

Effects of Various Polyurethanes on the Mechanical and Structural Properties of an Epoxy Resin

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ABSTRACT: Polyurethanes (PURs) obtained from poly(ethylene glycol)s (PEGs) and polyoxypropylene diols (POPDs) of different molecular weights were used as modifiers of diglycidyl ether of bisphenol A. The impact strength, critical stress intensity factor, stress, and strain during three-point bending were measured as functions of the PUR type and content. Scanning electron microscopy and infrared spectroscopy were employed for the structure and morphology analysis. The addition of 10 or 15% PUR to the epoxy resin resulted in the most enhanced mechanical properties. However, a modifier loading higher than

15% led to decreases in the impact strength, critical stress intensity factor, and flexural strength. Moreover, shorter flexible segments in PUR obtained from lower molecular weight PEG led to stronger composites, whereas composites containing PUR based on lower molecular weight POPD with long flexible segments exhibited higher toughness and strain at break and lower impact strength. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2925–2932, 2011

Key words: composites; mechanical properties; polyurethanes; resins

INTRODUCTION

Cured epoxy resins (EPs) form a special class of thermosetting polymeric materials with high dimensional stability and very good chemical resistance. Because of these properties, they are widely used as matrices for high-performance composite materials, surface coatings, printed circuit boards, electric insulators, and adhesive joints. However, because of their high crosslink density, cured EPs exhibit low impact strength (IS), poor resistance to crack propagation, and little elongation at break; that is, they are inherently brittle.

In the last few decades, a lot of effort has been invested in minimizing the brittleness and improving the elasticity and adhesive and mechanical strength of EPs and in simultaneously maintaining their thermal stability.^{1–3}

Inorganic and metallic solid particles,^{4–6} liquid rubbers with various reactive groups,^{7–17} nanoparticles,^{18–24} and engineering thermoplastics^{25–28} have been employed to overcome the drawbacks due to the incorporation of liquid rubber (e.g., reduced glass-transition temperatures and stiffness).

EPs have also been modified with other crosslinkable polymers to form full, grafted, and semi-interpenetrating polymer networks. Because of its excellent elasticity and good IS, polyurethane (PUR) has been successfully used to improve the elasticity and resistance to brittle fracture of EPs.

Frisch et al.²⁹ obtained interpenetrating polymer network systems with EPs and polyester- and polyether-based PURs. The presence of a single glass-transition temperature between the temperatures of the two components confirmed that phase separation did not take place.

The level of reaction between EPs and modifiers has been further increased with suitable PURs containing other reactive groups. For example, Wang and Chen³⁰ modified diglycidyl ether of bisphenol A with a PUR prepolymer terminated with aromatic amine groups as well as phenolic hydroxyl groups. The results of their work showed that an EP modified with PUR with phenol hydroxyl groups exhibited better fracture toughness than an EP containing PUR with amine groups.

PURs can be linked to EPs by physical entanglements and chemical bonding to form grafted interpenetrating polymer network structures. Hsieh and Han^{31,32} evaluated the mechanical properties of a grafted interpenetrating polymer network made of an EP and PURs based on polyols with different chain lengths. The results showed that the significant improvement in the tensile strength was due to the grafted structure as well as the shortness of the PUR chains.

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Stefani et al.^{33,34} studied a urethane prepolymer with isocyanate groups blocked with nonylphenol to modify an amine-cured EP. Compositions containing PUR with an excess of isocyanate groups showed increased IS without a decrease in the elastic modulus or the compressive yield stress.³³ The same authors compared the modification effect of a commercial PUR (Desmocap 12) and a synthesized PUR with blocked isocyanate groups.³⁴ The fracture toughness parameter increased approximately 270% after the addition of the synthesized PUR (20%) in comparison with the parameter of the unmodified EP. With Desmocap 12 (20%), the attained increase in the fracture toughness was only 70%. It was confirmed that the blocked isocyanate groups participated in the crosslinking of the EP, and they played a major role as proton donors and thus accelerated the crosslinking process of the matrix. Furthermore, the use of Desmocap 12 contributed to the increase in the matrix elasticity through copolymerization with the flexible prepolymer chain.

Harani et al.³⁵ proved that an isocyanate-terminated PUR could react with an EP and lead to a significant improvement in the fracture toughness. Moreover, the use of a chain extender with a PUR prepolymer caused a 7-fold increase in IS and an almost 2-fold increase in the critical stress intensity factor (K_C) in comparison with the unmodified EP.

Pokropski and Balas³⁶ characterized the effects of the EP/PUR weight ratio, the molecular weight of the isocyanate component, and the grafting degree on the morphology and thermal and mechanical properties of an EP. They also analyzed the relationship between EP and PUR phase separation and the elasticity of the obtained products.

In a separate work, Park and Jin³⁷ evaluated the glass-transition temperatures, contact angles, and mechanical properties of EP/PUR systems. They used the Owens–Wendt and Wu models to evaluate the surface free energies of the EP/PUR compositions. 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, which resulted in increases in K_C and the low-temperature IS. The enhancement of the mechanical properties was explained as a result of an improvement in the hydrogen bonding between the EP hydroxyl groups and the PUR isocyanate groups.

More recently, we investigated the effects of PURs with different isocyanate indices on the mechanical and thermal properties of EPs.³⁸ The maximum improvement in the fracture toughness was reached with the PUR with the highest isocyanate index. Moreover, the elastic modulus decreased, and this implied softening of the epoxy-based compositions. The infra-

red (IR) spectra indicated that an excess of isocyanate groups led to a grafting process between the modifier and the matrix, and this explained the toughening of the latter. The purpose of this work was to investigate the properties and morphology of an EP modified with PURs based on different polyols.

EXPERIMENTAL

Materials

The following substances were used in this work:

- Diglycidyl ether of bisphenol A (Epidian 5, Organika Sarzyna, Nowa Sarzyna, Poland) as the EP with a molecular weight of approximately 400 g/mol, a maximum viscosity at 25°C of 30 Pa s, and an epoxy number of 0.49–0.52 mL/100 g.
- Poly(ethylene glycol) 400 (PEG 400) with a molecular weight of 400 g/mol and a hydroxyl number of 277 mg/g and poly(ethylene glycol) 600 (PEG 600) with a molecular weight of 600 g/mol and a hydroxyl number of 234 mg/g (Merck, Darmstadt, Germany).
- Polyoxypropylene diol 1002 (POPD 1002) with a molecular weight of 1000 g/mol and a hydroxyl number of 180 mg/g and polyoxypropylene diol 2002 (POPD 2002) with a molecular weight of 2000 g/mol and a hydroxyl number of 46 mg/g (Rokita, Brzeg Dolny, Poland).
- Triethylene tetramine (Z-1, Organika Sarzyna) as the curing agent.
- 2,4-Toluene diisocyanate (TDI; Merck).
- Dibutyltin dilaurate (Merck) as the catalyst.
- Toluene and acetone as the solvents.

Synthesis of the PURs

Four types of PURs were prepared from TDI and polyols: PUR based on PEG 400 (PUR 400), PUR based on PEG 600 (PUR 600), PUR obtained from POPD 1002 (PUR 1002), and PUR obtained from POPD 2002 (PUR 2002). The appropriate amounts of TDI were calculated as follows: 45.1 g for PUR 400, 38.1 g for PUR 600, 29.3 g for PUR 1002, and 7.5 g for PUR 2002. Polyols were purified by azeotropic and vacuum distillation with toluene to eliminate water. First, 50 g of polyol and 0.25 cm³ of dibutyltin dilaurate were stirred for 15 min *in vacuo*, and then they were heated to 40°C. One half of the TDI amount was added drop by drop over 15 min. The reaction was performed under a nitrogen atmosphere for 30 min, and the temperature was maintained below 60°C. Furthermore, the PUR was cooled to 25°C, and 50 cm³ of acetone was added to decrease the mixture viscosity. Finally, the rest of the TDI was added drop by drop over another 15

TABLE I
Effects of the PUR Content on Selected Mechanical Properties of the EP

Type of modifier	PUR content (wt %)	IS (kJ/m ²)	K _C (MPa m ^{1/2})	Flexural stress at break (MPa)	Flexural strain at break (×10 ⁻²)	Energy at break (kJ/m ²)
PUR 400	0	0.97 ± 0.09	1.18 ± 0.10	41.2 ± 0.3	0.53 ± 0.02	4.3 ± 0.3
	5	1.20 ± 0.10	2.13 ± 0.02	74.6 ± 0.6	3.94 ± 0.13	10.6 ± 0.4
	10	1.33 ± 0.06	2.23 ± 0.12	82.3 ± 1.0	4.26 ± 0.26	13.2 ± 0.4
	15	2.30 ± 0.20	1.72 ± 0.09	52.4 ± 1.6	3.78 ± 0.16	8.3 ± 0.8
	20	2.20 ± 0.17	1.24 ± 0.13	50.4 ± 1.8	4.66 ± 0.36	9.5 ± 0.5
PUR 600	0	0.97 ± 0.09	1.18 ± 0.10	41.2 ± 0.3	0.53 ± 0.02	4.3 ± 0.3
	5	1.93 ± 0.17	1.95 ± 0.03	78.0 ± 0.5	3.78 ± 0.05	9.7 ± 0.3
	10	2.00 ± 0.19	1.95 ± 0.09	87.1 ± 2.4	3.83 ± 0.07	9.9 ± 0.2
	15	1.95 ± 0.18	2.59 ± 0.17	63.0 ± 0.5	7.13 ± 0.05	19.8 ± 1.2
	20	1.13 ± 0.06	1.45 ± 0.11	44.4 ± 1.9	8.78 ± 0.07	19.5 ± 0.9
PUR 1002	0	0.97 ± 0.09	1.18 ± 0.10	41.2 ± 0.3	0.53 ± 0.02	4.3 ± 0.3
	5	1.05 ± 0.10	1.47 ± 0.15	51.3 ± 2.1	2.63 ± 0.03	4.6 ± 0.5
	10	1.40 ± 0.10	2.98 ± 0.12	53.2 ± 2.6	2.78 ± 0.04	5.9 ± 0.3
	15	2.03 ± 0.18	2.16 ± 0.19	60.6 ± 3.1	6.58 ± 0.02	17.2 ± 1.1
	20	1.53 ± 0.06	2.17 ± 0.17	41.9 ± 2.9	8.85 ± 0.03	13.8 ± 1.3
PUR 2002	0	0.97 ± 0.09	1.18 ± 0.10	41.2 ± 0.3	0.53 ± 0.02	4.3 ± 0.3
	5	1.57 ± 0.12	3.00 ± 0.25	59.5 ± 2.1	2.43 ± 0.05	5.6 ± 0.7
	10	1.43 ± 0.06	2.62 ± 0.19	63.9 ± 3.6	5.23 ± 0.04	13.4 ± 0.9
	15	1.40 ± 0.10	1.76 ± 0.10	43.0 ± 3.2	6.53 ± 0.03	11.0 ± 0.8
	20	1.43 ± 0.06	0.97 ± 0.08	23.5 ± 1.9	13.33 ± 0.01	10.9 ± 0.9

min, and the mixture temperature was maintained below 40°C. All prepared PURs had an isocyanate index equal to 1.05.

Preparation of the modified EPs

PURs (5, 10, 15, and 20 wt %) were mixed with the EP at room temperature with a homogenizer for 15 to 20 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 was continued for another 5 min before the obtained compositions were poured into a mold with standard geometries for mechanical tests. The curing process was carried out at room temperature for 48 h, and postcuring took place for 3 h at 80°C.

Testing methods

IS was measured according to the Charpy method (ISO 179) with a Zwick 5012 (Ulm, Germany) apparatus on rectangular samples (80 mm long, 10 mm wide, and 4 mm thick) with a notch length of 1 mm.

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

The same testing mode was applied to the notched samples to obtain K_C :¹

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

where P is the load at break, L is the span distance, a is the notch length, w is the sample width, B is the sample thickness, and Y is the geometry factor.

Y was calculated according to the following equation:¹

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

Fourier transform infrared (FTIR) spectroscopy was performed on a PerkinElmer 1000 PC (Waltham, Massachusetts) spectrophotometer recording IR spectra from 400 to 4000 cm⁻¹. Scanning electron microscopy (SEM; S-2460 N, Hitachi, Tokyo, Japan) was employed to examine the fracture surfaces of specimens obtained from the impact tests.

RESULTS AND DISCUSSION

The mechanical properties determined for the pure EP and modified PURs are depicted in Table I. The addition of PUR led to a significant increase in the stress at break under three-point bending. The highest flexural strength (a 2-fold increase versus that of the neat EP) was attributed to the compositions with 10% PUR based on PEG 400 and PEG 600. PUR also enhanced the flexural strain at break of the EP measured in the three-point bending mode. The highest value, which was found for the sample based on PUR 2002, was attributed to the length of the PUR segments.

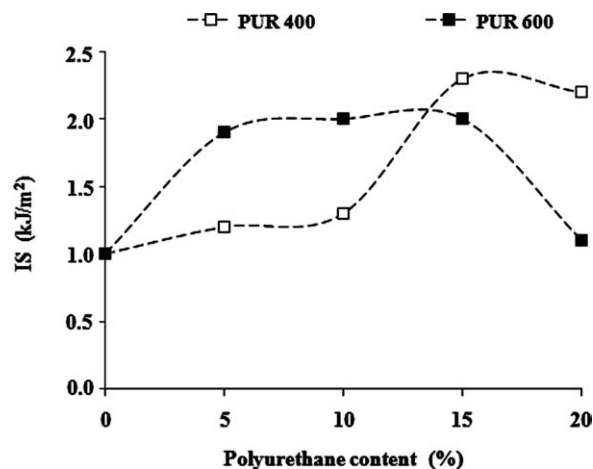


Figure 1 Effect of the PEG-based PUR content on IS of the EP.

Furthermore, the energy at break (obtained from the area under the load–displacement curve during flexural testing) rose with the addition of PUR. The flexural energy at break increased from 4.3 kJ/m² for the unmodified EP to 19.8 kJ/m² for the composition containing 15% PUR based on PEG 600; this represented a maximum improvement of 360% in comparison with the neat EP.

As shown in Figures 1 and 2, the effect of PUR modification on the IS of the EP was not uniform with the various PURs used. Except for the composition based on PUR 2002, which exhibited a 60% IS improvement with only 5% modifier, the maximum IS values were reached with a modifier concentration of 15%. The IS was enhanced approximately 130 and 100% upon modification with PUR 400 and PUR 1002, respectively.

Similarly to the IS results, the K_C values increased and then decreased with increasing amounts of PUR, and K_C reached maximum values with modi-

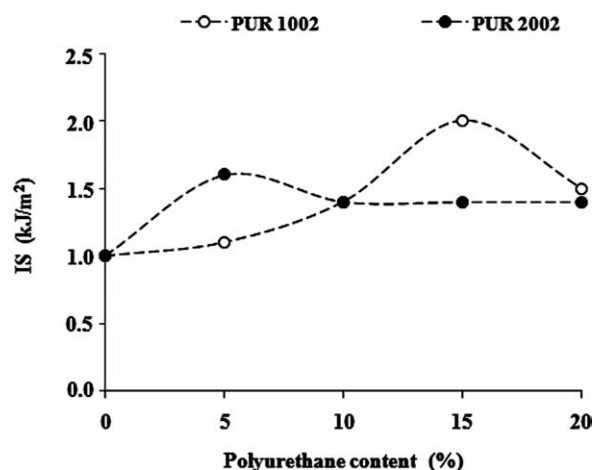


Figure 2 Effect of the POPD-based PUR content on IS of the EP.

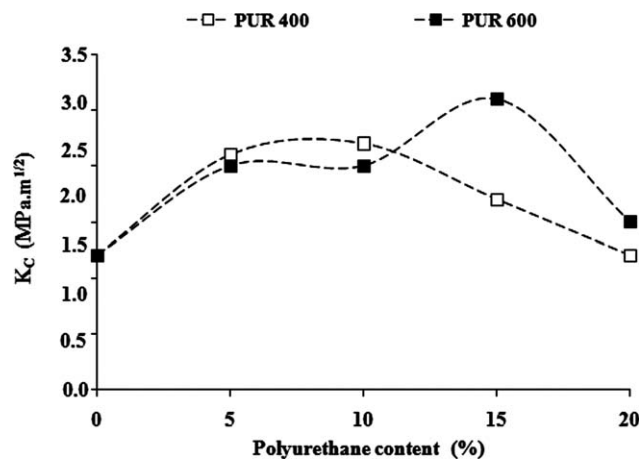


Figure 3 Effect of the PEG-based PUR content on K_C of the EP.

fier concentrations of 10–15% (Figs. 3 and 4). Peak K_C values of approximately 3 MPa m^{1/2} were obtained with compositions containing 10% PUR 1002 or 5% PUR 2002 (K_C was calculated to be 1.18 MPa m^{1/2} for the neat EP). These modifiers (i.e., PUR 1002 and PUR 2002) had the longest flexible segments as well as the highest average molecular weights (1000 and 2000 g/mol). The improvements of the IS and K_C values might be related to the high flexibility of the PUR prepolymers and the formation of an interpenetrating polymer network structure.

SEM micrographs obtained from fracture surfaces of pristine EP samples and samples containing PUR allowed us to clarify the modifying mechanism induced by PUR incorporation. The SEM image of the unmodified epoxy fracture surface presented in Figure 5 exhibits a glassy structure indicating a regular, uninterrupted crack propagation path.

On the other hand, Figures 6 and 7 present micrographs of the fractured surfaces of the EPs containing 10 or 15% PUR 400, respectively. Figure 6 shows

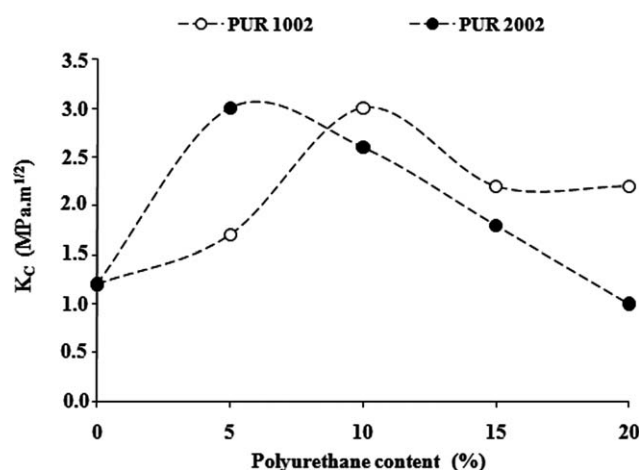


Figure 4 Effect of the POPD-based PUR content on K_C of the EP.

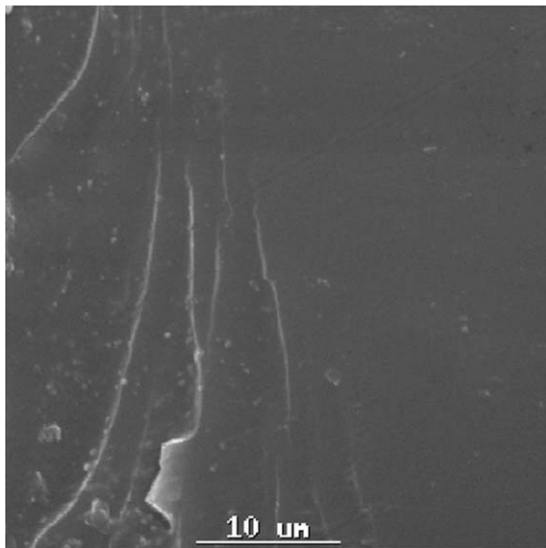


Figure 5 SEM micrograph of the unmodified EP.

an elongated structure most likely due to the occurrence of plastic yielding. SEM revealed two-phase systems with several microcracks near the notch tip. The enhancement of IS and K_C can thus be explained by the formation of new surfaces as well as plastic yielding of the polymer matrix. The incorporated PUR acted as a plasticizer, led to increased elasticity and consequently higher energy at break, and thus provided the obtained materials with toughness.

Moreover, the addition of a modifier to an EP generally leads to a decrease in the degree of its reticulation and thus an increase in the free volume together with the formation of plastic yielding zones. This can also be related to the observed IS increase.

The addition of a higher amount (15%) of PUR 400, as shown in Figure 7, contributed to the forma-

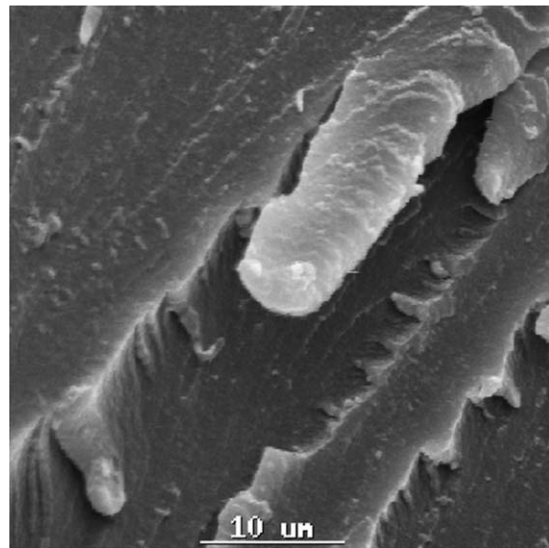


Figure 7 SEM micrograph of the EP modified with 15% PUR based on PEG 400.

tion of a structure similar to that found previously, and this might explain why the tested composition had the highest IS value.

Furthermore, as shown in Figure 8, the modification with 15% PUR based on PEG 600 resulted in a fracture surface that was almost glassy with insignificant plastic yielding.

EP compositions based on polyoxypropylene diols (POPDs) generally exhibited lower IS values than those synthesized from poly(ethylene glycol)s (PEGs). The compositions not following this trend were 15% PUR 1002 and 5% PUR 2002; their SEM micrographs (Figs. 9 and 10) show that their surfaces were elongated to a certain extent. This may explain

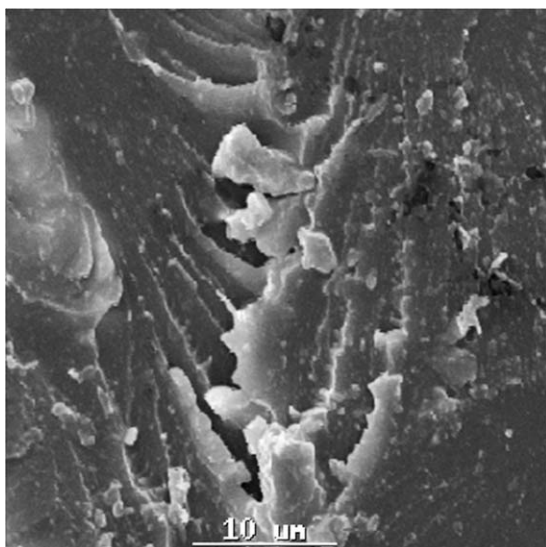


Figure 6 SEM micrograph of the EP modified with 10% PUR based on PEG 400.

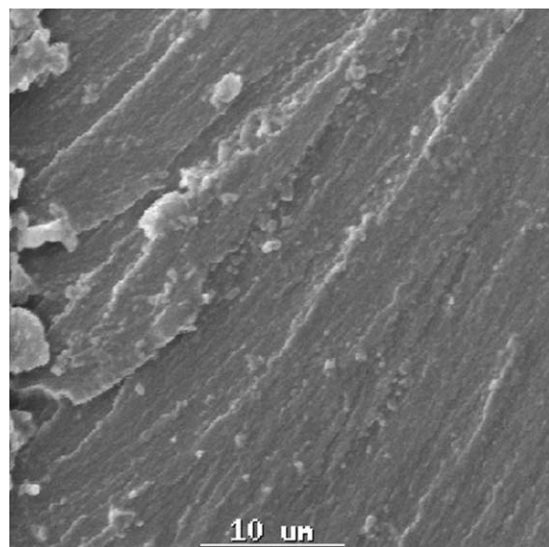


Figure 8 SEM micrograph of the EP modified with 15% PUR based on PEG 600.

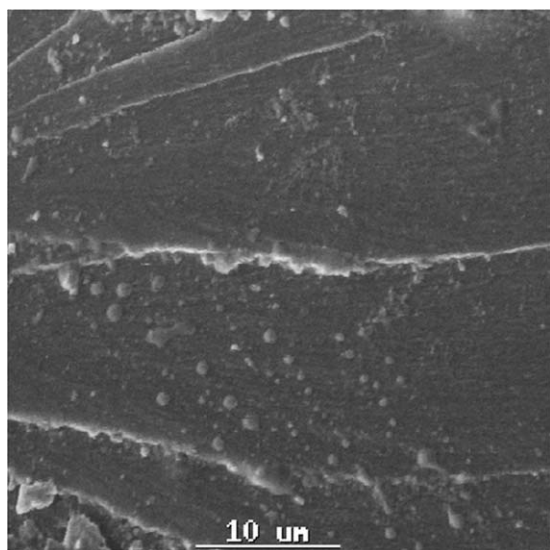


Figure 9 SEM micrograph of the EP modified with 15% PUR based on POPD 1002.

the higher IS and K_C values, respectively, of these compositions.

Figure 11 presents the IR spectra of the cured EP without PUR and the compositions containing 10% PUR 400 or 15% PUR 600. There are two characteristic peaks at 3400 and 920 cm^{-1} corresponding to the stretching vibrations of hydroxyl and epoxy groups, respectively. The peaks detected between 1600 and 830 cm^{-1} are usually associated with aromatic rings.

The EP modification with PUR 400 as well as PUR 600 showed a decrease in the hydroxyl group peak intensity in comparison with neat EP, and this might have arisen from the reactions taking place between the PUR isocyanate groups and the EP hydroxyl groups. Moreover, there was an increase in the peak

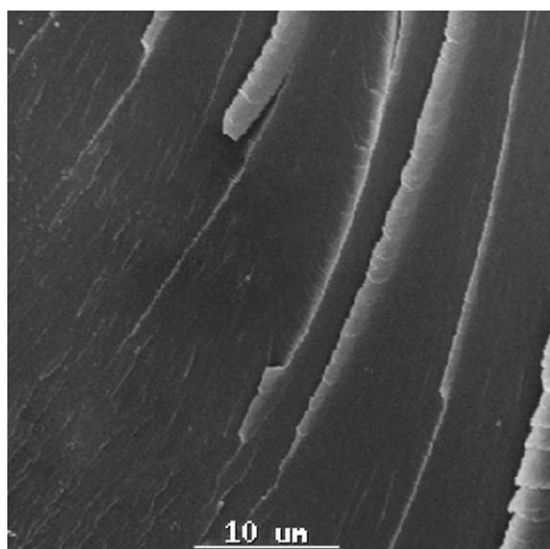


Figure 10 SEM micrograph of the EP modified with 5% PUR based on POPD 2002.

intensity from allophanate and urethane groups. Thus, FTIR spectroscopy confirmed the presumption of the improvement of mechanical properties due to the formation of strong grafted interpenetrating polymer network structures within this composition. The peaks corresponding to epoxy groups (920 cm^{-1}) remained unchanged, and this revealed an absence of reaction during the modification process.

Figure 12 presents the FTIR spectra of the pure EP and the compositions containing 15% PUR 1002 or 5% PUR 2002. The increase in the intensity peak at 1730 cm^{-1} confirmed the presence of higher numbers of allophanate and urethane groups in the composition containing PUR 1002 versus the composition modified with PUR 2002.

Furthermore, the peaks of the hydroxyl groups had considerably lower heights than those of the neat EP, and this indicated the formation of bonds between the PUR and EP. The epoxy group peak appearing at 935 cm^{-1} for the unmodified EP had almost the same intensity as the epoxy compositions modified with all the PUR types (PUR 400, PUR 600, PUR 1002, and PUR 2002). FTIR analysis also revealed that the composition based on PUR 1002 had two separate phases forming weak interphase bonds. This may explain the low IS of the PUR 1002 based compositions (except for the 15% composition). The composition containing 15% PUR 1002 exhibited a higher IS value (2.03 kJ/m^2) than the neat EP (0.97 kJ/m^2). This can be related to the formation of urethane and allophanate groups, as confirmed by the presence of an intensity peak at 1700 cm^{-1} .

There was a less pronounced peak at 1700 cm^{-1} for the composition based on 5% PUR 2002. This might be connected to the existence of urethane and

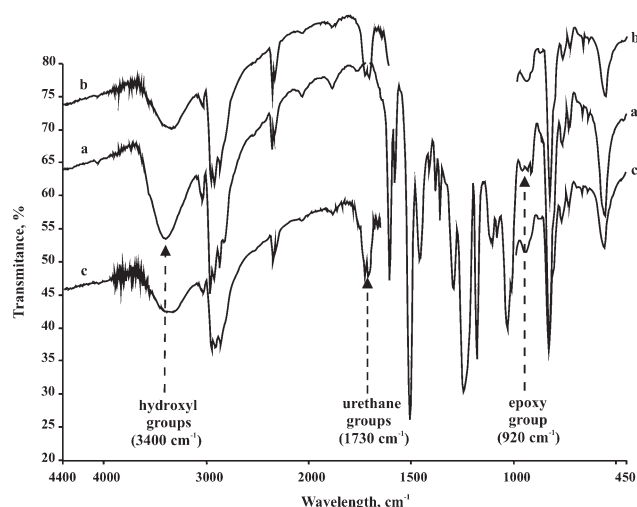


Figure 11 FTIR spectra of (a) the virgin EP, (b) the modified composition containing 10% PUR 400, and (c) the modified composition containing 15% PUR 600.

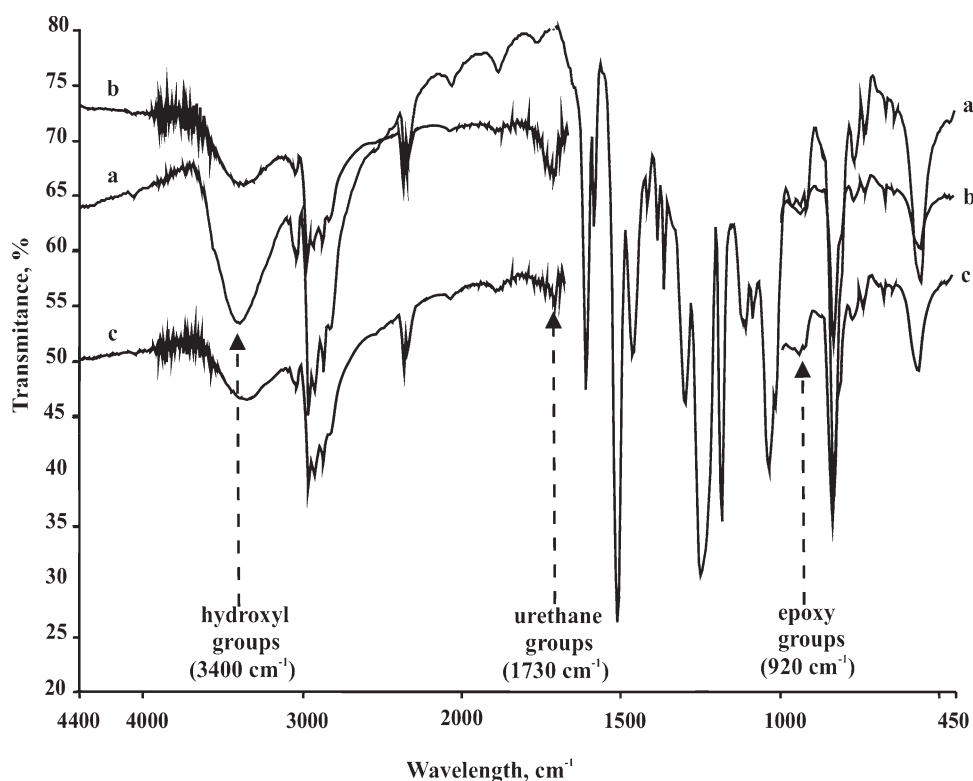


Figure 12 FTIR spectra of (a) the pure EP, (b) the modified composition containing 15% PUR 1002, and (c) the modified composition containing 5% PUR 2002.

allophanate groups and confirmed the lack of chemical reactions between the EP and PUR. In this specific case, the PUR modifier and EP formed two distinct phases without interchain reactions or with very rare interchain reactions, and this resulted in compositions with low impact resistance. However, this type of composite was more flexible than those containing PURs obtained from PEGs.

CONCLUSIONS

The mechanical properties determined for the EP modified with PURs, supported by IR spectroscopy and SEM analysis, revealed that PUR chains might contribute to the flexibility increase in the EP through the formation of grafted interpenetrating polymer networks.

The addition of PURs obtained from PEGs (PUR 400 and PUR 600) as well as POPDs (PUR 1002 and PUR 2002) resulted in increases in the IS and K_C values as well as the flexural properties of diglycidyl ether of bisphenol A. The IS, representing rapid crack propagation, improved approximately 130% with the addition of 15% PUR 400. However, K_C , revealing slow crack propagation, reached a maximum value of $3 \text{ MPa m}^{1/2}$ for compositions containing 5% PUR 2002 or 10% PUR 1002 versus $1.18 \text{ MPa m}^{1/2}$ for the virgin EP.

The flexural strength was maximally improved by a 10% addition of both PEG-based PURs. The composition containing 15% PUR 600 exhibited the highest flexural energy at break, probably because of its balanced rigid and flexible segment content in comparison with the neat EP. Modification with POPD-based PURs created two-phase flexible systems.

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