Composite materials from fully bio-based thermosetting resins and recycled waste poly(ethylene terephthalate)

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ABSTRACT

During the last two decades, interest in bio-based polymers, especially in bio-based composite materials, has grown as a result of environmental concerns. In this paper new composites obtained from fully bio-based unsaturated polyester resin (UPR) and waste poly(ethylene terephthalate) (PET) were studied for the first time. The composites were prepared by crosslinking the UPR in the presence of functionalized PET particles (3, 6 and 9 wt %), using dimethyl itaconate as reactive diluent. The results showed that the incorporation of the PET particles led to the increase in mechanical properties. However, higher PET loading caused a decrease in the mechanical properties of the composites because of the PET particle agglomeration.

1. Introduction

Due to a good balance between mechanical properties, cost, processability and adaptability to the various industries, unsaturated polyester resins (UPR) are widely used among the thermoset polymer materials [1]. Almost exclusively commercial UPRs have a petrochemical origin which could be seen as a serious disadvantage from both economic and environmental perspective [1]. Furthermore, recent studies showed that UPRs pose health risk due to the use of styrene as almost the exclusive reactive diluent of choice for UPRs. Namely, styrene is classified as a suspected carcinogen, neurotoxin, and respiratory tract irritant and poses a health risk for employees who are exposed to either vapours or physical contact with the styrene monomer [2]. To overcome or mitigate such disadvantages, in the last years, several UPRs based on 'green' monomers, i.e. derived from biomass, have been synthesized. The majority of studies investigated fatty acid-based monomers as bio-based alternative to petrochemical UPRs [3–6]. Although these resins showed low volatility, their moderately high viscosity limited their usage. Also, UPRs from this group showed elastomeric properties as a consequence of lower crosslinking density and higher content of aliphatic chains i.e. the lack of stiff aromatic groups from styrene. Aromatic bio-based monomers, mostly lignin derivate, were investigated as a promising way to increase UPR stiffness

[7,8]. These resins showed high values of storage moduli (over 3 GPa), still relatively high viscosity of aromatic monomers limited their usage due to the processing issue. In order to lower viscosity of bio-based UPRs, some authors designed systems composed of oligomers and/or monomers [9–12]. These UPRs also possessed elastomeric behaviour (low storage moduli and glass transition temperature and high elongation at break). Unsaturated cyclocarbonates were investigated as low viscosity styrene replacement. They have been proven as less harmful compounds but their lower reactivity has made them unsuitable as reactive diluents for UPRs. Cousinet et al. achieved promising results using vinyl levulinate as reactive diluent [13]. This UPR exhibited lower α relaxation temperature, elastic moduli at the rubbery plateau and mechanical properties determined by the three points bending test. UPRs with good mechanical properties were prepared using various bio-based methacrylates as styrene replacement [14]. Bearing in mind that there is no industrial production of bio-based methacrylates, the usage of these monomers will lower the bio-based content of the resin.

As presented, a variety of UPRs derived from bio-based monomers have been investigated, still these materials cannot keep appropriate features of ones with styrene. An increase in resin viscosities, low glass transition temperature, low elastic and storage modulus were the main problems which can be attributed to unusual reactivity of the prepolymer fumarate groups with other kinds of the double bonds on the

bio-based reactive diluent [14]. To overcome this issue, in our previous studies, we synthesized several UPRs where prepolymer and reactive diluent were both based on itaconic acid [15,16]. The UPR where prepolymer was prepared from itaconic acid, succinic acid and propylene glycol, while dimethyl itaconate was used as reactive diluent exhibited good applicative properties. We showed that this resin could be used for the preparation of gel coat. In order to be used for other applications, the mechanical properties of these resins should be further improved.

The development of novel composites has attracted the attention of material scientists as efficient, easy and cost-effective method to improve bio-based UPRs properties. Various fillers have been used for this purpose such as glass fibre [1], natural fibre [17], nano clay [18], lignin [19], etc. In the recent years, there has been increased interest in the preparation of UPR composites using waste materials because of their availability, low cost, and low carbon footprint. The use of waste paper [20,21], agricultural wastes [22,23], waste printed circuit board [24], scrap tire [25], waste Tetra Pak [26], waste fabric [27], waste grass broom fibre [28], etc have been investigated. These studies indicate a wide variety of pathways that have unfortunately not yet led to widespread application and use of effective filler for bio-based UPRs. Factors such as high viscosity, low mechanical properties, and/or application issues have limited their use to many applications.

As a ductile material, PET has been used as filler in various composites to enhance material properties [29–33]. It has excellent mechanical strength, inertness to many chemical reactions, and good thermal resistance [29]. Additionally, similarity of PET and UPR chemical structure will ensure good miscibility and moderate interface adhesion leading to improved physical–chemical properties. Furthermore, waste PET is present in abundant amount worldwide because of its widely usage for bottles, containers, woven sacks, and food packaging [34]. Nowadays, around a million of PET bottles per minute are discarded worldwide and it is expected to increase by 20% by the 2021 [35]. Unfortunately, the discard rate of PET bottles is greater than its recycling rate [36], and can lead to serious environmental problems due to littering, illegal landfilling, and incinerating [37]. One of the best ways to lower the environmental risk is to reduce PET waste by recycling. This research paper focuses on the investigation of waste PET as a suitable reinforcement for bio-based UPRs. The aim of this paper is particularly targeted at the establishing structural/properties relationship using mechanical, dynamic mechanical and thermomechanical analysis.

2. Experimental

2.1. Materials

The itaconic acid, succinic acid, 1,2-propandiol, hydroquinone, and dimethyl itaconate were supplied by Sigma Aldrich and are used as received. Methyl ethyl ketone peroxide (MEKPO) was used as the initiator. Recycled PET flakes were purchased from Jugoplastic recycling, RS (transparent, whit dimension of flakes 8 × 12 mm) and were used as received.

2.2. Extrusion of recycled PET fibers

The small laboratorial vertical extruder was used to homogenize and even recycled PET flakes. The inlet temperature of extruder was 265 °C while the output temperature was 165 °C. The extruder was set at those temperatures for 30 min before the initial feeding and continuously monitored during operating time. Extrusions process was carried out under atmospheric pressure. The raw material was fed using one batch charge of 100 g. Recycled PET fibers were automatically hauled on the coil. The obtained fibers had diameter of 50 ± 10 μm. After cooling the recycled PET fibers were chopped to a length of 3 ± 0.2 mm.

2.3. Chemical surfaced activation of recycled PET fibers - aminolysis reactions

The aminolysis reactions were carried out according to Bech et al. [38]. PET (1.5 g) was added in a round-bottom flask containing 25 mL of the corresponding diamine (1,6-diaminohexane or 3,6-dioxa-1,8-diaminooctane), which was previously thermostated at 50 °C in an oil bath. The reaction mixture was moderately stirred for 20 min. The PET particles were then carefully removed from the liquid phase, washed successively with methanol and water, and dried in vacuum at room temperature for ca. 8 h. The weight loss was around 5% for both methods. The aminated PET particles (1.0 g) were dispersed in 20 mL of dichloromethane and itaconyl chloride (0.055 mL) and triethylamine (0.65 mL) were added. The reaction mixture was moderately stirred for 1 h at room temperature. The particles were then separated from the solution, washed successively with aqueous solution of $NaHCO_3$ and water, and dried in vacuum at room temperature for ca. 8 h.

2.4. Synthesis of UPRs reinforced with recycled PET

The prepolymer was synthesized by melt polycondensation with diacids and 1,2-propanediol as described in detail by Fidanovski et al. [16]. The synthetized UPR was mixed with MEKPO (2.5% w/w) and with functionalized recycled PET particles in amounts of 3, 6 and 9 wt %, homogenized and poured into Teflon molds. The samples were cured at 60 °C for 24 h and at 120 °C for additional hour.

2.5. Functionalized PET particles characterization

Functionalized PET particles size and size distribution were determined by optical microscope (Olympus CX41RF, Tokyo, Japan) using ImageJ software.

2.6. Characterization of composite materials

The cross-section morphology of composite materials was studied by JEOL JSM–6610L scanning electron microscope (SEM). All the SEM samples were coated with platinum using LEICA SCD005 nebulizer. The dynamic mechanical properties of prepared composites were examined by Discovery Hybrid Rheometer HR2 (TA Instruments, New Castle, DE, USA) in the torsion deformation mode. Dimensions of tested samples were: 58 mm × 12 mm × 2 mm. The experiments were performed in the temperature range from 25 °C to 150 °C, at fixed strain amplitude of 0.1% and a single angular frequency of 1 Hz. The storage modulus (G'/GPa), loss modulus (G''/MPa) and damping factor ($tan\ \delta$) were determined. The mechanical properties of the composites were tested through both uniaxial tensile testing and dynamic mechanical testing (DMA). Tensile testing was performed with the Shimadzu Servopulser according to ASTM D638. Five specimens of each sample were tested at a rate of 0.5 mm min^{-1}.The elastic moduli, tensile strength and elongation at break were calculated and analyzed. DMA testing was conducted with the Discovery Hybrid Rheometer HR2 (TA Instruments), in which the thin rectangular samples (58 mm × 12 mm × 2 mm) were loaded into a tension fixture and subjected to a test at fixed strain amplitude of 0.1% and a single angular frequency of 1 Hz at a temperature range from 25 °C to 150 °C. The values of storage modulus (G'/GPa), loss modulus (G''/MPa) and damping factor ($tan\ \delta$) were obtained. The glass transition temperature (T_g/°C) was obtained as the temperature at which tan δ had a maximum value. The coefficients of thermal expansion of the prepared samples were determined by thermal-mechanical analysis (TMA) in the expansion mode by Q400 (TA Instrument). The experiments were performed at constant load of 10 mN under argon atmosphere (100 mL min^{-1}). The temperature range was from 0 °C to 115 °C and a heating rate was 10 °C min^{-1}.
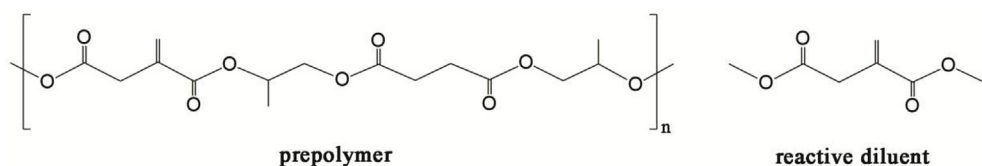
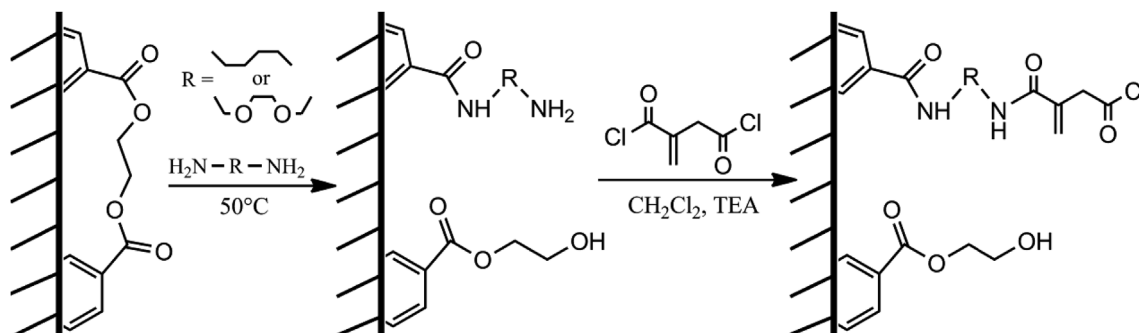Fig. 1. Chemical structure of prepolymer and reactive diluent.

Fig. 2. Surface functionalization of PET by diamines and itaconyl chloride.

3. Results and discussion

In this study fully bio-based UPR was prepared by environmental benign bulk polycondensation. Prepolymer was synthesized from itaconic acid, succinic acid and propylene glycol while dimethyl itaconate was used as bio-based reactive diluent. The chemical structures of prepolymer and reactive diluent are presented in Fig. 1.

The recycled PET particles were used as active filler to enhance mechanical and thermal properties of prepared bio-based resins. Bearing in mind that active filler efficiency mainly depends on filler/matrix interaction, PET surface was modified by incorporation of double bond functionality via two step modification (Fig. 2). In the first step, amine groups have been incorporated into PET surface throughout aminolysis. Two amines have been used, 1,6-diaminohexane and 3,6-dioxa-1,8-diaminooctane. The sample modified with 1,6-diaminohexane was denoted as PET-H while the sample modified with 3,6-dioxa-1,8-diaminooctane was denoted as PET-O. Composites prepared using modified samples were denoted as UPR-H and UPR-O.

3.1. Optical microscopy

After the functionalization PET particles size were reduced. This reduction was not result of weight loss (due PET dissolution) but the result of particle splintering. Namely, recycled PET flakes were extruded under atmospheric pressure and, due to this low pressure, there were a large number of small cracks and other micro defects in the extruded fibers structure. During the surface functionalization, these micro defects caused particles splintering. The final PET particles size distribution is presented in Fig. 3.

The results of optical microscopy showed that functionalization process with 3,6-dioxa-1,8-diaminooctane gave particles with smaller size. This was due to more effective interactions of 3,6-dioxa-1,8-diaminooctane with PET compared to 1,6-diaminohexane. Namely, ether groups from 3,6-dioxa-1,8-diaminooctane interacted with PET macromolecule via dipole-dipole interactions and thus faster diffuse into PET micro defects and enhance fiber splintering.

3.2. Scanning electron microscopy

Using SEM, high definition images were obtained from tensile test specimens' fracture surfaces to observe the level of dispersibility of PET particles and nature of the fractures. As presented in Fig. 4, PET particles were uniformly dispersed in the samples with 3 and 6 wt% of PET

particles. On the other hand, some agglomeration of the PET particles could be observed in the samples with 9 wt% of PET particles (area indicated with red ellipses in Fig. 4).

After fracture, the fracture surface morphologies of modified and unmodified UPR were observed. Many slim river lines distribute on the fracture surface of unmodified UPR could be seen, which present the typical brittle fracture. Similar fracture surface was observed for samples modified with 3 wt% of PET. On the other hand, samples with higher amount of PET particles exhibited ridges and protruding pieces on the fracture surface indicating plastic deformation and shear yielding. The addition of a dispersed ductile phase (PET particles) in a brittle matrix toughened material mainly due to plastic dissipation during crack-bridging, crack-trapping, crackshielding, or a combination of the above [39]. Furthermore, the fact that fracture mechanism changed from brittle to ductile indicated that PET particles were strongly bonded to a brittle matrix and were free from internal stresses [40].

3.3. Dynamic mechanical analysis

The dynamic mechanical analysis of composites is very useful to analyze the potential of the reinforcement and to probe the interfacial properties of the filler, namely in the presence of a coupling agent. The dependence of storage modulus (G') and loss tangent ($tan\ \delta$) on temperature are presented in Fig. 5. The storage moduli of the composites were found to decrease with temperature. The reduction in storage modulus is associated with an energy dissipation phenomenon involving cooperative motions of the polymer chains with temperature. Incorporating PET particles into the polymer increases the storage modulus over the entire temperature range measured. This increase could be attributed to the reinforcing behaviour of the PET particles. The highest increase in G' values were observed when 6 wt% of PET is added in UPRs. However, further increase in PET content led to the decrease in G' values. This may be associated with the poorer dispersion of PET particles. Namely, filler–polymer reinforcing network, which mainly contributes to the reinforcement, was distorted by agglomeration of PET particles. Comparing DMA results of samples prepared from PET-H and PET-O it could easily be seen that PET-O samples showed better mechanical properties. The key factors affecting the reinforcement are considered to be the microstructure of the filler (particle size, shape, and eventual agglomeration), the polymer's segmental mobility, and the chemistry-specific polymer–filler interactions [41]. In this case it could be assumed that the chemistry-specific polymer–filler
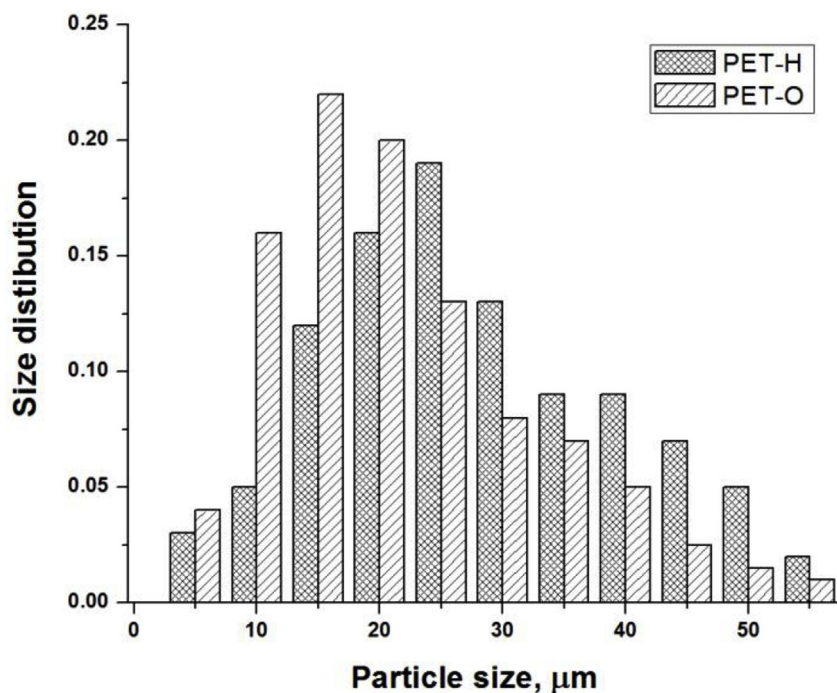
Fig. 3. Size distribution of functionalized PET particles.

interactions were similar because coupling agents had similar structure. Also, the influence of polymer's segmental mobility is the same in all samples because the same resin was used. Thus, it could be concluded that PET particle shape and structure was the governing factor of improved properties. Namely, the higher increase in G' for PET-O samples compared to PET-H samples could be explained by smaller size of PET-O particles and, thus, their higher specific surface area that resulted in formation of denser reinforcing network. In order to further verify aforementioned assumption the experimental crosslink density (n_e) was determined based on the kinetic theory of rubber elasticity using equation (1) [42]:

$$G' = 3n_e RT \tag{1}$$

where G' represents the storage modulus of the cured resin in the rubbery plateau region, R is the gas constant (8.314 J K^{-1} mol^{-1}), T the absolute temperature in K. The calculated values of crosslink density (Table 1) prove our assumption that samples prepared using PET-O exhibited denser reinforcing network. After the glass transition temperature a huge decrease in G' by about two decades is noted followed by the rubbery plateau. This decrease could be explained by the huge increase in polymer chain mobility above T_g. Interestingly, this decrease of storage moduli was less pronounced in samples with 9 wt% of PET compared to other samples, indicating that the agglomerated PET particles restrain the molecular mobility and deformability of the rubbery matrix.

The "C" parameter (equation (2)) is a relative measurement of the decrease in modulus of composites compared to neat resin when temperature increases and the material pass through its glass transition. The lower values of C indicate higher reinforcement of composites at rubbery state.

$$C = \frac{\left(\frac{G'}{G'_{125°C}}\right)_{composites}}{\left(\frac{G'}{G'_{125°C}}\right)_{resin}} \tag{2}$$

The calculated values of C parameter, presented in Table 1 were close to 1 indicating that filler particles equally reinforced material at glass and rubbery state. This is expected because PET has a T_g at around 76 °C, thus above composites' T_g (around 75 °C), filler particles were,

also as matrix, at rubbery state. Interestingly, higher reinforcement was observed for samples prepared with 9 wt% of PET particles. The most likely reason for this was higher interference of neighboring segments, since there must be greater molecular cooperation for the relaxation process to occur [43].

As mentioned before, the reactivity of DMI is lower compared to styrene, and therefore UPRs cured by DMI are more susceptible to various influences. Paauw and Pizzi found that organic fillers are more likely to interact with reactive diluent during curing and affect network structure, and, therefore, cured resin properties [44]. The shape of $tan\,\delta$ curve is indicative of the structure and properties of a particular composite material. The similar shape of $tan\,\delta$ curves (Fig. 5) indicates that all samples had similar network homogeneity, and that PET particles had no significant effect on resin curing and network formation. The T_g values of composites and neat resin were obtained as a peak temperature of $tan\,\delta$ curves. The T_g values, presented in Table 1, were slightly higher for composites than the neat resin duo to the interference of chain segments movement at the particle-resin interface.

3.4. Tensile test

Generally, one of the main drawbacks of bio-based materials are their lower mechanical properties compared to petrochemically based ones. Bio-based unsaturated polyester resins are no exception. The values of tensile strength and elongation at break are usually low. Bearing in mind that PET is ductile material, its incorporation into bio-based resin should improve these properties. Table 2 summarize the effect of different contents of PET particles on tensile properties of bio-based resins.

It can be noticed that the tensile strength and elastic modulus of unsaturated polyester composites increased with increasing PET content. Interestingly, samples with 9 wt% of PET showed the highest values of tensile strength, while samples with 6 wt% of PET showed the highest values of elastic moduli (same as for storage moduli). At first glance these results might be contradictory, but they could be explained by taking into consideration strain at which they are measured. Namely, elastic and storage moduli are measured under very small strains 0.2 and 0.1%, respectively while tensile strength is obtained at
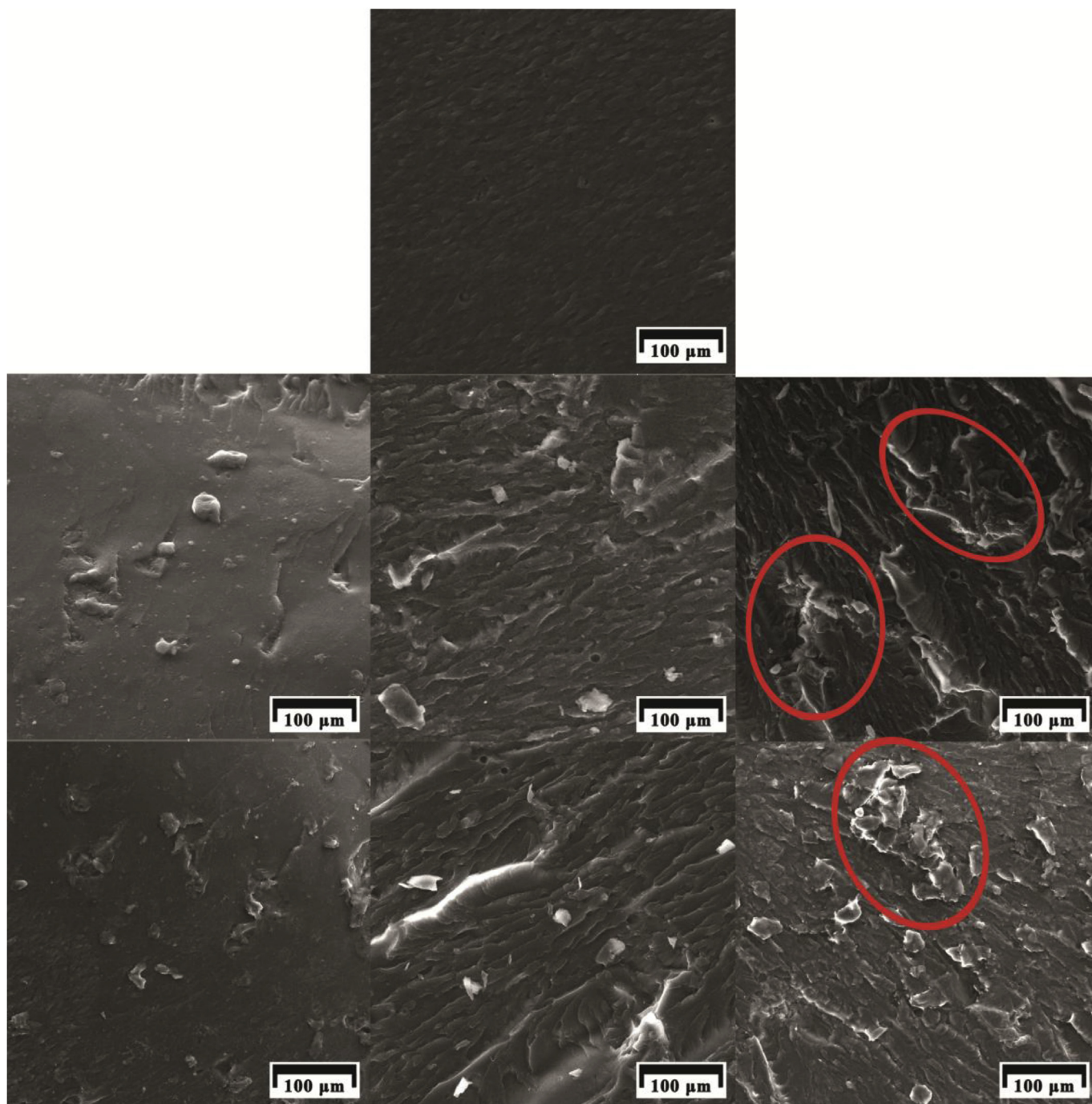
Fig. 4. SEM micrograph of the fractured surface.

much higher strains, more than 4.5% (Table 2). At low strain, the main factor that influenced the mechanical properties are intermolecular forces. Materials with strong intermolecular forces exhibit higher values of moduli. In this work samples with 6 wt% of PET showed the highest values of crosslink density duo to the good dispersibility of PET particles. The elastic and storage moduli of these samples were the highest, because the rate of matrix yielding was reduced due to the high crosslink density [45]. Also, these samples had lower capacity to absorb energy of deformation leading to fracture at lower strains (Table 2). On the other hand, with the increase in PET content, some of the PET particles agglomerated leading to lower crosslink density. Due to this, material had higher ability of energy absorption by matrix yielding and hence lower chance of rapid and catastrophic crack propagation [45].

Furthermore, agglomeration of PET particles led to the formation of microvoids and it is generally accepted that microvoiding of ductile filler particles itself does make a small contribution to absorption of the fracture energy. Namely, voided particles can relax the locally triaxial stress state which favors brittle fracture and then promote energy dissipation through initiating crazing and/or shear yielding of the matrix around them [46–48]. Because of these two factors, samples with 9 wt% of PET particles showed the highest values of tensile strength and elongation at break compared to the other samples.

Although composite materials showed enhanced mechanical properties compared to the neat bio-based resin, they were still lower compared to the mechanical properties of petroleum based UPRs. Namely, petroleum based resins (used for the production of high
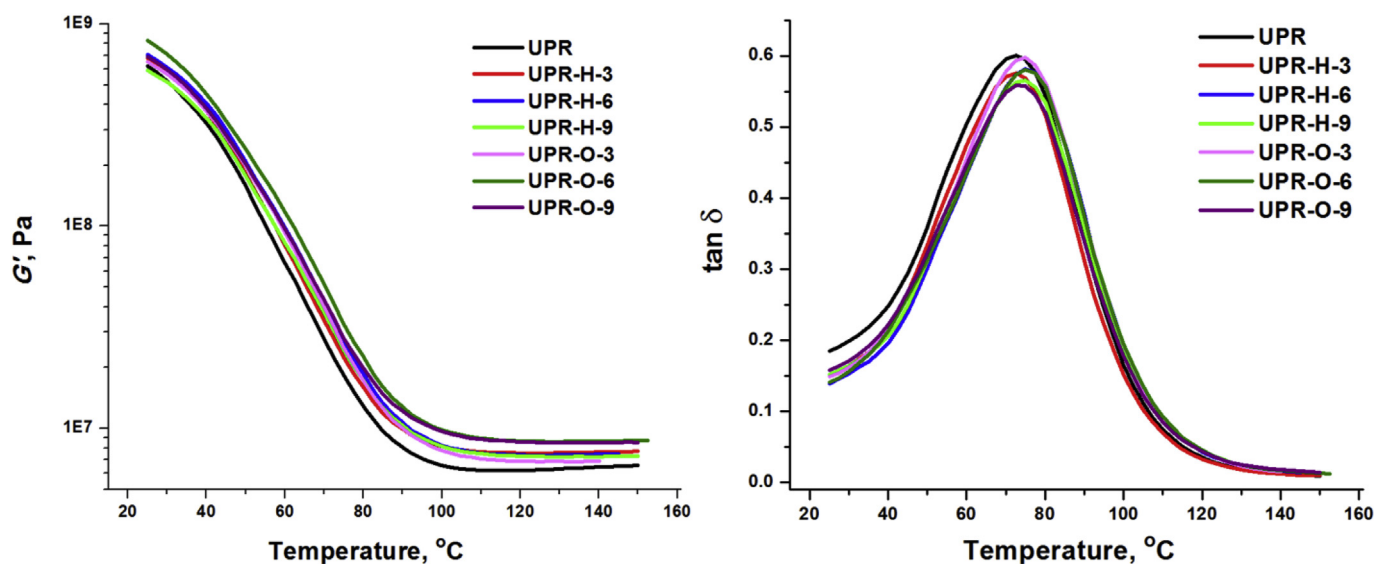
Fig. 5. The dependences of (a) the storage modulus and (b) the loss tangent of the cured resins on temperature.

Table 1
The storage moduli at 25 °C (G') and 125 °C ($G'_{125°C}$), crosslink density (n_e) and glass transition temperature (T_g) of prepared composite materials and neat UPR.

Sample	G', GPa	$G'_{125°C}$, MPa	n_e, mol m^{-3}	T_g, °C	C
UPR	0.62	6.17	1918	72.3	/
UPR-H-3	0.68	7.55	2289	72.5	0.90
UPR-H-6	0.71	7.39	2238	75.2	0.96
UPR-H-9	0.59	7.26	2198	74.3	0.81
UPR-O-3	0.65	6.86	2077	74.4	0.94
UPR-O-6	0.83	8.62	2611	75.3	0.96
UPR-O-9	0.69	8.52	2580	73.5	0.81

Table 2
Tensile strength (σ), elongation at break (ε), elastic modulus (E) and average values of *CTE* in the temperature range of 20–45 °C and 90–115 °C of prepared composite materials and neat UPR.

Sample	σ, MPa	ε, %	E, MPa	CTE, 10^{-6} °C^{-1}	
				20–45 °C	90–115 °C
UPR	20.68	7.32	198	96.8	141.4
UPR-H-3	19.53	5.71	303	96.4	127.4
UPR-H-6	30.51	4.96	652	94.1	126.2
UPR-H-9	36.49	6.24	569	77.3	117.0
UPR-O-3	24.06	4.46	344	96.4	137.2
UPR-O-6	30.27	4.92	807	91.3	124.7
UPR-O-9	34.50	5.72	627	88.6	121.3

performance composite materials) usually have G' in the range of 2–3 GPa, σ in the range of 55–75 MPa, E in the range of 2–3 GPa and T_g in the range of 100–150 °C. These high values are results of high crosslink density and high content of aromatic groups, as a consequence of usage of styrene as reactive diluent. Thus, in the future studies efforts have to be paid to the selection of an aromatic bio-based co-diluent with good miscibility with DMI and ability to homopolimerize, and to copolymerize with DMI and unsaturation in prepolymer. In this case, DMI would be used to control UPR viscosity, while aromatic co-diluent will be used to tune final network properties yielding materials exhibiting a compromise in properties.

3.5. Thermomechanical analysis

In polymers, especially thermosetting resins, the *CTE* is an important thermophysical property because it governs many applicative properties, such as dimensional stability [49]. The *CTE* of the samples was determined from the slope of the heating part of the second thermal cycles in two different intervals, below and above the expected glass transition temperature. The obtained values of *CTE* are presented in Table 2. Generally, expansion of polymer materials shows a gradual increase with temperature [50], but this increase is negligible compared with the variations of the *CTE* on passing through the glass transition regions.

A decrease in *CTE* values with an increase in PET content could be observed in the first temperature region (20–45 °C). Below the T_g, the expansivity is much reduced because the polymer chains have less room to "wiggle" due to the closer packing and stronger intermolecular forces. The increase in crosslink density with the increase in PET content led to the decrease in *CTE* values. Moreover, the CTE of the composites were reduced due the existence of voids in the matrix. This effect of voids on lowering composite *CTE* was also observed by other authors [51]. The lowest values of *CTE* were observed for samples with 9 wt% of PET due to the highest void concentration.

The same trend for *CTE* was observed in the second temperature range (90–115 °C). However, the lower values of *CTE* of composites compared to neat resin were more pronounced in rubbery region than in the glassy region. This fact indicates good dispersibility of PET particles and good adhesion between particles and resin which omits polymer chain movement and thus reduces *CTE*.

4. Conclusion

In this study, novel composite materials were prepared by crosslinking fully bio-based UPR in the presence of recycled PET particles (3, 6 and 9 wt%), using dimethyl itaconate as reactive diluent. In order to enhance interactions and compatibility between PET and UPR, PET surface was modified by grafting of itaconyl groups. The grafting has been done via PET aminolysis (1,6-diaminohexane and 3,6-dioxa-1,8-diaminooctane) followed by amidation with itaconyl chloride. The SEM analysis showed that, up to 6 wt%, PET particles were homogenously dispersed throughout polymer matrix. However, further increase in PET content led to the slight particle agglomeration and void formation between agglomerated particles. The DMA and tensile tests showed that composites exhibit better mechanical properties compared to neat resin. The storage moduli of composites ranged from 0.65 to 0.83 GPa, while elastic moduli ranged from 0.30 to 0.81 GPa. Storage and elastic moduli of neat resin were 0.62 and 0.20, respectively. The higher

values of storage moduli (0.65–0.83 GPa) and elastic moduli (0.30–0.81 GPa) of composites compared to neat resin (G' = 0.62, E = 0.20) could be explained by reduced rate of matrix yielding due to the higher crosslink density of composites. Tensile strengths of the composite materials were also increased due to the higher crosslink density. The coefficients of thermal expansion of the composites were found to be lower than the neat resin due to the two factors: increased crosslink density and existence of voids in the matrix.

The obtained results from the DMA, TMA and mechanical analysis showed that the variation of mechanical properties, between composites prepared from PET particles functionalized by two different methods, was consequence of different PET particle size and size distribution. The similar shape of *tan δ* curves indicates that all samples had similar network homogeneity, and that PET particles had no significant effect on resin curing and network formation.

These results show that the mechanical properties of composites cannot entirely compete with commercial glass fiber reinforced unsaturated polyester composites. Nonetheless, considering the high renewable ratio, relatively low price for the recycled PET, and very low carbon footprint these composites show promising properties for making commercial products with a high renewable content.

Acknowledgment

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.compositesb.2018.07.034.

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