Tomas Bata University in Zlin

Faculty of Technology

Doctoral Thesis

Modification of Epoxy Resin with Polyurethane and Montmorillonite

Úprava epoxidových pryskyřic přídavkem polyuretanu a nanojílu

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ABSTRACT

The aim of this doctoral thesis is the chemical and physical modification of brittle epoxy resin (EP) using two different modifiers – polyurethanes and montmorillonite nanoclay – with the purpose to improve its mechanical properties.

The use of polyurethanes (PUR) is motivated by the versatility of their structure, which can be easily modulated with appropriate substrates. Those utilized in the thesis were synthesized from polyols (polyethylene glycols and polyoxypropylene diols) with different molecular weights, and two diisocyanates: 2,4-toluene diisocyanate (TDI) and 4,4'-diphenylmethane diisocyanate (MDI).

It was determined that the short soft segments in polyurethane (polyethylene glycol based PUR) increase the flexural strength of EP, while composites containing polyurethanes with longer soft segments (synthesized from polyoxypropylene diols) are tougher. The addition of MDI based PUR results in a greater improvement of epoxy resin's mechanical properties than in the case of TDI application.

Montmorillonite (MMT) is known to significantly improve fracture toughness and strength of polymers even if added in amounts considerably lower than used for μ-sized fillers. Epoxy composites containing 1 % MMT demonstrate increased impact strength, whereas 2 % addition of MMT to EP enhances its flexural properties. However, higher MMT concentrations lead to reduction of EP mechanical properties.

Hybrid composites containing 1 or 2 % MMT and 5 to 15 % PUR (both MDI and TDI based) exhibit improved mechanical properties in comparison to neat epoxy resin. Moreover, hybrid composites prepared with MDI based PUR show more pronounced enhancement in comparison to those containing TDI, because the increase of fracture toughness and flexural strength is achieved without deterioration of the thermal properties.

For optimum strength enhancement the loading level of 1 % MMT and 15 % of MDI-PUR synthesized from polyethylene glycol is intercepted with two mechanisms involved in the improvement: exfoliation of nanoclay depicted with X-ray diffraction, and formation of chemical bonding between hydroxyl groups of epoxy resin with isocyanate groups from polyurethane confirmed with infrared spectroscopy as well as differential scanning calorimetry. Furthermore, polyurethane modifier acts as a compatibilizer for epoxy resin and montmorillonite mixtures and promotes the exfoliation process of the latter.

Taking into account all results obtained from mechanical tests and structural analyses, it might be assumed that the obtained EP/PUR/MMT hybrid composites are formed from grafted EP/PUR interpenetrating polymer networks and exfoliated montmorillonite acting as nanofiller.

ABSTRACT IN CZECH

Disertační práce se zabývá chemickou a fyzikální úpravou vlastností epoxidové pryskyřice (EP) přídavkem nanojílu a polyuretanů s cílem - za předpokladu synergie působení obou modifikátorů - zlepšení jejích mechanických vlastností.

Výběr polyuretanu (PUR) je motivován flexibilitou a universalitou jeho struktury/vlastností použitím vhodných kombinací výchozích látek pro jeho přípravu. Polyuretany použité v disertační práci byly syntetizovány z polyolů (polyetylénglykolů a polyoxypropylénů) s různou molekulovou hmotností a dvou diisokyanátů: 2,4–toluen diisokyanát (TDI) a difenylmethan 4,4’–diisokyanát (MDI).

Bylo zjištěno, že krátké segmenty (PUR na bázi polyetylénglykolů) zvyšují ohybovou pevnost EP, zatímco kompozity obsahující PUR s dlouhými segmenty (syntetizované z polyoxypropylénů) jsou tužší. Použití MDI přináší výraznější zlepšení mechanických vlastností EP, než je tomu v případě aplikace TDI.

Montmorillonit (MMT) je nanojíl známý svou schopností pozitivně ovlivnit lomovou houževnatost a pevnost polymerů, i když je k jejich modifikaci použit ve značně nižších koncentracích, než je tomu u plniv v mikronových rozměrech. Kompozity obsahující 1 % MMT se vyznačují zvýšenou pevností v rázu, zatímco 2 % MMT zlepšují především ohybové vlastnosti EP. Je však třeba zmínit, že vyšší stupeň plnění MMT má za následek zhoršení mechanických vlastností epoxidové pryskyřice.

Hybridní kompozity obsahující 1 nebo 2 % MMT a 5 až 15 % PUR (MDI i TDI) vykazují zlepšené mechanické vlastnosti EP matrice. Jako optimální bylo vyhodnoceno plnění obsahující 1 % MMT a 15 % PUR připraveného z polyetylénglykolů s molekulovou hmotností 400 g/mol a MDI, kde strukturní analýza ukázala působení dvou mechanismů směřujících k zlepšení vlastností EP: exfoliace nanojílu a formace chemických vazeb mezi hydroxylovými skupinami EP a izokyanátovými skupinami PUR. Ke zlepšení mechanických vlastností EP tak došlo díky synergii modifikace přídavkem PUR a MMT; exfoliace nanojílu byla potvrzena rentgenovou difrakcí, a formace chemických vazeb infračervenou spektroskopií i kalorimetricky. K dalšímu zlepšení užitných parametrů EP přispívá i flexibilita řetězců polymerního modifikátoru. V případě použití MDI navíc dochází ke zlepšení houževnatosti bez zhoršení teplotních charakteristik, jak dokládají výsledky kalorimetrických zkoušek.

Shrnutím dosažených výsledků lze vyvodit závěr, že připravené EP/PUR/MMT hybridní kompozity tvoří tzv. inter-penetrační EP/PUR síť, kde polyuretan hraje roli kompatibilizátoru mezi epoxidovou pryskyřicí a nanojílem, a podporuje tak jeho exfoliaci.

ABSTRACT IN POLISH

Rozprawa doktorska dotyczy chemicznej i fizycznej modyfikacji kruchej żywicy epoksydowej (EP) w celu otrzymania kompozytu hybrydowego o poprawionych właściwościach mechanicznych przez jednoczesne zastosowanie dwóch modyfikatorów: poliuretanu (PUR) i glinokrzemianu warstwowego – monmorylonitu (MMT).

Poliuretany zostały wybrane jako modyfikatory polimeryczne żywicy epoksydowej z uwagi na możliwość zmiany ich właściwości poprzez zastosowanie odpowiednio dobranych substratów. W niniejszej pracy do syntezy poliuretanów użyto polieteroli o różnej masie cząsteczkowej (glikoli polietylenowych oraz poliksypropylenodioli) oraz dwóch diizocyjanianów: 2,4-diizocyjanianu toluenu (TDI) i 4,4’-diizocyjanianu difenylometanu (MDI).

Wyniki badań właściwości mechanicznych wskazują, że krótkie giętkie segmenty pochodzące od poliuretanów otrzymanych z glikolu polietylenowego powodują wzrost odporności na zginanie zmodyfikowanej żywicy epoksydowej, podczas gdy poliuretany zawierające długie łańcuchy polieterowe pochodzące od polioksypropylenodiolu wykazują większą odporność na propagację pęknięcia przy niskiej prędkości deformacji.

Jako drugi modyfikator został wybrany montmorylonit (MMT) z uwagi na jego bardzo specyficzne właściwości fizykochemiczne. Na podstawie przeprowadzonych badań mechanicznych stwierdzono, że żywica epoksydowa zawierająca 1 % MMT wykazuje lepszą udarność, natomiast przy zawartości 2 % MMT kompozycje wykazują większą odporność na zginanie.

Rezultaty badań żywicy epoksydowej zawierającej 1 lub 2 % MMT oraz 5 – 15 % poliuretanów otrzymanych z TDI lub MDI wykazują, że kompozyty hybrydowe zawierające poliuretany na bazie MDI wykazują lepsze właściwości wytrzymałościowe w porównaniu do czystej żywicy epoksydowej jak również w porównaniu do kompozytów hybrydowych zawierających poliuretany otrzymane z TDI. Analiza struktury i morfologii przy użyciu spektroskopii w podczerwieni (FTIR), dyfrakcji promieni rentgena (XRD) oraz skaningowej mikroskopii elektronowej (SEM) wykazała, że w otrzymanych kompozytach hybrydowych matryca polimerowa EP/PUR ma strukturę szczepionego IPN, w której zdyspergowany jest eksfoliowany montmorylonit. W efekcie otrzymane kompozyty wykazują znacznie polepszone właściwości mechaniczne bez pogorszenia właściwości termicznych, co potwierdzają wyniki badań przy użyciu różnicowej kalorymetrii skaningowej (DSC). Ponadto otrzymane rezultaty sugerują, że poliuretan działa jako kompatybilizator dla układu EP/MMT oraz pełni rolę czynnika wspomagającego proces eksfoliacji w matrycy polimerowej.

LIST OF PAPERS

The following papers are included in the presented doctoral thesis:

I **Effects of various polyurethanes on the mechanical and structural properties of an epoxy resin**
Kostrzewa M., Hausnerova B., Bakar M., Siwek E.
Journal of Applied Polymer Science 2011, vol. 119, no. 5, 2925–2932.

II **Property evaluation and structure analysis of polyurethane/epoxy graft interpenetrating polymer networks**
Kostrzewa M., Hausnerova B., Bakar M., Dalka M.
Journal of Applied Polymer Science 2011, vol. 122, no. 3, 1722 – 1730.

III **Preparation and property evaluation of nanocomposites based on polyurethane-modified epoxy/montmorillonite systems**
Bakar M., Kostrzewa M., Hausnerova B., Sar K.
Advances in Polymer Technology 2010, vol. 29, no. 4, 237–248.

IV **Preparation and characterization of an epoxy resin modified by a combination of MDI-based polyurethane and montmorillonite**
Kostrzewa M., Hausnerova B., Bakar M., Pająk K.
Journal of Applied Polymer Science 2011, vol. 122, no. 5, 3237 – 3247.

V **Effect of diisocyanate type on the properties and morphology of epoxy/polyurethane interpenetrating polymer networks**
Bakar M., Hausnerova B., Kostrzewa M.
Journal of Thermoplastic Composite Materials, submitted November 2011.

1. THEORETICAL BACKGROUND

1.1. Epoxy resins: structure, properties and applications

Epoxy resins are low molecular weight, oligomeric or polymeric compounds consisting of more than one epoxy group. They are liquids with high viscosity that undergo a cross-linking process and transform to insoluble and hard plastics. They can be cured at high or low temperatures by using curing agents (or hardeners). Cured epoxy resins are characterized by high chemical and corrosion resistance, good mechanical properties as well as acceptable thermal stability. Moreover, they exhibit convenient adhesive strength to metals and other materials. However, due to high cross-link density, they are inherently brittle with low impact strength and small elongation at break.

The first epoxy resin was synthesized in 1936 by Castan from the reaction of 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) with epichlorohydrin in an alkaline medium, and was commercialized by Ciba Co. in 1946. Industrial grade epoxy resins obtained from bisphenol A and epichlorohydrin have molecular weights ranging from 400 to 4200 g/mol and an average degree of polymerization between 0.2 and 12 [1].

There are four main types of epoxy resin:

a) The oldest and still very common is bifunctional epoxy resin - the diglycidyl ether of bisphenol A (DGEBA) with the following structure, Figure 1.

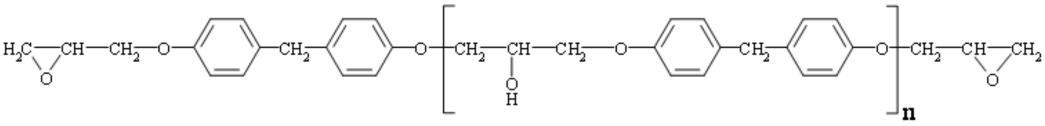


Figure 1. Chemical structure of diglycidyl ether of bisphenol A

b) Multifunctional epoxy resins containing three, four or more epoxy groups and characterized by very high glass transition temperature (up to 300 °C) as well as excellent mechanical and adhesive properties and thermal resistance. For these reasons, they have found multiple applications mainly in the aerospace industry as matrices for carbon fiber composites. One of the most widely used resins for such applications is N,N’-tetraglycidyl-4,4’-diaminodiphenylmethane (Figure 2), which is generally cured with 4,4'-diaminodiphenylsulphone.

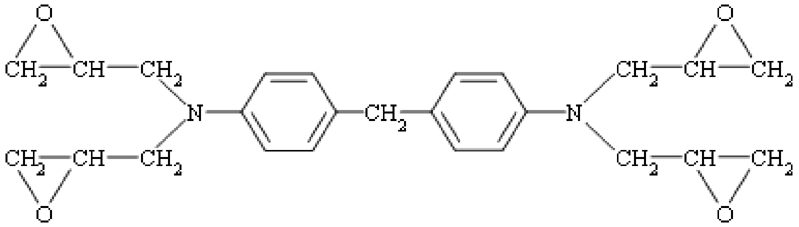


Figure 2. Chemical structure of N,N'- tetraglycidyl -4,4'-diamino diphenylmethane

c) Novolac epoxy resins (Figure 3) can contain from two to more than five epoxy groups. The multiple epoxy groups allow these resins to achieve high cross-link density resulting in excellent thermal and chemical resistance.

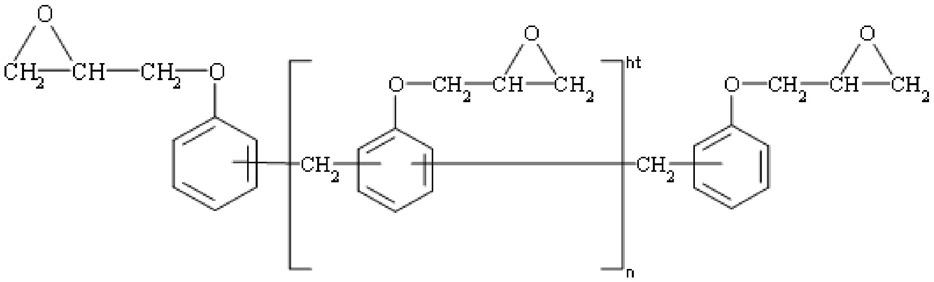


Figure 3. Chemical structure of novolac epoxy resin

Typical hardeners to be used for novolac epoxy resin include anhydrides, amines as well as diamino diphenyl sulphone. Furthermore, because of their superior performance at elevated temperatures and very good electrical properties, novolac epoxy resins are widely used in microelectronics and coating industries.

d) Cycloaliphatic epoxy resins are most widely used in the electrical industry. The absence of aromatic groups confers upon these epoxy resins superior electrical properties, particularly tracking resistance. A typical cycloaliphatic resin structure is shown in Figure 4. Polyamines and anhydrides are used as curing agents for cycloaliphatic epoxy resins.

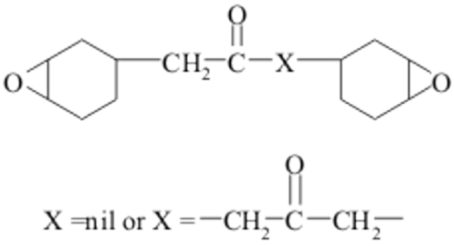


Figure 4. Chemical structure of cycloaliphatic epoxy resin

The applications of epoxy resins are extensive and include coatings, adhesives and matrices for high performance composite materials containing carbon and glass fibers as well as electronic packaging. However, their field of applications is seriously limited by their poor resistance to crack propagation, low impact strength and small elongation at break, i.e. their brittleness [1-4].

1.2. Modification of epoxy resin

In the last few decades, much work has been devoted to the methods for minimizing brittleness and improving elasticity, adhesive and mechanical strength, while simultaneously maintaining the thermal stability and chemical resistance of epoxy based materials.

The disadvantage of epoxy resins induced by their brittleness associated with low impact strength and small elongation at break can be reduced through physical and chemical modification. Attempts are made to increase epoxy resin toughness without significantly decreasing other important properties such as modulus and heat distortion temperature. Most of the reported studies were carried out using solid particles (glass beads, aluminum trihydroxide, silica, kaolin), rubbers, thermoplastic polymers, core-shell particles and nanoparticles. One of the most successful methods involves the addition of a suitable rubber such as copolymers of butadiene and acrylonitrile terminated with amine, carboxyl, hydroxyl and epoxy groups.

Scientific works noted in the literature section deal with the effects of particulate fillers on the mechanical properties of epoxy resin. Parameters such as the volume fraction of a filler, particle characteristics as well as their influence on modulus, strength, and toughness of the matrix have been extensively studied [5-11]. The variation of some of these parameters results in the improved toughness of the filled material while increasing its strength and modulus. Indeed, several studies have demonstrated that the fracture energy of filled epoxides reaches a maximum value at a specific filler content [4,7,11]. Moreover, highly cross-linked thermosetting resins have been strengthened by tough, ductile, chemically and thermally stable engineering thermoplastics such as polyethersulfones, polyetherimides, polysulfone and polyphenylene oxide, ABS, polyamides and polycarbonates [4,12 -15]. It has been well documented that the modification of polymers may not result in the improvement of all properties of a polymer matrix. In this respect, the formation of interpenetrating polymer network structures with other cross-linkable polymers such as polyurethanes seems to be a very promising method for epoxy resin modification [16-18].

1.2.1. Interpenetrating polymer networks

Interpenetrating Polymer Networks (IPNs) represent a novel type of polymer system, intended to modify epoxy resins by improving their impact strength and increasing their elongation at break. IPNs are defined as a combination of two or more polymers in a network form, in which one of the polymers is cross-linked or synthesized in the presence of the other. Interpenetration or permanent entanglements usually lead to improved compatibility between the blend's components, which means a decreased degree of phase separation. Morphology, which plays a major role in affecting IPN properties, is controlled by the chemical compatibility of the polymers, interfacial tension, cross-linking densities of the networks, polymerization method, and IPN composition [16-18].

However, most IPNs do not interpenetrate on a molecular scale but may instead form finely divided phases of only tens of nanometers in size. Many IPNs exhibit dual phase continuity, meaning that two or more polymers form a continuous phase on a macroscopic scale. It has to be mentioned that the cross-link density (related to chain length between cross-links) plays a major role in determining the domain size of IPNs. Generally, it is well accepted that the presence of short chain segments between cross-links can form smaller domains, which may increase the miscibility between IPN components. However, in some cases, strong evidence suggests that the cross-links' density might lead to the decrease of the miscibility between polymer components [19].

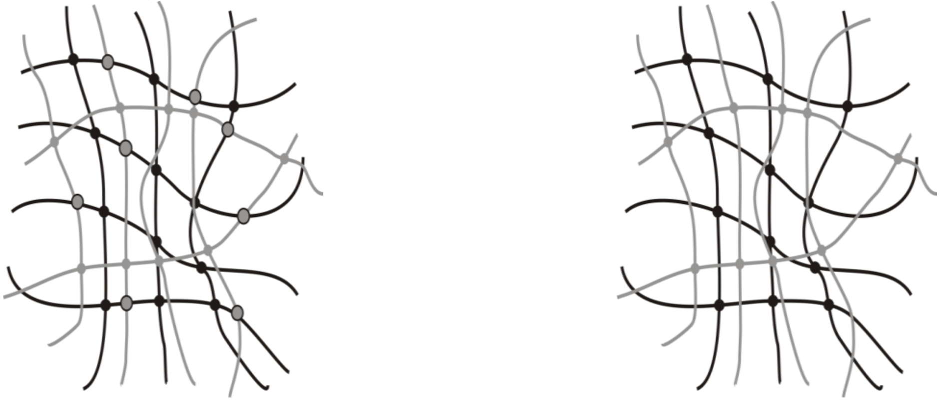
Several types of IPNs can be distinguished [20]:

- full IPNs, where two or more cross-linkable polymers are mixed on the molecular scale and form a three-dimensional network. The mixed polymers cross-link separately and are physically entangled without the formation of covalent bonds;
- grafted IPNs, in which interchain bonds are created within the network structure;
- semi IPNs, where one polymer remains linear or branched but not reticulated, while the second one is cross-linked;
- sequential IPNs, where a polymer network is made first, and then a second monomer, cross-linker and activator are swollen into the network and polymerized in situ. The sequential IPNs include many possible materials where the synthesis of one network follows the other;
- simultaneous IPNs, in which the monomers or prepolymers plus cross-linkers and activators of both networks are mixed. The reactions are carried out simultaneously, but by non-interfering reactions. For example, consider chain and step polymerization kinetics;
- latex IPNs are made in the form of latexes, frequently with a core and shell structure. A variation is to mix two different latexes, and then form a film, which cross-links both polymers. This variation is sometimes called an interpenetrating elastomer network;
- gradient IPNs are polymeric materials in which the overall composition or cross-link density of the material varies from location to location on the macroscopic level. For example, a film can be made with the first network predominantly on one surface, with the second network on the other surface and a gradient in composition throughout the interior;

- thermoplastic IPNs are hybrids between polymer blends and IPNs that involve physical cross-links rather than chemical cross-links. Thus, these materials flow at elevated temperatures, similar to thermoplastic elastomers, and they are cross-linked and behave like IPNs at the temperature of use. The types of cross-links include block copolymer morphologies, ionic groups and semi-crystalline structures.

Some of the IPN structures are presented in Figure 5. Although the preceding definitions are idealized and simple, many combinations may be envisioned that form the basis for broad scientific research as well as patented applications.

Homopolymer structure Semi IPN structure



Grafted IPN structure Full IPN structure

Figure 5. Examples of IPN structures

To summarize, interpenetrating polymer networks can produce materials which may have completely different properties from the base components. Such IPN systems, composed of two different polymers, might exhibit advantages of both components with minimized drawbacks. Moreover, it is possible to adjust the structure of an interpenetrating polymer network such that an enhancement in the epoxy resin properties can be achieved.

1.2.2. Modification of epoxy resin with polyurethane

Polyurethane characterization

Polyurethane polymers were introduced by Otto Bayer and his coworkers in 1937 in the I.G. Farben laboratories in Leverkusen, Germany [21]. They used the polyaddition principle to produce polyurethanes from liquid diisocyanates and liquid polyether or polyester diols. The obtained polymer exhibited special opportunities, especially when compared to already existing plastics which were made by polymerization of olefins, or the other compounds.

Polyurethane (IUPAC abbreviation PUR) is any polymer consisting of a chain of organic units joined by urethane (carbamate) links. Polyurethane polymers are formed through step-growth polymerization. A urethane linkage -RNHCOOR'- is produced by reacting an isocyanate group –N=C=O with a hydroxyl (alcohol) group –OH, in the presence of a catalyst. Figure 6 shows a schematic reaction between polyol and diisocyanate leading to polyurethane formation.

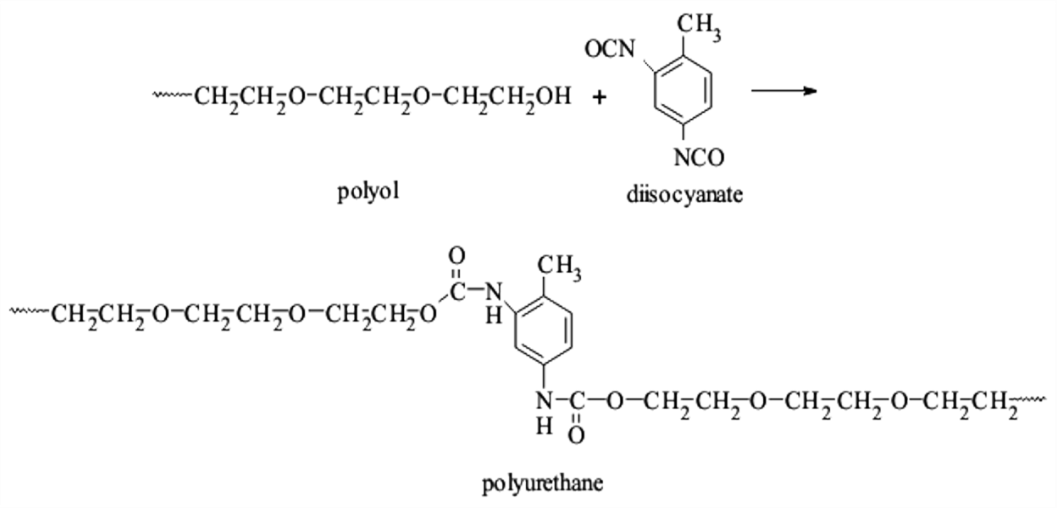


Figure 6. Synthesis of the polyurethane

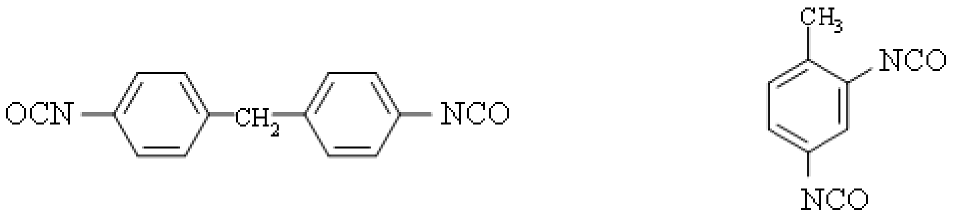
The step-growth polymerization is catalyzed by tertiary amines, such as dimethylcyclohexylamine, and organometallic compounds, such as dibutyltin dilaurate or bismuth octanoate. The choice of catalysts is furthermore governed by the urethane (gel) reaction, such as 1,4-diazabicyclo[2.2.2]octane. The physical and chemical character, structure and molecular size of these compounds influence the polymerization reaction as well as the processability and resulting physical properties of polyurethane.

Two main components are used to prepare polyurethanes - isocyanate and polyol. Molecules containing two isocyanate groups are called diisocyanates. These molecules are also referred to as monomers or monomer units, since they themselves are used to produce polymeric isocyanates containing three or more isocyanate functional groups.

Isocyanates can be classified as aromatic diphenylmethane diisocyanate (MDI) or toluene diisocyanate (TDI), and aliphatic 1,6-hexane diisocyanate (HDI) or isophorone diisocyanate (IPDI). An example of a polymeric isocyanate is polymeric diphenylmethane diisocyanate (PMDI), a blend of molecules with two or more isocyanate groups, with an average functionality of 2.7.

Isocyanates can be further modified by partial reaction with a polyol to form a prepolymer. A quasi-prepolymer is formed when the stoichiometric ratio of isocyanate to hydroxyl groups is greater than 2:1. A true prepolymer is formed when the stoichiometric ratio is equal to 2:1. Important characteristics of isocyanates are their molecular backbone, NCO group content, functionality and viscosity.

The two most important aromatic isocyanates, TDI and MDI, are shown in Figure 7. TDI is a mixture of toluene 2,4- and 2,6-diisocyanate isomers. The most important product is TDI-80, consisting of 80 % of the 2,4-isomer and 20 % of the 2,6-isomer. This blend is used extensively in the production of polyurethane flexible slabstock and molded foams. TDI, and especially crude TDI and TDI/MDI blends can be used in rigid foam applications, but have been supplanted by polymeric MDI. TDI-polyether and TDI-polyester prepolymers are used in high performance coating and elastomer applications [22].



MDI TDI

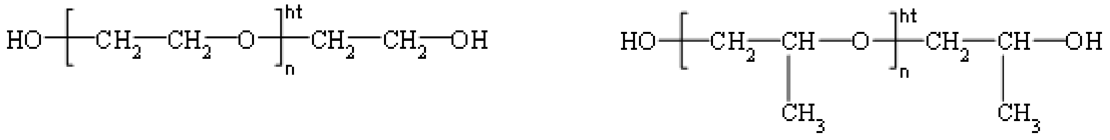
Figure 7. Chemical structure of most important aromatic isocyanates

MDI has three isomers - 4,4'-MDI, 2,4'-MDI and 2,2'-MDI, and is also polymerized to provide oligomers of functionality three and higher. Only the 4,4'-MDI monomer is commercialized as a single isomer. It is provided either as a frozen solid or flake, or in molten form, and is used to manufacture high performance prepolymers. It is also available in liquid form as a 50:50 mixture of the 4,4'-isomer and the 2,4'-isomer. The 4,4'-MDI-glycol prepolymers offer increased mechanical properties for similar applications, but they are solid at temperatures below 20 °C. A polymeric MDI that contains a rather large portion of high-functionality oligomers is used to produce polyurethane and polyisocyanurate rigid insulation boardstocks.

Modified PMDI, which contains a high level of MDI monomer, is used in the production of polyurethane flexible molded and microcellular foams. Other aromatic isocyanate include p-phenylene diisocyanate, naphthalene diisocyanate and o-tolidine diisocyanate [23,24].

The most important aliphatic and cycloaliphatic isocyanate is 1,6-hexane diisocyanate (HDI), which is used to produce light, stable, non-yellowing polyurethane coatings and elastomers. Isocyanates will react with any molecule that contains active hydrogens, for example alcohols, amines or water.

The second essential component of a polyurethane polymer is the polyol. Polyols are higher molecular weight materials classified as polyether polyols, which are made by the reaction of epoxides (oxiranes) with active hydrogen containing starter compounds, or polyester polyols, which are made by the polycondensation of multifunctional carboxylic acids and hydroxyl compounds. They can be further classified according to their end use as flexible or rigid polyols, depending on the functionality of the initiator and their molecular weight. Taking functionality into account, flexible polyols have molecular weights from 2000 to 10000 (hydroxyl groups number from 18 to 56). Rigid polyols have molecular weights from 250 to 700 (hydroxyl groups number from 300 to 700). Polyols with molecular weights from 700 to 2000 (hydroxyl groups number from 60 to 280) are used for stiffness or flexibility increase purposes in base systems, as well as solubility increase of low molecular weight glycols into high molecular weight polyols. Molecules containing two hydroxyl groups are called diols, while those having three hydroxyl groups are called triols. The structures of typical polydiols are presented in Figure 8. In practice, polyols are distinguished from short chain or low-molecular weight glycol chain extenders and cross-linkers such as ethylene glycol, 1,4-butanediol, diethylene glycol, glycerine, and trimethylolpropane. Polyols are formed by a base-catalyzed addition of propylene oxide or ethylene oxide onto a hydroxyl or amine containing initiator, or by polyesterification of diacids (adipic acid) with glycols (ethylene glycol or propylene glycol). Polyols extended with propylene oxide or ethylene oxide are polyether polyols, while those formed by polyesterification are polyester polyols.



Polyethylene glycol Polypropylene glycol

Figure 8. Examples of chemical structure of polydiols

Polyester polyols fall into two distinct categories according to composition and application. Conventional polyester polyols are based on a virgin raw material and are manufactured by the direct polyesterification of high-purity diacids and glycols, such as adipic acid and 1,4-butanediol. They are distinguished by the choice of monomers, molecular weight, and degree of branching. While costly and difficult-to-handle because of their high viscosity, they offer physical properties not obtainable with polyether polyols, including superior solvent, abrasion, and cut resistance. Other polyester polyols are based on reclaimed raw materials. They are manufactured by transesterification (glycolysis) of recycled poly(ethylene terephthalate).

Though the properties of polyurethane are determined mainly by the choice of polyol, the diisocyanate exerts some influence and must be selected according to PUR application. The cure rate is influenced by the functional group reactivity and the number of functional isocyanate groups. The mechanical properties are influenced by the functionality and the molecular shape. The choice of diisocyanate also affects the stability of the polyurethane upon exposure to light. Polyurethanes made from aromatic diisocyanates yellow under exposure to light, whereas those based on aliphatic diisocyanates are colour-stable [23-25].

Softer, elastic, and more flexible polyurethanes result when linear bifunctional polyethylene glycol segments, commonly called polyether polyols, are used to create the urethane links. This strategy is used to make spandex elastomeric fibers and soft rubber parts, as well as foam rubber. More rigid products result if polyfunctional polyols are used, as these create a three-dimensional cross-linked structure.

Commercially, polyurethanes are produced by reacting a liquid isocyanate with a liquid blend of polyols, a catalyst, and other additives. The additives may include chain extenders, cross-linkers, surfactants, flame retardants, blowing agents, pigments, and fillers to control and modify the reaction process and performance characteristics of polymer.

Chain extenders (2-functional) and cross-linkers (3- and higher functional) are low molecular weight hydroxyl and amine terminated compounds playing an important role in the morphology of polyurethane fibers, elastomers, adhesives, and certain integral skin and microcellular foams. The elastomeric properties of these materials are derived from the phase separation of the hard and soft copolymer segments of the polymer, where the urethane hard segment domains serve as cross-links between the amorphous polyether (or polyester) soft segment domains. The phase separation occurs as a result of incompatibility between non-polar, low melting, soft segments and polar, high melting hard segments. The soft segments, which are formed from high molecular weight polyols, are mobile and are normally present in a coiled formation, while the hard segments, which are formed from the isocyanate and chain extenders, are stiff and immobile. The structure of polyurethane is shown in Figure 9.

Because the hard segments are covalently coupled to the soft segments, they inhibit plastic flow of the polymer chains, thus creating elastomeric resiliency. Upon mechanical deformation, a portion of the soft segments are stressed by uncoiling, and the hard segments become aligned in the stress direction. This reorientation of the hard segments and consequent powerful hydrogen bonding contributes to high tensile strength, elongation, and tear resistance values [23, 25-27]. The choice of chain extender also determines the flexural, heat, and chemical resistance properties. The most important chain extenders are ethylene glycol, 1,4-butanediol and 1,6-hexanediol.

One of the most desirable attributes of polyurethanes is their ability to be turned into foam. Blowing agents such as water, certain halocarbons and hydrocarbons (e.g. n-pentane) can be incorporated into the poly-side or added as an auxiliary stream. It is important to note that surfactants are also used to modify the characteristics of the polymer during the foaming process. Commercial production of flexible polyurethane foam began in 1954, based on toluene diisocyanate and polyester polyols.

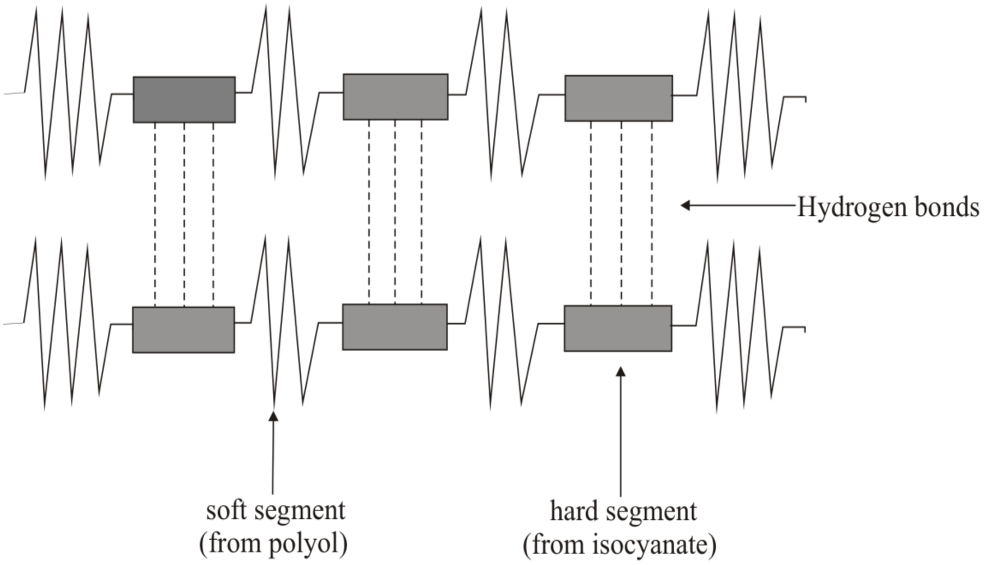


Figure 9. Segmented structure of polyurethane

Polyurethanes are widely used in high resiliency flexible foam seatings, rigid foams, elastomers, insulation panels, sealants, gaskets, durable elastomeric wheels and tires, automotive suspension bushings, electrical potting compounds, high performance adhesives, fibers and hard plastic parts (e.g. for electronic instruments).

Polyurethane as an epoxy resin modifier

Due to their excellent properties which might be modified by structural elements, polyurethanes have been used to improve the toughness of epoxy resins. Polyurethane/epoxy resin graft interpenetrating polymer networks (IPN) with combined advantages of both polymers were first reported by Frisch et al. [28].

Polyurethane can be linked to epoxy resin through physical entanglements as well as chemical bonding to form a grafted IPN. Hsieh and Han evaluated the mechanical properties of grafted IPNs based on epoxy resin and polyurethanes based on polyols with different chain lengths. They concluded that the significant improvement of the tensile strength was due to the grafted structure but also to the shortening of polyurethane chains [29].

However, Harani et al. [30] modified epoxy resin using a polyurethane prepolymer based on hydroxyl-terminated polyester. They proved that isocyanate-terminated polyurethane reacts with epoxy resin leading to significant improvement in fracture toughness. Moreover, the use of a chain extender with the polyurethane prepolymer caused a seven-fold increase in the impact strength and an almost two-fold increase in the critical stress intensity factor in comparison with unmodified epoxy resin.

Raymond and Bui [31] modified epoxy resin using urethane prepolymers based on TDI and castor oil with a molar ratio NCO/OH equal to 1.5. The epoxy resin was cross-linked by 2,4,6-tris(dimethylaminomethyl)phenol. They confirmed the occurrence of chemical reactions between isocyantae groups of PUR phase and hydroxyl groups of the epoxy matrix resulting in thermal resistance and tensile property enhancement. However, their results did not show an increase in impact resistance. Moreover, the thermo-mechanical tests demonstrated that the glass transition temperature peak of the mixtures was shifted towards lower temperatures as polyurethane content increased.

In order to further enhance the level of reaction between epoxy resin and polyurethane, it is appropriate to use polyurethane containing reactive groups. For example Wang and Chen [32] modified diglycidyl ether of bisphenol A with a polyurethane prepolymer terminated with aromatic amine groups as well as phenol hydroxyl groups. Moreover, they determined the effect of the diol type and content in polyurethane on the final properties and morphology of the obtained compositions. They concluded that epoxy resin modified with polyurethane with phenol hydroxyl groups exhibits better resistance properties and a higher glass transition temperature than epoxy resin containing polyurethane with amine groups.

Li and Mao [33] 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 the poor dispersion of polyurethane in the epoxy resin matrix.

In a separate work, Sung and Wu [34] 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 Jin [35] evaluated the glass transition temperature, contact angle and mechanical properties of 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 and low-temperature impact strength. The enhancement of the mechanical properties was explained as being the result of the improvement of hydrogen bonding between hydroxyl groups of EP and isocyanate groups of PUR.

Recently, Chen et al. [36] mixed polypropylene glycol, toluene diisocyanate, and 1,4-butanediol with diglycidyl ether of bisphenol A and stannous caprylate (as a catalyst) to obtain epoxy resin/polyurethane networks via frontal polymerization. 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 network synthesized by frontal polymerization has shown the same properties as those synthesized by batch polymerization. Moreover, it was confirmed that the frontal polymerization method requires significantly less time and lower energy input.

More recently, Bakar et al. [37] investigated the effect of PUR with a different isocyanate index on the 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 leads to a grafting process between the modifier and the matrix, explaining the toughening of the latter.

However, only a few articles have investigated the properties and morphologies of composites based on epoxy resin and polyurethane based on other diisocyanates such as 4,4’-diphenylmethane diisocyanate (MDI) or 1,6-hexane diisocyanate (HDI). A series of semi-interpenetrated polymer networks based on polyurethane and epoxy resin were also obtained and characterized by Cristea et al. [38]. They synthesized PUR from poly(ethylene adipate) diol, MDI and butylene glycol, and further modified with the addition of epoxy resin. They studied the damping properties of the obtained semi-IPNs and found that the heat treatment conditions affect significantly the viscoelastic properties of the blend. Moreover, weak softening and completion of the cross-linking were observed upon temperature increase.

In another work [39], Wang and Chen modified an epoxy resin based on bisphenol A using a 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 revealed also that the use of hydroxyl terminated PUR gives the composite with the best mechanical properties in comparison with amine or anhydride terminated PUR. The analysis of the SEM and TEM pictures showed that phase separation occurs for the obtained composites, which might take part in the toughening mechanism.

Pan et al. [40] 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.

However, Ismail et al. [41] modified an epoxy resin with an aliphatic polyurethane synthesized from poly(ethylene glycol) and 4,4'-diisocyanatodicyclohexylmethan (HMDI) without a solvent. An amine-cured epoxy composition containing 5 phr PUR exhibited enhanced thermal stability, flexural strength, storage modulus and adhesion strength.

It has to be mentioned that most of the published works describe epoxy modification with polyurethanes synthesized from TDI and selected polyols or very specific types of polyurethanes obtained from natural compounds, for example with castor oil [31]. However, there are only a few papers dealing with MDI-based polyurethanes.

Generally, polyurethane/epoxy systems can form several types of IPN structures depending on the reactive groups existing in the polymeric chains, leading to different levels of mechanical and thermal property improvements. However, there is a lack of information concerning the relationships between polyurethane structure and the mechanical properties of epoxy-based composites. The present thesis will attempt to investigate the effect of PUR structures on the ultimate properties of the base epoxy resin.

1.2.3. Modification of epoxy resin with nanoclay

Montmorillonite characterization

Nanostructured materials have completely different properties than dimensionally larger materials of the same composition because the transition from microparticles to nanoparticles yields pronounced changes in physical properties. Nanoparticles have a large surface area in comparison to occupied volume, inducing strong chemical and physical interactions governed by surface properties.

Generally, nanomaterials are classified according to their geometries as nanoparticles (e.g. carbon black, silica), nanofibers (e.g. glass nanofibers), carbon nanotubes and layered nanoparticles, where the filler has a plate-like structure (e.g. organosilicate clays - natural or synthesized).

During the last two decades, a great number of studies have been devoted to the application of natural clays as additives for polymers and composites preparation. Attempts of specific additive incorporation such as with montmorillonite, hectorite, vermiculite, saponite, illite and kaolinite were reported upon [42].

Montmorillonite (MMT) is a soft, natural clay that belongs to the smectite mineral family. It is named after Montmorillon, a place in France where MMT was discovered. MMT is composed of two tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately one micrometer [43,44].

The layers are continuous in the x- and y-directions, and stacked one above the other in the z-direction. Gallery is a term used to describe the stacked array of clay sheets separated by a regular spacing. The structure of the clay particle is presented in Figure 10.

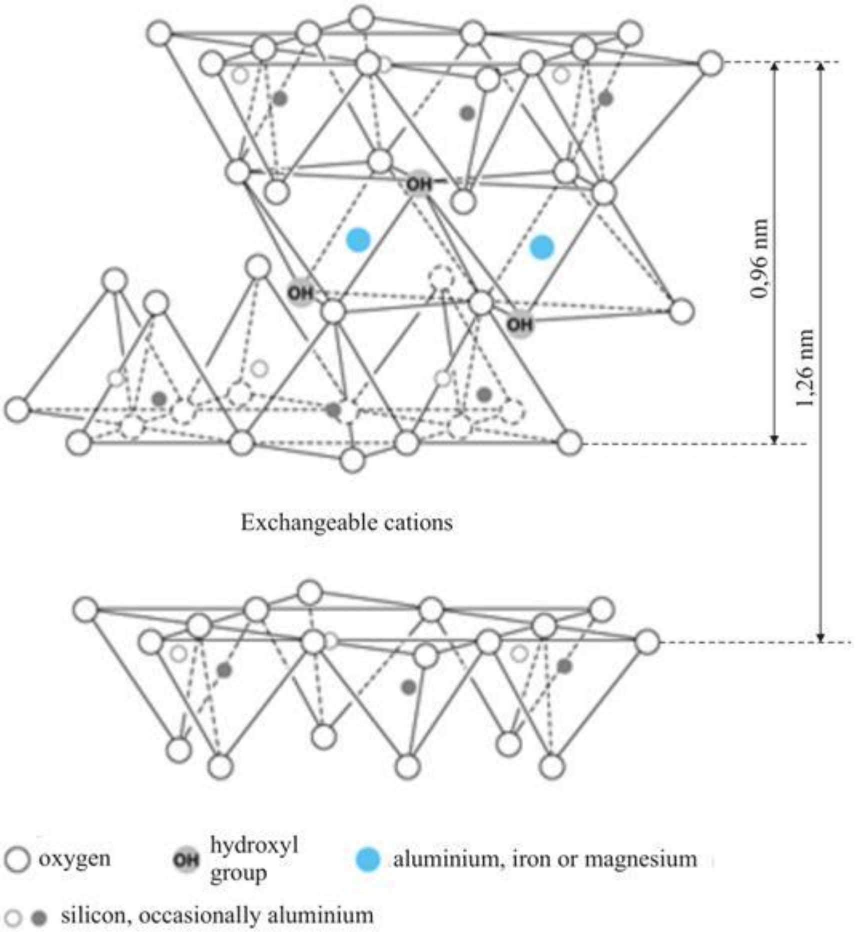


Figure 10. Layered structure of Montmorillonite

Chemically, MMT is hydrated sodium calcium aluminum magnesium silicate hydroxide $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2\cdot nH_2O$. Potassium, iron, and other cations are common substitutes, too.

Similarly to many other clays, montmorillonite swells upon addition of water. However, some montmorillonites expand considerably more than other clays due to water penetration into the interlayer spaces and the concomitant adsorption. The amount of expansion is largely due to the type of exchangeable cation existing in the sample. The presence of sodium as the predominant exchangeable cation can result in the clay swelling to several times its original volume.

Montmorillonite is known for its adsorbent quality; it has proven effective as an adsorptive of heavy metals, toxins, and hazardous chemicals [45-48] or moisture from air and gases. MMT is also widely used in the cosmetic and paper industries, and in pharmacology for a variety of applications such as stabilization of suspensions and emulsions, viscosity modifier, adhesion to the skin, and tablet making [49], drug carrier [50,51] or a part of a drug delivery system [52,53] for controlled drug release [54], and for tissue engineering [55].

A particular feature of the montmorillonite structure is that water and other polar molecules can enter among the unit layers because of the relatively weak forces between them, causing the lattice to expand. Due to the substitution of ions of different valence there is a charge deficiency on the sheet surface, and this charge is typically balanced by exchangeable cations adsorbed between the unit layers and around their edges. Usually, montmorillonite clays are modified by an onium ion substitution reaction with surface sodium ions, rendering the normally hydrophobic silicate surface organophilic and enabling the insertion of organic materials (including polymers). The alkyl ammonium cations provide functional groups which can react with the polymer or initiate polymerization of monomers [56-58].

As shown in Figure 11, there are three main structures possibly occurring in the polymer matrix/MMT system:

- an exfoliated structure formed when the clay layers are well separated from each other and individually dispersed in the continuous polymer matrix;
- an intercalated structure formed when there is a limited inclusion of polymer chains among the clay layers with a corresponding small increase in the interlayer spacing of a few nanometers;
- a microcomposite structure which occurs when montmorillonite particles are dispersed in the polymeric phase without nanoclay layers exfoliation.

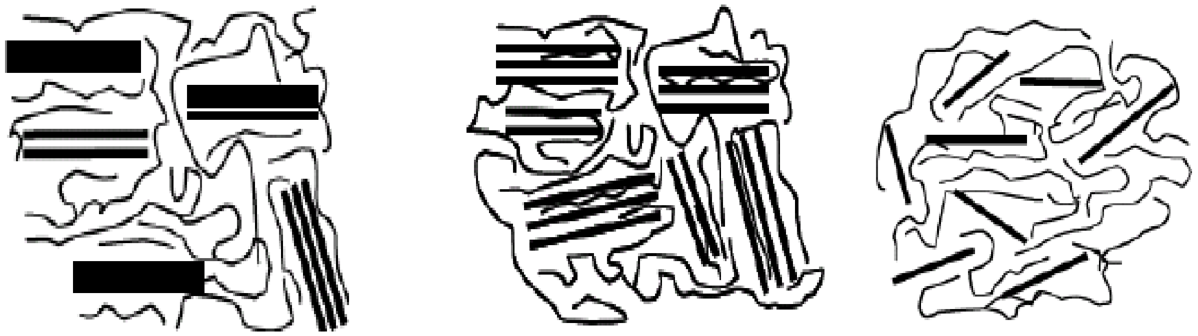

Microcomposite structure Intercalated structure Exfoliated structure

Figure 11. Polymer matrix/MMT structures

Exfoliated nanocomposites have higher phase homogeneity than the intercalated counterpart. The exfoliated structure is more desirable for enhancing the mechanical properties of a polymer matrix. However, it is not easy to achieve complete exfoliation of clays and, indeed with few exceptions, the majority of the polymer nanocomposites reported in the literature were found to have intercalated nanostructures. During the last two decades, montmorillonite has been used extensively as a modifier for epoxy resin in particular, and thermoplastics and thermosets in general [59-62].

Nanoclay as epoxy resin modifier

Hussain et al. [63] prepared a comprehensive and very interesting basis for polymer nanocomposite researchers. It is focused on scientific principles and mechanisms in relation to the methods of processing and manufacturing with a discussion on commercial applications of various kinds of nanocomposites. Generally nanoclay can be incorporated into a polymer matrix by several methods:

- the direct mixing of nanoclay powder with a polymer in a liquid state;
- nanoclay dispersing in the polymer solution followed by evaporation of the solvent;
- mixing of the nanoclay dispersion in a organic solvent with a melted or dissolved polymer and evaporation of the solvent;
- intercalative polymerization in situ when the polymer is formed in between the intercalated sheets. This technique is realized through the swelling of layered silicate within the liquid monomer and polymerization initiated by a suitable organic initiator or irradiation (e.g. heat, UV). This is a very popular method in the case of nanocomposite preparation based on thermoplastics as the polymer matrix.

The mixing process plays a very important role in composite preparation. It can be achieved by using a high speed mechanical stirrer, mechanical homogenizer or extruder or by applying an ultrasonic disintegrator to obtain ideal dispersion of the nanofiller [35,63]

A literature review dealing with energy absorption mechanisms in nanocomposites as a function of shape, dimension and stiffness of particles, type of matrix, particle volume fraction, distribution of particles and the particle/matrix interfacial properties by both experiments and simulation methods was presented by Sun et al. [64]. They reported various expressions of nanocomposite energy absorption from the nano- to the macro-scale, with more emphasis on the nano-scale composite.

Moreover, many papers present results on nanocomposite preparation, characterization and properties. For example, Ganguli et al. [65] prepared nanocomposites based on bifunctional epoxy resin modified with 4 % (by weight if not specified otherwise) organically modified silicate and evaluated its influence on viscoelastic, thermal properties and reinforcement. They compared the obtained results with neat epoxy resin as well as epoxy resin modified with 1 % multi-walled carbon nanotubes. They concluded that modification with carbon nanotubes creates a tougher nanocomposite than that containing layered silicate, although they applied different concentrations of nanofillers (1 % for nanotubes and 4 % for silicate).

Yilmazer et al. [66] used an unmodified montmorillonite (Cloisite Na+) and an organically modified one (Cloisite 30B) as reinforcing agents for diglycidyl ether of bisphenol-A (DGEBA). Their results demonstrate an increase in the glass transition temperature by more than 10 °C upon the addition of 9 % Cloisite 30B. The addition of 0.5 and 1 % Cloisite 30B resulted in maximum improvement of impact strength of DGEBA. The tensile strength also exhibited maximum value at 1 % modified clay loading.

In another work, Messersmith and Giannelis [67] prepared an exfoliated layered silicate epoxy nanocomposite based on DGEBA cured with nadic methyl anhydride in the presence of dimethylbenzylamine. Their results depict a significant increase in the storage modulus of the epoxy nanocomposite using 4 % organoclay modified with bis (2-hydroxyethyl) methyl tallow-alkyl ammonium chloride - approximately 58 % in the glassy region and 450 % in the rubbery plateau region compared to that of virgin epoxy.

The mechanism of the exfoliation of the nanoclays was analyzed by Lan et al. [68] for nanocomposites based on DGEBA cured with m-phenylenediamine. The exfoliation of the clay was not only dependent on the reactivity of the epoxy system but also on the accessibility of the matrix and the curing agent to the clay galleries. Moreover, the exfoliation was facilitated by the exchange of cations, which catalyze the intragallery polymerization of epoxy resin.

Kornmann et al. [69] prepared exfoliated nanocomposites using diglycidyl ether of bisphenol A and polyoxyalkylene diamine as a curing agent. They studied the dependence of the cation exchange capacities (CEC) on the synthesis and structure of epoxy/nanoclay nanocomposites. The exfoliation of montmorillonite takes place at low CEC during the swelling stage of the epoxy resin, which undergoes homopolymerization during swelling prior to cross-linking reactions because of the large space available between the galleries.

Shabeer and coworkers [70] prepared nanocomposites using a soy-based epoxy resin cured by anhydride and montmorillonite with two different dispersion techniques - pneumatic and sonication. They obtained composites with significantly improved tensile modulus and strength by 625 % and 340 % respectively. The glass transition temperature of the polymer decreased with increasing clay loading for a constant ratio of anhydride to epoxy. This decrease was attributed to reduced cross-link density. Moreover, rheological measurements showed that the addition of clay to the resin did not show a pronounced viscosity change. The dielectric constant and the dielectric loss of the nanocomposites increased linearly with nanoclay concentration increase.

Mittal [71] prepared epoxy nanocomposites with organically modified vermiculite to examine the influence of nanoclay structure on the barrier properties of nanocomposites. He employed ammonium ions of different chemical architecture in order to analyze the effect on the final composite properties. He concluded that the basal spacing values were enhanced after nanocomposite synthesis, confirming inter-gallery polymerization, despite the fact that a complete exfoliation could not be achieved. Moreover, a TEM analysis showed the presence of a mixed morphology with tactoids of varying thicknesses present along with a small number of single layers. The permeation properties were significantly improved (about 30 % improvement) but no significant effect of the chemical architecture was observed on the composite properties that were more affected by filler matrix interactions.

Zhao and Hoa [72] studied the correlation between particle size and volume fraction of nanofillers as well as microfillers and possible maximum energy release value to determine the upper limit of toughness improvement. They proposed some theoretical models which can predict the mechanical characteristics of the composites. The theory was compared with experimental results for epoxy resin modified by fillers with different particle sizes, structures and concentrations.

Lam and Lau [73] found that the micro-hardness of epoxy-based nanocomposites increased to a certain level with increasing nanoclay content. They related the hardness increase to the size increase of nanoclay clusters within polymer nanocomposites. In fact, micro-hardness and the flexural strength tests are governed by the nanoclay cluster size. Furthermore, it was found that mechanical properties are increased as the nanoclay amount in the nanocomposite is raised, albeit only in the certain range of nanoclay loading. Above this range, nanoclay reinforcement decreases due to the decreased distance between nanoclay clusters accompanying a larger amount of the total number of clusters in the composite. It leads to a reduction of contact surface area between nanoclays and the epoxy resin, causing reduced effectiveness of nanoclay strengthening. Moreover, they concluded that the application of MMT in the optimal limit can produce composites containing MMT clusters perfectly dispersed and with significantly improved mechanical properties without focusing on the formation of exfoliated and intercalated nanoclay structures within the composite.

A series of epoxy- based nanocomposites was prepared and characterized by Garea et al. [74]. As nanofiller they applied selected types of organo-modified MMT containing different organo-modifying agents - quaternaryammonium salts and epoxy-amine adducts. Results showed that modified montmorillonite with epoxy-amine adducts exhibits a higher compatibility with an epoxy polymer matrix than commercially modified montmorillonites, and that the glass transition temperature (T_g) of epoxy systems containing modified montmorillonite with epoxy-amine adducts as reinforcing agents decreased.

Rýznarová et al. [75] studied the effect of the clay surface modification on the structure of epoxy-clay nanocomposites. They prepared several organoclays via cation exchange reaction between inorganic cations naturally occurring in the clay gallery and different alkylammonium ions. They confirmed that various clay surface modifiers exhibit different catalytic effects on the curing of epoxy inside the clay gallery as observed by the measurement of the gel time with dynamic mechanical analysis.

Organophilic nanoclays are still very interesting mineral modifiers which can produce materials with improved toughness, strength and barrier properties, and with low loading. The properties of obtained composites are strongly dependent on the nanoclay type and concentration, their dispersion as well as arrangement within the polymer matrix. The exfoliation of nanoclay is the most desired arrangement because it leads to increased strength and enhanced fracture parameters. Moreover, in comparison to other nanofillers (eg. carbon nanotubes), it is relatively cheap and available in the market. Nanocomposites containing this type of nanoclay exhibit enhanced mechanical properties; in many cases the increase was higher than 100 % in comparison to the raw materials.

1.2.4. Hybrid epoxy composites

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 the mechanical and thermal properties of brittle epoxy resins via synergy 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. Due to the positive deviation generated from the combination of two different toughening mechanisms, hybrid composites are expected to exhibit better properties than neat resin.

Mülhaupt and coworkers [76] used both inorganic nanofillers and compatibilized polyether liquid rubbers to modify an epoxy resin. They found enhanced toughness of the epoxy resin due to the presence of a compatibilizer which induced phase separation of the rubber.

Furthermore, Ramos et al. [77] 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.

Qi et al. [78] modified epoxy resin by using a combination of SiO_2 nanoparticles and carboxyl-randomized liquid butadiene–acrylonitrile rubber (CRBN) nanocomposites. They found that a nanocomposite containing 2 % SiO_2 and 5 % CRBN showed improved impact strength and modulus. Moreover, the nanocomposite's morphology analysis by means of scanning electron microscopy and transmission electron microscopy showed a three-phase system as well as the uniform dispersion of both the rubber and the SiO_2 nanoparticles in the epoxy 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 [79]. 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 Zavareh [80] evaluated the impact strength and tensile properties and analyzed the structure of diglycidyl ether of bisphenol A reinforced with a thermoplastic acrylonitrile-butadiene-styrene terpolymer (ABS) and organically modified clay. Their results showed that the impact strength of an epoxy matrix increased significantly upon the addition of 2.5 % clay and 4 phr ABS. Moreover, the impact and tensile strengths of ternary nanocomposites were higher than those of binary systems. An exfoliated clay structure was obtained for a hybrid material composed of an epoxy/ABS/clay system.

Wang et al. prepared hybrid epoxy composites by using potassium titanate whiskers and castor oil-based polyurethane [81]. Their results showed that the addition of whiskers improves the damping properties and the tensile strength of the polyurethane/epoxy interpenetrating polymer network composites. In a separate work [82], the same authors used short carbon fiber, hollow glass beads and polyurethane to modify epoxy resin. The damping properties and tensile strength of the polyurethane/epoxy interpenetrating polymer network (IPN) were improved after the incorporation of carbon fiber and glass beads.

Shetty and Rai [83, 84] toughened diglycidyl ether of Bisphenol A-based epoxy resin with thermoplastic hydroxyl-terminated polyurethane elastomer and fly ash as well as hydroxyl-terminated polyurethane elastomer and a silane coupling agent treated granite powder. In both cases, the results demonstrated that toughened composites exhibited enhanced properties in comparison to the neat matrix.

Bakar and Kostrzewa [85] used a combination of polyether and toluene diisocyanate-based polyurethane and glass beads for epoxy resin modification. 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 a composition containing only 10 phr PUR.

Zheng et al. [86] used nanosized silicon dioxide particles to modify IPNs based on polyurethane and epoxy resin. They showed that an addition of nanoparticles improves the compatibility between the components as well as the mechanical properties and water resistance of epoxy/polyurethane nanocomposites.

Liu et al. [87] prepared epoxy hybrid composites containing carboxyl-terminated butadiene acrylonitrile (CTBN) rubber and organoclay, evaluated their properties and studied their morphology with X-ray diffraction, atomic force microscopy and scanning electron microscopy. Their results showed the improvement of fracture toughness, compressive modulus, yield strength and ultimate strength of the polymer matrix due to the exfoliation of the organoclay in the obtained nanocomposites. Epoxy modification with nanoclay and reactive rubber improves the fracture toughness parameters by 2 to more than 7 times at 6 phr nanonoclay loading and 20 phr CTBN. The glass transition temperature, yield strength and ultimate strength were also enhanced in comparison to the rubber-modified epoxy (with the same content of CTBN).

However, Alagar and his research group [88] prepared epoxy based IPNs with different amounts of caprolactam-blocked diphenylmethane diisocyanate (CMDI) and organophilic montmorillonite (MMT). The differential scanning calorimetry and dynamic mechanical analyses data indicated a significant decrease in the glass transition temperature of MMT-based hybrid epoxy systems when compared with that of neat epoxy resin. The mechanical tests indicated that the CMDI-toughened epoxy and organoclay/CMDI/epoxy systems had improved mechanical properties in comparison with neat epoxy resin. The X-ray diffraction analysis indicated the formation of an intercalated clay structure and a scanning electron microscope showed the homogeneous surface morphologies of CMDI-toughened epoxy and organoclay/ CMDI/epoxy systems. The same authors prepared nanoclay-filled polyethylene glycol (PEG)/1,8-octanediol (OCT) to modify epoxy resin with 4,4′-diaminodiphenylmethane as a curing agent [89], and reported improvement of impact strength for 3 % nanoclay-filled PEG and OCT modified epoxy systems. Homogeneous and heterogeneous morphologies were ascertained with a scanning electron microscope. From the X-ray diffraction analysis it was observed that the nanoclay filled PEG/OCT modified epoxy systems indicated the formation of exfoliated nanohybrids. A significant improvement in impact strength was achieved without any reduction in glass transition temperature due to the incorporation of nanoclay.

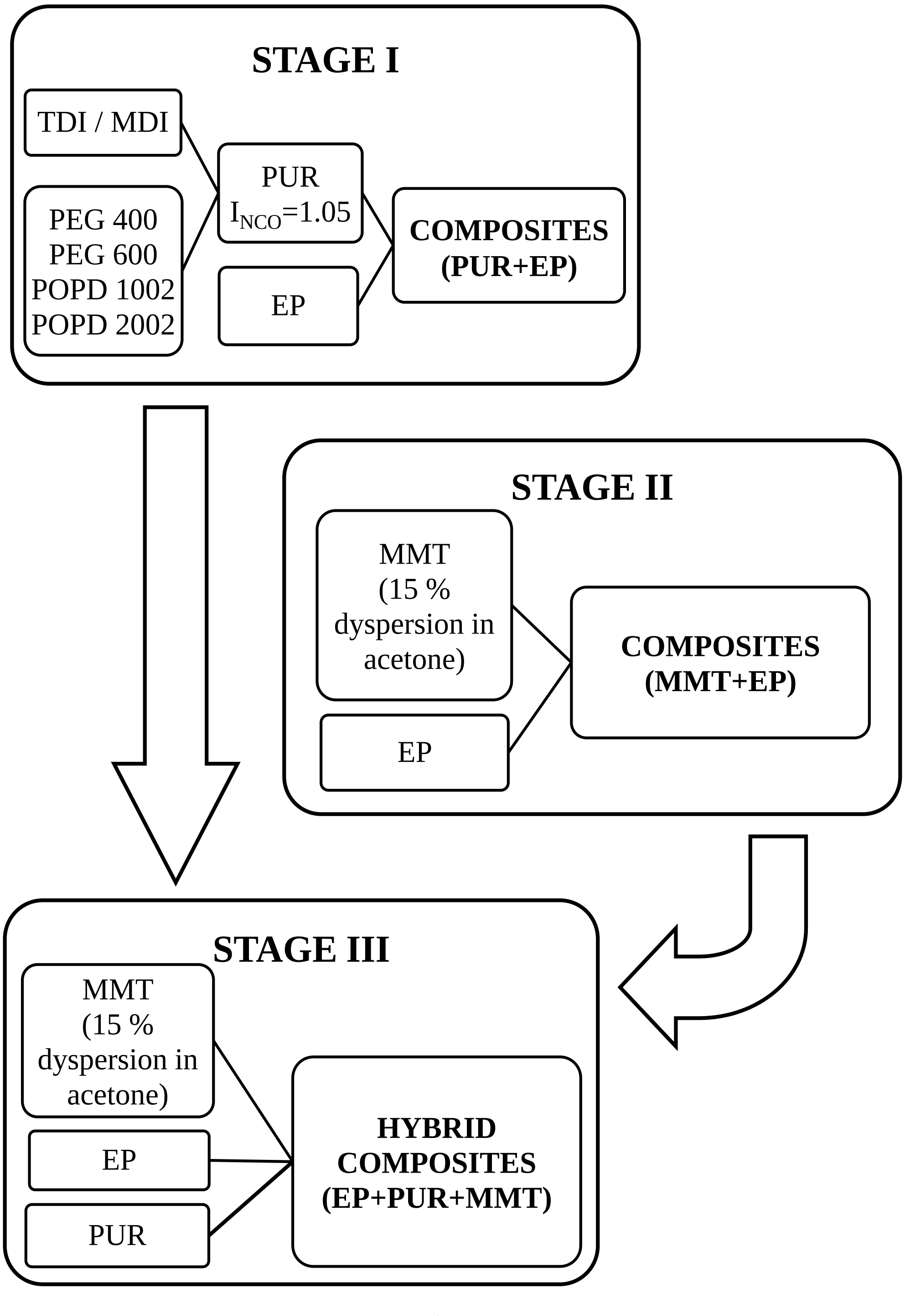
Lee et al. [90] investigated the effect of montmorillonite content on the mechanical properties and morphology of a carboxyl-terminated butadiene acrylonitrile toughened epoxy resin cured with polyetheramine. It was shown that the curing agent contributed to the intercalation of nanoclay, and the preparation method of the nanocomposite had only a slight effect on the mechanical properties.

Despite a few studies dealing with hybrid composites based on polyurethane and nanoclay, thorough investigation of the relationship between structure, morphology and strength of composites and added polyurethanes is still needed. Most of the studies are dealing with the effect of nanoclay structure and content on their thermal, dynamic mechanical properties and the free volume of obtained composites [91-94].

The presented thesis concentrates on the preparation and mechanical property evaluation of hybrid composites containing epoxy resin modified with polyurethanes and montmorillonite. The choice of two modifiers arose from the assumption that an epoxy resin with the combined advantages of both might be obtained.

2. AIM AND METHODOLOGY OF THE WORK

The aim of the doctoral thesis is modification of epoxy resin (EP) with polyurethane (PUR) and montmorillonite (MMT) to enhance fracture toughness and flexural strength without loss of thermal properties. To fulfill this intention several milestones are considered according to the procedure described in Scheme 1.



Scheme 1. Methodology of the work - a schematic view

First, polyurethanes are synthesized from the selected raw materials and mixed with epoxy resin to form compositions of the interpenetrating polymer network structure (Stage I). The EP/PUR mechanical properties in terms of impact strength, flexural strength and critical stress intensity factor are evaluated. The relationship between polyurethane structure used as modifier and its effect on toughness (strength) of epoxy resin is investigated

Simultaneously, epoxy resin is modified with 1, 2 and 3 % of montmorillonite to select concentration resulting in the most pronounced enhancement of epoxy resin's mechanical properties (Stage II).

Based on the obtained results series of EP/PUR/MMT hybrid composites are prepared with the expectation to achieve the synergic effect of both modifiers (Stage III). Thus, fracture toughness and flexural strength of hybrid composites are evaluated, and structure and morphology analyzed to confirm and explain mechanisms leading to the desired enhancement.

3. DISSCUSION OF THE RESULTS

Modification of epoxy resin with PUR based on toluene diisocyanate (TDI) or diphenylmethane diisocyanate (MDI) and two types of polyethylene glycol with molecular weights 400 and 600 g/mol as well as two polyoxypropylene diols having molecular weights 1000 and 2000 g/mol resulted in an enhancement of all tested mechanical properties as it can be seen in Table 1.

Table 1. Mechanical properties of epoxy resin modified with different type of polyurethane (data derived from Paper I and Paper II)

Sample symbol	**PUR**	**IS**	**K_C**	**Flexural strength**	**Flexural strain at break**	**Energy at break**
	%	**kJ/m^2**	**$MPa\ m^{1/2}$**	**MPa**	**$\cdot 10^{-2}$**	**kJ/m^2**
EP		1.0 ± 0.1	1.2 ± 0.1	41 ± 0	0.5 ± 0.0	4.3 ± 0.3
PUR400T	5	1.2 ±0.1	2.1 ± 0.0	75 ± 1	3.9 ± 0.1	10.6 ± 0.4
	10	1.3 ± 0.1	2.2 ± 0.1	82 ± 1	4.3 ± 0.3	13.2 ± 0.4
	15	2.3 ± 0.1	1.7 ± 0.1	52 ± 2	3.8 ±0.2	8.3 ± 0.8
PUR600T	5	1.9 ± 0.2	2.0 ± 0.0	78 ± 1	3.8 ± 0.1	9.7 ± 0.3
	10	2.0 ±0.2	2.0 ± 0.1	87 ± 2	3.8 ± 0.1	9.9 ± 0.2
	15	2.0 ± 0.2	2.6 ± 0.2	63 ± 1	7.1 ± 0.1	19.8 ± 1.2
PUR1002T	5	1.1 ± 0.1	1.5 ± 0.2	51 ± 2	2.6 ± 0.0	4.6 ± 0.5
	10	1.4 ± 0.1	3.0 ± 0.1	53 ± 3	2.8 ± 0.0	5.9 ± 0.3
	15	2.0 ± 0.2	2.2 ± 0.2	61 ± 3	6.6 ± 0.0	17.2 ± 1.1
PUR2002T	5	1.6 ± 0.1	3.0 ± 0.3	60 ± 2	2.4 ± 0.1	5.6 ± 0.7
	10	1.4 ± 0.1	2.6 ± 0.2	64 ± 4	5.2 ± 0.0	13.4 ± 0.9
	15	1.4 ± 0.1	1.8 ± 0.1	43 ± 3	6.5 ± 0.0	11.0 ± 0.8
PUR400M	5	1.5 ± 0.1	2.9 ± 0.3	98 ± 10	4.0 ± 0.4	18.5 ± 1.9
	10	1.4 ± 0.2	2.5 ± 0.3	89 ± 10	5.1 ± 0.5	16.5 ± 1.7
	15	1.5 ± 0.1	2.4 ± 0.2	90 ± 6	4.9 ± 0.5	14.4 ± 1.5
PUR1002M	5	2.0 ± 0.2	2.9 ± 0.2	91 ± 8	4.7 ± 0.5	14.0 ± 1.4
	10	2.3 ± 0.2	2.8 ± 0.3	80 ± 7	4.3 ± 0.4	12.9 ± 1.3
	15	1.6 ± 0.1	2.0 ± 0.2	73 ± 6	4.4 ± 0.4	12.3 ± 1.2
PUR2002M	5	1.9 ± 0.2	3.1 ± 0.2	83 ± 8	4.6 ± 0.5	15.7 ± 1.6
	10	1.8 ± 0.2	1.6 ± 0.2	80 ± 8	4.5 ± 0.2	12.9 ± 1.3
	15	1.6 ± 0.1	1.6 ± 0.1	76 ± 7	3.9 ± 0.4	10.6 ± 1.1

PUR-polyurethane content, **IS**-impact strength, **K_C**-critical stress intensity factor

The addition of 5 % MDI based PURs resulted in a twofold increase of impact strength (IS) and threefold increase of critical stress intensity factor (K_C) values. Moreover, the flexural strength and strain at break values increased by more than two times and ten times, respectively, in comparison to neat epoxy resin. The addition of 5 to 10 % of TDI based polyurethanes (PUR) with longer flexible segments (PUR prepared from polyoxypropylene diols) is needed to improve the resistance of epoxy resin to slow crack propagation expressed by K_C value. Moreover, PUR containing shorter flexible segments (PUR based on TDI and polyethylene glycols) produced composites with higher flexural strength.

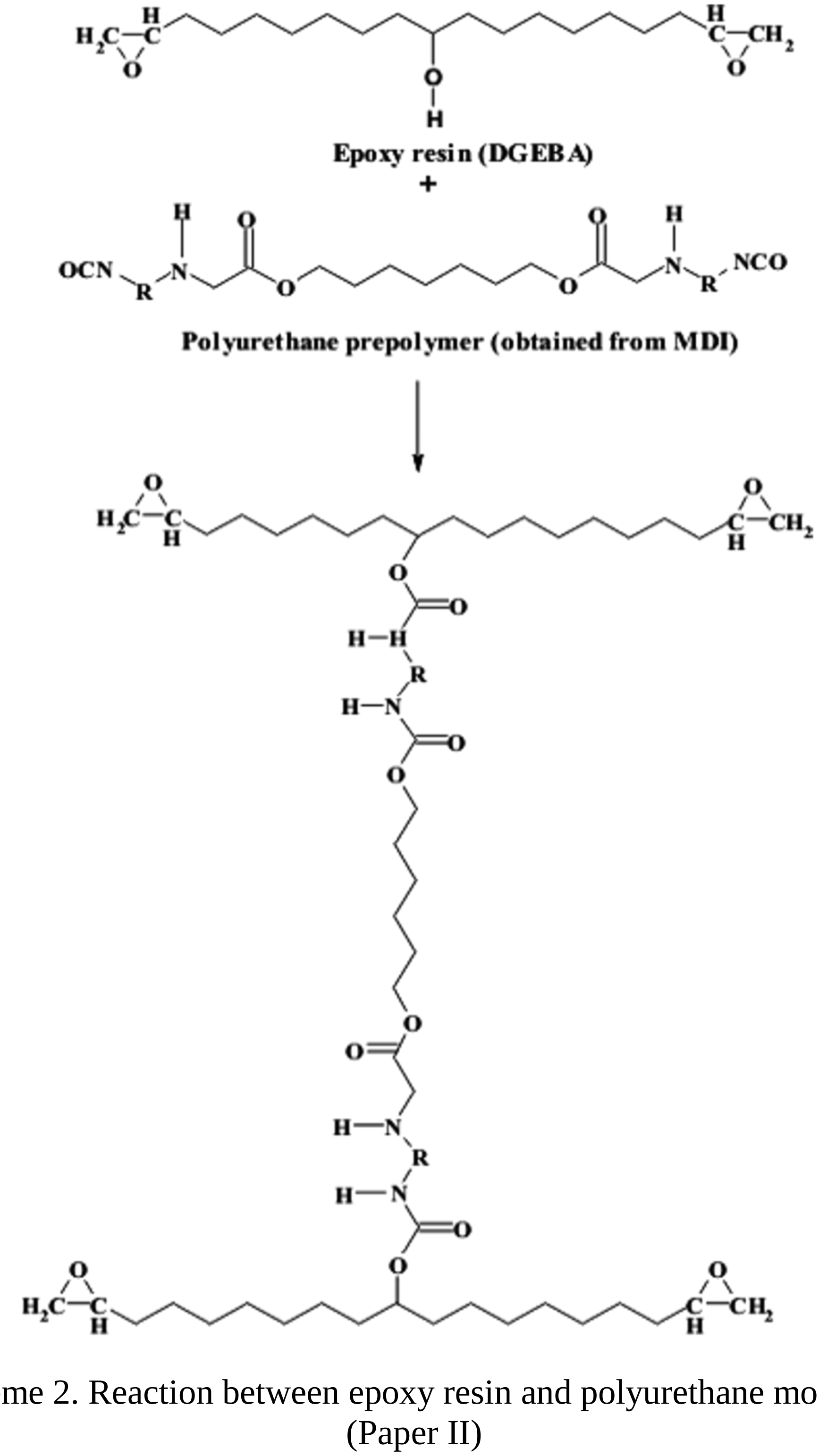
Overall, lower concentration of MDI based polyurethanes than TDI based polyurethanes was sufficient to obtain significant improvement of epoxy resin mechanical properties regardless of used polyols. These findings are in agreement with the results reported in the literature dealing with modification of epoxy resin with different polyurethanes, where an increase of tensile strength and strain at break of epoxy resin with increasing amount of PUR was attributed to the rubberlike properties and plasticizing effect of the latter [29, 31-34].

Moreover, the incorporation of polyurethanes having an excess of reactive groups might contribute to the improvement of epoxy resin properties by a grafting process [29-34, 37]. FTIR spectra of epoxy resin modified with MDI based PUR (Figure 12) reveal that peak intensity connected to the hydroxyl groups from epoxy resin decreases upon an incorporation of polyurethane. This might be indication of grafting reaction between hydroxyl groups and isocyanate groups as described in the Scheme 2. The occurrence of the grafting reaction between isocyanate and hydroxyl groups leading to the increase of mechanical properties of epoxy resin was also notified by other researchers [30, 31, 37].

Moreover, comparison of glass transition temperatures (T_g) of neat epoxy resin and those modified with PUR (Table 2) shows shifts towards slightly higher temperatures. Another aspect supporting the idea of grafted IPN structure formation is the increase of flexural strength.

Table 2. Glass transition temperature of epoxy resin modified with PUR (data derived from Paper I and Paper II)

Composition	**T_g °C**	**Composition**	**T_g °C**
EP	63	EP+10 % PUR400M	67
EP+10 % PUR400T	68	EP+10 % PUR1002M	63
EP+10 % PUR1002T	67	EP+10 % PUR2002M	65



Scheme 2. Reaction between epoxy resin and polyurethane modifier (Paper II)

All above mentioned facts result in the conclusion that obtained EP/PUR composites have grafted IPN structure responsible for improved flexural strength and fracture toughness parameters even for EP modification with low content of polyurethane.

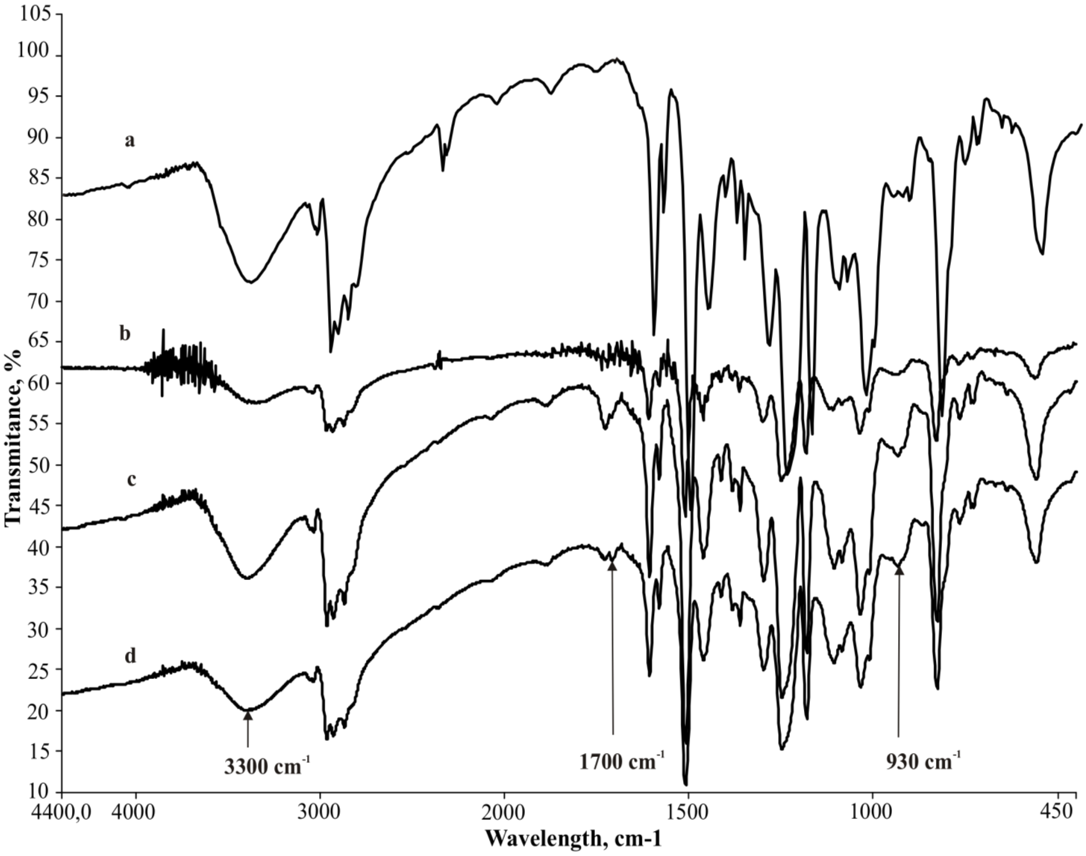


Figure 12. FTIR spectra of (a) neat epoxy resin and epoxy resin modified with (b) 10 % PUR400M, (c) 10 % PUR1002M, and (d) 10 % PUR2002M (Paper II)

Simultaneously, the epoxy resin composites containing various amounts of montmorillonite (MMT) were prepared and their mechanical properties tested as demonstrated in Table 3. It can be noted that the addition of MMT increased the mechanical properties of epoxy resin. In fact, 1 % of MMT gives composites having enhanced fracture toughness, while composites containing 2 % of MMT exhibit the highest value of flexural strength.

Since the major role in mechanical properties enhancement plays nanoclay distribution within a polymer matrix, X-ray diffraction was employed for the MMT arrangement investigation. It has been demonstrated that low concentration of the organomodified nanoclay in a composite exhibits better dispersion and lower degree of agglomeration [63, 66], and an improvement of mechanical properties is achieved only for composites with a uniform dispersion of exfoliated nanoclay. Thus, admixing of nanoclay is a key parameter that should be considered in the production of nanocomposites [35,63].

Table 3. Mechanical properties of composites (Paper III)

Sample symbol	**IS** **kJ/m^2**	**K_C** **MPa m$^{1/2}$**	**Flexural strength** **MPa**	**Flexural strain at break** **$\cdot 10^{-2}$**	**Energy at break** **kJ/m^2**
EP	1.0 ± 0.1	1.2 ± 0.1	41 ± 0	0.5 ± 0.0	4.3 ± 0.3
EP + 1 % MMT	1.5 ± 0.2	2.2 ± 0.2	55 ± 5	1.9 ± 0.1	3.7 ± 0.4
EP + 2 % MMT	1.4 ± 0.1	2.1 ± 0.2	77 ± 7	2.0 ± 0.2	5.9 ± 0.5
EP + 3 % MMT	1.4 ± 0.1	2.0 ± 0.2	44 ± 4	1.5 ± 0.2	2.3 ± 0.3

IS-impact strength, **K_C**-critical stress intensity factor

Diffractograms presented in Figure 13 show that MMT in epoxy resin forms in majority intercalated structure due to the presence of peaks in the 2θ range from 1 to 10 ° connected to enlarged distance between MMT plates.

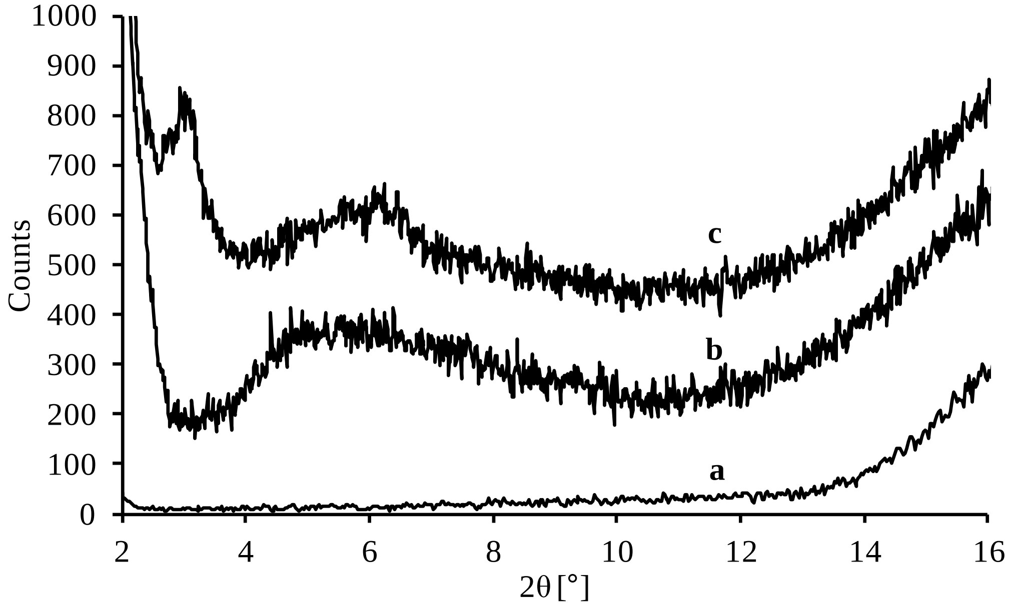
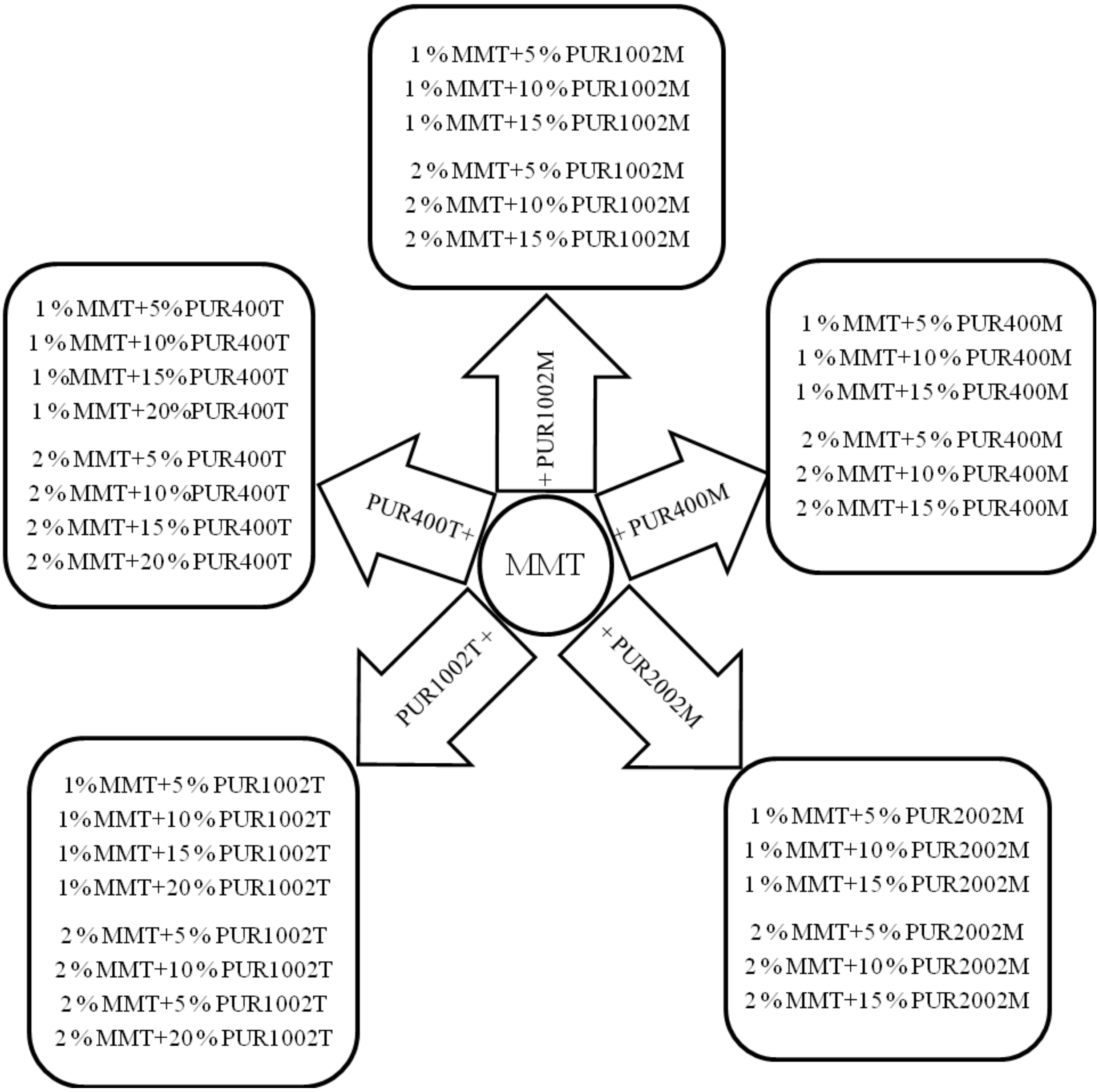


Figure 13. Diffractograms of (a) EP, (b) EP+1 % MMT and (c) EP+2 % MMT (according to the results of Paper III)

Furthermore, the influence of MMT loading on thermal properties was examined (Table 4), and the shifts in T_g values were evaluated. The addition of 2 % MMT resulting in a T_g decay can be related to the reduction of the cross-linking density within polymer matrix as supported by a similar finding reported in [92].

Based on the results obtained for EP/PUR composites containing one modifier the following polyurethanes were selected for the preparation of hybrid composites with 1 and 2 % MMT: PUR400T, PUR1002T, PUR400M, PUR1002M and PUR2002M. The selection was motivated by the conclusion that EP containing TDI based PURs such as 10 % PUR1002T and 5 % PUR2002T have the maximum K_C values, 10 % PUR400T or PUR600T have the most enhanced flexural properties, and usage of MDI results in improvement of all mechanical properties tested (Scheme 3).



Scheme 3. Composition of hybrid composites

Table 4. Glass transition temperature of EP/MMT composites

Composition	**T_g** **°C**
EP	63
EP + 1 % MMT	64
EP + 2 % MMT	59

The highest values of impact strength and critical stress intensity factor of hybrid composites obtained from TDI or MDI are shown in Figure 14 and Figure 15, respectively. The fracture toughness of EP represented by impact strength and critical stress intensity factor for hybrid composites becomes significantly improved in comparison to a neat epoxy resin, especially for composites containing MDI based polyurethanes, where the increase attained for IS is 200 % and more than 100 % for K_C.

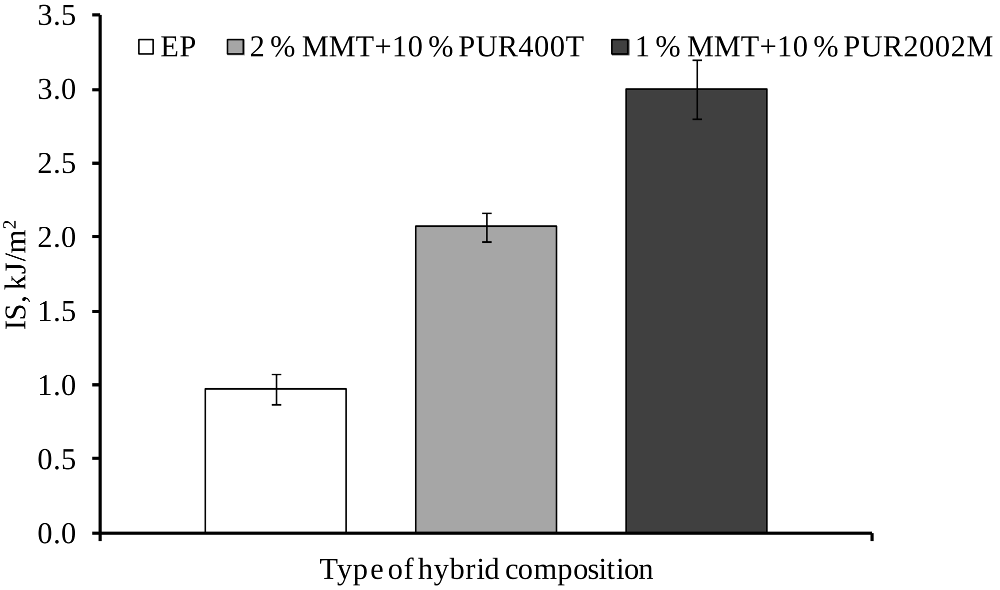


Figure 14. Comparison of hybrid composites impact strength
(data derived from Paper III and Paper IV)

The fracture toughness increase might be attributed to the intercalation/exfoliation of nanoclay (as mentioned heretofore) combined with high flexibility of polyurethane chains. Further it is supposed to be related to an IPN structure occurring in EP/PUR as it was reported also by other researchers [79, 80, 87-89].

Thus, FTIR spectroscopy was employed to confirm possible chemical reactions occurrence as well as IPN structure formation. FTIR spectra of hybrid composites presented in Figure 16 show characteristic peaks connected to hydroxyl groups (3300 cm^{-1}), urethane groups (1700 cm^{-1}) and epoxy groups

(930 cm^{-1}). The decrease of hydroxyl group peak associated with the presence of urethane groups implies the formation of grafted IPN structure between epoxy resin and polyurethane.

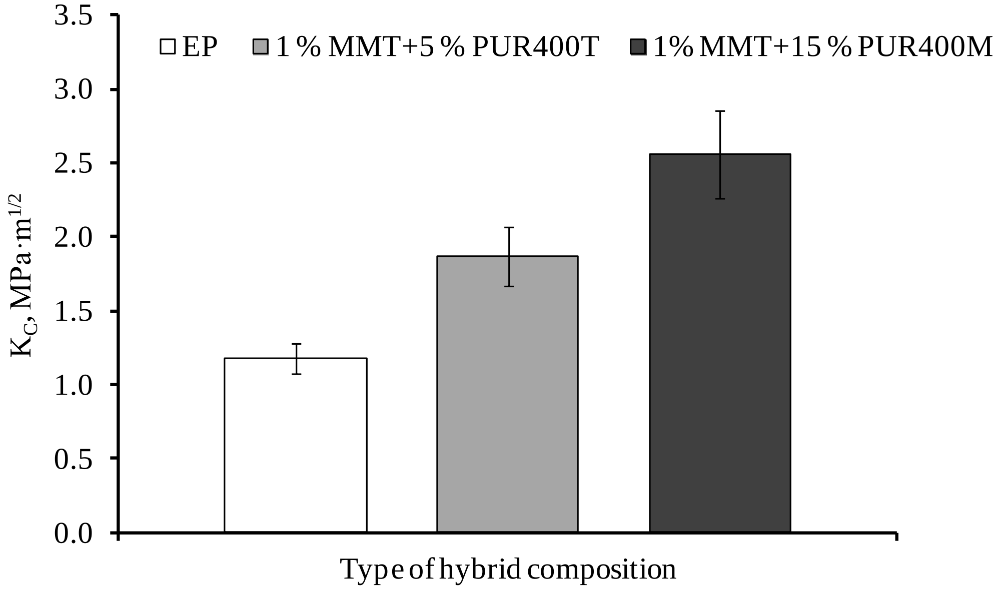


Figure 15. The critical stress intensity factor K_C of selected hybrid composites (data derived from Paper III and Paper IV)

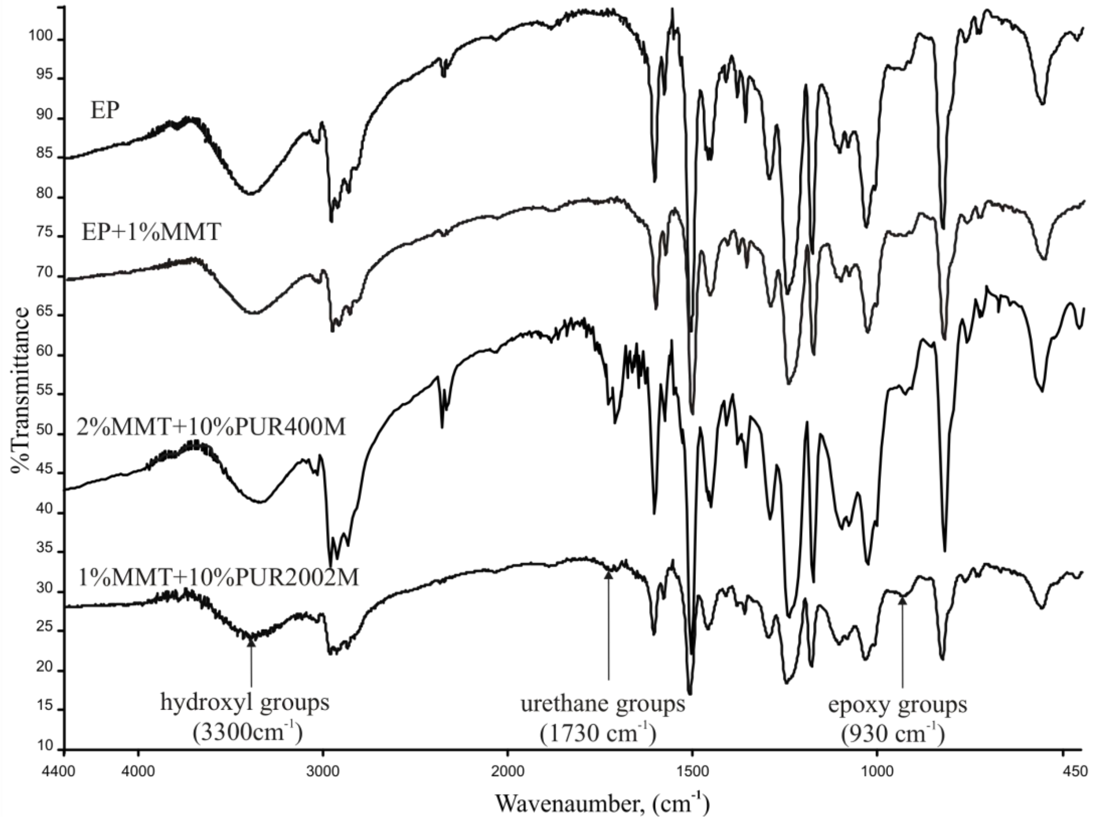


Figure 16. FTIR spectra of modified epoxy resin (Paper IV)

Differential scanning calorimetry (DSC) was used to investigate the effect of modification on thermal properties of epoxy resin. The obtained results are in an agreement with above mentioned conclusions. DSC results show a single glass transition temperature connected with one phase system created by interchain reaction between PUR and epoxy resin. Obtained results also prove that polyurethane does not act only as a plasticizer (as expected) but forms, together with epoxy resin, material exhibiting improved fracture toughness without loss of the thermal resistance.

From Table 5 it can be further observed that the concomitant addition of montmorillonite and polyurethanes do not affect significantly the glass transition temperature of epoxy resin. The shift in T_g towards higher values due to MMT and PUR400T addition may be related to the interactions between modifiers and epoxy resin matrix via chemical reaction of hydroxyl groups of epoxy resin with MMT layer surface with isocyanate groups from polyurethane. As was concluded earlier, it leads into the formation of a grafted IPN structure (confirmed by FTIR results, Figure 16).

Table 5. Glass transition temperatures (T_g) for selected composites (data derived from Paper III and Paper IV)

Composition	**T_g °C**	**Composition**	**T_g °C**
EP	63		
1 % MMT+10 % PUR400T	66	2 % MMT+10 % PUR400T	69
1 % MMT+10 % PUR400M	69	2 % MMT+10 % PUR400M	68
1 % MMT+10 % PUR1002T	65	2 % MMT+10 % PUR1002T	67
1 % MMT+10 % PUR1002M	68	2 % MMT+10 % PUR1002M	65
1 % MMT+10 % PUR2002M	66	2 % MMT+10 % PUR2002M	64

The similar findings can be drawn from the flexural strength values as shown in Figure 17. Hybrid composition containing 2 % of MMT and 5 % PUR400M showed about 150 % increase in flexural strength in comparison to a virgin epoxy resin, while flexural strength of hybrid composition with TDI based PUR attained only 50 %. The increase of flexural strength for hybrid composites might be treated as another proof that EP/PUR system has grafted IPN structure.

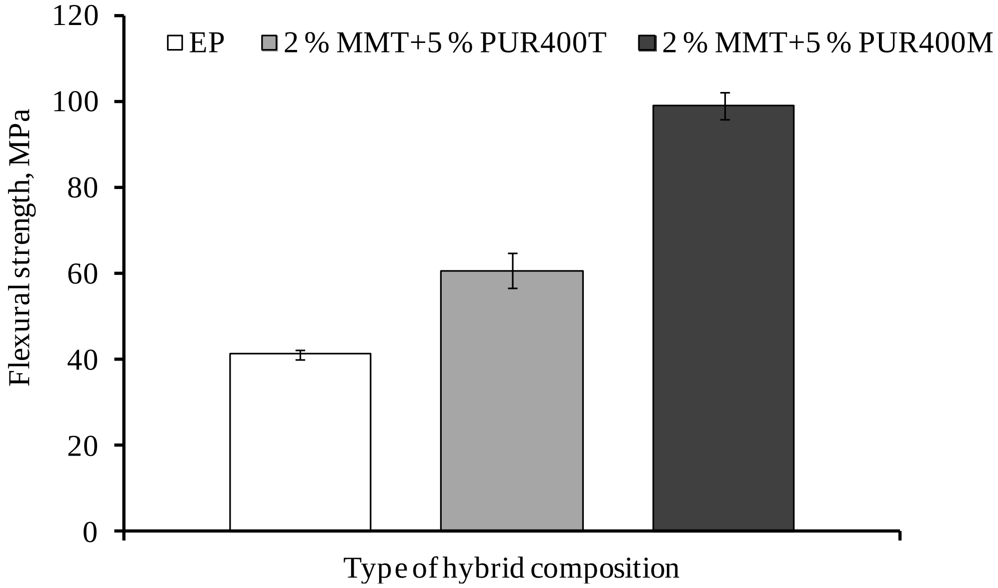


Figure 17. The flexural strength for selected hybrid composites (based on data from Paper III and Paper IV)

Similarly the values of flexural strain at break as well as energy at break of obtained hybrid composites are enhanced (Figures 18 and 19). The strain at break of hybrid composites containing 2 % MMT and 15 % PUR1002T (or PUR1002M) were eight to ten times higher than that of neat epoxy resin.

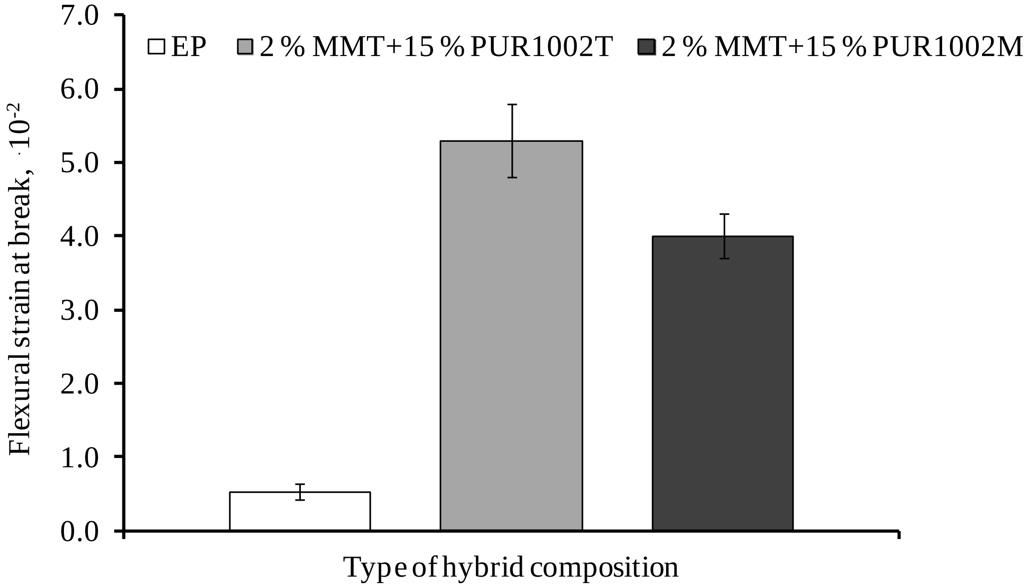


Figure 18. Strain at break for selected hybrid composites (data derived from Paper III and IV)

Moreover, the energy at break of the tested hybrid composites had values higher more than three times than unmodified epoxy resin, which is related to the significant increase of flexural stress and strain at break due to the presence of flexible polyurethane chains in composites.

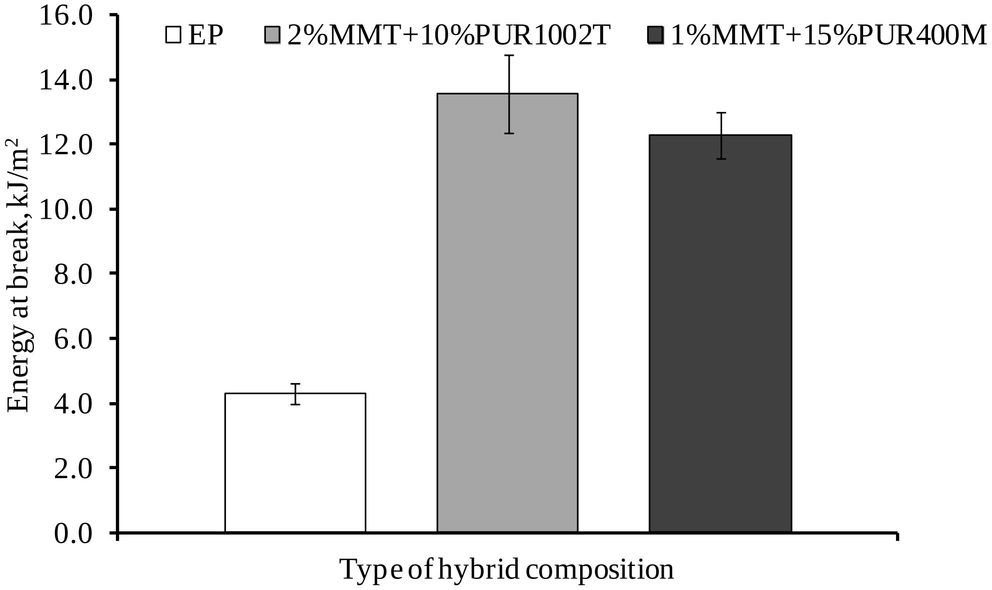


Figure 19. Energy at break for selected hybrid composites (data derived from Paper III and IV)

The structure and morphology of obtained hybrid composites were further examined by scanning electron microscopy and X-ray diffraction to explain the mechanism(s) of mechanical properties improvement.

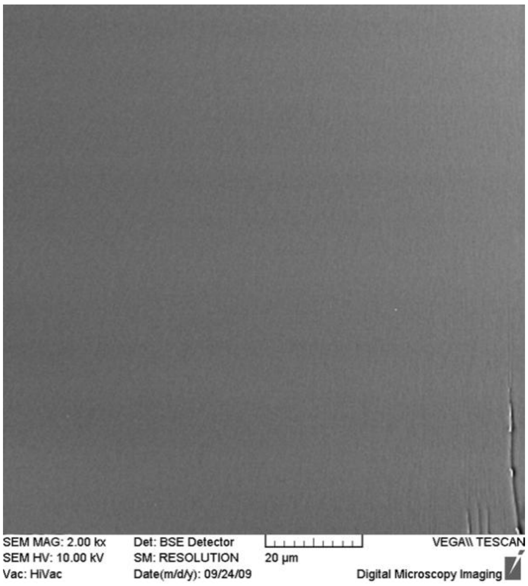


Figure 20. SEM micrograph of neat epoxy resin (Paper V)

SEM micrographs presented in Figures 20 and 21 were obtained from fractured surfaces of samples after impact tests near the crack tip. In comparison to the surface of epoxy resin (Figure 20) which is - typically for brittle materials - flat and smooth [95], micrographs of hybrid composites reveal the presence of a regular and homogeneous structure with nanoparticle aggregates embedded in the polymeric phases. It appears (Figure 21a) that the concomitant addition of 2 % MMT and 10 % PUR based on TDI and polyethylene glycol 400 (PUR400T) reached more stratified elongated structure between epoxy resin and modifiers with microcracks. Epoxy resin containing 1 % MMT and 10 % PUR2002M (Figure 21b), on the other hand, shows a rough fracture surface with larger elongated domains and well dispersed MMT particles within polymer matrix revealing good adhesion between MMT particles and EP/PUR supporting the significant improvement of the epoxy resin fracture toughness.

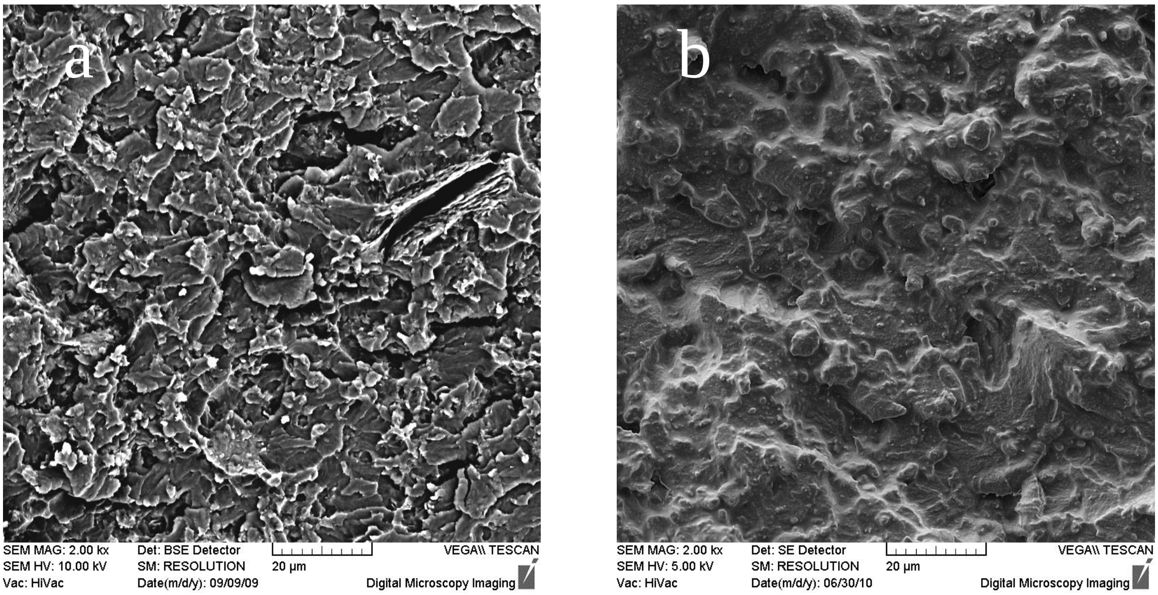


Figure 21. SEM micrographs of hybrid composites based on (a) 2 % MMT +10 % PUR400T and (b) 1 % MMT+10 % PUR2002M (Paper III and Paper IV)

X-ray diffraction applied in the 2θ range 2 ÷ 12 ° to characterize the nanoclay structure within the prepared hybrid composites (Figure 22) shows no diffraction peaks in the 2θ range from 2 to 10 °. Such lack of distinct diffraction peaks in this range confirms the randomization and exfoliation of MMT in these composites [78]. While, the presence of diffraction peaks associated with epoxy resin containing 2 % MMT suggests the formation of an intercalated structure.

Improvement of mechanical properties of epoxy resin investigated with various characterization techniques (FTIR, DSC, SEM and XRD) suggests that polyurethane promotes the exfoliation of the nanoclay.

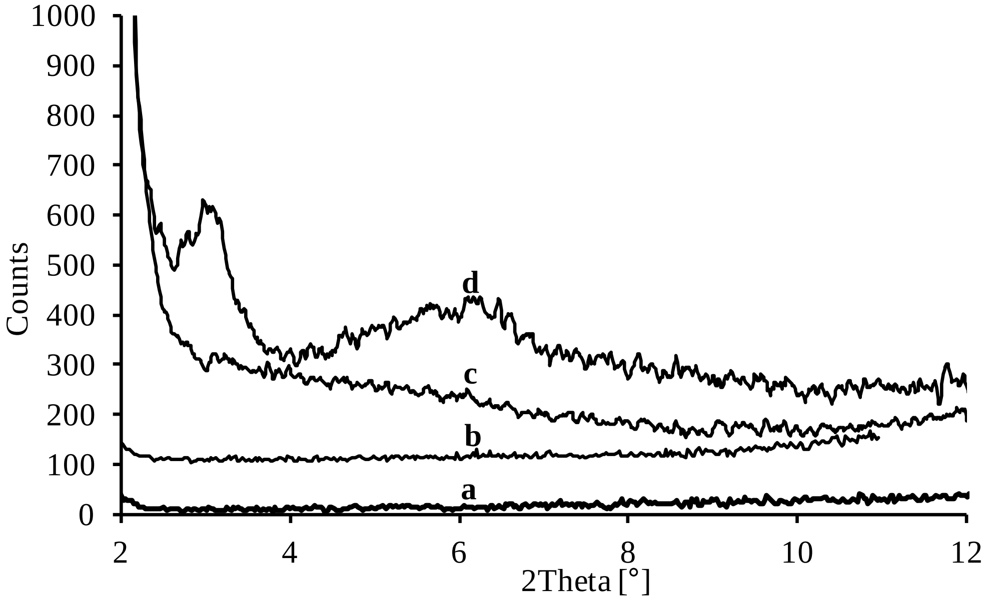


Figure 22. XRD diffractograms of epoxy based composites: (a) EP, (b) 1 % MMT+10 % PUR2002M, (c) 2 % MMT+10 % PUR400T, (d) EP+2 % MMT (data depicted from Paper III and IV)

The exfoliated nanoclay embedded in epoxy resin and flexible PUR phase lead to the significant enhancement of the fracture and flexural strengths of the brittle polymer matrix. It has been documented that the strength and fracture toughness parameters enhancement is strongly dependent on the nanoclay arrangement within the polymeric phase [44, 60-63, 65, 66, 69, 72, 86, 87] as well as grafted IPN structure formed [28-39]. Very important advantage for an end usage of the obtained hybrid composites is that thermal properties of epoxy resin maintained, while all strength parameters are significantly improved.

4. CONCLUSIONS

The aim of the doctoral thesis – preparation of hybrid epoxy/polyurethane/ montmorillonite composites with high performance properties – was achieved.

To the improvement of epoxy resin flexibility and toughness contributed especially the addition of polyurethanes based on polyols with longer flexible segments, since an excess of isocyanate groups in the polymeric modifier led to the formation of grafted interpenetrating polymer network structure with the polymer matrix.

Incorporation of diphenylmethane diisocyanate based polyurethane and montmorillonite resulted in the formation of a homogeneous and rough fractured surface with nanoclay particles well dispersed and embedded in the epoxy and polyurethane phases, while the usage of toluene diisocyanate created a stratified structure with the presence of microcracks.

Two mechanisms are supposed to be involved in the improvement of hybrid composites properties: exfoliation of nanoclay combined with the formation of chemical bonding between hydroxyl group of epoxy resin with isocyanate groups from polyurethane. Polyurethane promoted exfoliation process of nanoclay in the polymer matrix, and flexibility of its chains also contributed to the additional properties enhancement.

The selected hybrid composites, in particular epoxy resin modified with 1 % of nanoclay and 15 % of polyurethane synthesized from polyethylene glycol with molecular weight 400 g/mol and diphenylmethane diisocyanate, exhibited an optimal balance among the improvement of impact strength, critical stress intensity factor and flexural strength without deterioration of thermal properties.

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First of all, I would like to thank Mohamed Bakar for his help in making my ideas presented in this work a reality. More importantly, he showed me the way to do my scientific research. Moreover, he was and is always open to discussion and always willingly shared his knowledge and experience.

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I also would like to express my unending gratitude to my family and especially to my wife for her patience and faith in my abilities when I began to have doubts.

LIST OF SYMBOLS

ABS – acrylonitrile-butadiene-styrene terpolymer
CEC – the cation exchange capacities
CMDI – caprolactam-blocked diphenylmethane diisocyanate
CRBN – carboxyl-randomized liquid butadiene–acrylonitrile rubber
CTBN – carboxyl-terminated butadiene acrylonitrile copolymer
DGEBA – diglycidyl ether of bisphenol A
DSC – differential scanning calorimetry
EP – epoxy resin
f – number of functional group of isocyanate
FTIR – fourier transform infrared spectroscopy
HDI – 1,6-hexane diisocyanate
HMDI – 4,4'-diisocyanatodicyclohexylmethan
I_{NCO} – isocyanate index
IPDI – isophorone diisocyanate
IPN – interpenetrating polymer network
IS – impact strength, kJ/m^2
K_C – critical stress intensity factor, $MPa \cdot m^{1/2}$
LOH – hydroxyl number
MDI – 4,4'–diphenylmethane diisocyanate
$m_{isocyanate}$ – diisocyanate mass for polyurethane synthesis, g
$M_{isocyanate}$ – molecular weight of diisocyanate, g/mol
M_{KOH} – molecular weight of KOH, g/mol
MMT – montmorillonite
m_{POL} – polyol mass, g
OCT – 1,8-octanediol
PEG400 – polyethylene glycol with molecular weight 400 g/mol
PEG600 – polyethylene glycol with molecular weight 600 g/mol
PEG – polyethylene glycol
phr – part per hundred
PMDI – polymeric diphenylmethane diisocyanate
POPD1002 – polyoxyropylene diol with molecular weight 1000 g/mol
POPD2002 – polyoxyropylene diol with molecular weight 2000 g/mol
PUR – polyurethane
PUR1002M – polyurethane obtained from MDI and POPD 1002
PUR1002T – polyurethane obtained from TDI and POPD 1002
PUR2002M – polyurethane obtained from MDI and POPD 2002
PUR2002T – polyurethane obtained from TDI and POPD 2002
PUR400M – polyurethane obtained from MDI and PEG 400
PUR400T – polyurethane obtained from TDI and PEG 400
PUR600T – polyurethane obtained from TDI and PEG 600
R_{NCO} – isocyanate molar equivalent, g/mol

SEM – scanning electron microscopy
TDI – 2,4–toluene diisocyanate
TEM – transmission electron microscopy
T_g – glass transition temperature, °C
XRD – X-ray diffraction
2θ – the angle between the incident ray and the scattering planes, °

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PAPER I

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 Chen[30] 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 Balas[36] 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 Jin[37] 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 infrared (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 cm^3 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 cm^3 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]

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

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]

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

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.

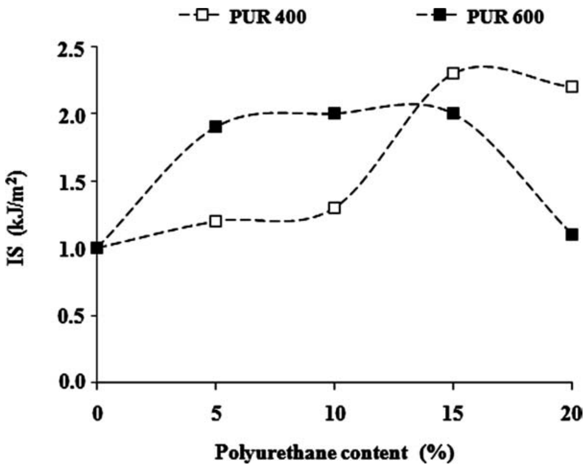

Figure 1 Effect of the PEG-based PUR content on IS of the EP.

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/m^2 for the unmodified EP to 19.8 kJ/m^2 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 modifier 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.

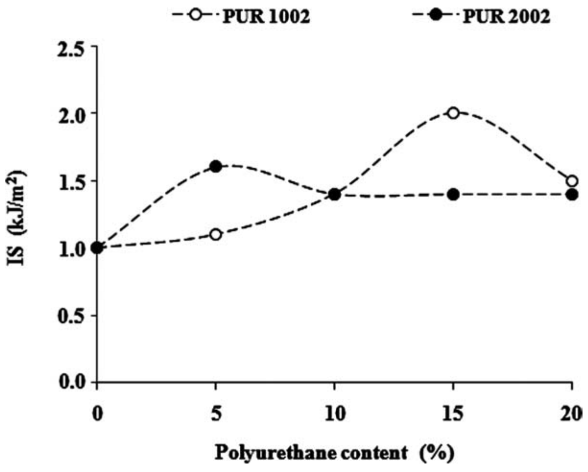

Figure 2 Effect of the POPD-based PUR content on IS of the EP.

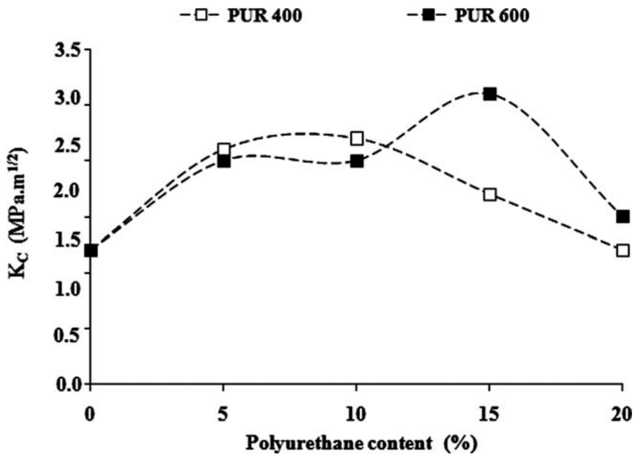

Figure 3 Effect of the PEG-based PUR content on K_C of the EP.

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

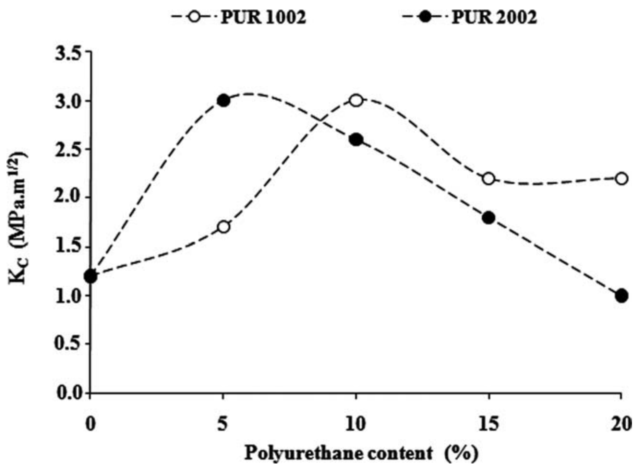

Figure 4 Effect of the POPD-based PUR content on K_C of the EP.

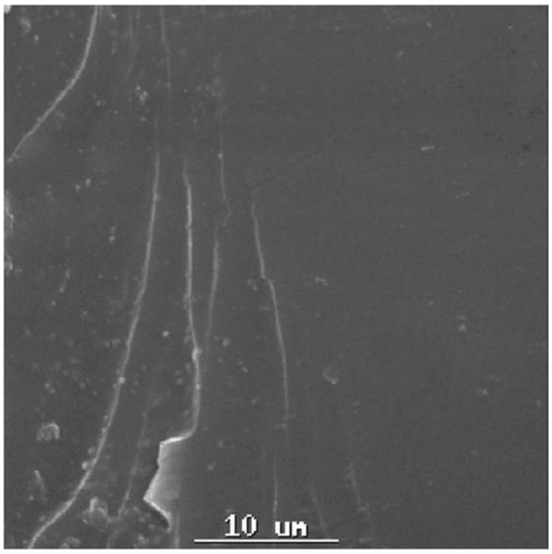

Figure 5 SEM micrograph of the unmodified EP.

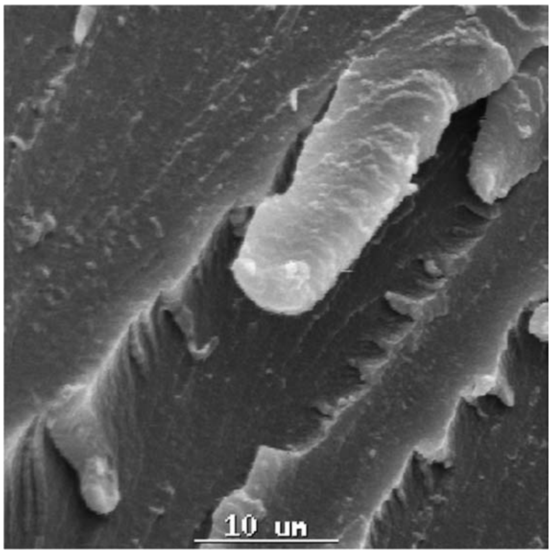

Figure 7 SEM micrograph of the EP modified with 15% PUR based on PEG 400.

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 formation 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

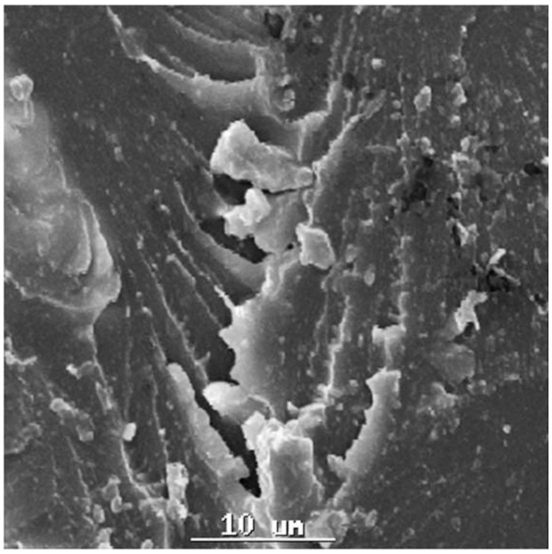

Figure 6 SEM micrograph of the EP modified with 10% PUR based on PEG 400.

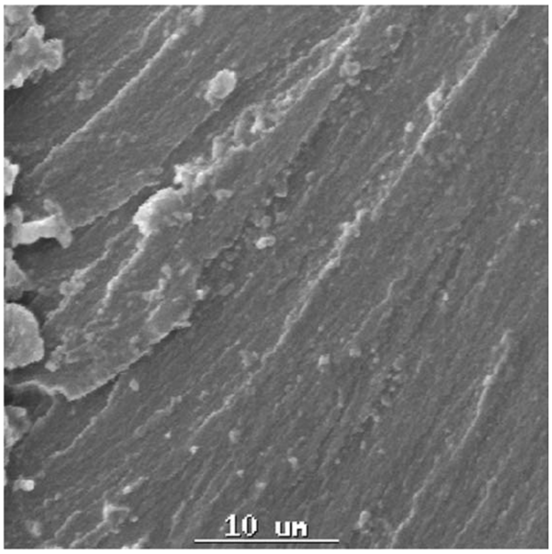

Figure 8 SEM micrograph of the EP modified with 15% PUR based on PEG 600.

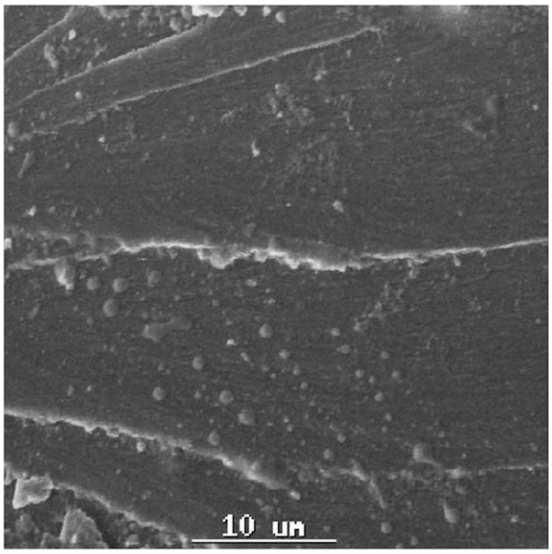

Figure 9 SEM micrograph of the EP modified with 15% PUR based on POPD 1002.

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 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.

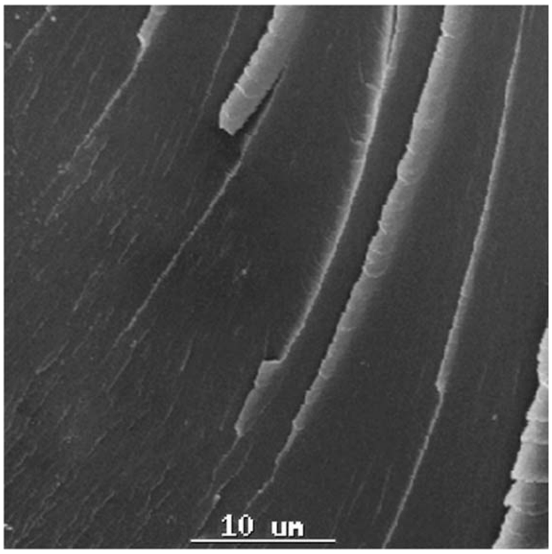

Figure 10 SEM micrograph of the EP modified with 5% PUR based on POPD 2002.

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

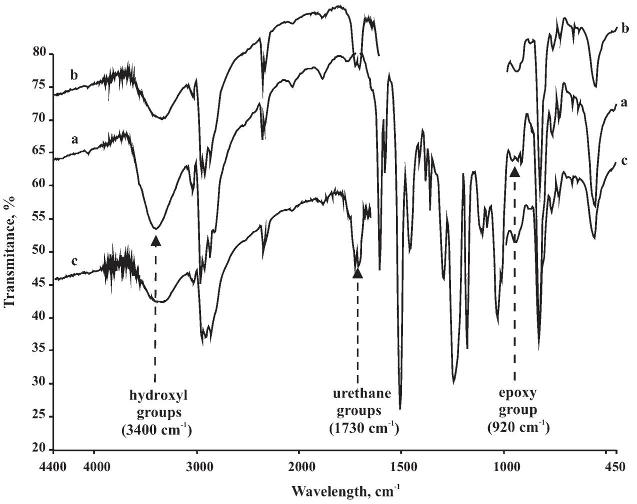

Figure 11 FTIR spectra of (a) the virgin EP, (b) the modified composition containing 10% PUR 400, and (c) the modified composition containing 15% PUR 600.

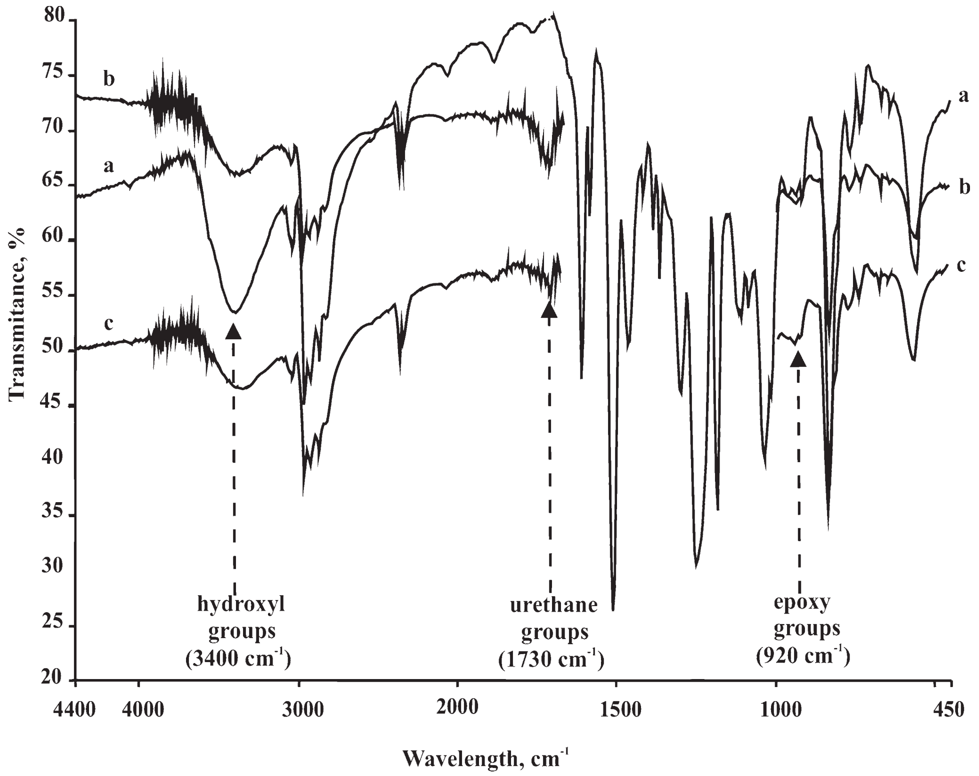

Figure 12 FTIR spectra of (a) the pure EP, (b) the modified composition containing 15% PUR 1002, and (c) the modified composition containing 5% PUR 2002.

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.

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.

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 MPa $m^{1/2}$ for compositions containing 5% PUR 2002 or 10% PUR 1002 versus 1.18 MPa $m^{1/2}$ for the virgin EP.

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PAPER II

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_C), 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 Mao[3] 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 Bui[4] 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 Wu[9] 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 Jin[10] 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 Chen[15] 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.

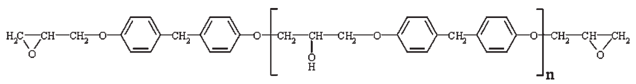
EXPERIMENTAL

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;

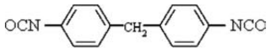
TABLE I
Structures of Main Raw Materials



Diglicidyl ether of bisphenlol A (Epidian 5, epoxy resin)

$H_2N—CH_2—CH_2—NH—CH_2—CH_2—NH—CH_2—CH_2—NH_2$

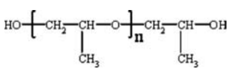
Triethylene tetramine (Z-1, curing agent)



4,4′-diphenylomethane diisocyanate (MDI)

$HO{-}[CH_2—CH_2—O]_n{-}CH_2—CH_2—OH$

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



$HO{-}[CH_2—CH(CH_3)—O]_n{-}CH_2—CH(CH_3)—OH$

Polyoxypropylene diol (POPD 1002-$M_w = 1000$ g/mol, POPD 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 (POPD 1002) with 1000 g/mol molecular weight and a hydroxyl number of 180 mg/g obtained from Rokita, Poland
- polyoxypropylene diol (POPD 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′-diphenylomethane 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′-diphenylomethane 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 cm^3 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.

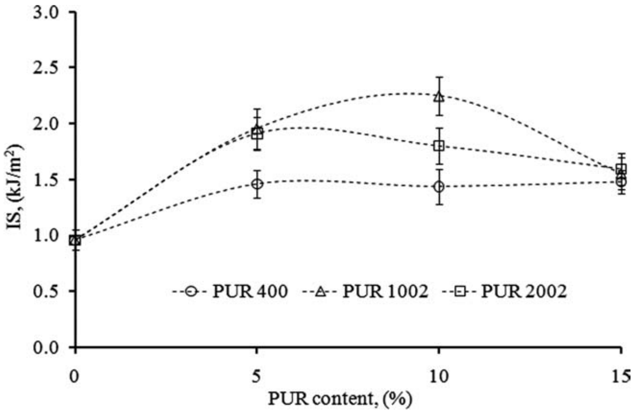


Figure 1 Effect of polyurethane content on impact strength (IS) of epoxy resin.

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 1mm 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]:

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

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 equation[18]:

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

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°C/min, temperature range −100 to 200°C and 10 mg ± 0.1 of sample weight. Nitrogen flow 20 mL/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 MPa·m$^{1/2}$ is reached by the epoxy composition containing 5% of each polyurethane compared with the 1.53 MPa·m$^{1/2}$ of the unmodified epoxy resin. The values of K_C parameter decrease when increasing the amount of polyurethanes above 5%.

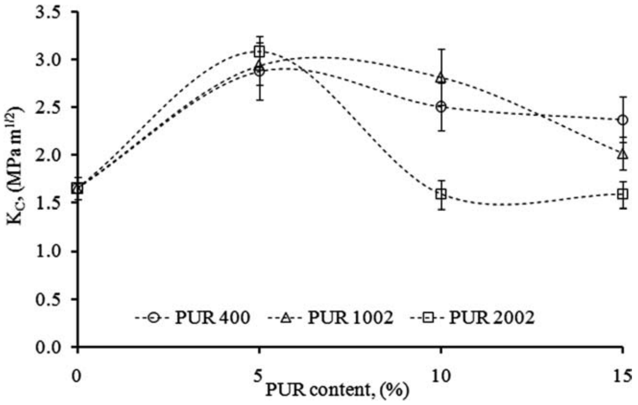


Figure 2 Critical stress intensity factor (K_C) as function of polyurethane content.

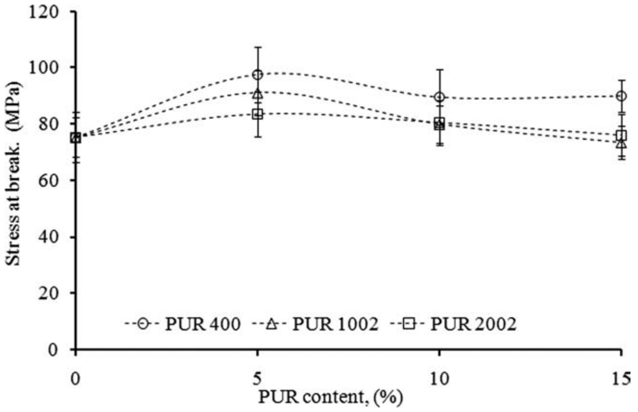


Figure 3 Flexural stress at break of epoxy resin modified with polyurethane.

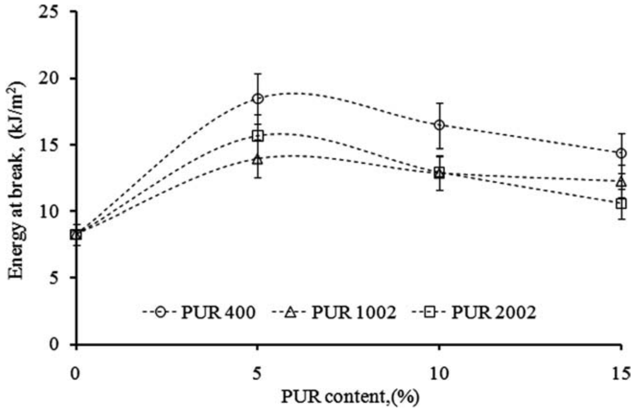


Figure 5 Effect of polyurethane content on the flexural energy at break of epoxy resin.

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 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

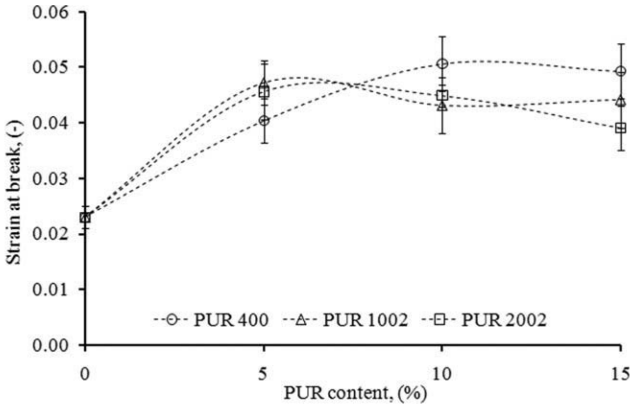


Figure 4 Strain at break of epoxy resin containing different amounts of polyurethanes.

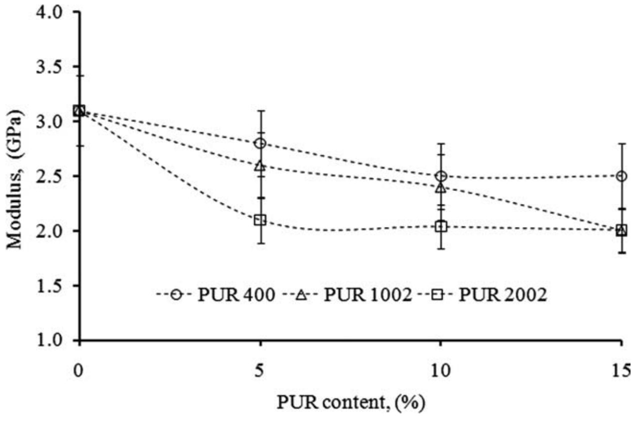


Figure 6 Flexural modulus as function of polyurethane content.

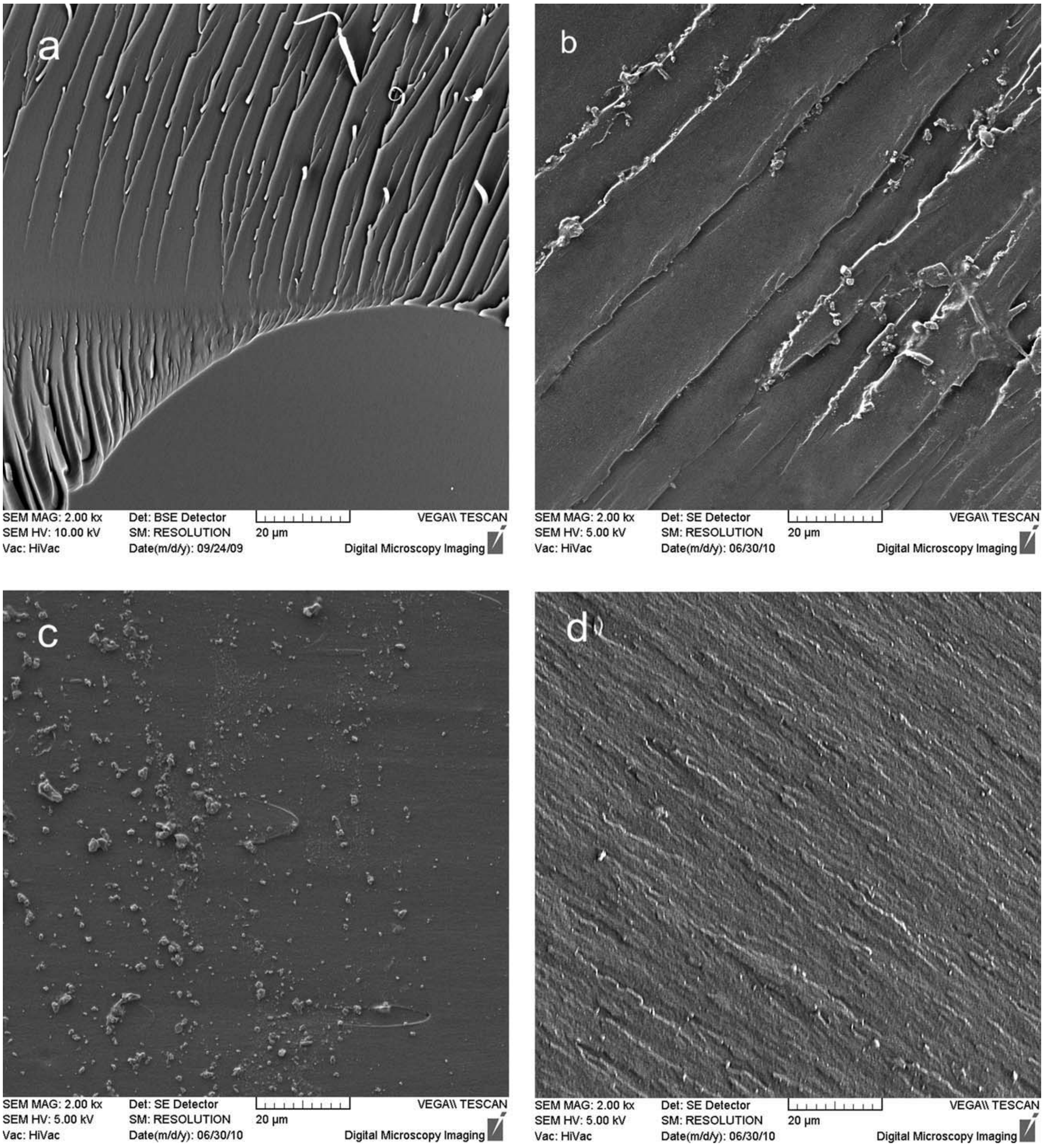


Figure 7 SEM images of fracture surface: epoxy resin (a) and composition containing 10% PUR 400 (b), 10% PUR 1002 (c), 10% PUR 2002 (d).

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-

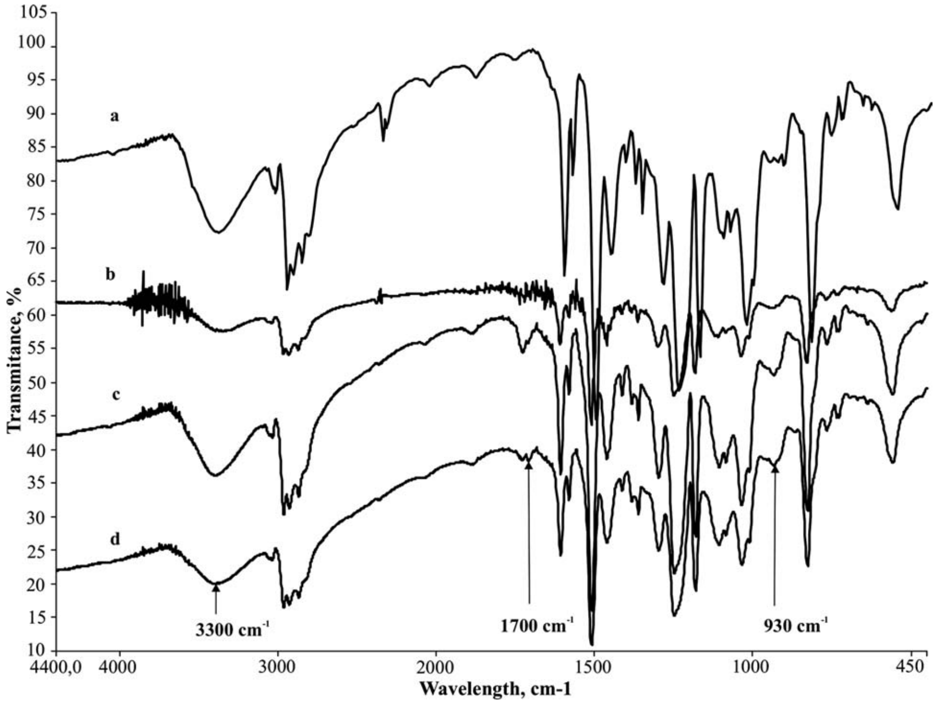


Figure 8 FTIR spectra of epoxy resin (a) and composites modified with 10% PUR 400*M* (b), 10% PUR 1002*M* (c), and 10% PUR 2002*M* (d).

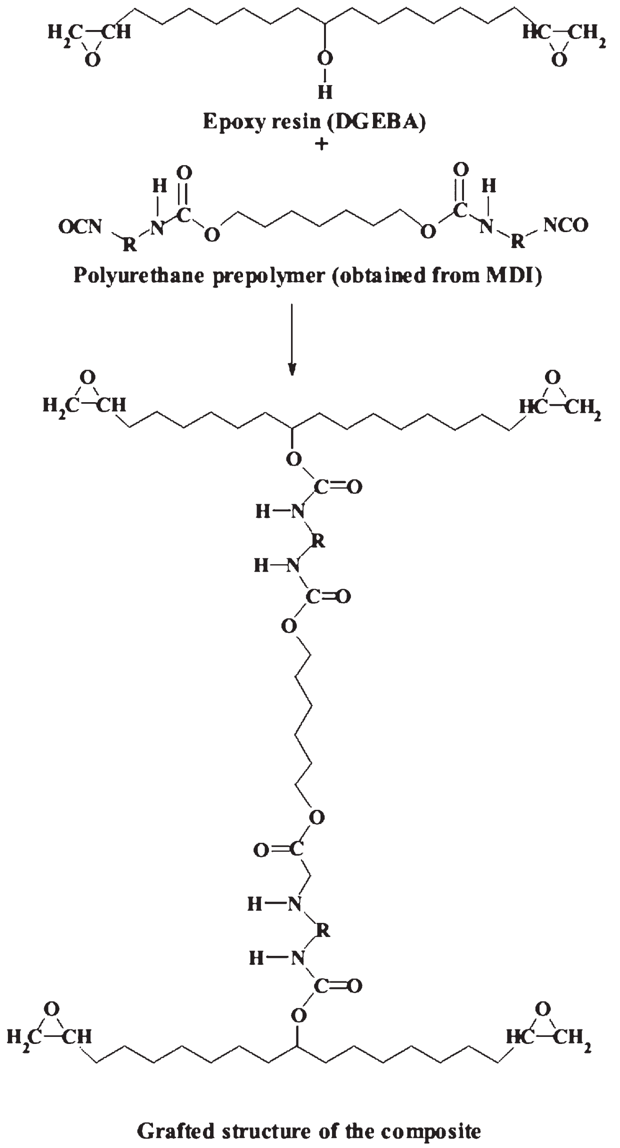
thane. As can be observed, the flexural modulus decreases as the amount of polyurethane is increased. The lowest modulus value is reached with compositions containing 15% of PUR 1002 or 15% PUR 2002. The modulus value decreased by about 30% in comparison to neat epoxy resin.

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 microcraks 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 allophonate 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_C 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 confirmed 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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PAPER III

Preparation and Property Evaluation of Nanocomposites Based on Polyurethane-Modified Epoxy/Montmorillonite Systems

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ABSTRACT: Montmorillonite nanoclay and polyurethanes obtained from polyethylene glycol (PUR 400) and polyoxypropylene diol (PUR 1002) were used to enhance the mechanical properties of an epoxy resin. Maximum impact strength improvement was obtained with compositions containing 2% nanoclay and 10% PUR 400 as well as that with 1% nanoclay and 15% PUR 400, corresponding to 110% and 75%, respectively, in relation to the unmodified epoxy resin. Moreover, a 10-fold increase was observed with respect to the flexural strain at break for the composition containing 15% PUR 1002 and 2% nanoclay.

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SEM micrographs have indicated that the mechanism of mechanical property enhancement is associated with increased yield of the epoxy matrix. Moreover, FTIR results showed that some chemical reactions have taken place between the hydroxyl groups of epoxy resin and the isocyanate groups of polyurethane, explaining partly the improvement in the mechanical properties of the polymer matrix. Adv Polym Techn 29: 237–248, 2010; View this article online at wileyonlinelibrary.com. DOI 10.1002/adv.20192

KEY WORDS: Epoxy, Mechanical properties, Nanocomposites, Polyurethanes, Structure

Introduction

Because of their high-dimensional stability, as well as the very good chemical resistance, epoxy resins are widely used as matrices for high-performance composite materials, surface coatings, and adhesives. However, cured epoxy resins exhibit low impact strength, poor resistance to crack propagation, and low elongation at break.

In the past few decades, a considerable amount of work has been devoted to improve the mechanical and thermal properties of epoxy resins. Approaches to enhance the adhesive and mechanical strength of the final products have included the addition of particulate fillers,[1–3] reactive liquid rubbers,[4–10] and thermoplastic polymers.[11–15] Epoxy resin's properties have also been improved by using nanoparticles[16–20] as well as other cross-linkable polymers to form full- or semi-interpenetrating polymer networks.[21–29]

Yilmazer and co-workers[16] have used unmodified montmorillonite (Cloisite Na^+) and organically modified Cloisite 30B as reinforcing agents for diglycidyl ether of bisphenol-A (DGEBA). Their results have shown an increase in the glass transition temperature (T_g) by more than 10°C with the addition of 9 wt% of a modified montmorillonite (MMT). The addition of 0.5 and 1 wt% of Cloisite 30B resulted in a maximum improvement in the impact strength of DGEBA. The tensile strength also exhibited the maximum value at 1 wt% modified clay loading.

In another work, Messersmith and Giannelis[17] have prepared exfoliated layered silicate epoxy nanocomposite based on DGEBA cured with nadic methyl anhydride in the presence of benzyldimethylamine. Their results have shown a significant increase in the modulus of the epoxy nanocomposite using 4 wt% of organoclay modified with bis(2-hydroxyethyl) methyl tallow-alkyl ammonium chloride. The dynamic storage modulus of the nanocomposite containing 4 wt% silicate was approximately 58% higher in the glassy region and 450% higher in the rubbery plateau region compared to that of virgin epoxy.

The mechanism of the exfoliation of the filler was also analyzed by Lan et al.[18] for nanocomposites based on DGEBA cured with *m*-phenylenediamine. The exfoliation of the clay was not only dependent on the reactivity of epoxy system but also on the accessibility of the matrix and the curing agent into the clay galleries. Moreover, the exfoliation was facilitated by the exchange of cations, which catalyze the intragallery polymerization of the epoxy resin.

Kornmann et al.[19] have prepared exfoliated nanocomposites using diglycidyl ether of bisphenol A and polyoxyalkylene diamine as a curing agent. They have studied the dependence of the cation-exchange capacities (CEC) on the synthesis and structure of epoxy–nanoclay nanocomposites. The exfoliation of montmorillonite takes place at low CEC during the swelling stage of the epoxy resin, which undergoes homopolymerization during swelling prior to cross-linking reactions because of the large space available between the galleries.

Polyurethanes (PUR) have also been used to improve the toughness of epoxy resins. Wang and Chen[20] modified diglicydyl 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 the epoxy modified with PUR containing phenol hydroxyl groups had higher fracture toughness than the corresponding system containing PUR with amine groups.

Polyurethane chains can be linked to the epoxy network through physical entanglements as well as chemical bonding to form graft interpenetrating polymer network (IPN) structures. Hsieh and Han[21] have evaluated the mechanical properties of graft IPN of an epoxy and a PUR based on polyols with different chain lengths. The results showed that the significant improvement in the tensile strength was related to the grafted structure and to the length of PUR chains. Harani and co-authors[22] have also proved that the addition of isocyanate-terminated polyurethanes significantly improved the fracture toughness of epoxy resin. Moreover, the use of a chain extender with polyurethane prepolymer caused a sevenfold increase in the impact strength and almost twofold increase in the critical stress intensity factor, K_C, in comparison with the unmodified epoxy resin. In a separate work, Park and Jin[23] have evaluated the mechanical properties, as well as surface free energy, of epoxy resin—polyurethane systems. The polar components of the surface free energy of the composition were largely influenced by the addition of PUR, which caused an increase in K_C and impact strength at low-temperatures. The improvement in the mechanical properties was explained as a result of the increase in the strength of the hydrogen bonds between the hydroxyl groups of the epoxy resin and the isocyanate groups of the PUR.

More recently, we have investigated the effect of polyurethanes having different isocyanate index on the mechanical and thermal properties of epoxy resin.[24] The largest improvement in the fracture toughness was achieved with the PUR having the highest isocyanate content. The infrared spectra have indicated that the excess of isocyanate groups has produced grafting reactions between the modifier and the epoxy matrix, which explained the observed toughening effect.

The aim of the present work is to investigate the properties and morphology of an epoxy resin modified with polyurethane and reinforced with an organomodified montmorillonite. Reactions are to be expected between the $-CH_2CH_2OH$ groups of the quaternary ammonium salt in the nanoclay and the isocyanate groups of PUR, enhancing the stability of the nanoclay dispersion after exfoliation.

Experimental

MATERIALS

The following components were used in the present work:

- epoxy resin–diglycidyl ether of bisphenol A (Epidian 5, Organika Sarzyna, Nowa Sarzyna, Poland) with a molecular weight of 400 g/mol, viscosity at 25°C around 30 Pa·s, and epoxy number of 0.49–0.52 mol/100 g;
- triethylenetetramine hardener (trade name Z1, Organika Sarzyna, Nowa Sarzyna, Poland);
- polyethylene glycol with molecular weight of 400 g/mol (PEG 400) and 277 mg/g hydroxyl number (Merck, Darmstadt, Germany);
- polyoxypropylene diol with 1000 g/mol molecular weight (POPD 1002) and hydroxyl number of 180 mg/g (Rokita, Poland);
- 2,4-toluene diisocyanate (TDI) for synthesis produced by Merck (Germany);
- dibutyltin dilaurate catalyst (Merck, Germany);
- montmorillonite nanoclay modified with tallow-quarternary ammonium salt (Cloisite 30B, Southern Clay Products Inc., Gonzales, TX); and
- toluene and acetone solvents (Merck, Germany).

SYNTHESIS OF POLYURETHANE

Two types of polyurethanes were prepared from toluene di-isocyanate (TDI) and polyols, based on polyethylene glycol (PUR 400) and polyoxypropylene diol (PUR 1002).

First, 50 g of polyol and 0.25 cm^3 of dibutyltin dilaurate were mixed with a mechanical stirrer for 15 min under vacuum and then heated to 40°C. One half of the amount of TDI was added dropwise over 15 min. The reaction was then carried in a nitrogen atmosphere for 30 min, while the temperature was maintained below 60°C. Then, the PUR was cooled to 25°C and 50 cm^3 of acetone was added to reduce the viscosity of the mixture. Finally, the rest of TDI was added dropwise for another 15 min and the temperature of the mixture was maintained below 40°C.

For 50 g of polyol, we needed 45.1 g TDI for PUR 400 and 29.3 g for PUR 1002, to obtain a PUR having an isocyanate index of 1.05. The polyols were purified by azeotropic vacuum distillation of toluene to remove the water.

PREPARATION OF POLYURETHANE-MODIFIED EPOXY RESINS AND EPOXY–MONTMORILLONITE COMPOSITES

The polyurethane was mixed with the epoxy resin in amounts of 5, 10, 15, and 20 wt% using a homogenizer for 20 min at a rotational speed of 2500 rpm, at room temperature. The mixtures were then placed in a vacuum oven to remove air bubbles. The curing agent was then added, and mixing was 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 postcuring for 3 h at 80°C.

The epoxy–MMT composites were prepared using 1, 2, and 3 wt% of Cloisite 30B (MMT). 10 g of MMT was added to 40 cm^3 of acetone to disperse the nanoclay and then poured in a preheated epoxy resin (40°C), followed by mechanical stirring for 15 min at 2500 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 described for epoxy/PUR compositions.

PREPARATION OF EPOXY NANOCOMPOSITES MODIFIED WITH POLYURETHANE

Compositions containing 1 and 2 wt% Cloisite 30B and different amounts of PUR were prepared. First, the solvent dispersion with a specific amount of MMT was mixed with epoxy resin for 20 min prior to the PUR incorporation and mixture homogenization. After degassing in a vacuum oven, the curing agent was added and the compositions were placed in the mold. Curing and postcuring processes were carried out as described previously.

MECHANICAL PROPERTIES MEASUREMENTS

Impact strength was measured according to Charpy method using a Zwick 5012 apparatus (ISO 179) on rectangular-shaped samples (80 mm long, 10 mm wide, 4 mm thick, with a 1-mm notch).

Three-point bending tests (ISO 178) were carried out at room temperature on specimens of the same dimensions as for impact tests using an Instron 5566 at deformation rate of 5 mm/min. The distance between the spans was 60 mm.

The critical stress intensity factor K_C was evaluated using Eq. (1) by means of three-point bending tests on notched (1 mm) specimens having the same dimensions as impact. The test was carried out using an Instron 5566 with a deformation rate of 5 mm/min and a distance between the spans of 60 mm [25]:

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

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 equation[25]:

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

CHARACTERIZATION

Infrared spectroscopy (FTIR) was performed on a Perkin–Elmer spectrophotometer (1000 PC) recording the IR spectra from 450 to 4000 cm^{-1}. Scanning electron microscope (Hitachi S-2460 N) was employed to examine the fracture surfaces of specimens obtained from the impact tests. X-ray diffraction (XRD) tests were performed using X′ PERT PRO Panalytical X-ray diffractometer with a Cu $K_{\alpha 1} = 1.54$ Å radiation source operating at 40 kV and 30 mA.

Differential scanning calorimetric (DSC) tests were carried out on a Pyris 1 Perkin-Elmer apparatus to measure the T_g of selected compositions. The scan rate was 10°C/min within a temperature ranging from −25 to 200°C under nitrogen atmosphere. The T_g was taken at the median point in the range of glass transition.

Results and Discussion

MECHANICAL PROPERTIES

The impact strength (IS), the critical stress intensity factor (K_C), and the flexural properties (stress at break, the strain at break, and the energy at break) are measured for epoxy resin containing different amounts of montmorillonite (MMT). The obtained results are summarized in Table I. It can be noted that the IS and K_C values increase with increasing amount of MMT. These properties were improved

TABLE I

Properties of Epoxy-Based Compositions Containing Different Amounts of Montmorillonite

MMT Content (wt%)	Impact Strength (kJ/m^2)	K_C (MPa m$^{1/2}$)	Stress at Break (MPa)	Strain at Break (m/m)	Energy at Break (kJ/m^2)
0	1.0	1.2	41.2	0.005	4.3
1	1.5	2.2	54.6	0.019	3.7
2	1.4	2.1	77.3	0.020	5.9
3	1.4	2.0	44.1	0.015	2.3

up to 50% and 85%, respectively, for the composition containing 1 wt% MMT in comparison to the neat epoxy resin. The composition containing 2 wt% MMT shows the highest flexural properties (both flexural strength and strain at break) in comparison with the nonreinforced epoxy samples, showing a twofold and fourfold increase in the flexural strength and strain at break. Moreover, the fracture energy, expressed as the area under the force/deflection curve, increased from 4.3 to 5.9 kJ/m^2.

The decrease in the tensile strength and flexural energy at break exhibited by the epoxy resin nanocomposite containing 3 wt% MMT could be due to the presence of nanoclay particles aggregates.

Our previous results[26] have confirmed that the addition of polyurethanes (PUR 400 and PUR 1002) produces a large increase in impact strength and K_C values. The IS values were increased by approximately 130% upon addition of 15 wt% PUR 400, whereas K_C increased by approximately 150% when 10 wt% PUR obtained from Rokopol D1002 (PUR 1002) was added.

It is in light of these results that these two types of polyurethanes (i.e., PUR 400 and PUR 1002) were chosen to prepare the modified epoxy nancomposites (i.e., epoxy resin modified with MMT, PUR 400 and PUR 1002).

In Fig. 1, the effect of the PUR 400 modification on the impact strength of the epoxy nancomposites with 1 and 2 wt% of montmorillonite is shown. These results show that the addition of both polyurethane and montmorillonite improves the impact strength of epoxy resin. All modified compositions exhibited higher impact strength than the unmodified epoxy resin. However, the best results were obtained with epoxy nancomposite containing 2 wt% MMT and 10 wt% PUR 400 as well as that with 1 wt% MMT and 15 wt% PUR 400, representing 110% and 75% improvement, respectively, in relation to the virgin epoxy resin (composition 0/0).

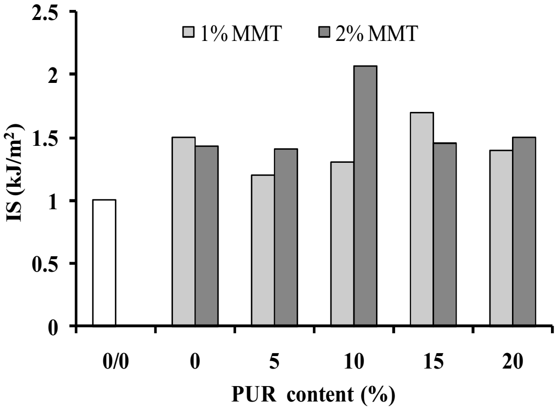


FIGURE 1. IS of modified epoxy nanocomposites as a function of polyurethane (PUR 400) content.

The improvements in the impact strength can be attributed to the good dispersion of nanoclay particles, as well as to the intrinsic properties of the modified epoxy resin network.

In Fig. 2, the impact strength of the modified epoxy nanocomposites containing PUR 1002 is shown. However, all compositions exhibited higher impact strength values than the base (0/0) epoxy resin without modifier. Comparing these results with those shown in Fig. 1, it can be noted that the polyurethane with longer flexible segments did not cause a significant improvement in the impact strength of the nanocomposites.

Chen and Evans[27] have shown that higher molecular mass fractions of polymer intercalate preferentially into clay during the nanocomposite

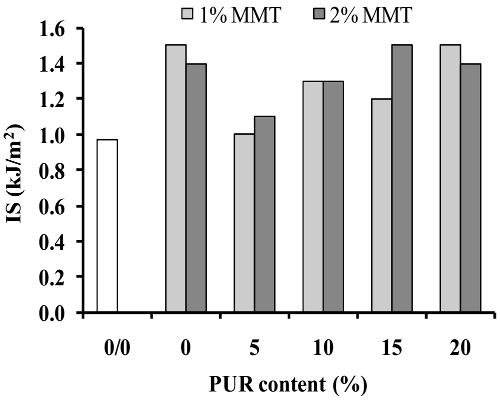


FIGURE 2. IS of epoxy nanocomposites as a function of polyurethane (PUR 1002) content.

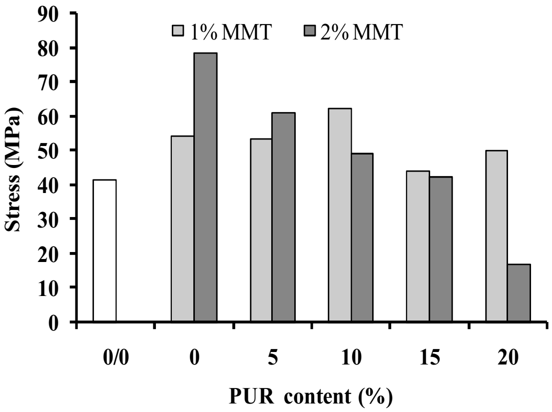


FIGURE 3. Effect of polyurethane (PUR 400) modification on the flexural stress at break of epoxy nanocomposites with 1% and 2% MMT.

preparation and, therefore, this could explain the effect reported above.

The stress at break values measured in the three-point bending test is shown in Figs. 3 and 4 for nanocomposites based on both PUR 400 and PUR 1002. From these data, it can be observed that maximum strength improvement was obtained for epoxy hybrid nanocomposites containing 10 wt% PUR and 1 wt% MMT.

The strength improvements achieved are 50% and 25%, in comparison, respectively, to neat epoxy resin and 1 wt% MMT/epoxy resin nanocomposites.

From the results shown in Fig. 4, one can observe that the incorporation of the polyurethane synthesized from polyoxypropylene diol (PUR1002) did not show a significant effect on the flexural strength of epoxy nanocomposite containing 1 wt% of montmorillonite. Moreover, the epoxy nanocomposite based on 2 wt% MMT and containing 5% and 10% PUR exhibits higher flexural strength than virgin epoxy compositions. However, similarly to PUR 400 nancomposites (Fig. 3), a deterioration effect can be noted for nancomposites with 2 wt% MMT.

Therefore, it seems that the incorporation of polyurethane with long flexible segments leads to an improvement in flexural strength without significant deterioration of the impact strength. However, the polyurethane with shorter segments and low molecular weight contributes more effectively to impact strength improvement.

A decrease in the flexural strength of epoxy nanocomposites based on 2% MMT and higher polyurethane content might be related to the reduction in the interaction between the epoxy resin and the incorporated modifiers.

In Fig. 5, it is shown that the flexural strain at break increases with increasing PUR content. The highest value (10 times higher than that of original epoxy resin) was obtained for nanocomposites containing 15% PUR 1002 and MMT. However, the flexural strain at break increased to 165 and 125% levels, respectively, with 2 and 1 wt% MMT in comparison with the flexural strain of epoxy nanocomposites containing, respectively, 2 wt% MMT and that with 1 wt% MMT. The incorporation of relatively long flexible PUR chains to epoxy resin contributes to more movements, thus allowing the samples to reach higher strains before fracture occurs.

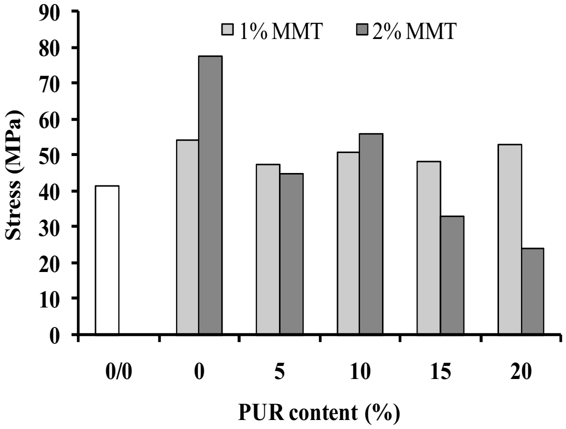


FIGURE 4. Effect of polyurethane (PUR 1002) modification on flexural stress at break of epoxy nanocomposites with 1 and 2% MMT.

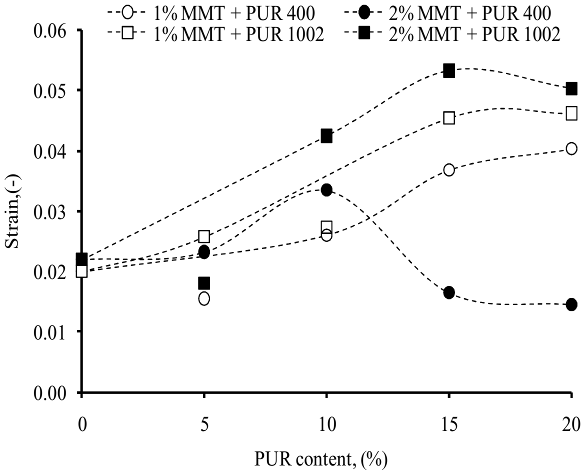


FIGURE 5. Effect of PUR content on flexural strain of epoxy nanocomposites with 1% and 2% MMT.

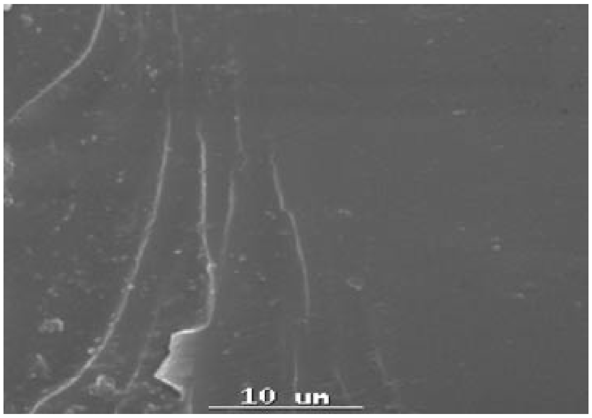


FIGURE 6. SEM micrograph of an unmodified epoxy resin.

Nevertheless, these results demonstrate the need to use less nanoclay within the polymer matrix to obtain epoxy nanocomposites with enhanced properties.

FRACTURE SURFACE ANALYSIS

SEM micrographs obtained from fracture surfaces of pristine samples and compositions containing polyurethanes based on polyethylene glycol and polyoxypropylene diol can help to understand the toughening mechanism induced by PUR incorporation. All obtained micrographs were scanned on samples after impact tests near the crack tip.

The micrograph of the unmodified epoxy composition fracture surface is flat and glassy (Fig. 6), indicating the occurrence of regular uninterrupted and an elastic crack propagation path.

In Fig. 7, a micrograph of the epoxy resin composites containing 1% MMT is shown. The fractured surface is rough and contains larger domains. The concomitant addition of MMT and 10% PUR based on polyethylene glycol 400 (PUR 400) gave a more stratified elongated structure between epoxy resin and modifier (Fig. 7b).

However, the micrographs in Figs. 8a and 8b show a rather different structure for systems with the incorporation of PUR 1002, when compared with the micrograph for the pure epoxy resin (Fig. 6), the surface is no more smoother but reveals the presence of elongated domains. This may explain the higher values of the flexural strain at break as shown in Fig. 5 as well as the resistance to crack propagation as expressed by K_C and the impact strength data. The occurrence of plastic yielding and the formation of the second phase within the polymer matrix are usually associated with higher energy absorption during the crack propagation processes either under impact or low-speed conditions.

Figure 9 shows SEM micrographs of epoxy nanocomposites (2 wt% MMT) modified with 10 wt% PUR 400 (Fig. 9a) and 15 wt% PUR 1002 (Fig. 9b). The composition containing PUR 400 has a more stratified structure due to MMT particles surrounded by the polymer matrix. The SEM micrograph shows the phase separation, i.e., larger number of microvoids, which could be the reason for the observed decrease in the fracture toughness. This composite also exhibits a lower value of the impact strength in comparison with composite containing 1 wt% of MMT.

It can be mentioned that the structure of epoxy nanocomposite based on 2 wt% MMT and 15 wt% PUR 1002 (Fig. 9b) is similar to that of nanocomposite containing 1 wt% MMT and 10 wt% PUR 400 as depicted in Fig. 7b. These nanocomposites also exhibit a lower value of the impact strength in comparison with nanocomposites containing 1 wt% of MMT.

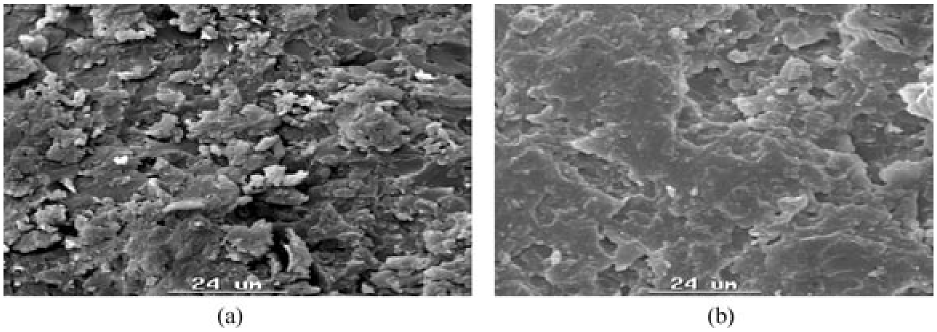
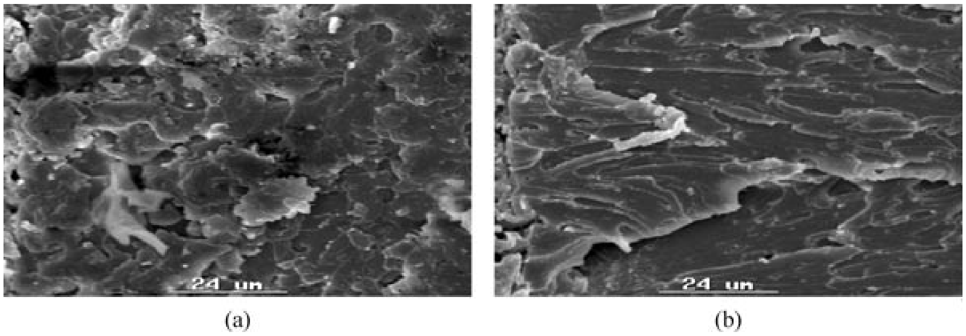
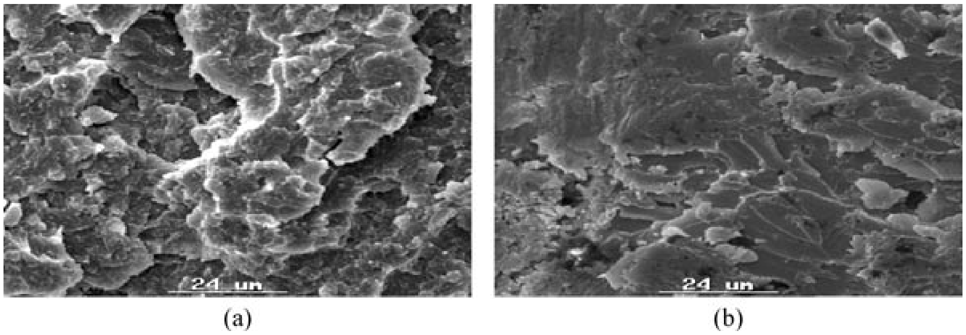


FIGURE 7. SEM micrograph of an epoxy resin modified with (a) 1% MMT and (b) 1% MMT and 10% PUR 400.



(a) (b)

FIGURE 8. SEM micrograph of epoxy nanocomposites (1% MMT) modified with (a) 15% PUR 1002 and (b) 20% PUR 1002.



(a) (b)

FIGURE 9. SEM micrographs of epoxy nanocomposites (2% MMT) modified with (a) 10% PUR 400 and (b) 15% PUR 1002.

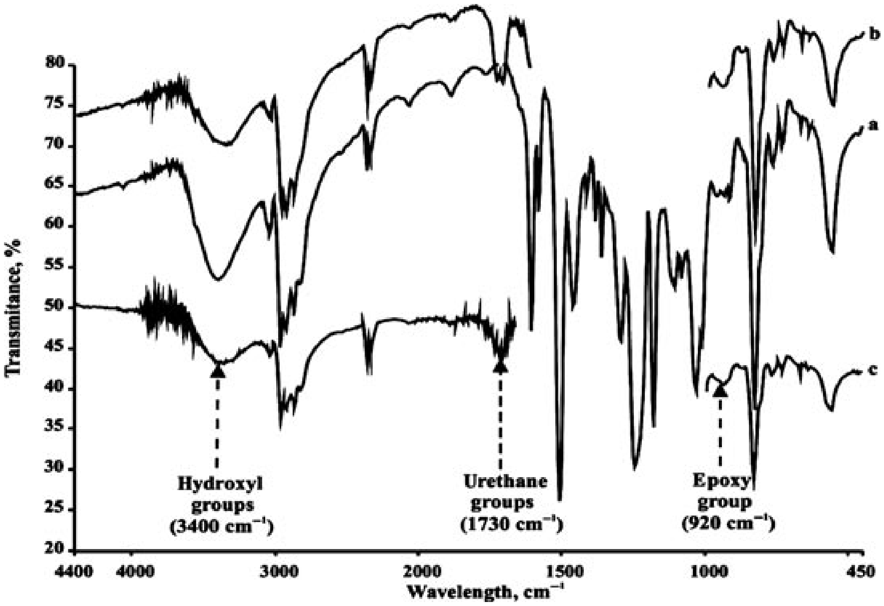


FIGURE 10. FTIR spectra of virgin epoxy resin (a) and modified compositions containing 10% PUR 400 (b) and 15% PUR 1002 (c).

TABLE II
Peak Heights of Hydroxyl Groups of Selected Epoxy Resin Based Compositions

Composition	Peak Height (%T)	Composition	Peak Height (%T)
Virgin EP	11.4	Virgin EP	11.4
EP + 10% PUR 400	5.9	EP + 1% MMT	7.7
EP + 15% PUR 1002	3.8	EP + 2% MMT + 10% PUR 400	6.0
		EP + 2% MMT + 15% PUR 1002	3.2

STRUCTURE CHARACTERIZATION

The FTIR spectra of compositions containing polyurethanes (PUR 400 and PUR 1002) are shown in Fig. 10 together with that of virgin epoxy resin. The epoxy resin modification with PUR 400 shows a decrease in the hydroxyl group peak intensity (as shown in Table II) approximately by 50% and peak area by 44.4% in comparison with neat epoxy resin. This may arise from the reactions taking place between isocyanate groups of polyurethane and hydroxyl groups of epoxy resin, as indicated by the absence of the isocyanate peak at 2270 cm^{-1} and is illustrated in Scheme 1. Moreover, the appearance of the peak at 1730 cm^{-1} confirms the presence of the allophonate and urethane groups in the epoxy compositions containing polyurethanes (PUR 400 and PUR 1002).

Thus, the FTIR spectra confirm the presumption of the improvement in mechanical properties due to the formation of grafted IPN structures within this composition.

The incorporation of PUR 1002 resulted in a decrease in the hydroxyl groups peak height by 65% and peak area by 64.4% in relation to neat epoxy resin, confirming the occurrence of interchain bonds between polyurethane and epoxy resin. Moreover, the epoxy group peak appearing at 920 cm^{-1} has an intensity similar to that found in both epoxy resin and the resin modified with PUR 400.

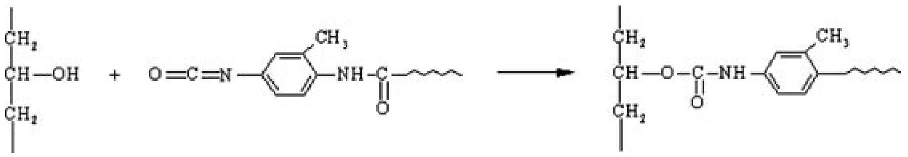
Zheng and co-workers[28] found that the addition of organically modified montmorillonite to epoxy/polyurethane IPNs systems promotes the compatibility of epoxy and polyurethane. Moreover, they confirmed that the degree of nanoclay dispersion is improved and results in modified nanocomposites with excellent mechanical properties.

In Fig. 11, the FTIR spectra of neat epoxy resin and nanocomposites (2% MMT) modified with 10 wt% PUR 400 and 15 wt% PUR 1002 are depicted. It can be observed that, for the nanocomposite containing 10% PUR 400 and PUR 1002, the peak connected with hydroxyl groups has lower intensities (Table II) than that arising from the unmodified epoxy resin. The decrease in the peak heights attained, respectively, 50% and 70% in comparison with an unreinforced epoxy resin. On the other hand, the peak areas decreased by, respectively, 44.2% and 11.5%.

This can be related to the formation of bonding between the free isocyanate groups from polyurethane and hydroxyl groups from epoxy, resulting in the formation of grafted IPN structure in the examined composition, which is responsible for the increase in the impact strength and flexural strength (see Scheme 1).

Table II contains values of peak heights of hydroxyl groups of selected epoxy resin compositions containing different amounts of polyurethanes and montmorillonite.

The X-Ray diffraction method is used to characterize the nanoclay structure within the epoxy nanocomposites. From Fig. 12 showing the XRD patterns of selected epoxy nanocomposites containing MMT, PUR 400, and PUR 1002, it can be seen that for epoxy nanocomposite containing only 2 wt% MMT the d-spacing value of the clay in the epoxy resin, estimated from the Bragg equation at 2θ of 5.3°, is 1.7 nm. Moreover, the lack of distinct diffraction peaks in the range 2.5–10.5 in the XRD pattern is



SCHEME 1.

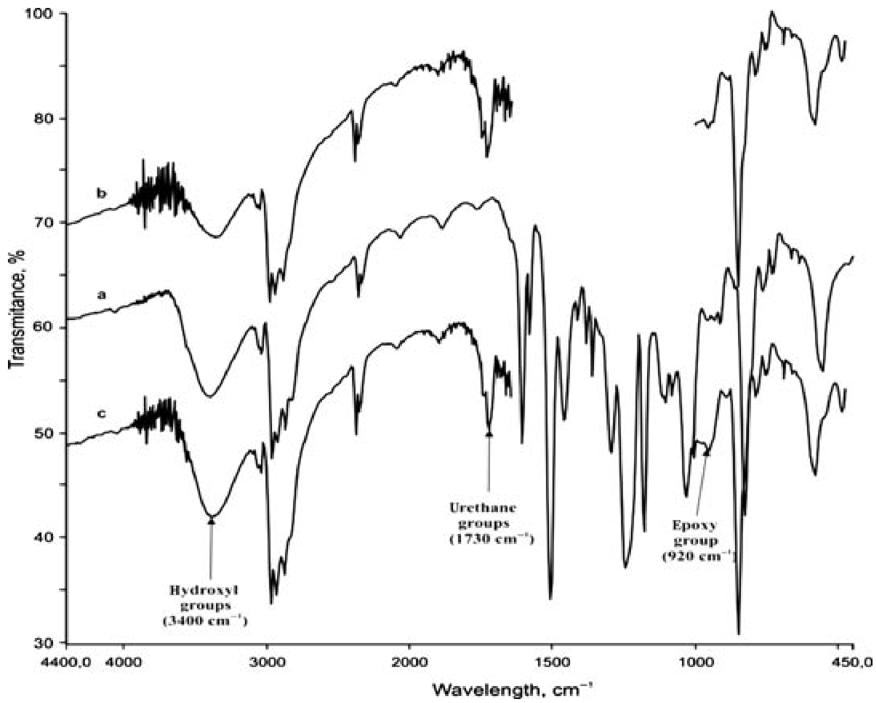


FIGURE 11. FTIR spectra for neat epoxy resin (a), epoxy resin modified with 2% MMT and 10% PUR 400 (b), and composite containing 2% MMT and 15% PUR 1002 (c).

observed, thus confirming the randomization or exfoliation structure of the nanoclay. Similar results were reported by other researchers.[29] Furthermore, the incorporation of 10 wt% of polyurethane to the nanocomposite (2% MMT) resulted in the disappearance of peaks in low values of 2θ in the range 2.5°–12.5°. One can confirm the presence of an intercalated structure for the composition containing only MMT and an exfoliated structure for the PUR-epoxy nanocomposites.

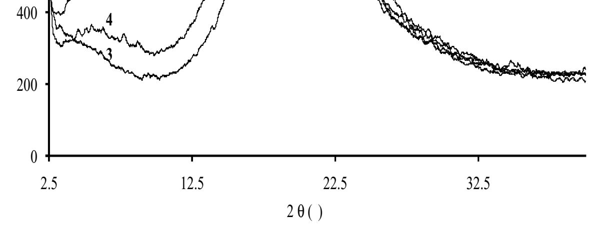


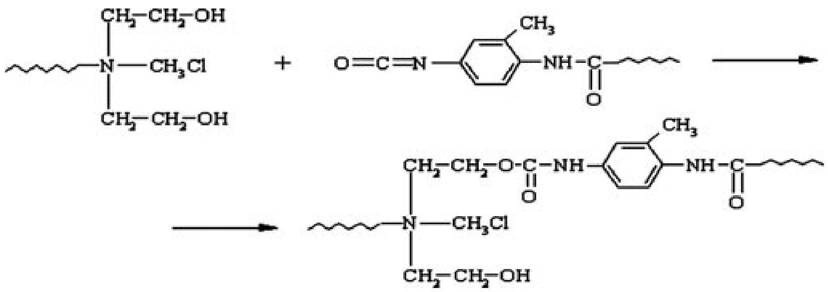
FIGURE 12. XRD patterns of epoxy resin (EP) containing montmorillonite (MMT) and different polyurethane (PUR).

The peak that appears at 2θ of about 20° for all nanocomposites as well as for the virgin epoxy resin is usually associated with the amorphous structure of epoxy resin.[29,30] It can be noted that the addition of PUR promotes the exfoliation process of MMT.

Furthermore, modified montmorillonite contains quaternary ammonium ions with two hydroxyethyl groups capable of reacting with the isocyanate groups of polyurethane according to Scheme 2.

Such reactions promote the exfoliation of montmorillonite and consequently lead to improvement in mechanical properties of epoxy resin.

It is well known that nanoclay exfoliation is a complex process, which depends on many factors, and involves polymer chain penetration into the nanoclay galleries as well as the development of mechanical stresses during the cross-linking reaction of epoxy resin.[31–33] Acetone, which was used as a dispersing agent for nanoclay, can easily penetrate clay galleries and enable epoxy resin to be placed between clay layers before the curing process.



SCHEME 2.

During the cross-linking reaction, a three-dimensional network structure was formed with an exfoliated epoxy/nanoclay nanocomposite.

Chen et al.[31] used a acetone–clay slurry to prepare a highly exfoliated epoxy nanocomposite. Their results confirmed the ease of epoxy resin penetration into clay galleries as well as its accelerated curing process. Moreover, Park and Jana[32] explained the nanoclay exfoliation by the elastic force exerted by the cross-linked molecules of epoxy resin inside the galleries.

Table III summarizes the values of the T_g of epoxy resin as a function of MMT and PUR contents. It is shown that the addition of 1 wt% of montmorillonite leads to a decrease in the T_g of epoxy resin by 3.5°C. An even larger decrease in T_g (8.4°C) can be observed when using 2 wt% MMT loading. Such findings, reported also by other researchers,[28,29] arise from the reduction in the cross-linking density due to the absorption of the hardener.

However, the incorporation of 5–10% of linear polyurethane (PUR 400 or PUR 1002) to the epoxy nanocomposites brings about an increase in T_g, in relation to the epoxy nanocomposites containing only MMT. This can be explained by the formation of a grafted IPN structure but also by the increase of crosslink density of the epoxy resin, as already confirmed by FTIR results.

Conclusions

A series of epoxy nanocomposites were prepared and tested. All nanocomposites showed higher impact strength than the unmodified epoxy resin. The highest increase in the impact strength was obtained for nanocomposites containing 2% MMT and 10% PUR 400, representing 110% enhancement in comparison with the unmodified epoxy resin. A 10-fold increase in relation to pristine epoxy resin samples was observed for the flexural strain of a nanocomposites containing 15% PUR 1002 and 2% MMT. Moreover, the addition of 10% PUR 400 to 1% MMT modified epoxy resin resulted in the highest improvement in the flexural strength.

The FTIR results showed that chemical reactions have occurred between the hydroxyl groups of the epoxy resin and the isocyanate groups of the polyurethane modifier, explaining the improvement in the fracture toughness of the polymer matrix. Moreover, SEM micrographs have indicated that the concomitant addition of 1% MMT and 10% PUR based on polyethylene glycol 400 (PUR 400) gave a more stratified elongated structure between epoxy resin and modifier as indicated by the rough surface and the presence of larger domains. However, the incorporation of PUR 1002 to epoxy nanocomposite

TABLE III
Glass Transition Temperatures for Selected Epoxy Compositions

Formulations	T_g (°C)	Formulations	Tg (°C)
EP	67.5		
1% MMT+EP	64.0	2% MMT+EP	59.1
1% MMT+10% PUR 400	65.6	2% MMT+10% PUR 400	68.8
1% MMT+15% PUR 1002	66.1	2% MMT+15% PUR 1002	66.5

(1% MMT) showed a rather different structure with elongated domains, which could be associated with the increase in the impact strength and K_C values.

The DSC results showed a slight decrease in the T_g with the addition of MMT, most probably due to a reduction in the cross-linking density of the polymer matrix. The XRD analysis has confirmed the formation of intercalated structure for the compositions containing only MMT and an exfoliated structure for the related nanocomposites.

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PAPER IV

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 intensity factor (K_C) 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 Zavareh[21] 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 SiO_2 nanoparticles and carboxyl-randomized liquid butadiene-acrylonitrile rubber (CRBN) nanocomposites. They found that nanocomposite containing 2% SiO_2 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 SiO_2 nanoparticles in the epoxy matrix.

In our previous work,[25] we have evaluated the properties and analyzed the morphology of an epoxy 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 tallow-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′-diphenylomethane 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 cm^3 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 cm^3 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 equation[26]:

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

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 equation[26]:

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

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 Panalytical X-ray diffractometer with a CuK$_{\alpha 1}$ = 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

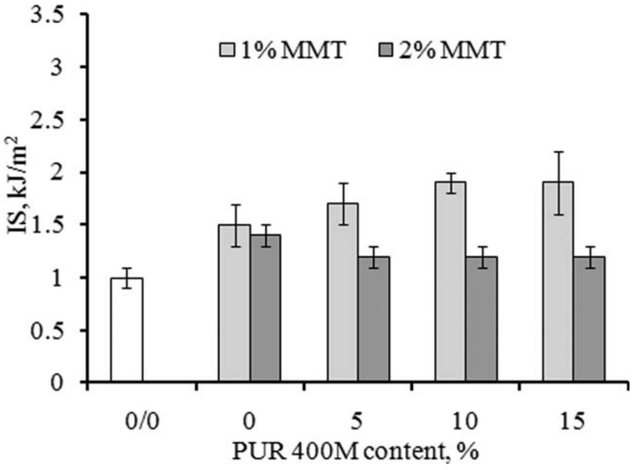


Figure 1 Effect of polyurethane (PUR 400M) content on impact strength (IS) of nanocomposites containing 1 and 2% montmorillonite (MMT).

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 investigation[27] 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/m^2) 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/m^2 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

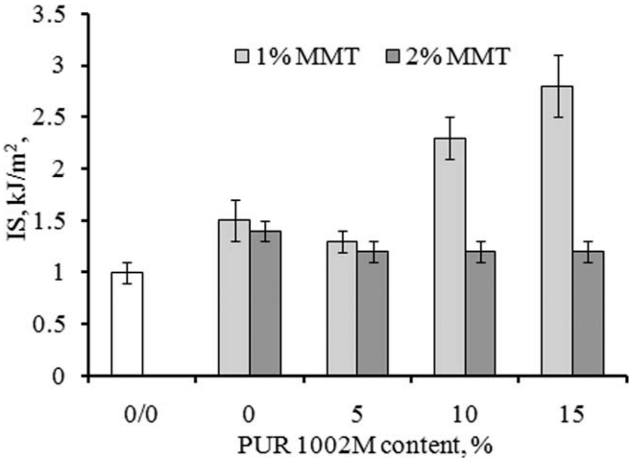


Figure 2 Impact strength (IS) of nanocomposites containing 1 and 2% montmorillonite (MMT) as function of polyurethane (PUR 1002M) content.

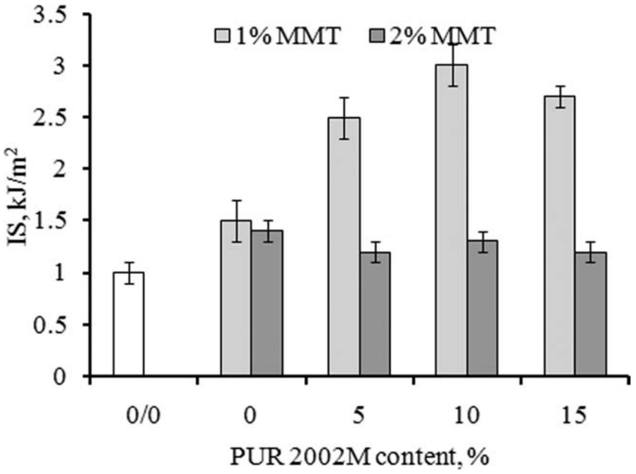


Figure 3 Impact strength of epoxy compositions containing montmorillonite (MMT) as a function of PUR 2002M content.

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.

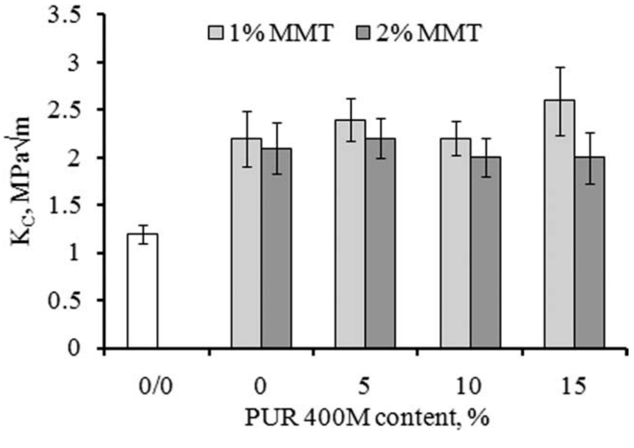


Figure 4 Effect of polyurethane (PUR 400M) and montmorillonite (MMT) contents on the critical stress intensity factor (K_C).

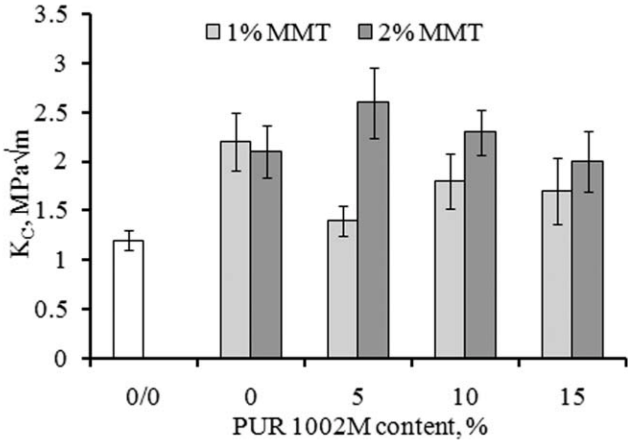


Figure 5 Critical stress intensity factor (K_C) values of epoxy nanocomposites modified with polyurethane (PUR 1002M).

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 MPa.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

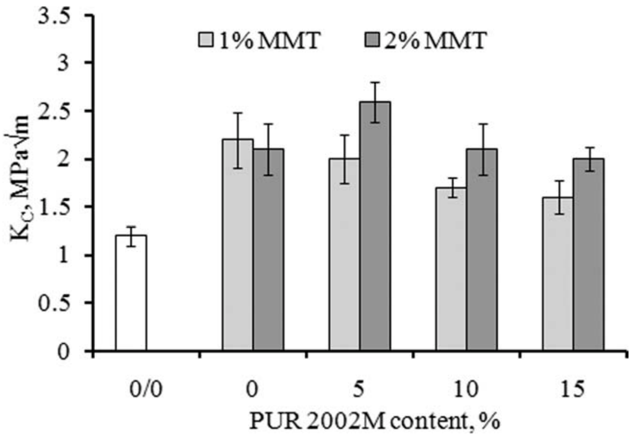


Figure 6 Effect of PUR 2002M and MMT content on critical stress intensity factor K_C values.

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

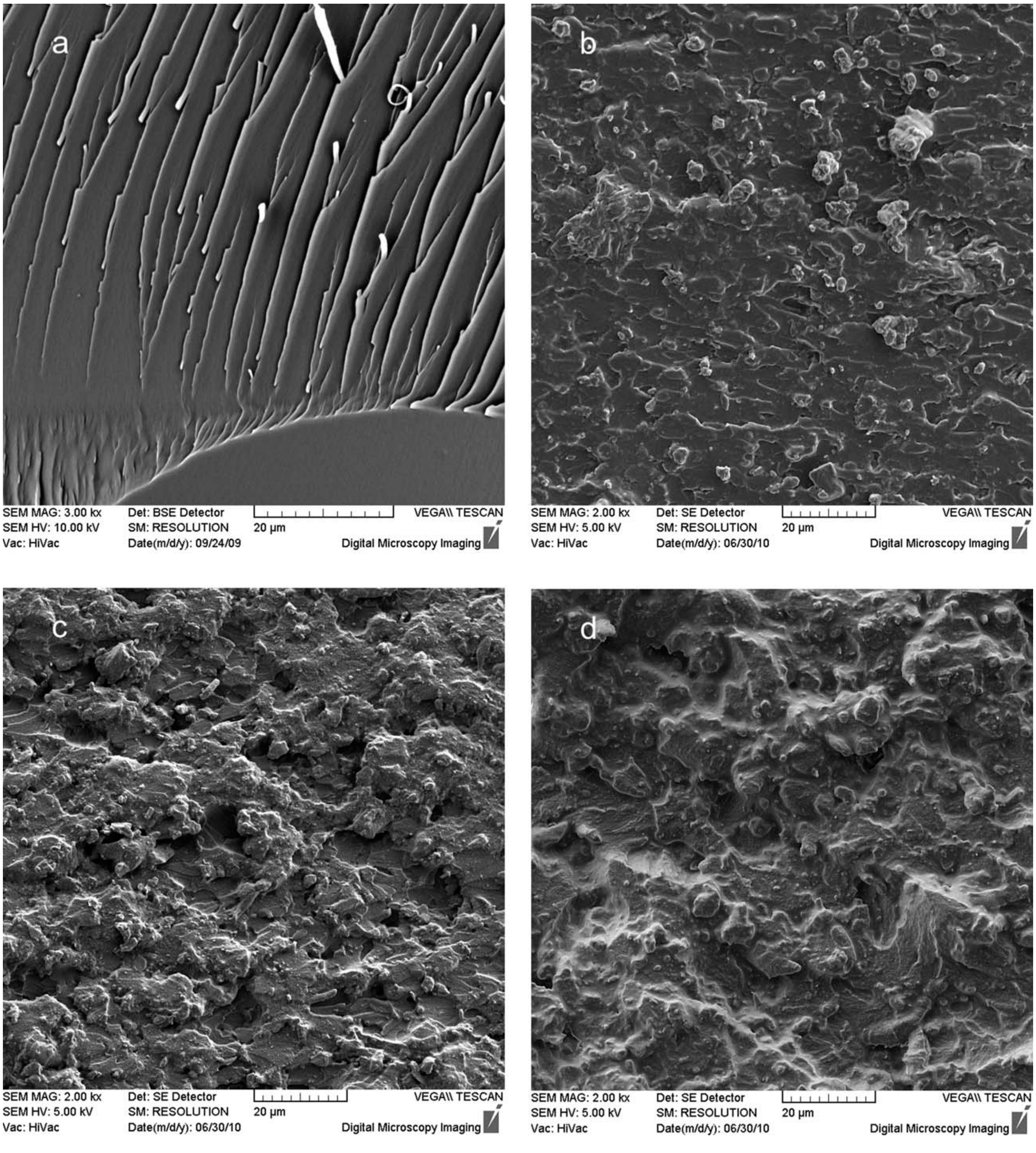


Figure 7 SEM micrographs of virgin epoxy resin (a) and compositions containing: 1% MMT + 10% PUR 400M (b), 1% MMT + 10% PUR 1002M (c), 1% MMT + 10% PUR 2002M (d).

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 allophonate 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 modifier 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).

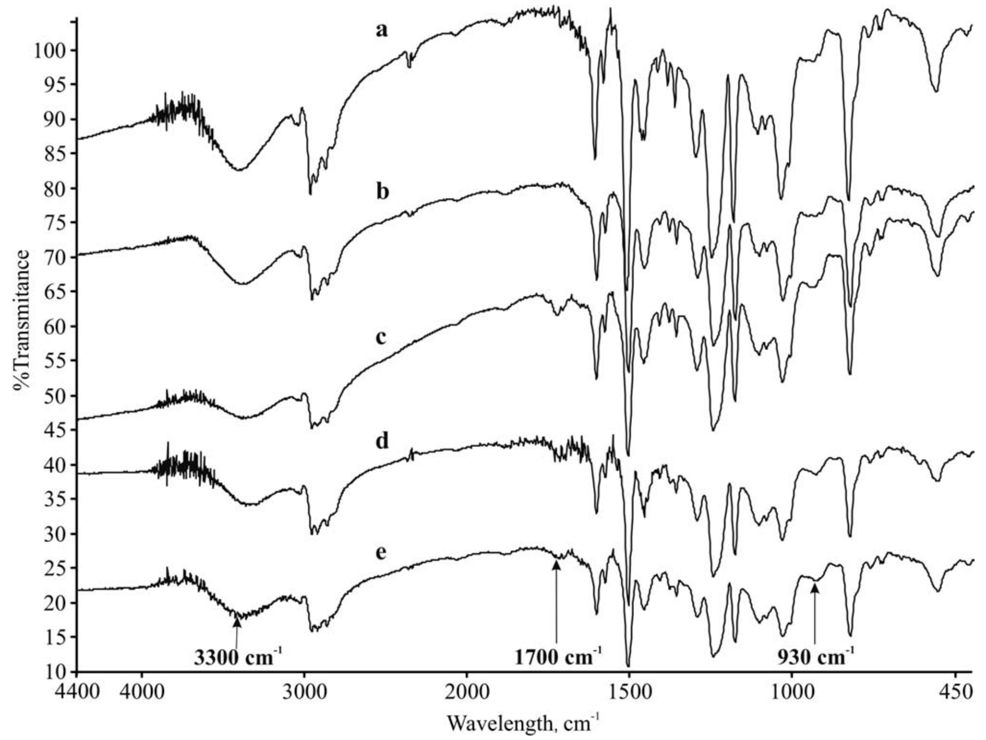
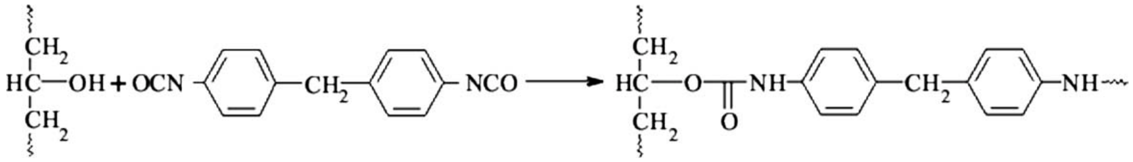


Figure 8 FTIR spectra of modified epoxy resin: neat epoxy resin (a), epoxy resin modified with 1% MMT (b) and hybrid composites containing: 1% MMT + 10% PUR 400M (c), 1% MMT + 10% PUR 1002M (d), 1% MMT + 10% PUR 2002M (e).



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

The characteristic peaks appearing at 1700 cm^{-1} are connected with allophonate 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 allophonate 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

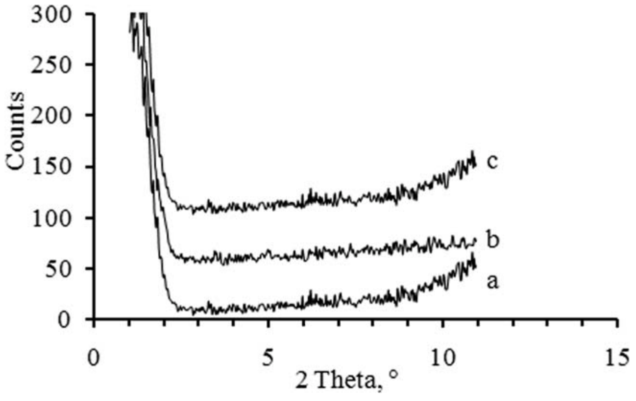


Figure 9 XRD patterns of epoxy resin formulations containing 1% montmorillonite (MMT) and 10% PUR 400M (a), 10% PUR 1002M (b), 10% PUR 2002M (c).

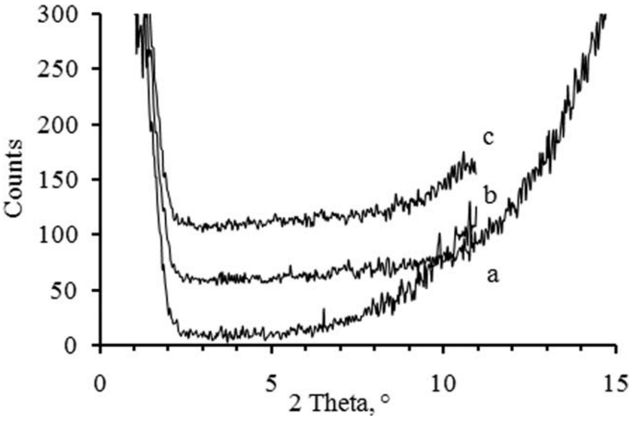


Figure 10 XRD patterns of epoxy resin formulations containing 2% montmorillonite (MMT) and 10% PUR 400M (a), 10% PUR 1002M (b), 10% PUR 2002M (c).

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 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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PAPER V

Effect of Diisocyanate Type on the Properties and Morphology of Epoxy/Polyurethane Interpenetrating Polymer Networks

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Abstract: The present work investigates the effect of epoxy resin modification with polyurethanes based on polyethylene glycol and two different diisocyanates: 4,4’-diphenylmethane diisocyanate and 2,4-toluene diisocyante. The impact strength of composition based on 15 % polyurethane with 2,4-toluene diisocyante was enhanced by 130 % while the critical stress intensity factor and the flexural strength of epoxy composition based on 5 % polyurethane based on 4,4’-diphenylmethane diisocyanate increased approximately 140 % in comparison with unmodified epoxy resin. Infrared spectroscopy confirmed chemical reactions occurrence between the hydroxyl groups of epoxy resin and isocyanate groups from polyurethane, explaining the improvement of the mechanical properties of epoxy resin. Moreover, scanning electron micrographs showed a rough surface with plastic yielding and several microcracks for the compositions containing 2,4-toluene diisocyante based polyurethane, and deformed leaf-like morphology with more elongated structure for the epoxy resin modified with 4,4’-diphenylmethane diisocyanate based polyurethane.

Keywords: epoxy resin, polyurethane, mechanical properties, DSC, FTIR, SEM.

1. INTRODUCTION

Epoxy resins are widely used as matrices for high performance composite materials, surface coatings and adhesives for metals. However, due to their low impact strength, poor resistance to crack propagation and low elongation at break, cured epoxy resins have limited range of applications [1,2]. Several methods, including the formation of interpenetrating polymer networks (IPNs), were used to toughen epoxy resin [1, 3-16]. In this respect, polyurethanes proved to be successful, mainly due to their high flexibility and versatile structure [17].

Polyurethane/epoxy resin graft interpenetrating polymer network (IPN) with combined advantages of both polymers were first reported by Frisch et al. [6]. It was demonstrated that polyurethane (PUR) can be linked to epoxy resin (EP) through physical entanglements as well as chemical bonding to form graft IPN. Li and Mao [7] prepared semi-IPN EP/PUR, and evaluated their thermal and mechanical properties demonstrating that the two polymers are compatible at weight ratio of EP/PUR equating 70/30. Moreover, SEM indicated that this semi-IPN has a two-phase continuous structure which changes with different weight compositions. Also, the occurrence of the glass transition temperature between those of epoxy resin and polyurethane was related to the EP/PUR interface.

Park and Jin [8] found that the polar components of the surface free energy of the EP/PUR composition is largely influenced by the addition of PUR resulting in an increase of critical stress intensity factor value as well as impact strength at low-temperatures. The improvement of the mechanical properties was explained as a result of the increase in the strength of the hydrogen bonds between the hydroxyl groups of epoxy resin and the isocyanate groups of PUR.

Cristea et al. [9] synthesized and studied the damping properties of semi-IPNs based on epoxy resin and polyurethane which was prepared using poly(ethyleneadipate) diol, MDI, and butylene glycol. They found that the heat treatment conditions affect significantly blend's viscoelastic properties. Moreover, a weak softening and a completion of the crosslinking were observed upon temperature increase.

Wang et al. [10] studied the damping, thermal, and mechanical properties of EP/PUR IPNs. Polyurethanes with various isocyanate indexes were synthesized using poly(tetramethylene glycol) and TDI. They found that the tensile strengths of the IPNs decreased while their impact strengths increased with increasing PUR content. Furthermore, the formation of EP/PUR interpenetrating polymer network might improve not only the damping capacity, but also the thermal stability.

Recently, the effect of isocyanate index of TDI based PUR on the mechanical and thermal properties of diglycidyl ether of Bisphenol A cured with triethylenetetramine was investigated [11], and the positive effect of the reactive groups was confirmed.

Further, 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. Hsieh and Han [12] evaluated the mechanical properties of graft-IPN based on epoxy resin and polyurethanes based on polyols with different chain length. They concluded that the significant improvement of the tensile strength was due to the grafted structure, and simultaneously the shortness of polyurethane chains. However, Raymond and Bui [13] prepared IPNs from epoxy resin, TDI based polyurethane and castor oil and confirmed the occurrence of chemical reactions between isocyanate groups of PUR with hydroxyl groups of the epoxy matrix leading to the thermal resistance and tensile properties enhancement. However, the paper did not report an increase of impact resistance.

In the separate work, Harani et al. [14] confirmed that isocyanate-terminated PUR reacts with EP leading to a significant fracture toughness improvement. Moreover, the use of chain extender with PUR prepolymer caused a seven-fold increase of impact strength and almost two-fold increase of critical stress intensity factor in comparison to the unmodified epoxy resin. The improvement of the EP fracture toughness was attributed to the grafting reactions between the polymer matrix and the modifier.

Wang and Chen [15] modified epoxy resin using polyurethane prepolymer synthesized from polyether diol and MDI with the support of a coupling agent. Polyurethane modifiers were terminated with hydroxyl, amine, and anhydride functional groups. They found that the addition of polyurethane improves the fracture energy of epoxy resin, and the most pronounced enhancement in mechanical properties is obtained with hydroxyl terminated PUR. Furthermore, the analysis of SEM and TEM scans depicted phase separation, which might influence toughening mechanism.

Chern et al. [16] prepared IPNs from polyurethane based on poly(oxypropylene)triol grafted with polyacrylonitrile and epoxy resin. The investigation of mechanical properties and morphology of the networks has shown that the tensile strength increased with increasing amount of epoxy resin and that some grafting reactions have taken place between polyurethane and hydroxyl group of epoxy.

The aim of the present work is to compare modification of epoxy resin with polyurethanes based on toluene isocyanate (TDI) and diphenylmethane diisocyanate (MDI).

2. EXPERIMENTAL

2.1. Materials

The following components were used in the present work:

- 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 of 0.49-0.52 mol/100g;
- triethylenetetramine hardener (Z1, Organika Sarzyna, Poland);
- polyethylene glycol with molecular weight of 400 g/mol (PEG 400) and 277 mg/g hydroxyl number (Merck, Germany);
- 2,4- toluene diisocyanate (TDI) for synthesis produced by Merck, Germany;
- 4,4'-diphenylmethane diisocyanate (MDI) produced by Merck, Germany; pure for synthesis
- dibutyltin dilaurate catalyst (Merck, Germany);
- toluene and acetone solvents (Merck Germany).

2.2. Samples preparation

2.2.1. Preparation of polyurethanes

Two types of polyurethanes were prepared: based on polyethylene glycol (PEG 400) and toluene diisocyanate (PUR400T) and PEG 400 and diphenylmethane diisocyanate (PUR400M).

The TDI based PUR was prepared as follows: 50 g of polyol and 0.25 cm^3 of dibutyltin dilaurate were mixed mechanically for 15 min under vacuum and then heated to 40 °C. Then, one half of the TDI amount (22.55 g) was added dropwise over 15 min and the reaction was carried in a nitrogen atmosphere for 30 min, while the temperature maintained below 60 °C. The mixture was cooled to 25°C before adding 50 cm^3 of acetone to reduce the viscosity. Finally, the rest of TDI was added dropwise for another 15 min and the temperature maintained below 40 °C.

For MDI based PUR, 50 g of polyol and 0.25 cm^3 of dibutyltin dilaurate were stirred for 5 min under vacuum and cooled dawn to below 10 °C to slow down the exothermic reaction between isocyanate and hydroxyl groups. Then, 27 g of MDI was added rapidly and the reaction was carried under nitrogen atmosphere with vigorously mixing for 10 min and temperature still maintained below 15 °C until the increase of reaction mixture viscosity.

All prepared polyurethanes had the isocyanate index equal to 1.05.

2.2.2. Preparation of polyurethane modified epoxy resins

Polyurethane was mixed with epoxy resin in amounts of 5, 10, 15 and 20 wt % for 20 min at a rotational speed of 2400 rpm at room temperature. The mixtures were then placed in a vacuum oven to remove air bubbles. Subsequently, the curing agent was added and mixing continued for 5 min before pouring the obtained compositions into the cavities of a mould to produce specimens for mechanical tests. The curing reactions were carried out at room temperature for 48 hours followed by post curing for 3 hours at 80 °C.

2.3. Mechanical properties measurements

Impact strength was measured according to Charpy method using a Zwick 5012 apparatus (ISO 179) on samples (80 x 10 x 4) mm and 1 mm notch.

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

The critical stress intensity factor K_C was evaluated by means of three point bending tests on the notched (1 mm) specimens having the same dimensions as impact test samples. The test was carried out using an Instron 5566 with a deformation rate of 5 mm/min and a distance between the spans of 60 mm [18].

2.4. Characterization

Infrared spectroscopy (FTIR) was performed on a Perkin Elmer spectrophotometer (1000 PC) recording the IR spectra from 450 to 4000 cm^{-1}. Scanning electron microscope (Hitachi S-2460 N) was employed to examine the fracture surfaces of specimens obtained from the impact tests. Differential scanning calorimetric (DSC) tests were carried out on a Perkin Elmer (Pyris 1) apparatus with the scan rate 10 °C/min within a temperature range from –25 to 200°C under nitrogen atmosphere. The T_g was recorded at the median point in the range of glass transition.

3. RESULTS AND DISCUSSION

3.1. Mechanical properties

The impact strength (IS), the critical stress intensity factor (K_C), the flexural properties (stress at break, strain at break and energy at break) were measured for epoxy resin containing various amounts of PUR400T and PUR400M. It can be noted from Figure 1 that all epoxy modified compositions exhibited higher IS values in comparison with neat epoxy resin; maximum IS improvement (about 130 %) was obtained with epoxy composition with 15 % PUR400T. The improvement in impact behavior may be explained by the presence of flexible polyurethane chains, which tend to decelerate the crack propagation process.

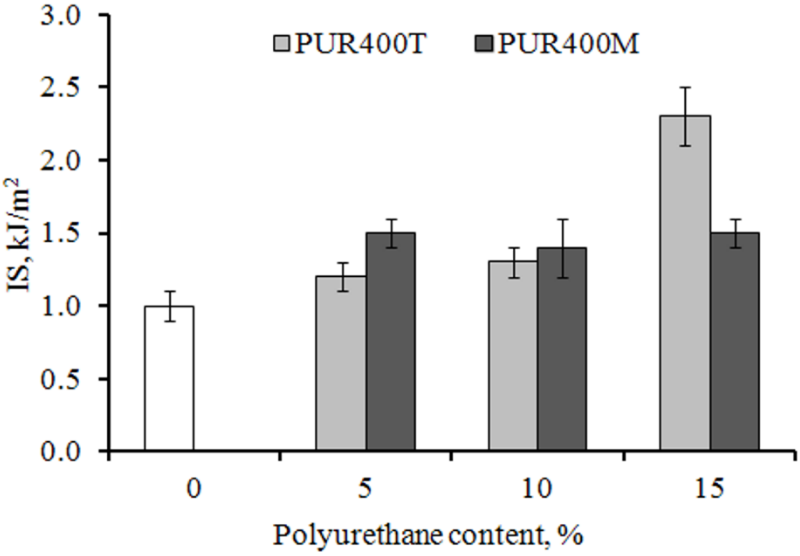


Figure 1. Effect of polyurethanes prepared from TDI (PUR400T) and MDI (PUR400M) on impact strength (IS) of epoxy resin

However, K_C values (Figure 2) point to higher resistance to crack propagation of modified compositions in relation to the pristine sample. Maximum K_C value, representing approximately 140 % improvement, was obtained for the composition based on 5 % PUR400M. The improvement of the resistance to slow crack propagation expressed by K_C or fast crack propagation represented by IS values might be attributed to the formation of interpenetrating polymer network (IPN) structure induced by polyurethane modifier within epoxy matrix. The presence of flexible PUR segments provided more free volume which in turn facilitates the movement of epoxy resin chains. Consequently, the resistance of EP/PUR system to crack propagation was enhanced in relation to unmodified epoxy resin.

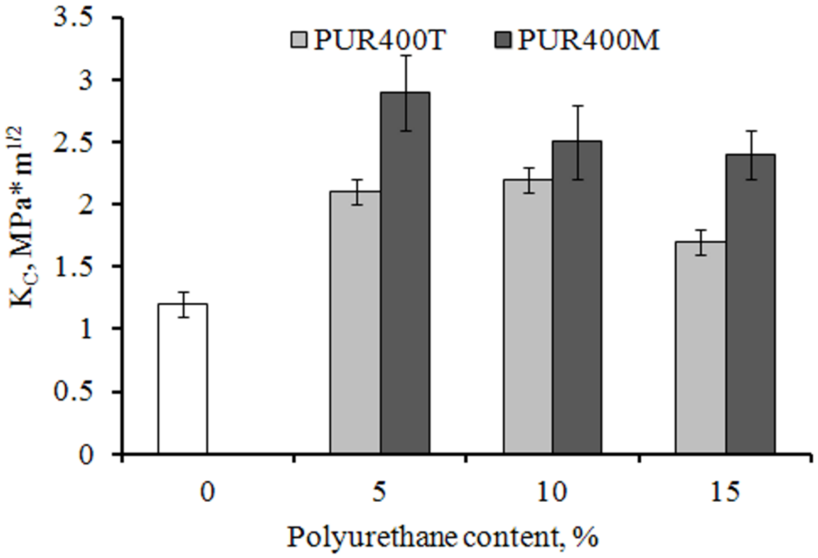


Figure 2. Effect of polyurethane based on TDI (PUR400T) and MDI (PUR400M) on critical stress intensity factor (K_C) of epoxy resin

The effect of PUR on flexural properties of EP in terms of flexural strength, strain at break and energy at break is demonstrated in Figures 3 to 5.

Similarly to IS and K_C results the modified epoxy compositions exhibited higher flexural strength than virgin polymer matrix. The addition of 5 % PUR400M to epoxy resin resulted in about 140 % increase of its flexural strength, and is attributed to the formation of an IPN structure combined with grafting reactions between epoxy resin and the polymeric modifier confirmed by FTIR analysis.

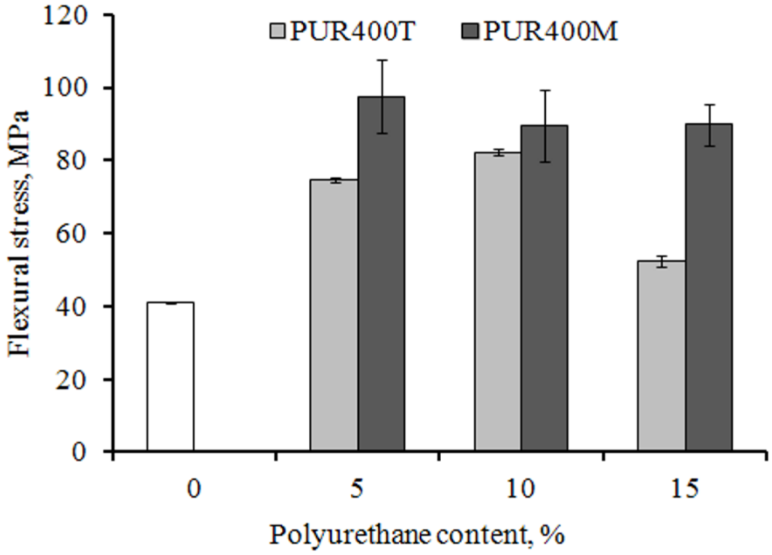


Figure 3. Effect of polyurethane based on TDI (PUR400T) and MDI (PUR400M) on the flexural stress at break of epoxy resin

Figures 4 and 5 show the evolution of flexural strain at break and energy at break of epoxy resin as function of PUR400 TDI and PUR400M content. The improvement of these two parameters was more pronounced than the flexural strength most probably due to the high elasticity of polyurethane modifier and the significant strain at break of PUR modified epoxy resin. The addition of soft segments was found to attribute to the improvement in tensile properties through better EP/PUR compatibility, and similar findings were reported for liquid rubbers [19, 20].

On the contrary, other researchers reported opposite results when different liquid rubbers were used to toughen diglycidyl ether of bisphenol A [21,22]. Ben Saleh et al. [21] attributed the reduction of the mechanical properties of epoxy resin to the presence of low modulus rubber, which was well distributed in the polymer matrix.

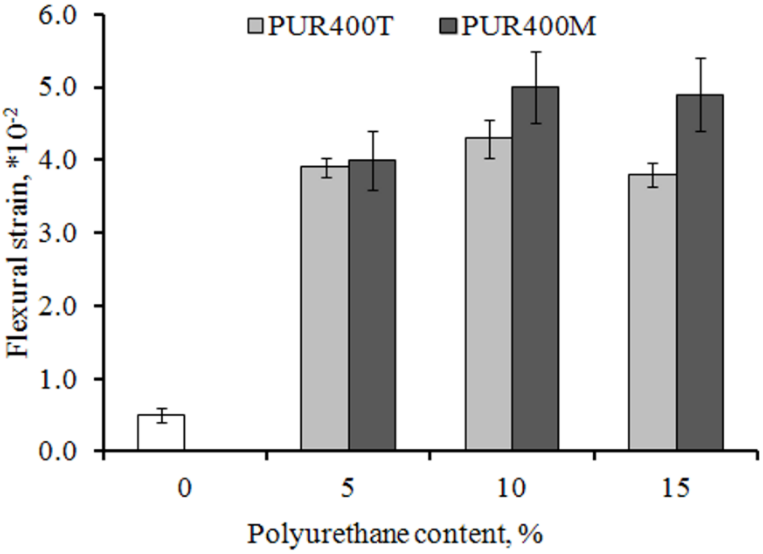


Figure 4: Effect of polyurethane based on TDI (PUR400T) and MDI (PUR 400M) on the flexural strain at break of epoxy resin

Compositions based on MDI showed higher values of strain and energy to break (obtained from the area under the load–displacement curve during flexural testing) as compared to TDI composites. With only 5 % PUR400M more than threefold improvement in energy at break and sevenfold increase in strain at break in comparison with virgin epoxy resin is achieved.

High values of elongation at break of EP/PUR400M can result from the flexibility of polyurethane chains giving rise to more free volume, and consequently more chain movement leading to high elongation before fracture occurrence.

It is seen that epoxy hydroxyl groups react with PUR isocyanate groups to yield more reticulate structure which may explain the improvement in epoxy resin mechanical properties. These findings were also reported by other researchers on similar systems [14].

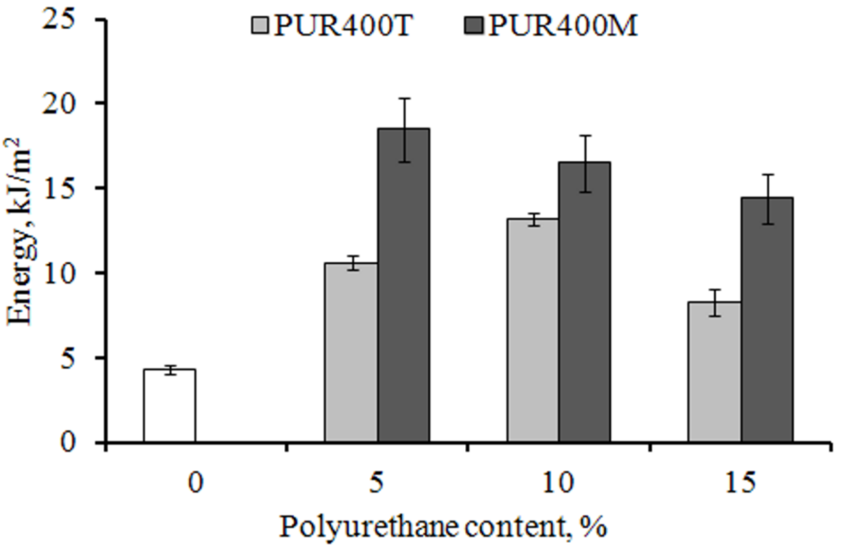


Figure 5: Effect of polyurethane based on TDI (PUR400T) and MDI (PUR400M) on flexural energy at break of epoxy resin

3.3. Structure characterization

FTIR spectra presented in Figure 6 were obtained for the structure characterization of virgin epoxy resin and compositions modified with PUR400T and PUR400M. We can observe characteristic peaks connected with functional groups of epoxy resin appearing at 3300 cm^{-1} for hydroxyl group and 920 cm^{-1} for epoxy groups. The series of peaks within the wavelength range 1000 - 1600 cm^{-1} are connected with aromatic rings.

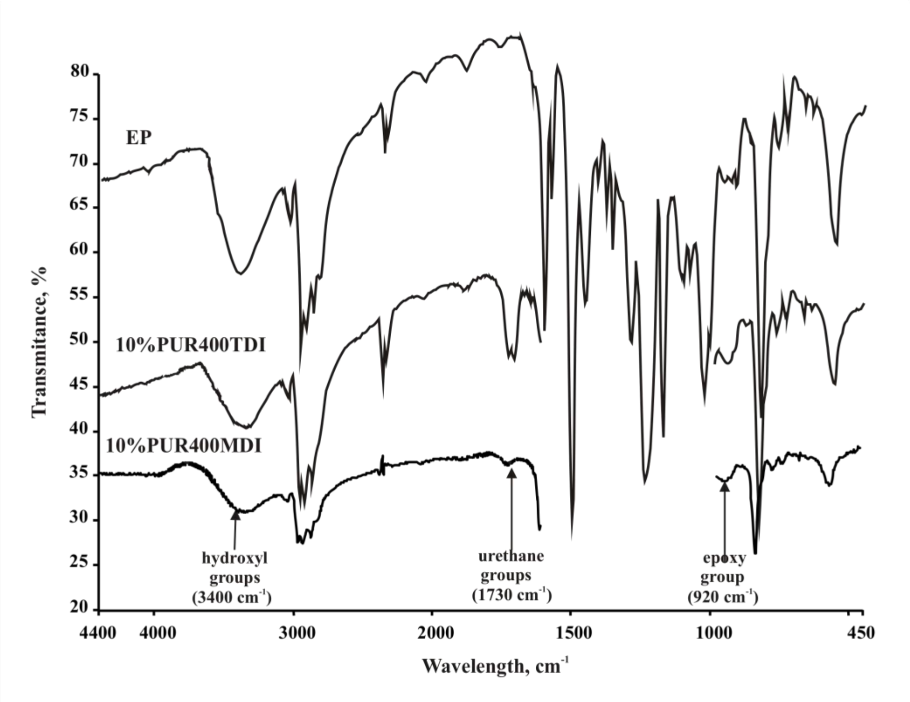
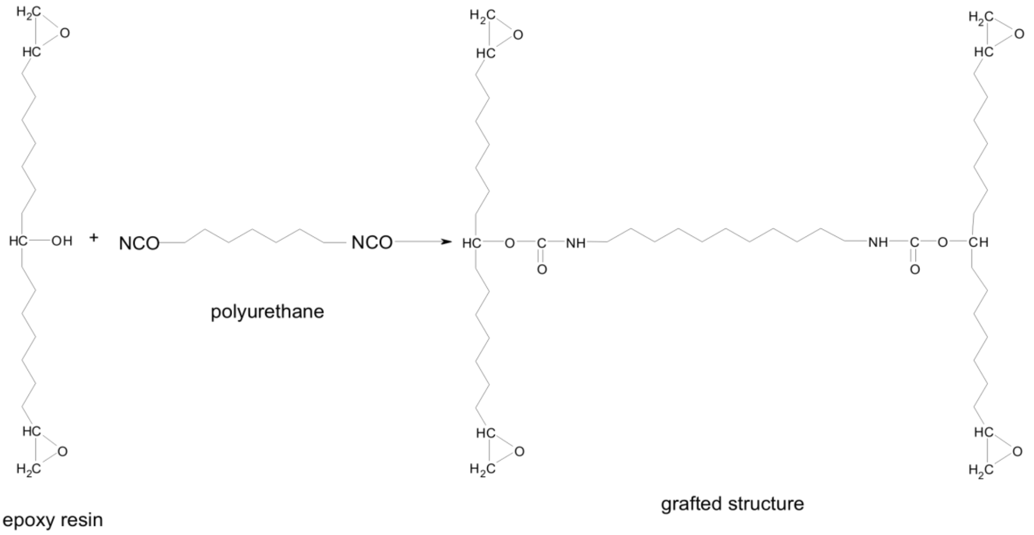


Figure 6. FTIR spectra of composite modified with polyurethane based on TDI and MDI

Allophonate and urethane groups from polyurethane modifier are represented by the peak at 1700 cm^{-1}. Moreover, the addition of TDI and MDI based polyurethanes resulted in the decrease of hydroxyl peak height by 52 and 74 % respectively. This finding proves the occurrence of grafting reaction between hydroxyl groups of epoxy resin and isocyanate groups of polyurethanes.

The grafting reaction is shown in scheme 1.



Scheme 1. Grafted structure of the obtained composites

The occurrence of grafting reactions as mentioned above and the formation of an interpenetrating polymer network structure between polyurethane and epoxy matrix chains could be related to the properties increase of this latter.

3.2. Fracture Surface Analysis

SEM micrographs were obtained from fractured surfaces of samples after impact tests near the crack tip, and are employed to explain the toughening mechanism induced by PUR incorporation. The micrograph of the unmodified epoxy composition fracture surface is flat and glassy (Fig. 7), indicating the occurrence of regular crack propagation path and low fracture energies of the tested samples. The lack of specific features or significant plastic deformation associated with the smooth surface indicates that the specimen fractured in a brittle manner.

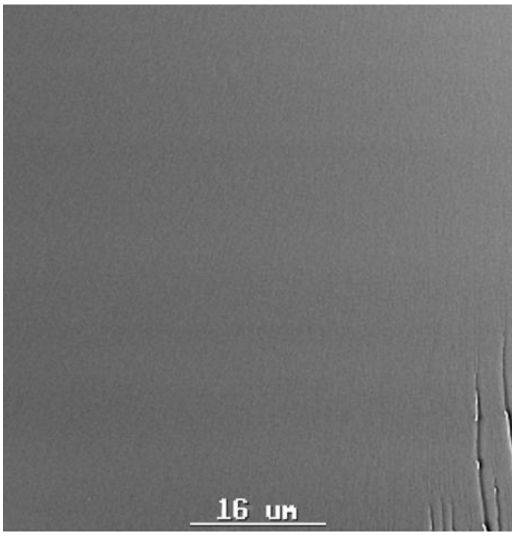
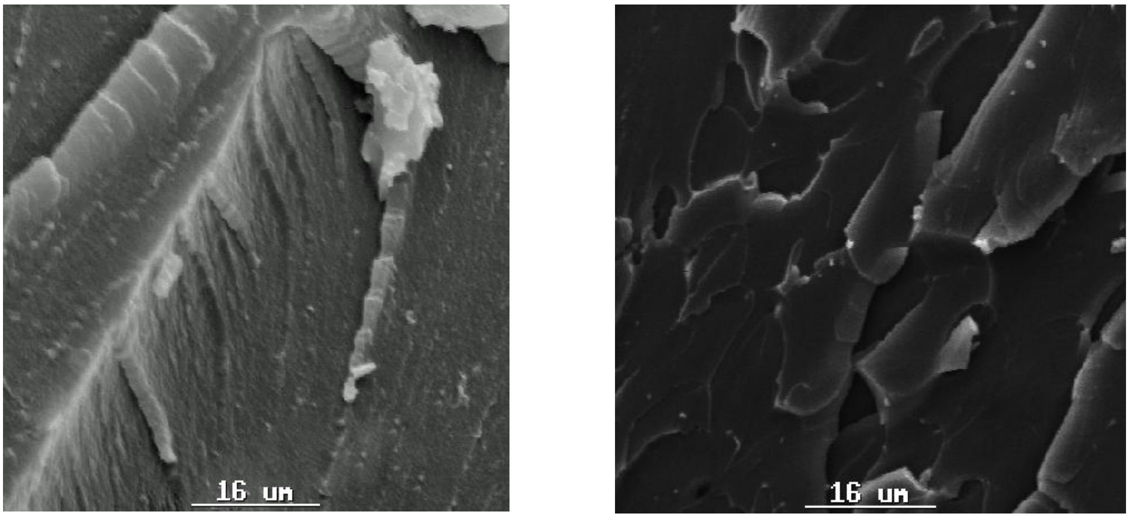


Figure 7. SEM micrograph of unmodified epoxy resin

Figure 8 shows the micrographs of epoxy resin containing 15 % of PUR prepared from TDI (PUR400T) and 15 % PUR400 based on MDI (PUR400M). It can be noted that the addition of polyurethane to the polymer matrix had resulted in an obvious change in the morphology of the neat polymer matrix. The fracture surface of composition containing 15 % PUR400T (Fig. 8a) is rougher with significant plastic deformations and several microcracks.

However, the micrograph of composition containing 15 % of MDI based PUR (Fig. 8b) presents a deformed leaf-like morphology and a more elongated structure. The observed significant structure deformation might be responsible for IS improvement due considerable absorbed energy during the crack propagation process.



a b

Figure 8. SEM image of the epoxy composite containing 15 % PUR400T (a) and 15 % PUR400M (b).

Differential scanning calorimetry (DSC) was employed for characterization of thermal behavior of the compositions containing 10 % of polyurethane based on TDI or MDI. Only one endothermic peak for each composition is obtained within the applied temperature range (from –100°C to +200 °C) confirming the existence of one glass transition temperature for all tested compositions (Table 1). Such obtained result might be attributed to the good compatibility between the epoxy resin and incorporated polyurethane modifier as well as the absence of two phase system.

Table 1. Glass transition temperature (T_g) of selected EP/PUR compositions

Composition	T_g (°C)
Virgin epoxy resin	63.2
EP + 10 % PUR400M	67.4
EP + 10 % PUR400T	67.6
EP + 15 % PUR400T	68.0

Furthermore, DSC analysis revealed that the glass transition temperature increased from 63°C to 68°C with the addition of 15 % PUR (see also in Table 1) which can be – with the support of FTIR - explained as the result of the formation of large amount of inter-chain bonding.

The increase of epoxy resin glass transition temperature due to polyurethane incorporation was attributed to grafting reaction by other authors [19, 23].

4. CONCLUSIONS

The addition of polyurethanes based on toluene diisocyanate (PUR400T) or diphenylmethane diisocyanate (PUR400M) resulted in improvement of mechanical properties of epoxy resin. All epoxy modified compositions exhibited higher impact strength (IS) and the critical stress intensity factor (K_C) values in comparison with neat epoxy resin. Maximum IS improvement, representing about 130 % in comparison with pristine epoxy samples, was obtained for epoxy composition modified with 15 % PUR400T, while the K_C and the flexural strength were the most enhanced (140 %) for 5 % PUR400M based composition.

The structure characterization by means of FTIR spectra indicated the occurrence of grafting reaction between hydroxyl groups of the polymer matrix and isocyanate groups of the modifier.

Moreover, SEM analysis of the fractured surfaces revealed the formation of elongated domains and regular parallel microcraks brought by incorporation of MDI based PUR, while the addition of TDI based PUR led to the formation of a homogenous elongated structure with significantly plastic deformations.

DSC results indicated the presence of a single glass transition temperature due to the good compatibility between the epoxy matrix and the modifier. The addition of this latter led to an increase of the glass transition temperature.

5. ACKNOWLEDGEMENT

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