Synergistic toughening and strengthening of an epoxy resin modified by simultaneous use of two different modifiers

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Abstract. The present work investigates the effect of modifying an epoxy resin using two different modifiers. The mechanical and thermal properties were evaluated as a function of modifier type and content. The structure and morphology were also analyzed and related to the measured properties. Polyurethane (PUR) was used as a liquid modifier, while Cloisite Na+ and Nanomer I.28E are solid nanoparticles. Impact strength (IS) of hybrid nanocomposites based on 3.5 wt% PUR and 2 wt% Cloisite or 3.5 wt% PUR and 1 wt% Nanomer was maximally increased by 55% and 30%, respectively, as compared to the virgin epoxy matrix, exceeding that of the two epoxy/nanoparticle binaries but not that of the epoxy/PUR binary. Furthermore, a maximum increase in IS of approximately 20% as compared to the pristine matrix was obtained with the hybrid epoxy nanocomposite containing 0.5 wt% Cloisite and 1 wt% Nanomer, including a synergistic effect, due most likely to specific interactions between the nanoparticles and the epoxy matrix. The addition of polyurethane and nanoclays increased the thermal stability of epoxy composites significantly. However, DSC results showed that the addition of flexible polyurethane chains decreased the glass transition temperatures, while the softening point and the service temperature range of epoxy nanocomposites containing nanofillers were increased. FTIR analysis confirmed the occurrence of interaction between the epoxy matrix and added modifiers. All SEM micrographs showed significant roughness of the fracture surfaces with the formation of elongated platelets, explaining the increase in mechanical properties of the epoxy matrix.

Keywords: epoxy resin; hybrid composites; mechanical and thermal properties; structure, morphology.

1. INTRODUCTION

Numerous studies have been devoted to the toughening and strengthening of epoxy resins using two different types of modifiers [1–6]. The production of epoxy-based hybrid composites aims to mainly reach a synergistic effect, where the properties are superior to those of binary systems. Various combinations of modifiers have been explored to prepare such composites with improved properties. The use of plasticizers or diluents generally results in an increase in ductility due to increased free volume [4,7–9], while a second phase can be formed by thermoplastics within the systems, which delays crack propagation, thus improving impact strength and fracture toughness [4,8,10,11]. The thermoplastic modifier can also form an interpenetrating polymer network structure with the possible occurrence of grafting reactions with the epoxy matrix, which would explain the improvement in the toughness and thermal resistance of the blend [12]. Due to their ability to form exfoliated and/or intercalated systems, solid nanoparticles have been shown to be very efficient modifiers for epoxy resins. Synthetic fibers are used for their high strength and stiffness, while natural fibers are

inexpensive and above all biodegradable [13–16]. The properties of a matrix can be further enhanced by means of combined reinforcement mechanisms of two modifiers as well as positive interactions between them and the polymer matrix [4,8,17,18]. A vast number of studies have been carried out on hybrid epoxy composites using different types of modifiers and having improved properties [3–5,8]. The present work focuses mainly on the use of solid nanoparticles and a liquid polymeric modifier.

Due to their specific morphologies, graphene and carbon nanotubes (CNTs) are considered the most promising candidates for the next generation of polymer nanocomposites. Recently, various researchers have studied the effects of both modifiers with the aim of obtaining synergistic effects on the properties of epoxy hybrid nanocomposites [19–27]. Shen *et al.* [19] showed that the friction coefficient of a hybrid composite with 0.5 phr multi-wall carbon nanotubes (MWCNTs) and 0.1 phr graphene oxide (GO) nanosheets, significantly increased with an appreciable reduction in the specific wear rate. However, the functionalization of MWCNTs was provided to avoid the formation of clusters in the matrix and further reinforce the matrix. Shukla *et al.* [20] investigated the effect of amine functionalized MWCNTs (A_f-MWCNT) and amine functionalized multi-layered graphene (A_f-MLG) on the thermo-mechanical properties of a bifunctional epoxy resin. Maximum increase of $\sim 50\%$ in tensile strength was obtained by the hybrid compos-

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ite containing 0.5 wt% of hybrid fillers, while the composite with 1 wt% of hybrid fillers showed the highest flexural strength and thermal properties as compared to the pristine matrix. The use of functionalized GO and CNTs resulted in improvement in tensile strength, critical stress intensity factor (K_{1C}) and critical strain energy release rate (G_{1C}) of the hybrid composite, resulting from good dispersion of the nanofillers in the matrix [21]. The synergistic effect was confirmed on the properties of epoxy hybrids due to crack deflection and bifurcation leading to a more tortuous crack propagation path. Bisht et al. [22] studied the effect of nanodiamond (ND) on the properties of epoxy resin modified with graphene (Gr) and CNTs, and confirmed the synergistic effect on the fracture toughness of the matrix. The tensile strength and toughness of the epoxy resin was improved due to very good dispersion and strong interfacial interaction between ND and the Gr-CNT hybrid. The effect of dimensions of graphene nanoplatelets (GnPs) on the properties of the epoxy resin containing (CNTs) was studied by Chatterjee et al. [23]. They confirmed that larger nanoparticles led to greater improvement in fracture toughness by ∼ 75% as compared to the pristine matrix. TEM analysis confirmed the uniform nanofiller dispersion in the nanocomposites. Yue et al. [24] showed that the use of CNTs and graphene nanoplatelets (GnPs) at the 8:2 ratio led to synergistic increase in flexural properties. In the study of the tensile and electrical properties of graphene nanopowders (GNPs) and CNTs-filled epoxy matrix, Ghaleb et al. [25] showed that improved tensile and electrical properties in the GNP–CNT/epoxy hybrid were achieved with a GNP–CNT ratio of 0.1:0.4, due to the uniform dispersion of nanofillers in the matrix. In another study, Singh et al. [26] used GNP and amine-functionalized MWCNTs to toughen an epoxy resin. The simultaneous use of nanofillers led to a synergistic effect on the flexural strength (121%) and tensile strength (132%) in a composite containing 0.17 wt% of the nanofiller. The properties improvement was attributed to the uniform dispersion of nanofillers and strong adhesion between the ingredients.

Graphene and CNTS were also combined with other nanofillers, such as montmorillonite (MMT), to enhance the properties of the epoxy matrix [28–30]. Yazik et al. [28] studied the properties of an epoxy resin modified with MWCNT and MMT at room temperature (RT) and high temperature (HT). The sample containing 3 wt% MMT and 1 wt% MWCNT showed maximum increase of 30% in tensile strength at RT. Kazemi-Khasragh et al. [29] confirmed a synergistic effect of GNPs combined with MMT on the wear resistance of hybrid epoxy nanocomposites. A synergistic effect of MWCNTs and MMT was reached on the mechanical and thermal properties of an epoxy resin as confirmed elsewhere [30]. However, thermal conductivity of MWCNTs/MMT epoxy nanocomposites was significantly improved with 0.5 wt% of hybrids.

The effect of metal oxide nanoparticles on the properties of the epoxy resin was investigated by various researchers [31–35]. Iron oxide (Fe_2O_3), copper oxide (CuO) nanoparticles and (MWCNT) were used by Gazderazi and Jamshidi [31] to modify an epoxy resin. Metal oxides combined with MWCNT led to significant increase in the tensile and flexural properties of epoxy samples as compared to those containing only MWCNT.

The best mechanical and thermal properties of epoxy nanocomposites were obtained with 1.5 wt% of MWCNT and 7 wt% of nanosize titanium dioxide (TiO_2) induced by better micro/nano dispersion. Similar results were obtained by Kumar et al. [32], who attributed the positive reinforcement of epoxy to crack bridging and the lack of nanoparticle pullout. In an another work, it was shown that tensile, flexural and impact strength increased by 56%, 81% and 112%, respectively, at 0.25 phr of hybrid fillers based on reduced graphene oxide (RGO) and iron oxide (Fe_2O_3) [33]. The fracture toughness and electrical conductivity of RGO–Fe_2O_3/epoxy nanocomposites showed significant improvement as compared to the neat epoxy matrix. A synergistic effect between graphene and CuO nanoparticles on the mechanical and thermal properties of the epoxy matrix was confirmed elsewhere [34]. Zirconium dioxide (ZrO_2) nanoparticles were also used with MWCNTs to synergistically reinforce the properties of epoxy resins [35]. The prepared nanocomposites showed superior thermo-mechanical properties, while the corrosion resistance of mild steel coated with a MWCNT/ZrO_2 hybrid epoxy nanocomposite (MNC) was significantly enhanced at 1 wt% of nanofiller hybrids. Moreover, the tensile strength and lap shear strength of the hybrid with the same content was increased by ∼ 68% and ∼ 58% as compared to neat epoxy resin.

The purpose of the present study was to prepare hybrid epoxy composites containing solid nanoparticles and a liquid modifier. We expected to obtain a synergistic effect on the properties of hybrid epoxy composites.

2. EXPERIMENTAL PHASE

2.1. Materials

The following ingredients were used in the present work:

- Epoxy resin (Epidian 52 from ZCh Sarzyna Co., Poland) with epoxy number in the range of 0.510–0.550 mol/100 g and viscosity of 400–800 mPas at 25°C;
- Triethylenetetramine (trade name Z1, produced by ZCh Sarzyna) was used as a curing agent for the epoxy matrix;
- Polyurethane (Desmocap 12) manufactured by Bayer AG;
- Cloisite Na+: natural nanoclay from BYK-Chemie GmbH;
- Nanomer I.28E: nanoclay modified with 25–30 wt% trimethyl stearyl ammonium, produced by Nanocor Inc.

2.2. Samples preparation

2.2.1. Epoxy based composites with one modifier

The epoxy resin was mixed with different amounts of polyurethane (2.5–15 wt%) with a mechanical stirrer for 10 min. However, Cloisite Na+ and Nanomer I.28E nanoparticles were mixed with the epoxy matrix using a mechanical stirrer and ultrasonic stirrer. First, the epoxy composition was mixed for 10 min with a mechanical stirrer followed by ultrasonic stirrer for 75 min at maximum amplitude of 270 µm. Then, 14 phr of a curing agent was added to the mixture and mixing continued for 5 min. The compositions were poured into metal molds, and then cured for 24 hours at room temperature and post cured for 3 hours at 80°C.

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2.2.2. Hybrid epoxy based composites

The following hybrid epoxy composites were prepared: PUR/Nanomer, PUR/Cloisite and Nanomer/Cloisite. The epoxy resin was mixed with the modifiers using a mechanical stirrer followed by ultrasonic mixing, as previously. Finally, 14 phr of a curing agent was added with additional 5 min of mixing before pouring into metal molds. Curing and post-curing was carried out as above. The mixing time and sonication amplitude were defined from the maximum impact strength of the tested nanocomposites. Studies have confirmed that the mixing sequence of components has an effect on the final properties of epoxy based composites [36, 37]. In order to obtain the desired mechanical properties, the ingredients were incorporated into the matrix in the following order: PUR – nanoclay – curing agent.

2.3. Evaluation of mechanical and thermal properties

Three-point bending: The test was carried out using the Zwick Roell tensile machine with samples 10 cm long, 1 cm wide and 0.5 cm thick. The deformation rate was fixed at 5 mm/min. The flexural strength (σ) and flexural strain (ε) are expressed by the following formula [38]:

$$\sigma = \frac{F \cdot L}{2b \cdot d^2}, \qquad \varepsilon = \frac{6d \cdot \delta}{L^2},$$

where: F – applied force, δ – deflection, L – distance between the support points, b – width of the sample, d – the depth or thickness of the sample.

Charpy impact strength: The test was conducted on a Zwick Roell device equipped with a hammer of 4 J using samples with the dimensions as above and 1 mm of notch length. The distance between the spans was fixed at 6 cm.

Resistance to crack propagation: Samples with dimensions and notch length as for the impact strength were used for the test which was carried out on Zwick Roell tensile device at a deformation rate of 5 mm/min. The critical stress intensity factor (K_C) was calculated as follows [39]:

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

where P – load at break, L – distance between the spans, a – notch length, w – sample width, B – sample thickness, Y – geometrical factor which depends on the a/w ratio.

Thermogravimetric analysis: The test was performed on a Q500 thermogravimetric analyzer (TA Instruments) in a nitrogen atmosphere and at a heating rate of 10°C/min. The temperature profile was set in the range of 25–1000°C.

Differential scanning calorimetry (DSC): The test was performed on a calorimeter 1 Star System (Mettler Toledo) under nitrogen atmosphere and at a scanning rate at 10°C/min.

2.4. Structure and morphology analysis

Fourier transform infrared spectroscopy (FTIR) was used to show the functional groups present in the samples. The test was carried out on the Nicolet 6700 spectrometer in the ATR mode with diamond crystal.

Morphology of the samples was analyzed using a scanning electron microscope (SEM) NovaNano SEM 450 (The Netherlands, produced by FEI). The images were taken using an ETD (topographic contrast) and CBS (material contrast) detector at accelerating 5 kV and 15 kV voltages, respectively.

3. RESULTS AND DISCUSSION

Table 1 contains the data of the mechanical properties of the epoxy resin as a function of the modifiers content. It can be noted that almost all mechanical properties have been improved by the added modifiers. The critical stress intensity factor (K_C), flexural strength and flexural strain at break of the composite containing 1 wt% Nanomer increased by ∼ 15%, ∼ 25% and ∼ 75%, respectively, as compared to the unmodified matrix. However, the epoxy resin modified with 1 wt% Cloisite showed a maximum improvement of ∼ 45% in flexural strength and more than 100% in strain at break, while the impact strength (IS) increased by 20% as compared to the pristine resin. The increase of polymer properties is generally explained by the exfoliation/interaction processes induced by the nanoparticles [40–42]. Unexpectedly, although not modified, Cloisite Na+ led to an appreciable improvement in the properties of the epoxy matrix, which can be compared to that of the Nanomer nanoclay. The nanoclay sheets are no longer parallel to each other, allowing the polymer chains to be placed between them, leading to an improvement in the mechanical, thermal and barrier properties of the polymer nanocomposites [4, 40, 41].

Table 1

Effect of modifier content on mechanical properties of epoxy resin

	Content (wt%)	Impact strength (kJ/m^2)	K_C (MPa·m$^{1/2}$)	Flexural strength (MPa)	Flexural strain at break (%)
Epoxy resin	–	2.78	2.46	71.1	2.6
Nanomer	0.50	2.73	2.37	72.14	5.40
	1.00	2.80	2.90	89.60	4.47
	2.00	2.80	1.90	69.70	3.20
	3.00	2.60	1.80	59.90	4.40
Cloisite	0.50	3.10	2.71	80.80	4.52
	1.00	3.30	2.51	101.90	5.43
	2.00	3.40	2.19	79.30	4.00
	3.00	2.70	2.23	81.30	3.87
PUR	2.50	5.10	2.59	59.48	6.23
	3.50	4.85	2.88	57.75	3.97
	5.00	4.70	2.62	58.08	6.50
	7.50	3.86	2.18	65.08	5.47
	10.00	3.16	2.03	51.65	7.70
	15.00	3.90	2.25	51.00	7.13

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In the case of the polymeric modifier (PUR), IS increased by about 90% at 2.50 wt% PUR, while the resistance to crack propagation expressed by K_C was 15% higher than that of the epoxy matrix containing 3.5% PUR. In addition, a maximum increase in IS of approximately 90% as compared to the neat matrix was obtained by the epoxy blend containing 2.50 wt% PUR. The improvement in IS due to the addition of PUR can be attributed to the formation of a flexible interpenetrating polymer network structure in the blend. The obtained results demonstrated that various properties were increased to different levels depending on the different toughening and strengthening mechanisms involved.

Figure 1 shows the effect of PUR on the impact strength (IS) of the epoxy resin modified with 1 wt% Nanomer or 2 wt% Cloisite. The composition designated 0/0 refers to the epoxy matrix without modifier. It is seen that IS increased then decreased with the increasing amount of the polymeric modifier. Maximum improvement of IS of approximately 55% and 30% as compared to the virgin epoxy matrix, was shown by the hybrid epoxy composite containing 3.5 wt% PUR and 2wt% Cloisite Na+ as well as that with 3.5 wt% PUR and 1wt% Nanomer, respectively. It should be noted that IS of the hybrid epoxy composites exceeded that of the two binary epoxy nanocomposites but not that of the binary epoxy/PUR blend.
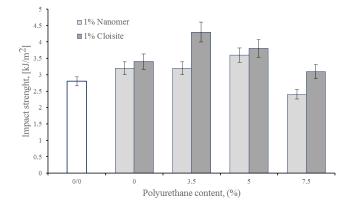

Fig. 1. Effect of polyurethane content on impact strength of epoxy resin modified with Nanomer or Cloisite

The flexibilization of the epoxy samples induced by the liquid modifier can be associated with the increase in the free volume, leading to an increase in movement of the polymer chains, and therefore to a significant ductile deformation before the rupture of the samples. The excess energy would be used to break up the samples, as confirmed by other studies [42, 43]. As already confirmed elsewhere, grafting reactions took place between the reactive groups of the epoxy resin and those of the polyurethane (Fig. 2). This can be easily verified with FTIR spectra with a decrease in the peak height of the reported OH groups at 3500 cm^{-1} [44, 45].

Figures 3 and 4 show the load-deflection curves of the epoxy resin modified with Cloisite and polyurethane, respectively. In the case of the nanoclay, the curves are more linear with a higher load per break. However, the epoxy/PUR blends exhibited non-

Fig. 2. Reaction between the epoxy and polyurethane reactive groups

linear behavior with more pronounced ductility. The energy at break of epoxy nanocomposites was higher than that of neat matrix and PUR based blends (Fig. 3).
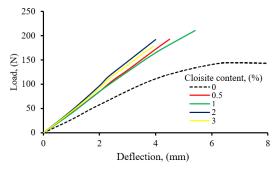

Fig. 3. Load-deflection curves of epoxy resin modified with different amounts of Cloisite
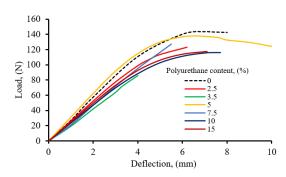

Fig. 4. Load-deflection curves of epoxy blends with different amounts of polyurethane

From Fig. 4, it is seen that the blend based on 5 wt% PUR showed the highest deflection at break and energy to break as compared to the other mixtures and the neat epoxy matrix. This finding can explain the significant improvement of impact strength of the epoxy hybrid nanocomposite (Fig. 1).

The effect of polyurethane content on the critical stress intensity factor (K_C) of the epoxy resin modified with 1 wt% Nanomer or 1 wt% Cloisite is shown in Fig. 5. Although both IS and K_C describe the resistance to crack propagation (fast for the first and slow for the second parameter), we noticed lower values for the latter, which can be explained by the slow release of energy during the process.
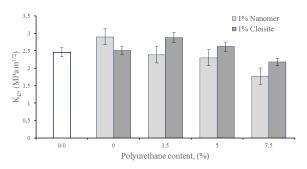
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Fig. 5. Effect of polyurethane content on the critical stress intensity factor (K_C) of epoxy resin modified with Nanomer or Cloisite

Indeed, the addition of Nanomer nanoparticles did not lead to K_C improvement, while maximum increase of the parameter was obtained with 3.5 wt% PUR and 1 wt% Cloisite. This finding might be explained by the different interactions between nanoparticles, the polymer matrix and PUR. The small or lack of improvement in K_C due to the existence of non-linear elastic behavior of epoxy compositions modified with liquid rubbers such as polyurethane was reported in other studies with similar systems [46, 47].

Figure 6 shows the effect of polyurethane (PUR) on the flexural strength of the polymer matrix modified with 1 wt% Nanomer or 1 wt% Cloisite. Although maximum values of flexural strength have been shown by the nanocomposites without the polymeric modifier (i.e. PUR), still higher strength was shown by Cloisite hybrid composites at 3.5 wt% and 5 wt% PUR as well as that of Nanomer at 3.5 wt% PUR. It can be mentioned that the lack of sufficient interaction between the nanoclays, the polyurethane and the epoxy resin did not lead to an improvement in the flexural strength of the polymer matrix. The decrease in flexural strength of the epoxy/nanoclay composites has been already reported elsewhere and has been attributed to the shear yielding upon nanoclay loading and the flexibilization of the polymer matrix [4, 42]. Furthermore, it is understandable that the existence of interactions between the hybrid polymer constituents can greatly improve the properties of the matrix.
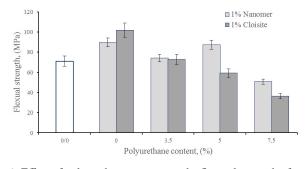

Fig. 6. Effect of polyurethane content on the flexural strength of epoxy resin modified with 1 wt% Nanomer or 1 wt% Cloisite

The effect of montmorillonite (Cloisite) content on impact strength (IS) of the hybrid epoxy matrix modified with 1 wt% Nanomer is shown in Fig. 7. A maximum increase in IS of approximately 18% as compared to the pristine matrix was ob-

tained with the hybrid epoxy nanocomposite containing 0.5 wt% Cloisite and 1 wt% Nanomer. The hybrid nanocomposite exhibited a synergistic effect towards the binary epoxy nanocomposites, due most likely to specific interactions between the nanoparticles and the epoxy matrix. It has already been reported that the nanoclays platelets display intercalated and/or exfoliated form within the nanocomposites, leading to improved mechanical properties of the polymer composite. Another aspect which can be considered is the interaction with the nanoclays themselves through the reactive groups of their respective modifier [38–40].
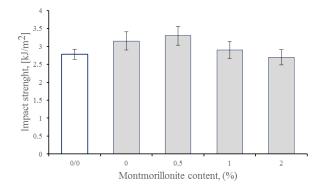

Fig. 7. Effect of Cloisite nanoclay content on impact strength of hybrid epoxy matrix modified with 1 wt% Nanomer

The variation of the critical stress intensity factor (K_C) of the epoxy resin modified with 1 wt% Nanomer as a function of Cloisite content is presented in Fig. 8. The resistance to slow crack propagation expressed by the K_C parameter was maximum at 1 wt% Nanomer without Cloisite nanoparticles. This finding proves that the two processes of crack propagation are different for Charpy and K_C tests.
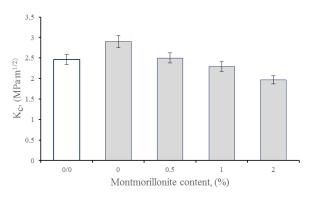

Fig. 8. Effect of montmorillonite (Cloisite) content on the critical stress intensity factor (K_C) of the epoxy matrix modified with 1 wt% Nanomer

The effect of Cloisite content on the flexural strength of the epoxy matrix modified with 1 wt% Nanomer is shown in Fig. 9. A synergistic epoxy composites strengthening was obtained with a hybrid nanocomposite prepared with 0.5 wt% Cloisite and 1 wt% Nanomer. Indeed, its strength (98.3 MPa) was higher than that of Nanomer and Cloisite based binary nanocomposites by about 10% and 22%, respectively, while IS exceeded that of virgin epoxy matrix by 38%.
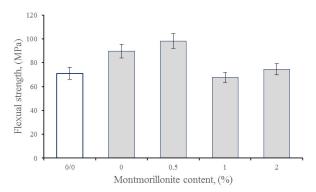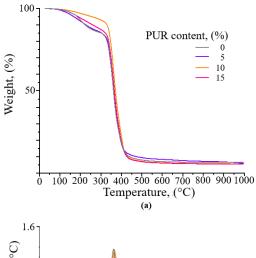
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Fig. 9. Effect of Cloisite content on the impact strength of epoxy resin modified with 1 wt% Nanomer

Thermal stability of the different epoxy samples was evaluated using thermogravimetric analysis (TGA) in the form of weight loss as a function of temperature. As shown graphically in Fig. 10, representing the thermograms of epoxy/polyurethane blends, the virgin epoxy resin was characterized by two stages of decomposition, at 128°C and 331°C. The decomposition process is in agreement with that of the epoxy composites based on microparticles [48].
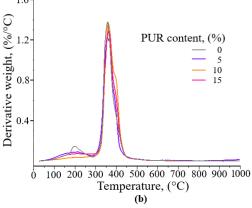

Fig. 10. TGA (a) and dTG (b) thermograms

The temperature corresponding to 5% of the weight loss of the sample was 192°C. The peaks of both stages of the decomposition process can be read accurately from the dTG curves.

The first stage occurred at 200°C and was associated with about 14% weight loss. The peak of the second stage was noted at 358°C with a total weight loss of 93.5%. However, the addition of 10 wt% PUR delayed the occurrence of the first stage of decomposition (corresponding to 5% weight loss) from 192°C to 254°C. The onset of decomposition temperature of two other EP/PUR blends was close to that of pure epoxy. The blend modified with 5 wt% PUR stands out because it had two peaks during the second stage of decomposition, which were observed at the temperatures of 357°C and 366°C.

The relevant decomposition temperatures of the epoxy composites containing Cloisite and Nanomer nanofillers are summarized in Table 2.

Table 2
Temperatures of degradation of epoxy nanocomposites modified with Cloisite and Nanomer

Nanoclay	Modifier content (%)	Temperature at 5% weight loss (°C)	Temperature at max. weight loss (°C)	Temperature of end of degradation (°C)
	0	192	358	430
Cloisite	0.5	334	370	429
	1	334	370	429
	2	334	370	432
Nanomer	1	330	368	434
	2	330	368	434
	3	200	363	426

Unlike the virgin epoxy matrix, these composites were characterized by a single-step decomposition process. The temperatures corresponding to 5% weight loss for both nanofillers were approximately 75% higher than those of the virgin polymer matrix. The temperature of greatest weight lost and that of end of degradation (lower plateau) were similar for all nanocomposites, and were at the level of 370°C and 430°C, respectively. The only sample deviating from this pattern was the one modified with 3 wt% Nanomer, which showed a slightly lower temperature.

Differential scanning calorimetry (DSC) thermograms of the epoxy resin modified with different amounts of polyurethane are shown in Fig. 11. It can be noted that the unmodified resin was characterized by a glass transition temperature of approximately 26°C recorded at endothermic peak. As expected, the addition of flexible chains of polyurethane shifted the glass transition temperatures (Tg) to a level below −60°C. It is well known that Tg of a polymer is associated with its degree of crosslinking during the curing process. The presence of a double peak appearing at the temperatures of 47°C and 56°C can indicate the crosslinking of the polymer matrix resin and its softening temperature, respectively. The range of use of pure epoxy resin was between +28 and +56°C for the unmodified matrix and changed with the addition of nanofillers. Regardless of the amount of polyurethane added, the glass transition temperature was approximately −60°C. For the sample modified with 10 wt% PUR, the peak corresponding to the curing of the resin and its softening temperature practi-

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cally disappeared completely. The softening temperature of the other composites modified with PUR did not change significantly. The range of use of the polyurethane-modified epoxy was the widest for the blend modified with 10 wt%, and was about 130°C higher than that of the pure resin.
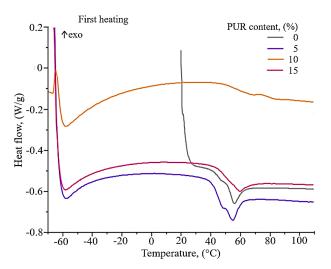

Fig. 11. DSC thermograms of epoxy resin modified with different amounts of polyurethane

Table 3 shows the transition temperature values of the epoxy resin modified with Cloisite and Nanomer nanofillers. It is seen that the glass transition temperature (Tg) did not change with the addition of nanofillers, in contrast with the softening point and degradation temperature, which both increased. However, epoxy nanocomposites prepared with 1 wt% and 2 wt% Nanomer nanofiller showed a significant increase in softening temperature of 167°C, which was about 30°C higher than that of the pure matrix. A similar trend was obtained with the degradation temperature of the nanocomposites, exceeding that of the unmodified matrix by 65°C.

Table 3

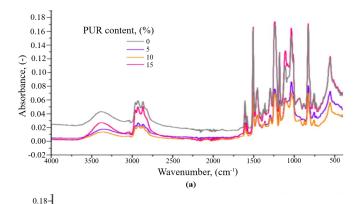Transition temperatures of epoxy resin modified with Cloisite and Nanomer

Nanoclay	Nanoclay content (%)	Glass transition temperature (°C)	Softening point (°C)	Degradation temperature (°C)	Range of use (°C)
	0	26	56	100	+26÷+56
Cloisite	0.5	26	88	166	+26÷+88
	1	27	88	166	+27÷+88
	2	27	88	166	+27÷+88
Nanomer	1	26	84	167	+26÷+84
	2	27	82	165	+27÷+82
	3	22	56	110	+22÷+56

Consequently, operating temperature range of the nanocomposites increased also approximately by 65°C, while the softening temperature of the sample containing 3 wt% Nanomer was

close to that of the pure resin. The increase in the degradation temperature of polymer nanocomposites with the addition of platelet nanofillers can be explained in a similar manner to the improvement in the barrier properties of the polymer nanocomposites by the blockage of heat transfer or gas path [48].

3.1. Structure and morphology analysis

Figure 12 shows the FTIR spectra of the unmodified epoxy resin, its blends with polyurethane (Fig. 12a), its nanocomposites with Cloisite (Fig. 12b) and those based on Nanomer (Fig. 13c). As we can see, the peaks appear at the same wavenumber ranges, regardless of sample composition. All the characteristic peaks of the matrix and modifiers were observed: a broad peak in the frequency range 3500–3000 cm^{-1}, which is attributed to OH stretching vibrations, asymmetric C-H stretching vibrations of the CH_3 groups (2967 cm^{-1}); asymmetric stretching vibrations C-H of the CH_2 groups (2947 cm^{-1}); symmetric C-H stretching vibrations of CH_2 and CH_3 groups (2880 cm^{-1}); C-C, C-N stretching vibrations (2880 cm^{-1}); (1606, 1582, 1496
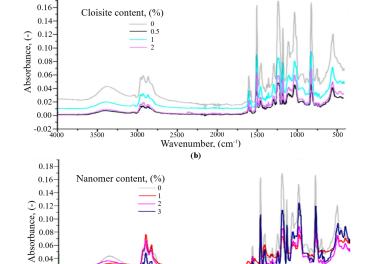

Fig. 12. FTIR spectra of epoxy resin and its blends with polyurethane (a), nanocomposites with Cloisite (b) and nanocomposites based on Nanomer (c)

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and 1455 cm^{-1}); asymmetric C-H bending vibration in CH$_2$ (1300 cm^{-1}); C-O aliphatic stretching vibrations (1250 cm^{-1} and 1195 cm^{-1}) and characteristic vibrations of the epoxy groups at 915 cm^{-1}.

Distinct differences were noted in the intensity of the OH group peaks of the samples containing polyurethane and those based on Cloisite and Nanomer. In the samples containing 5 wt% and 10 wt% PUR (Fig. 12a), the intensity of the peaks associated with the vibrations of the O-H groups (at 3300 cm^{-1} and 600 cm^{-1}) and epoxy groups (at 915 cm^{-1}) is significantly lower by about 60% as compared to pure epoxy resin. This may confirm the reaction between the OH groups of the epoxy matrix and the PUR reactive groups. It has already been reported that such grafting reaction explains the improvement of the mechanical properties of the polymer matrix [40, 43]. Similar changes were recorded for the epoxy nanocomposites based on 0.5 wt% and 2 wt% Cloisite, shown in Fig. 12b.

Indeed, we observed a decrease of the peaks height of the OH groups (at 3300 cm^{-1} and 600 cm^{-1}), epoxy groups (at 915 cm^{-1}) and C-H groups (at 2947 cm^{-1} and 2880 cm^{-1}) in CH$_2$ and CH$_3$, respectively, in the aliphatic chain. Similar results were obtained with nanocomposites containing 1 wt% and 2 wt% Nanomer, showing the greatest decrease of the peak height at the wavenumber of 3300 cm^{-1}. With the increase in the amount of added modifier, this peak became more and more distinct and for the composite modified with 3 wt% MMT, it was close to that of pure resin. However, it was shown that the addition of 1 wt% modifier caused the best interactions with the OH groups, and thus it was described as the optimum amount of the nanofiller to be used.

The confirmed interactions between the epoxy resin and the modifiers (Fig. 12a, Fig. 12b and Fig. 12c) resulted in improved mechanical properties of the epoxy resin but also allowed the determination of the reinforcement mechanisms of the polymer matrix.

SEM micrographs of unmodified epoxy resin and epoxy composites based on different amounts of modifiers are presented in Figs. 13 and 14, respectively. The images of the unmodified resin, epoxy blends and nanocomposites were obtained by scanning the fracture surfaces of the samples after their rupture under impact loading. As expected, the fracture surface of the neat resin is flat with a regular crack propagation path.
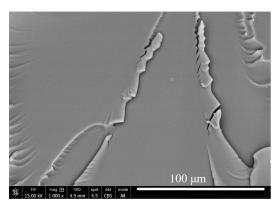
This image is typical for glassy and brittle materials, which in general exhibit a low impact strength. However, all other micrographs of the matrix modified with flexible polyurethane or solid nanoparticles show significant roughness of the fracture surfaces with the formation of elongated platelets, explaining the increase in mechanical properties of the epoxy matrix. As the amount of added PUR increased, the fracture surface was wrinkled, rougher and more uniform, most probably due to the flexible chains of the modifier. Unexpectedly, in the case of the Cloisite based nanocomposites, the fracture surface shows superimposed and aligned platelets, with shear yielding. However, the micrographs of the sample containing 2 wt% and 3 wt% Nanomer exhibited a more uniform surface with good distribution of nanoparticles within the matrix. Similar morphologies were observed with other polymer nanocomposites [49].
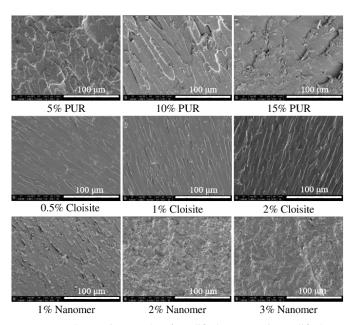

Fig. 14. SEM micrographs of modified epoxy resin modified

4. CONCLUSIONS

The following conclusions are drawn from the results obtained:

This work confirmed the successful preparation of epoxy hybrid composites with improved properties. The impact strength (IS) of the hybrid composites based on polyurethane/Cloisite and polyurethane/Nanomer was maximally increased by 55% and 30%, respectively, as compared to the neat epoxy matrix, exceeding that of the two binary epoxy nanocomposites. Maximum increase in IS of $\sim 20\%$ as compared to the matrix was shown by the hybrid nanocomposite containing 0.5 wt% Cloisite and 1 wt% Nanomer, with a synergistic effect towards the binary systems, due most probably to specific interaction between the nanoparticles and the polymer matrix.

The addition of polyurethane and nanoclays increased the thermal stability of epoxy composites significantly. As expected, the DSC results showed that the addition of flexible polyurethane chains decreased the glass transition temperatures, while the softening point and the temperature range of use of epoxy

Fig. 13. SEM micrograph of unmodified epoxy matrix

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nanocomposites containing nanofillers have increased. FTIR analysis confirmed the occurrence of interaction between the epoxy matrix and added modifiers. SEM micrographs of the epoxy composites showed significant roughness of the fracture surfaces with the formation of elongated platelets and some shear yielding, explaining the increase in mechanical properties of the epoxy matrix.

Hybrid epoxy composites with improved performance properties can be successfully used in applications of conventional epoxy composites but also under severe conditions.

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