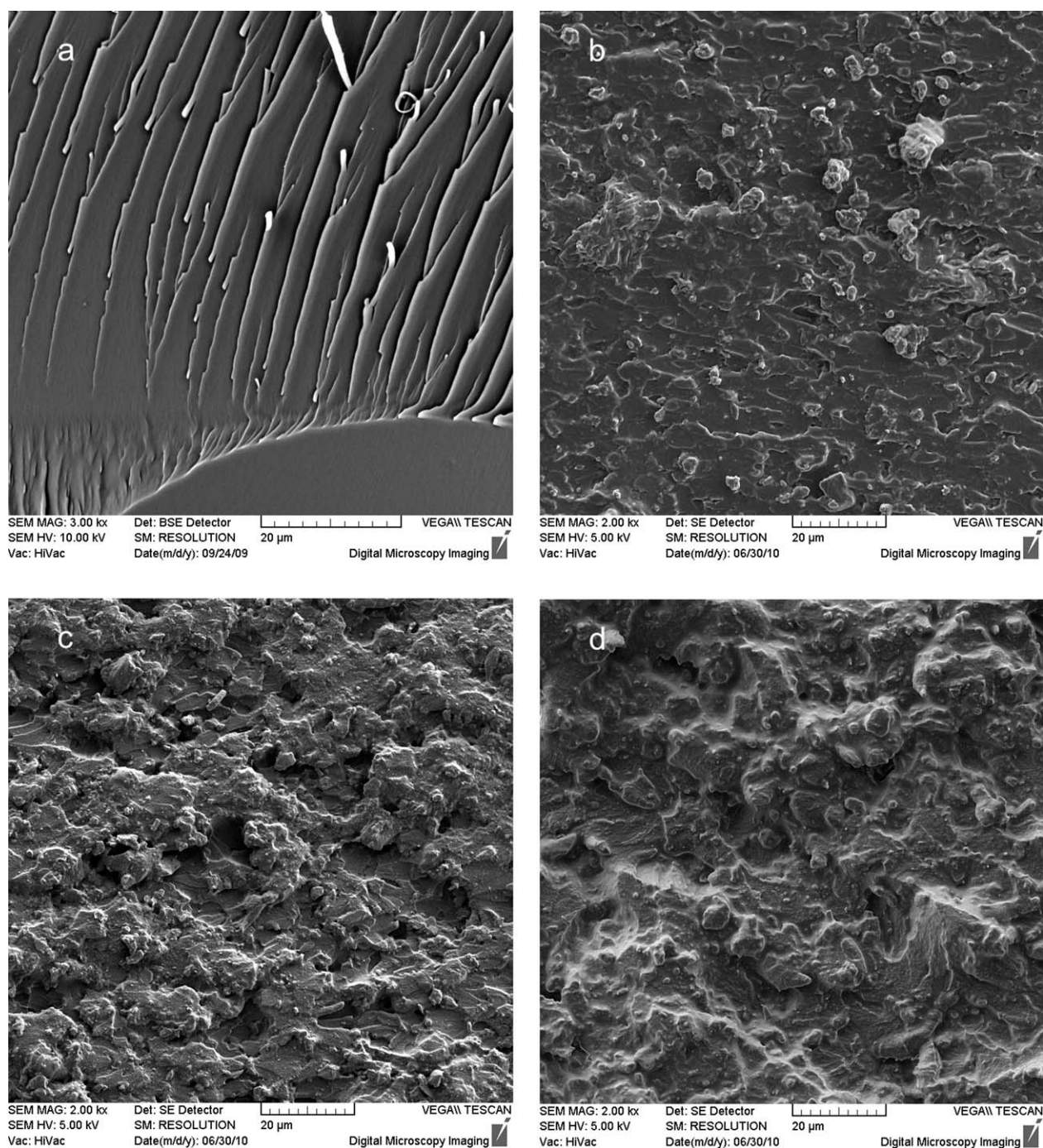


Figure 7 SEM micrographs of virgin epoxy resin (a) and compositions containing: 1% MMT + 10% PUR 400M (b), 1% MMT + 10% PUR 1002M (c), 1% MMT + 10% PUR 2002M (d).

matrix. It appears that the concomitant addition of MMT and 10% PUR based on polyethylene glycol 400 (PUR 400M) gave a more stratified elongated structure between epoxy resin and modifiers.

However, the micrographs depicted on Figure 7(c,d) show rather different structure for systems with the simultaneous incorporation of 1% MMT with 10% PUR 1002M or 10% PUR 2002M, when compared with the micrograph for the pure epoxy resin [Fig. 7(a)]. The surface is not smooth, but

reveals the presence of regular, homogenous stratified structure with nanoclay plates surrounded by polymer matrix. This may explain the higher values of the flexural strain at break as shown in Table II as well as the resistance to low and high speed crack propagation as expressed by K_C and IS values, respectively. SEM micrographs also confirm a good adhesion between MMT plates and polyurethane modifiers, especially those with longer flexible segments. This can be due to the occurrence of plastic

TABLE II
Peak Intensities of Hydroxyl Groups of Selected Epoxy Compositions

Compositions	Peak intensity (%)
Epoxy resin (EP)	8.4
EP + 1% MMT	6.0
EP + 1% MMT + 10% PUR 400M	3.1
EP + 1% MMT + 10% PUR 1002M	3.9
EP + 1% MMT + 10% PUR 2002M	4.5

yielding and the formation of second phase within polymer matrix associated with higher energy absorption during the crack propagation processes.

Structure characterization

FTIR spectra presented in Figure 8 were obtained for the structure characterization of virgin epoxy resin and selected modified compositions. As it can be seen, there are some characteristic peaks connected with functional groups present in the composite. First is a large peak at 3300 cm^{-1} wavelength associated with hydroxyl group of epoxy resin, second at 1700 cm^{-1} connected with allophanate and urethane groups from polyurethane modifier, and third is a small peak at 930 cm^{-1} arising from epoxy group of epoxy resin. The peaks appearing in the range from 2900 to 3000 cm^{-1} are connected with methylene groups existing in epoxy resin, polyurethane modi-

fier and quaternary ammonium salt of MMT. Moreover, one can observe a series of peaks, appearing at wavelength range 1000 to 1600 cm^{-1} , which are connected with aromatic rings.

As one can observe, all characteristic peaks of epoxy composites containing MMT exhibit relatively lower intensities. This can be partly explained by the formation of physical barriers by nanoparticles of MMT which might affect the absorption band intensity. The calculated intensity of the peak corresponding to hydroxyl groups are presented in Table II.

FTIR spectra show a decrease of hydroxyl group peak intensity in comparison to neat epoxy resin. This decay can be explained by the occurrence of reactions between isocyanate groups of polyurethane and hydroxyl groups of epoxy resin according to Scheme 1.

It has to be mentioned that the lowest peak intensity is observed for the composition containing 10% PUR 400M as a result of the grafted structure, most probably induced by the significant amount of interchain bonding formed between polymer matrix and modifier as well as to the highest amount of MDI contained in PUR 400M. It can be noted that composites containing polyurethanes based on POPD with higher molecular weight have a smaller amount of MDI, which explain the rare occurrence of crosslink reactions. The lowest density of interchain reaction occurs for composite containing PUR 2002M (i.e., PUR having the longest flexible segments).

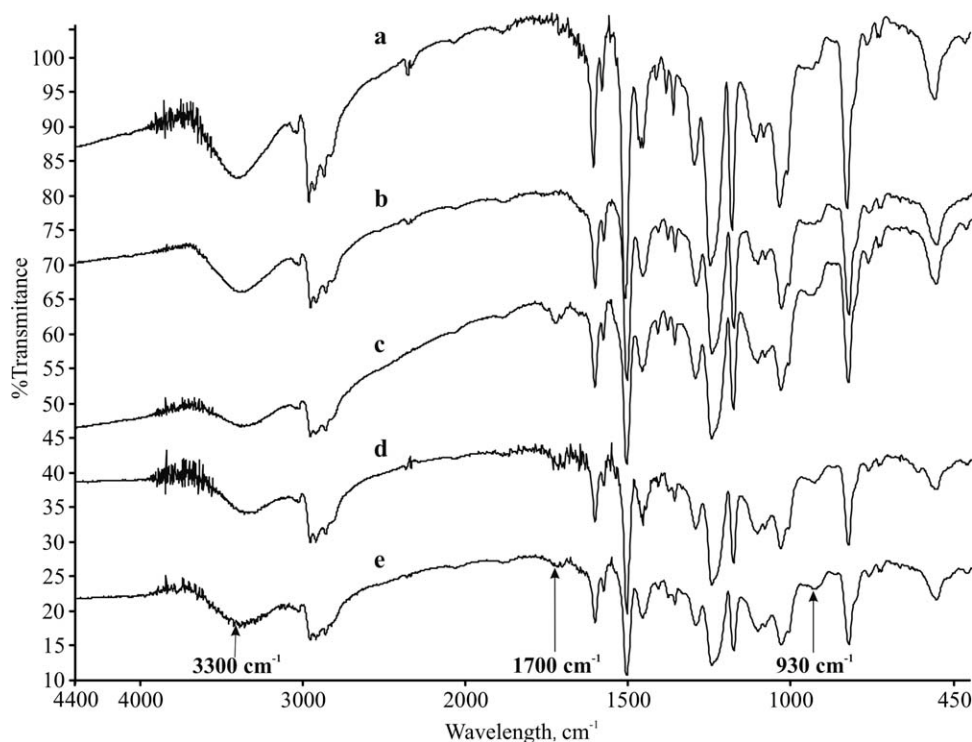
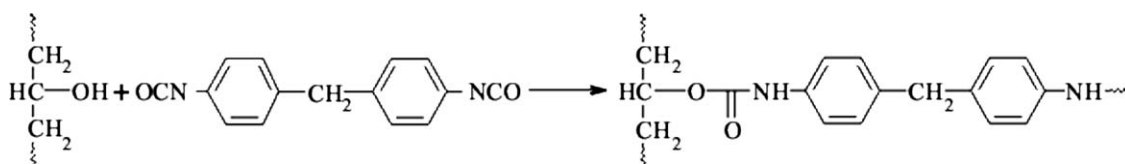


Figure 8 FTIR spectra of modified epoxy resin: neat epoxy resin (a), epoxy resin modified with 1% MMT (b) and hybrid composites containing: 1% MMT + 10% PUR 400M (c), 1% MMT + 10% PUR 1002M (d), 1% MMT + 10% PUR 2002M (e).



Scheme 1 Reaction between hydroxyl group from epoxy resin and diisocyanate.

The characteristic peaks appearing at 1700 cm^{-1} are connected with allophanate and urethane groups arising from polyurethane present in hybrid compositions. These peaks can also be associated with the grafted structure formation during the curing process due to the reaction that might take place between the amine groups of the curing agent and the isocyanate groups of polyurethane. Such reactions can further explain the appearance of allophanate and urethane groups of hybrid compositions at 1700 cm^{-1} , nevertheless it is difficult to establish a relationship between above-mentioned reactions and relevant peak intensity.

As one can expect, the lowest intensity is exhibited by the peak associated with urethane groups for composition containing 1% MMT and 10% PUR 2002M. The intensity of above-mentioned peak increases with decreasing length of flexible segments length. However, the largest urethane peak is attributed to the hybrid composite containing 1% MMT and 10% PUR 400M.

FTIR results confirm that hybrid compositions containing PUR 400M exhibit low impact strength and high flexural resistance because of grafted structure with high density of interchain bonding, whereas the combination of lower degree of grafting and longer flexible segments in polyurethane structure can give composite with improvement of all mechanical properties. These findings are in agreement with results of other published works, which claim that the addition of organically modified montmorillonite to epoxy/polyurethane IPNs systems promotes the compatibility between these two

latter components. Moreover, as confirmed by Zeng et al.,²⁴ the degree of nanoclay dispersion is improved leading to nanocomposites with excellent mechanical properties.

X-ray diffraction (XRD) technique was employed in the range 1° to 20° to characterize the nanoclay structure within the prepared nanocomposites. Figures 9 and 10 show XRD patterns of selected hybrid composites. The structure of montmorillonite (intercalated or exfoliated) is defined by means of Bragg's equation, which enables to calculate the d -spacing values between nanoclay plates. As can be seen, all selected compositions have no diffraction peaks in the range from 1° to 10° . The lack of distinct diffraction peaks in this range confirms that randomization and exfoliation occur in nanocomposite.^{24,25} Moreover, all tested composites exhibit large peak (not showed in the figures) at 2Θ equating 20° and connected with amorphous structure of epoxy resin.^{25,26}

The SEM micrographs showing very good and homogenous dispersion of MMT particles in polymer matrix, the absence of XRD diffraction peaks in the range between 1° and 10° as well as the improvement of mechanical properties might confirm the exfoliation structure of nanoclay within obtained hybrid compositions.

The exfoliation of montmorillonite via reactions with tallow surfactant takes place according to the scheme reported in our previous work.²⁵

The glass transition temperatures (T_g) of modified epoxy resin are shown in Table III as a function of

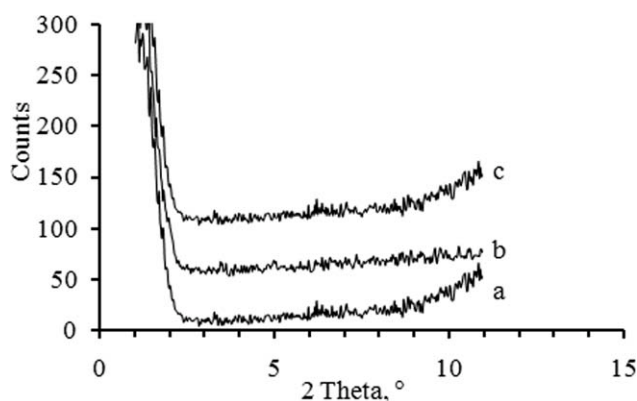


Figure 9 XRD patterns of epoxy resin formulations containing 1% montmorillonite (MMT) and 10% PUR 400M (a), 10% PUR 1002M (b), 10% PUR 2002M (c).

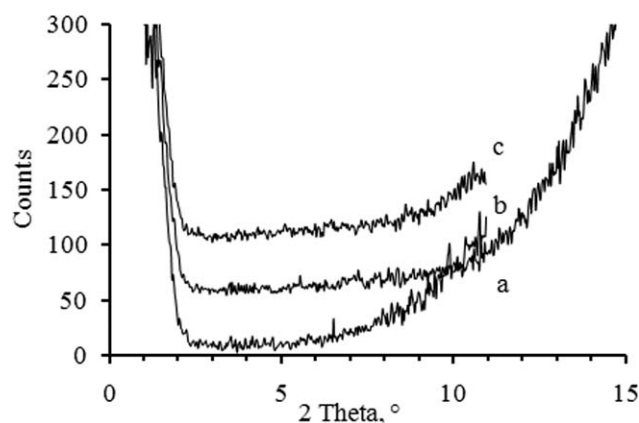


Figure 10 XRD patterns of epoxy resin formulations containing 2% montmorillonite (MMT) and 10% PUR 400M (a), 10% PUR 1002M (b), 10% PUR 2002M (c).

TABLE III
Glass Transition Temperatures (T_g) for Selected Epoxy Resin Based Compositions

Composition	T_g (°C)
EP	67.5
EP + 1 % MMT	64.0
EP + 2 % MMT	59.1
EP + 1 % MMT+10 % PUR 400M	69.4
EP + 1 % MMT + 10 % PUR 1002M	67.8
EP + 1 % MMT + 10 % PUR 2002M	65.8
EP + 2 % MMT + 10 % PUR 400M	68.2
EP + 2 % MMT + 10 % PUR 1002M	65.3
EP + 2 % MMT + 10 % PUR 2002M	63.8

montmorillonite and polyurethane content. It can be observed that T_g slightly decreases (from 67.5°C to 59.1°C) with increasing amount of MMT, which is in agreement with results reported in literature.^{22,25,28,29} Such findings are most probably due to the reduction in crosslinking density arising from the absorption of the hardener. Furthermore, it is worth mentioning that T_g of hybrid compositions containing both nanoclay and polyurethane remains almost unchanged. Moreover, for compositions based on PUR 400M and containing 1% as well as 2% MMT the T_g are slightly higher than the value obtained for neat epoxy resin (69.4°C and 68.2°C compared with 67.5°C). It might be related to the increase of the crosslinked density and the formation of a grafted IPN structures. However, the addition of polyurethanes based on polyoxypropylene diol with higher molecular weight (especially PUR 2002M) affects the glass transition temperature of epoxy resin only slightly. Hence, the T_g increase might be also understood as a confirmation of a grafted structure formation in the case of using PUR 1002M and PUR 2002M.

CONCLUSIONS

A series of epoxy nanocomposites was prepared and their mechanical properties tested.

All nanocomposites showed higher impact strength than the unmodified epoxy resin with a maximum (300%) improvement obtained for epoxy resin modified with 1% MMT and 10% PUR 2002M (or 15% PUR 1002M). The flexural strain at break of the hybrid composition containing 15% of any polyurethane and MMT increased approximately eight times in relation with a pristine epoxy resin sample. Moreover, the addition of 10% PUR 400M to epoxy resin modified with 1% MMT resulted in a maximum enhancement of flexural strength.

FTIR analysis confirmed chemical reactions between the isocyanate groups of polyurethane and the hydroxyl groups of epoxy resin as well as amine groups from curing agent, explaining the improvement of the mechanical properties of epoxy resin.

Furthermore, SEM micrographs indicated that the concomitant addition of 1% MMT and 10% PUR based on polyethylene glycol 400 (PUR 400M) results in a EP/PUR system with a more stratified elongated structure. However, the incorporation of PUR 1002M to epoxy nanocomposite containing 1% MMT showed a stratified structure with MMT nanoparticles embedded in polymer matrix, explaining the improvement of impact strength and stress intensity factor values.

The DSC results showed a slight decrease of the glass transition temperature with MMT loading due most probably to the reduction in crosslinking density arising from the absorption of the hardener.

XRD analysis, the improvement of mechanical properties as well as SEM micrographs showing the very good dispersion of MMT particles in polymer matrix, might confirm the exfoliation structure of nanoclay within obtained hybrid compositions.

A combination of the formation of epoxy resin/polyurethane strong grafted interpenetrating polymer network structure with montmorillonite exfoliation might explain the improvement of the mechanical properties of the polymer matrix.

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