

Property Evaluation and Structure Analysis of Polyurethane/Epoxy Graft Interpenetrating Polymer Networks

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ABSTRACT: Polyurethanes obtained from 4,4'-diphenylmethane diisocyanate (MDI) and polydiols with different molecular weights (polyethylene glycol and polyoxypropylene diols) were used as modifiers for diglycidyl ether of bisphenol A. Impact strength (IS), critical stress intensity factor (K_{IC}), flexural strength and flexural strain at break were measured as a function of polyurethane (PUR) type and content. Scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and infrared spectroscopy (FTIR) were employed for the structure and morphology analysis. It was found that the addition of polyurethane with an excess of isocyanate groups to epoxy resin resulted in the formation of a grafted interpenetrating

polymer network structure. The mechanical properties of epoxy resin were improved with 5 and 10% PUR. Moreover, it was observed that composites containing PUR based on higher molecular weight (PUR 1002 and PUR 2002) with long flexible segments exhibited higher impact strength while PUR prepared from polyethylene glycol had a higher flexural energy to break and a higher flexural modulus. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 1722–1730, 2011

Key words: resins; polyurethanes; mechanical properties; interpenetrating polymer networks (IPN); composites

INTRODUCTION

Cured epoxy resins are brittle materials with low impact strength, poor resistance to crack propagation and small elongation at break. Several methods used to overcome these drawbacks include their modification with other crosslinkable polymers to form full, grafted, or semi-interpenetrating polymer networks (IPN).

Polyurethanes (PUR) belongs to a versatile family of polymers, which can exhibit a wide variety of physical properties depending on their chemical composition and structure.^{1,2}

Polyurethane elastomers, which are characterized by excellent elasticity and good abrasion resistance and impact strength as well as low temperature performance, prove to be very effective modifiers for epoxy resins. Furthermore, they have a segmented structure consisting generally of continuous soft domains providing elastomeric features, and hard domains imparting rigidity to the system.

The majority of the scientific studies have focused on the modification of epoxy resin (EP) by using polyurethanes prepared from 2,4-toluene diisocyanate (TDI).^{3–12}

Li and Mao³ found that composites containing 20–30% polyurethane have improved stress at break, strain at break, Young modulus and thermal stability without impact strength improvement. They explained their findings as being the result of the physical entanglement of polymer chains and poor dispersion of polyurethane in an epoxy resin matrix. Raymond and Bui⁴ prepared and tested interpenetrating polymer networks from epoxy and castor oil-based polyurethane (PUR). They confirmed the occurrence of chemical reactions between isocyanate groups of PUR phase with hydroxyl groups of the epoxy matrix, leading to the thermal resistance and tensile properties enhancement. However, their results did not show an increase of impact resistance.

Sung and Wu⁹ investigated the dynamic mechanical properties of polyurethane-grafted epoxy polymer networks. Their results showed that tensile strength increases with increasing PUR content, reaching a maximum value at 20% PUR. The glass transition region was broadened upon variation of the degree of phase separation.

Park and Jin¹⁰ evaluated the glass transition temperature, contact angle and mechanical properties of

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EP/PUR systems. Their results indicated that the interfacial and mechanical properties reached maximum values at 40 phr PUR. Furthermore, the polar components of the surface free energy of the composition were largely influenced by the addition of PUR, resulting in an increase of critical stress intensity factor (K_C) and low-temperature impact strength. The enhancement of the mechanical properties was explained as a result of the improvement of hydrogen bonding between hydroxyl groups of EP and isocyanate groups of PUR.

Recently, Chen et al.¹¹ mixed polypropylene oxide glycol, toluene diisocyanate, and 1,4-butanediol with diglycidyl ether of bisphenol A and stannous caprylate (as a catalyst) to obtain resin/polyurethane (EP/PUR) networks via frontal polymerization (FP). As a result of the reaction, they obtained a stable epoxy resin connected by a polyurethane chain with end oxirane groups which can react with the curing agent. The structure analysis of the EP/PUR network synthesized by FP have shown the same properties as those synthesized by batch polymerization. Moreover, it was determined that the frontal polymerization method requires significantly less time and lower energy input.

More recently, Bakar et al.¹² investigated the effect of PUR with different isocyanate index on mechanical and thermal properties of EP. Maximum improvement of the fracture toughness was reached with PUR having the highest isocyanate index. Moreover, the elastic modulus decreased, implying the softening of epoxy-based compositions. The infrared spectra indicated that an excess of isocyanate groups lead to a grafting process between the modifier and the matrix, explaining the toughening of the latter.

In our previous work,¹³ we have investigated the effect of polyurethane based on toluene diisocyanate and on polyethylene glycols (PEG) or polyoxypropylene diols (POPD). The obtained results showed that the addition of 10 or 15% PUR to the epoxy resin resulted in enhancement of mechanical properties. Moreover, it was confirmed that shorter flexible segments in PUR obtained from lower molecular weight PEG led to stronger composites, whereas composites containing PUR based on higher molecular weight POPD with long flexible segments exhibited higher toughness and strain at break and lower impact strength.

However, only few articles investigated the properties and morphologies of composites based on epoxy resin and polyurethane based on other diisocyanates for example: 4,4'-diphenyl-methane diisocyanate (MDI) or hexamethylene diisocyanate (HMDI).

A series of semi-interpenetrated polymer networks (IPN) based on polyurethane and epoxy resin were

also obtained and characterized by Cristea et al.¹⁴ They synthesized PUR from poly(ethylene adipate) diol, MDI, and butylene glycol, and then it was modified with the addition of epoxy resin. They studied the damping properties of the obtained semi-IPNs. They found that the heat treatment conditions affect significantly the viscoelastic properties of the blend. Moreover, a weak softening and a completion of the crosslinking were observed upon temperature increase.

Wang and Chen¹⁵ modified epoxy resin based on bisphenol A using polyurethane prepolymer synthesized from polyether diol and MDI with the use of a coupling agent. The applied polyurethane modifiers were terminated with hydroxyl, amine, and anhydride functional groups. They found that the addition of polyurethane to epoxy resin improves the fracture energy upon an increase of modifier content. The study also revealed that an application of hydroxyl terminated PUR results in a composite with the best mechanical properties among those three tested. The analysis of the SEM and TEM pictures showed that phase separation occurs for the obtained composites, which might take a part in the toughening mechanism.

Pan et al.¹⁶ studied the effect of PUR prepolymers based on MDI and HMDI on the epoxy group conversion and thermal stability of the obtained compositions. The results showed that with the increase of polyurethane loading, the glass transition temperature and thermal stability decrease, but PUR modified epoxy resin exhibits improved tensile strength and shear strength.

Ismail et al.¹⁷ modified an epoxy resin with an aliphatic polyurethane synthesized from poly(ethylene glycol) and HMDI without a solvent. An amine-cured epoxy composition containing 5 phr PUR exhibited enhanced thermal stability, flexural strength, storage modulus, and adhesion strength.

The purpose of this work is to investigate the effect of 4,4'-diphenyl-methane diisocyanate based polyurethane on the mechanical properties and morphology of diglycidyl ether of bisphenol A, aiming at improving the fracture toughness of the latter.

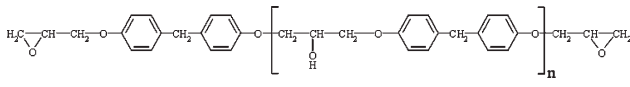
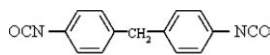
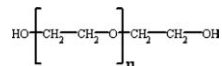
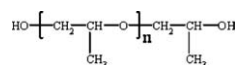
EXPERIMENTAL

Materials

For preparation of the composites, we used the following substances:

- epoxy resin-diglycidyl ether of bisphenol A (Epidian 5, Organika Sarzyna, Poland) with a molecular weight of about 380 g/mol, viscosity at 25°C max 30 Pa.s, epoxy number 0.49–0.52 mol/100g;

TABLE I
Structures of Main Raw Materials


Diglicidyl ether of bisphenol A (Epidian 5, epoxy resin)
$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$
Triethylene tetramine (Z-1, curing agent)

4,4'-diphenylmethane diisocyanate (MDI)

Polyethylene glycol (PEG 400, $M_w = 400$ g/mol)

Polyoxypropylene diol (POP 1002- $M_w = 1000$ g/mol, POP 2002- $M_w = 2000$ g/mol)

- polyethylene glycol 400 (PEG 400) with a molecular weight of 400 g/mol and 277 mg/g hydroxyl number produced by Merck, Germany;
- polyoxypropylene diol (POP 1002) with 1000 g/mol molecular weight and a hydroxyl number of 180 mg/g obtained from Rokita, Poland
- polyoxypropylene diol (POP 2002) with a molecular weight of 2000 g/mol and a 46 mg/g hydroxyl number obtained from Rokita, Poland;
- curing agent triethylene tetramine (Organika Sarzyna, Poland);
- 4,4'-diphenylmethane diisocyanate (MDI) for synthesis, obtained from Merck, Germany;
- catalyst: dibutyltin dilaurate (Merck, Germany);
- solvents: toluene and acetone (Lahner, Czech Republic).

The structures of the main raw materials used in the present study are shown in Table I.

Synthesis of polyurethane

Three types of polyurethanes (PUR) were prepared using 4,4'-diphenylmethane diisocyanate (MDI) and polyols: PUR based on PEG 400 (designated PUR 400), polyoxypropylene diol POPD 1002 (PUR 1002) and polyoxypropylene diol POPD 2002 (PUR 2002). 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 the exothermic reaction between isocyanate and hydroxyl groups and finally MDI was rapidly added. The reaction was performed in a nitrogen atmosphere with vigorous mixing for 10 min and the temperature was maintained below 15°C until the mixture demonstrated an increased viscosity. All prepared polyurethanes had an isocyanate index equal to 1.05.

The appropriate calculated amounts of MDI were the following: 27 g for PUR 400, 13.5 g for PUR 1002 and 6.6 g for PUR 2002.

Preparation of modified epoxy resins

Polyurethanes in the amounts of 5, 10, and 15 wt % were mixed with epoxy resin at room temperature using a homogenizer for 15 min at a rotational speed of 2400 rpm. The mixtures were then placed in a vacuum oven to eliminate air bubbles. Finally, the curing agent was added, and the mixing continued for an additional 5 min before pouring the obtained compositions into a mold with standard geometries prior to mechanical tests. The curing process was carried out at room temperature for 48 h and post-curing took place in an air circulating oven for 3 h at 80°C.

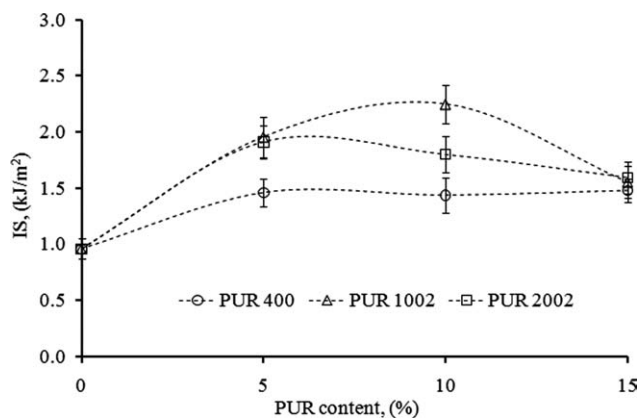


Figure 1 Effect of polyurethane content on impact strength (IS) of epoxy resin.

Evaluation of properties

Impact strength was measured according to the Charpy method (ISO 179) using a Zwick 5012 apparatus on rectangular shaped samples 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 conducted using an Instron 5566 tensile machine on samples of the same dimensions as for impact. The tests were carried out at room temperature with a deformation rate of 5 mm/min and 60 mm of distance between the spans.

The same testing mode was applied on the notched samples to obtain critical stress intensity factor K_C ¹⁸:

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

where P stands for load at break, L represents spans distance, a is notch length, w stands for sample width, B is sample thickness, and Y means a geometry factor.

The geometry factor was calculated according to the following equation¹⁸:

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

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

A scanning electron microscope SEM was combined with a TESCAN VEGA/LMU instrument produced in the Czech Republic to examine the fracture

surfaces of specimens obtained from the impact tests.

DSC test was carried out using a PYRIS 1 instrument produced by Perkin–Elmer with a heating rate of $10^\circ\text{C}/\text{min}$, temperature range -100 to 200°C and $10 \text{ mg} \pm 0.1$ of sample weight. Nitrogen flow $20 \text{ mL}/\text{min}$ was applied as a purge gas.

RESULTS AND DISCUSSION

Mechanical properties

The impact strength, critical stress intensity factor as well as flexural properties including stress at break, strain at break, energy to break and flexural modulus values of all the compositions prepared in this study, together with the values of corresponding neat epoxy resin were evaluated, and the collected data is shown in Figures 1–6. Figure 1 shows the effect of added polyurethanes on the impact strength (IS) of epoxy resin. It can be observed that all tested compositions exhibit higher impact strength values than unmodified epoxy resin. Nevertheless, the composition containing 10% PUR 1002 shows maximum IS improvement representing approximately 125% in comparison with the IS of pristine epoxy samples. However, the maximum IS increase with PUR 400 is only about 25%. Polyurethanes with longer flexible segments (PUR 1002 and PUR 2002) are more effective modifier than polyurethanes with shorter flexible segments (PUR 400). We can observe about a 100% IS increase with only 5% of the former.

The values of critical stress intensity factor (K_C) are presented in Figure 2 as a function of polyurethane content. It can be observed that the maximum value of $3.0 \text{ MPa}\cdot\text{m}^{1/2}$ is reached by the epoxy composition containing 5% of each polyurethane compared with the $1.53 \text{ MPa}\cdot\text{m}^{1/2}$ of the unmodified epoxy resin. The values of K_C parameter decrease when increasing the amount of polyurethanes above 5%.

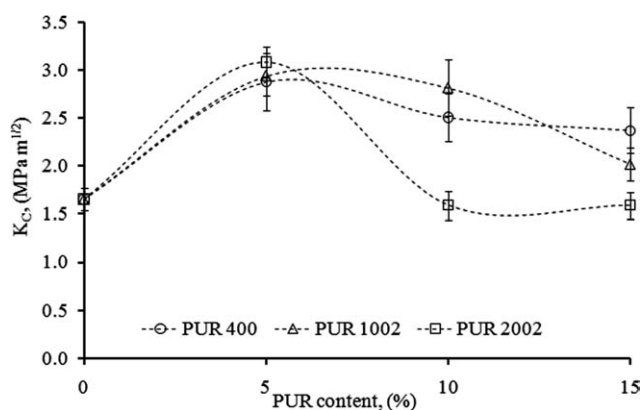


Figure 2 Critical stress intensity factor (K_C) as function of polyurethane content.

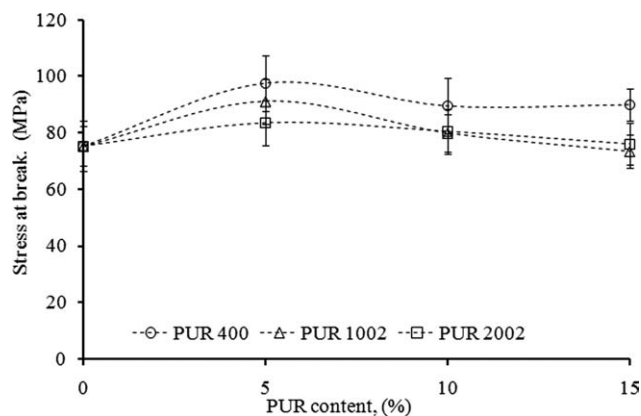


Figure 3 Flexural stress at break of epoxy resin modified with polyurethane.

It should be noted that the obtained K_C parameter results are compatible with IS data, indicating that the resistance of epoxy resin to high speed (IS tests) and low speed crack propagation as expressed by K_C parameter tests is enhanced by the addition of 5% PUR. The best property improvement is obtained with polyurethanes containing longer flexible segments (i.e., polyurethanes based on ROKOPOL 1002 and ROKOPOL 2002).

The improvement of impact strength and critical stress intensity factor through the addition of polyurethanes with shorter and longer flexible segments might attributed to the formation of an interpenetrating polymer network structure with the polymer matrix. The incorporated flexible polyurethane chains will provide more free volume to the system and hence increase its flexibility and the energy required to break the samples. The main reason for the significant improvement in the resistance to fast and slow crack propagation as expressed by respectively, impact strength and critical stress intensity factor values is the strong interaction between the well distributed polymeric modifier chains and the

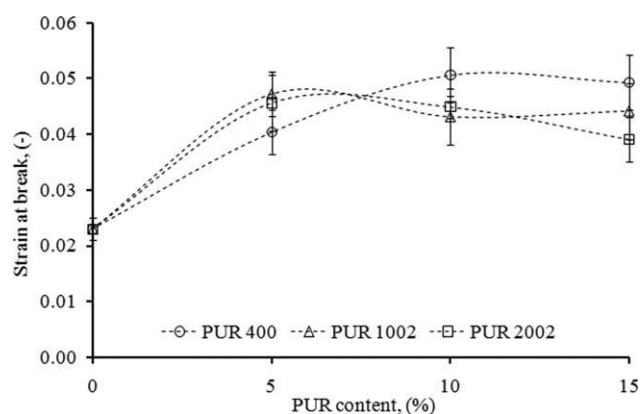


Figure 4 Strain at break of epoxy resin containing different amounts of polyurethanes.

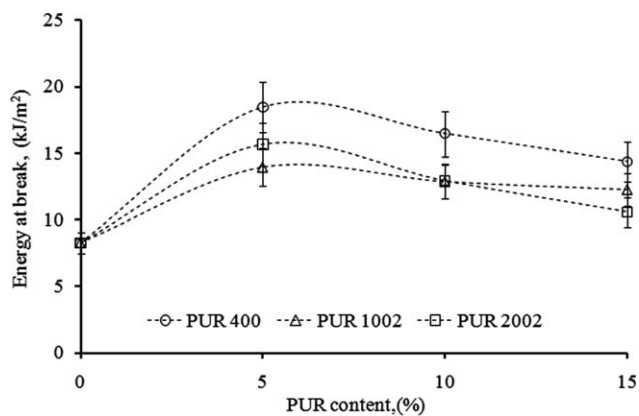


Figure 5 Effect of polyurethane content on the flexural energy at break of epoxy resin.

matrix through the formation of grafted interpenetrating polymer networks systems.

The data of the three point bending test is presented in terms of stress at break and strain at break respectively, in Figures 3 and 4. In polyurethane-modified epoxy resin, the stress at break value expresses the ultimate strength that the material can bear before its breakage, and depends significantly on the nature of the interactions as well as the system formed between the matrix and the polymeric modifier chains.^{12,17} Figure 3 confirms that the addition of polyurethanes slightly affects the flexural stress at break of epoxy resin. The maximum values of flexural stress at break is demonstrated by the compositions containing 5% PUR. The flexural strength increased from 75 MPa (neat epoxy resin) to maximally 95 MPa for the composition with 5% PUR 400.

As expected, epoxy resin modified with polyurethane shows increased strain at break. The addition of 5% of each polyurethane is sufficient to give an almost twofold increase of strain at break under three point bending. This is most probably due to

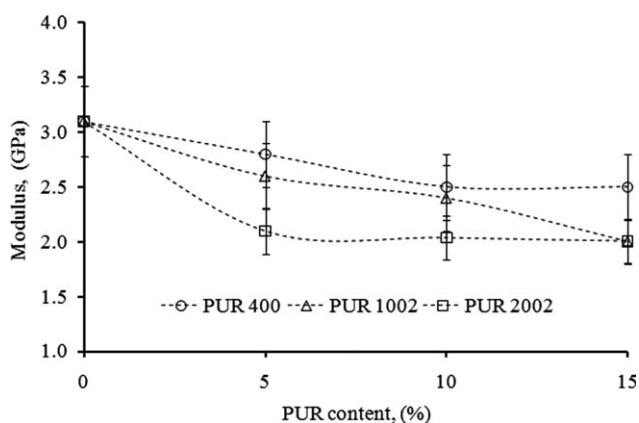


Figure 6 Flexural modulus as function of polyurethane content.

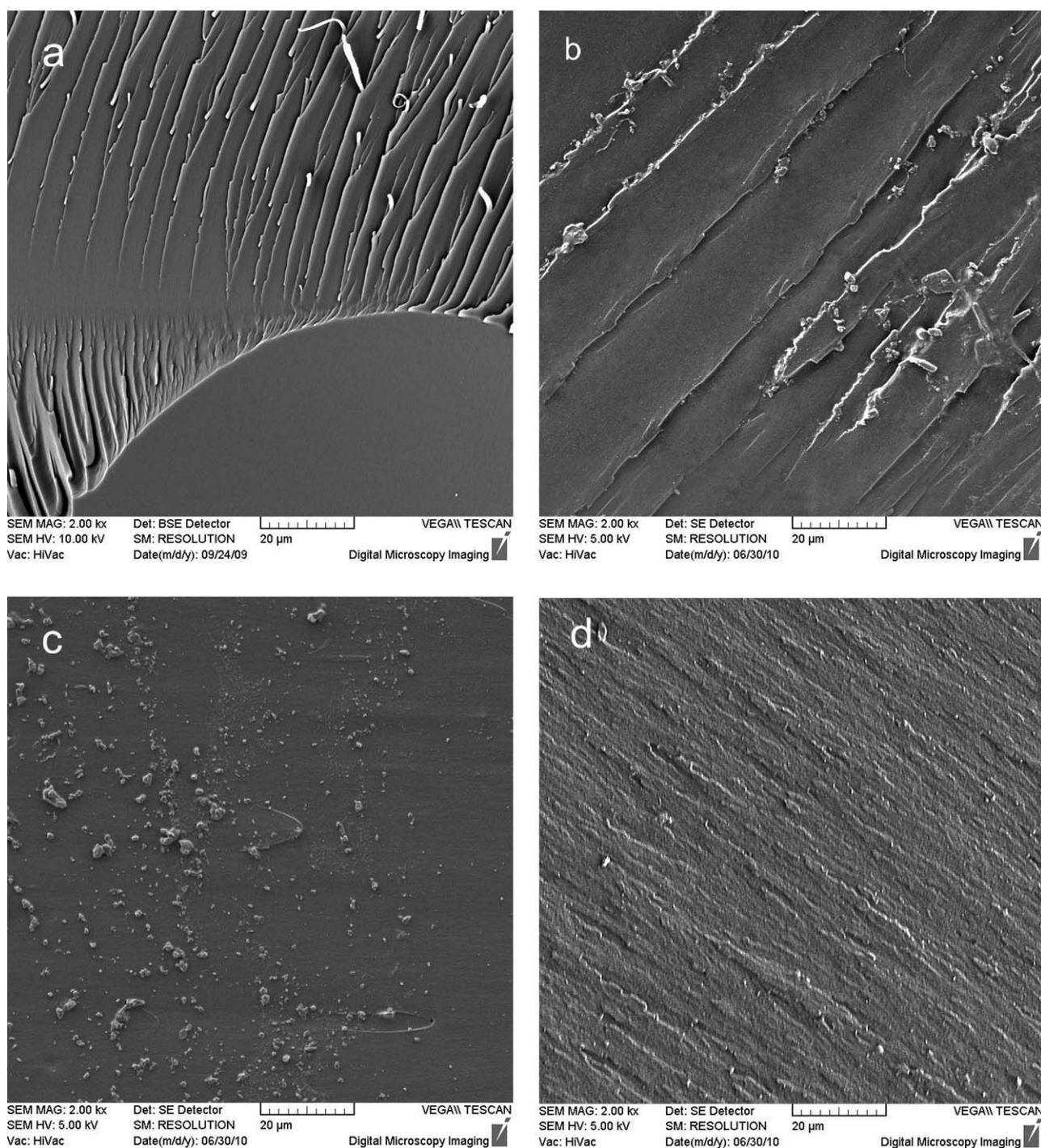


Figure 7 SEM images of fracture surface: epoxy resin (a) and composition containing 10% PUR 400 (b), 10% PUR 1002 (c), 10% PUR 2002 (d).

the incorporation of flexible segments in the polymer matrix. Maximum strain increase is reached with only 5% of polydiols (PUR 1002 and PUR 2002) based compositions with longer flexible segments, and 10% PUR 400. However, a higher amount of added polyurethane maintains the strain at break at the same level to that of virgin epoxy resin.

Figure 5 portrays the effect of modifier content on the flexural energy at break. This was calculated

from the area under stress-strain curve from the flexural test. The results confirm that the addition of 5% PUR is sufficient for maximal improvement of composites toughness. Maximum value of energy at break is shown by the composition containing 5% PUR 400 and represents about a 125% increase in comparison with neat epoxy resin.

Figure 6 shows the flexural modulus of epoxy resin modified with different amounts of polyure-

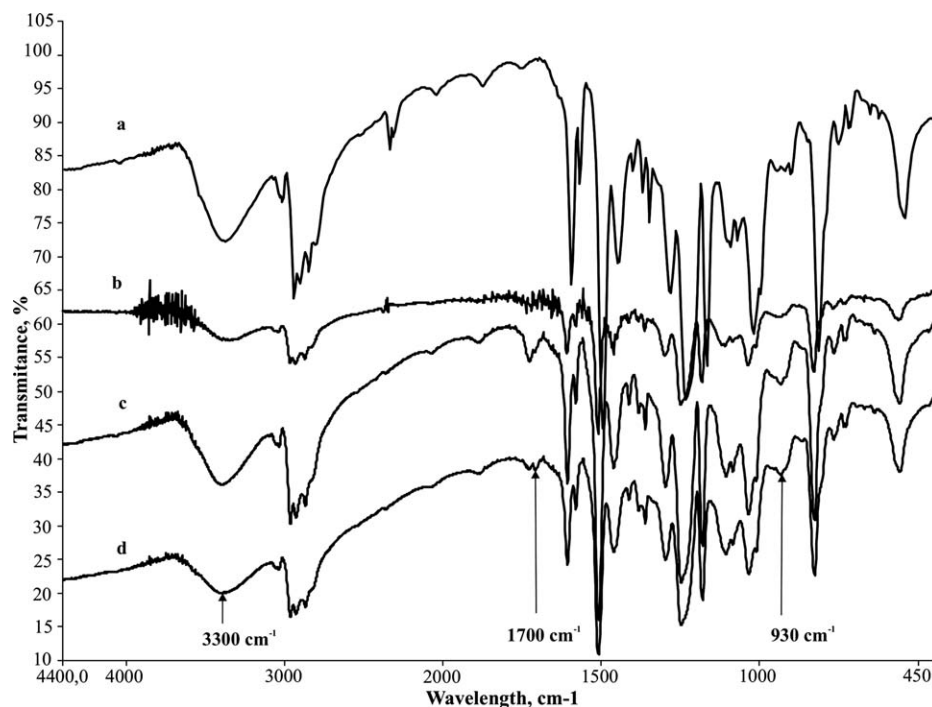


Figure 8 FTIR spectra of epoxy resin (a) and composites modified with 10% PUR 400M (b), 10% PUR 1002M (c), and 10% PUR 2002M (d).

thane. As can be observed, the flexural modulus decreases as the amount of polyurethane is increased. The lowest modulus value is reached with compositions containing 15% of PUR 1002 or 15% PUR 2002. The modulus value decreased by about 30% in comparison to neat epoxy resin.

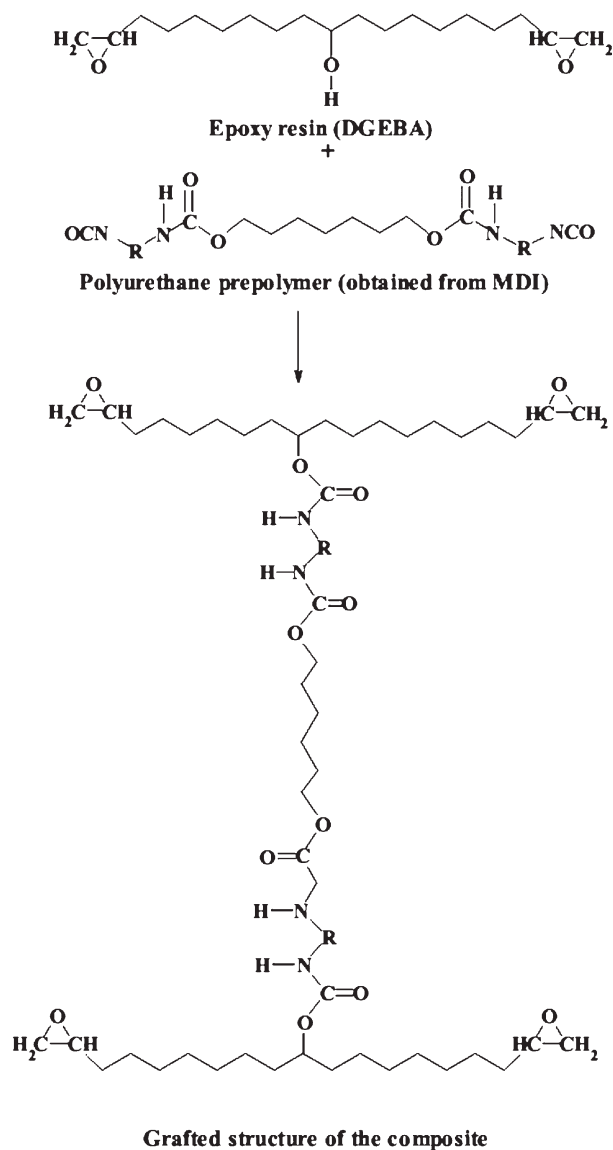
Morphology characterization

SEM micrographs were obtained from impact test samples near the crack tip for neat epoxy resin and selected compositions containing 10% of each polyurethane (PUR 400, PUR 1002 and PUR 2002). Figure 7(a) is micrograph of cured unmodified epoxy resin which exhibits a rather smooth surface and few crack propagation lines. The fractured surface shows a quite large glassy area with several microcracks formed during impact tests. This is a typical fracture surface of brittle glassy polymers having low impact strength. It should be noted that the micrographs of composites modified with polyurethane show completely different material structures in comparison to unmodified epoxy resin. However, Figure 7(b) depicts the fracture surface of epoxy resin modified with 10% PUR 400 with the presence of river-like lines. The formation of regular straight river lines might which may reflect some extent of shear plastic deformations, can be responsible for epoxy resin impact strength improvement due to the formation of a new surface that absorbs more energy before fracture occurrence. As demonstrated, the addition

of polymeric modifier has resulted in an obvious change in the morphology of the neat polymer matrix, leading thus to its fracture properties enhancement.

Figure 7(c,d) show that polyurethanes with longer flexible segments exhibit different fracture surfaces and consequently a different fracture toughness mechanism. It can be observed that the same polyurethane particles with different size are uniformly dispersed on the surface of the polymer matrix. This suggests that polyurethane acts as a barrier for crack propagation. Macroscopic observations of epoxy samples modified with PUR 1002 and PUR 2002 also confirm that phase separation occurs due to the opacity of epoxy compositions after curing. The fracture surface of composition containing PUR 2002 has a very regular structure of microcracks which can explain its higher mechanical properties in comparison to neat epoxy resin as well as the epoxy composition modified with PUR 1002.

Infrared spectra of selected compositions are presented in Figure 8. The peaks with wavelength 3300 cm^{-1} [Fig. 8(a)] are characteristic for hydroxyl groups of epoxy resin. Those at 1700 cm^{-1} indicate the presence of urethane and allophanate groups, while the peaks appearing at 930 cm^{-1} are associated with epoxy groups. The comparison of FTIR spectra for neat epoxy resin and composites with 10% polyurethane content shows that the intensity of the peak at 3300 cm^{-1} decreases. Furthermore, the absence of characteristic peak for free -NCO groups



Scheme 1 Formation of epoxy grafted structure.

in the wavelength range from 2270 to 2100 cm^{-1} confirms the formation of interchain bonds due to the reaction between free isocyanate groups from polyurethane and hydroxyl groups from epoxy resin within an interpenetrating polymer network (IPN) system as presented in Scheme 1. Consequently, a grafted IPN structure was formed, leading to the improvement of mechanical properties of epoxy resin. This kind of IPN structure was also reported by other researchers.^{4,8,11}

Figure 8(b) demonstrates that the addition of 10% PUR 400 forms an IPN structure with a high density of interchain bonds. This is shown by the significant reduction of the peak intensity of hydroxyl groups at 3300 cm^{-1} as well as by the disappearance of the urethane peak from polyurethane PUR 400 at 1700

cm^{-1} . This can explain the lower values of IS and K_C , since a stiffer material is formed in comparison to composites containing 10% PUR 1002 (8c) and PUR 2002 (8d), where the above-mentioned peak was detected. However, a composite modified with PUR 2002 demonstrates a significant decrease of hydroxyl group peak intensity, which confirms that the reaction between polyurethane and the epoxy resin matrix took place. In this case, we obtain a composite exhibiting improved mechanical properties due most probably to a good balance between flexible and rigid polyurethane segments and the hydrogen bond formation between polyurethane and epoxy resin chains.

Differential scanning calorimetry (DSC) was employed for thermal characterization of epoxy compositions containing 10% polyurethane with different flexible segment lengths. The DSC diagrams demonstrate, that within the applied temperature range (100 to + 200°C), only one endothermic peak for each composition, confirming therefore the existence of one glass transition temperature for all tested compositions. This can be related to the good compatibility between the polymer matrix and the incorporated polymeric modifier and the absence of a two phase system. Moreover, the DSC results reveal a glass transition temperature increase from 63.2 to 67.4°C with the addition of 10% PUR 400, which confirms the FTIR results depicting a large amount of interchain bonds. The results of glass transition temperatures are summarized in Table II as a function of PUR content.

Furthermore, the addition of a polyurethane with longer flexible segments (PUR 1002) causes a very small decrease in glass transition temperature (T_g), an improvement of IS , K_C , and strain at break without deteriorating the flexural strength, which has a comparable value to unmodified epoxy resin. The increase of T_g for composite containing 10% PUR 2002 can be also connected with the grafted structure formation confirmed by the FTIR spectra. Therefore, the use of polyurethane with longer flexible segments (PUR 1002 and PUR 2002) due to plasticizing effect and grafted structure formation produces tougher composites without thermal property deterioration.

TABLE II
Glass Transition Temperature (T_g) of Selected Epoxy (EP) Compositions

Composition	T_g (°C)
Virgin epoxy resin	63.2
EP + 10% PUR 400	67.4
EP + 10% PUR 1002	62.5
EP + 10% PUR 2002	65.3

CONCLUSIONS

Compositions based on diglycidyl ether of bisphenol A and polyurethanes (PUR) obtained from 4,4'-diphenylmethane diisocyanate (MDI) with different molecular weights were produced. Their mechanical properties and morphology were investigated as a function of modifier type and content. From the obtained results we can conclude that the addition of 5–10% PUR based on MDI and polyols with different length of flexible segments can be successfully applied as a modifier for epoxy resin. An excess of isocyanate groups in the polymeric modifier led to grafted IPN structure formation, as confirmed by FTIR and DSC measurements, with enhanced mechanical properties. Epoxy resin modified with 5 and 10% PUR exhibits maximally increased impact strength, critical stress intensity factor K_{IC} and flexural property values. A further addition of modifier causes only a small improvement in some mechanical properties. Composites containing 5% PUR with longer flexible segments (i.e., PUR 1002 and PUR 2002) exhibited higher impact strength in comparison to neat epoxy resin without a deterioration of thermal properties. However, PUR prepared from polyethylene glycol had a higher flexural energy (to the break) and a higher flexural modulus.

“SEM micrographs showed that the smooth surface of the pristine epoxy resin disappeared with PUR incorporation. Indeed, we observed in SEM micrographs of PUR based epoxy compositions the formation of river-like lines reflecting some extent of shear plastic deformations and that may act as a barrier for crack propagation. However, FTIR data con-

firmed the grafted IPN structure formation, which further contributes to the enhancement of mechanical properties of epoxy resin. DSC results confirmed the presence of one single glass transition temperature and the absence of phase separation within PUR modified epoxy compositions.”

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