



Hyperbranched polymers as modifiers of epoxy adhesives



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ABSTRACT

A novel hyperbranched poly(amide-ester)s (HBP) has been synthesized through the AB₂ approach in one-step polycondensation without solvents. The synthesized HBP has been characterized and used as filler for epoxy resin with the aim obtain materials which exhibit improved toughness. Composites containing 6% and 12% wt/wt of HBP in diglycidylether of bisphenol A (DGEBA) were produced and characterized. Results obtained from DMA tests showed that HBP has good compatibility with the epoxy resin. Impact tests proved that composites containing 12% HBP showed an improvement of about 25% on impact strength with respect to neat DGEBA. Moreover, adhesive properties were evaluated in terms of the lap-shear strength value of composite joints bonded using the investigated blend. Results showed an improvement of shear strength value of DGEBA added with 12% HBP with respect to neat DGEBA. The water uptake behavior was also evaluated.

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1. Introduction

Polymeric adhesives can offer several advantages compared to the traditional joining methods as the ability to join different materials coupled with the obtainment of a light-weight, but strong and stiff structures. Also, polymeric adhesives may be used to efficiently join thin-sheet materials which, due to their low bearing strength, cannot be readily joined by other methods [1]. Epoxy adhesives represent the most common type of structural adhesives. When polymerized, epoxy adhesives are amorphous and highly-crosslinked materials and this microstructure results in many useful properties for structural engineering applications, such as a high modulus and failure strength, low creep, and, good performance at elevated temperatures. However, they can be relatively brittle materials, with a poor resistance to crack initiation and propagation. Nevertheless, the incorporation of a second phase of dispersed rubbery particles into the epoxy polymer can greatly increase their toughness without significantly impairing the other desirable engineering properties. In the literature, several works are reported dealing with the obtainment of rubber-toughened epoxy adhesives [2–4]. They can be used, for example, in applications where a very high impact resistance is required for the adhesively-bonded joint.

In the last decade, hyperbranched polymers (HBPs) have been synthesized as a new class of three-dimensional macromolecules [5,6]. Hyperbranched polymers, because of their unique structure, are known to exhibit lower melt and solution viscosities than lin-

ear polymers of the same molar mass. A significant advantage of hyperbranched polymers is the high density of functional end groups on the shell.

The use of suitable end groups, such as amine and carboxylic groups, can enhance the compatibility between HBP and other polymeric matrices. Because of these properties, hyperbranched polymers constitute a new class of modifiers for epoxy resins. In the literature, several works deal with the modification of epoxy resins with hyperbranched polymers [7–9]. In particular, the use of hyperbranched polymers (HBPs) as toughener for thermoset resins has been reported [10–14]. Some papers deal with the use of aliphatic polyesters based on bis-hydroxymethyl propionic acid, others deal with the use of a novel synthesized polyimide and of a commercially available aliphatic poly(ester-amide). The structure of this latter one presents the advantages that hydroxylic groups at the chain end allow the covalent bonding of the HBP to the matrix, the aliphatic structure can increase the flexibility of the network and the presence of secondary alkyl esters can help to increase the thermal degradability of the materials.

The novelty of the present work is the use of a novel synthesized hyperbranched poly(amide-ester)s (HBPs) through the AB₂ approach in one-step polycondensation without solvents, as filler for an epoxy resin. The synthesized HBP has been characterized and used as filler for the epoxy resin diglycidylether of bisphenol A (DGEBA) with the aim to improve the toughness of the obtained composites materials. Thermal, mechanical and adhesive properties of the DGEBA/HBP composite have been investigated.

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2. Experimental section

2.1. Materials

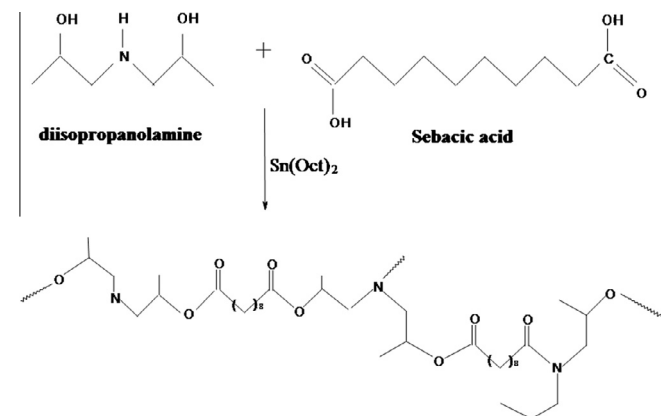
Diisopropanolamine (DIPA), sebacic acid (SA) and Stannous 2-ethylhexanoate, $[\text{Sn}(\text{Oct})_2]$ used for the synthesis of hyperbranched polymers, tetrahydrofuran (THF) and dimethyl sulfoxide (DMSO) were purchased from Sigma–Aldrich. Diglycidylether of bisphenol A, Epon-828, (DGEBA) and Epicure curing agent 3234, triethylene tetramine (TETA) were supplied by Hexion Speciality Chemicals. All chemicals were analytical grade and used without further purification.

2.2. Hyperbranched polymers synthesis

Equimolecular amounts of DIPA and SA were placed and pre-mixed in a vessel immersed in an oil bath and maintained at 140 °C for 10 min, with sufficient stirring provided. The reactants were pre-mixed in the presence of a catalytic amount of $[\text{Sn}(\text{Oct})_2]$ ($\approx 0.20\%$ mol). Then the reaction was carried out controlling the temperature at 185 °C by a thermocouple for 4 h under vacuum in a oven, followed by slow cooling to room temperature. The resulting material was purified by washing with methanol and then dried under vacuum at 80 °C until a slightly yellow soft polymer was obtained. The hyperbranched polyesteramide reaction scheme is shown in Scheme 1.

2.3. Preparation of DGEBA/HBP mixtures

The DGEBA epoxy resin was obtained choosing an amine-to-epoxy ratio of 13.1 phr (parts of curing agent per hundred parts of resin by weight). HBP was dissolved completely in few millilitres of DMSO at 170 °C and, after cooling, the obtained solution was added to the DGEBA epoxy resins. DMSO was removed under reduced pressure and then required amount of TETA were added to the mixture at room temperature ([10]). The mixtures containing



Scheme 1. Hyperbranched polyesteramide reaction scheme.

different amount of HBP (0%, 6% and 12% w/w) were cured at 70 °C for 1 h [15] and post-cured at 120 °C for 2 h. The obtained samples were coded DGEBA, DGEBA/6%HBP and DGEBA/12%HBP.

2.4. Preparation of composite joints bonded with DGEBA/HBP systems

Two composite panel sheets were carefully bonded with DGEBA epoxy resins and DGEBA/12%HBP blends. The used composite panels were produced using a bi-component epoxy resin (I-SX 10 produced by Mates Italiana) and carbon fiber (Toho Tenax HTA 5131 filament Yarn) cured at $T = 90$ °C for $t = 45$ min (cured cycle previously obtained by DSC measurements). Eight plies of unidirectional carbon fibers were positioned in $[0^\circ, 90^\circ]_n$ and the composite sheets were made up by VARTM (vacuum assistant resin transfer molding), obtaining 65% $[\text{wt}(\text{fibers})/\text{wt}(\text{epoxy})]$ of fibers. The adhesives used to join the composite sheets were spread on the overlap area. The sheets were cured at ambient temperature for about 70 h and then post-cured at $T = 120$ °C for 2 h. After the post-cure the panels were cut to obtain the test specimens having dimensions reported in ASTM D1002.

2.5. Measurements and characterizations

The intrinsic viscosity of the HBP was measured with a Cannon–Ubbelohde (State College, PA) microviscometer in DMSO at 30 °C. Gel permeation chromatography was performed on a Waters Model 150-C ALC (Waters Associates, Milford, MA) using THF as solvent and monodisperse polystyrene standards were used to create a calibration curve. Infrared absorption spectra were recorded from potassium bromide pellets with a Nicolet model 60SX FT-IR spectrometer (Nicolet Analytical Instruments, Madison, WI) in the 4000–500 cm^{-1} range.

Thermal analysis was performed by differential scanning calorimetry (DSC) with a DSC-Q1000 (TA Instrument, New Castle, US) in nitrogen atmosphere from -20 to 220 °C at a rate of 10 °C/

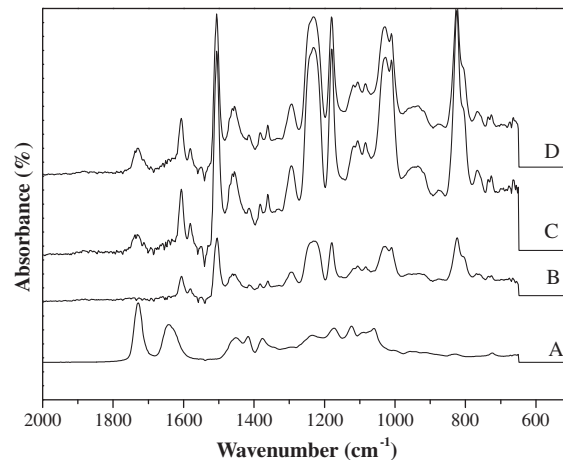


Fig. 1. ATR-FTIR spectra of free HBP (A), neat DGEBA (B), DGEBA/6%HBP (C), and DGEBA/12%HBP (D).

Table 1

Thermal and mechanical parameters from TGA, DMA analysis, nanoindentation tests and tensile tests for HBP/DGEBA blends containing 0, 6 or 12 wt% HBP.

Sample	T_{IDT} (°C)	T_g (DMA) (°C)	Elastic modulus E (Nanoindentation) (GPa)	Hardness (Nanoindentation) (GPa)	E (Tensile tests) (GPa)	Tensile strength (Tensile tests) (MPa)
DGEBA	337	127	4.41 ± 0.075	0.324 ± 0.016	2.48 ± 0.13	100.57 ± 3.14
DGEBA/ 6%HBP	330	118	3.75 ± 0.202	0.260 ± 0.023	2.65 ± 0.12	97.45 ± 10.19
DGEBA/ 12%HBP	326	108	3.90 ± 0.104	0.269 ± 0.010	2.68 ± 0.20	108.01 ± 6.18

min. Thermogravimetric analysis (TGA) was performed with a TA Instrument TGA – 2950 (TA Instrument, New Castle, US) to analyze the thermal stabilities of samples from 30° to 700 °C at 10 °C/min under nitrogen flow. The dynamic mechanical properties of the

samples were investigated with DMA-Q800 (TA Instrument, New Castle, US) at a frequency of 1 Hz, in the range 0–200 °C at a heating rate of 5 °C min⁻¹. Dynamic moduli and loss factors were obtained by single cantilever mode for the sample of size 17.5 mm × 11.6 mm × 1.9 mm.

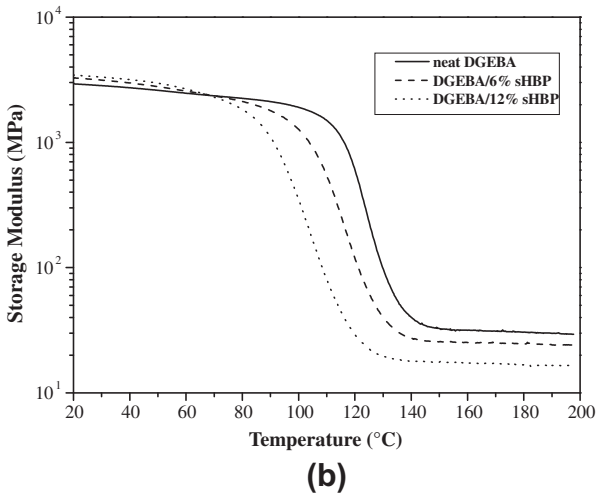
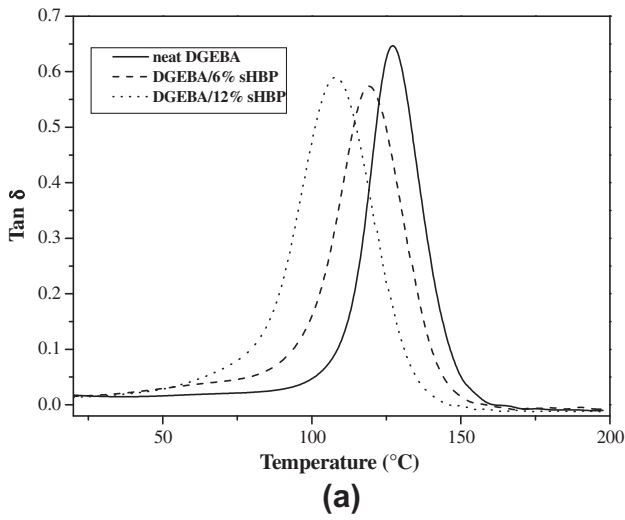


Fig. 2. Tan δ (a) and storage modulus (b) versus temperature plot for DGEBA/HBP blends containing 0, 6 and 12 wt% HBP.

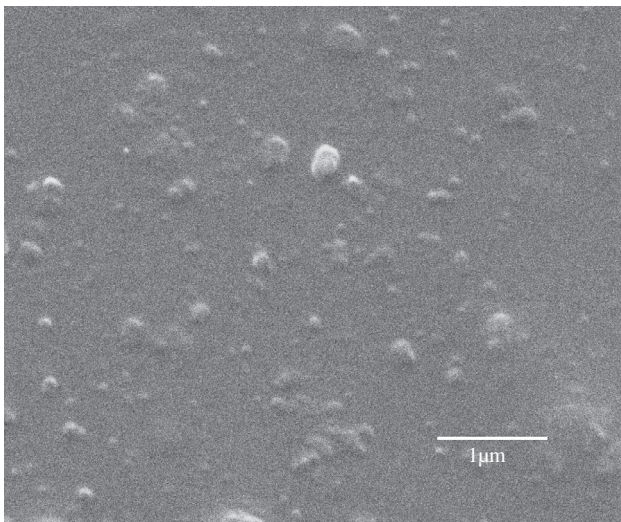


Fig. 3. SEM analysis of blend DGEBA/12%HBP.

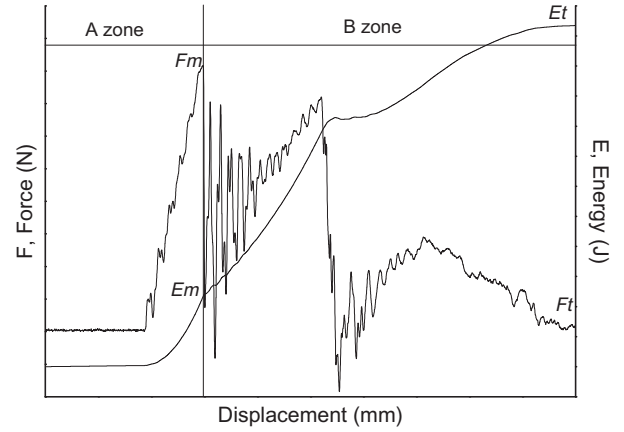


Fig. 4. Schematic load–displacement and energy–displacement curves obtained for neat DGEBA.

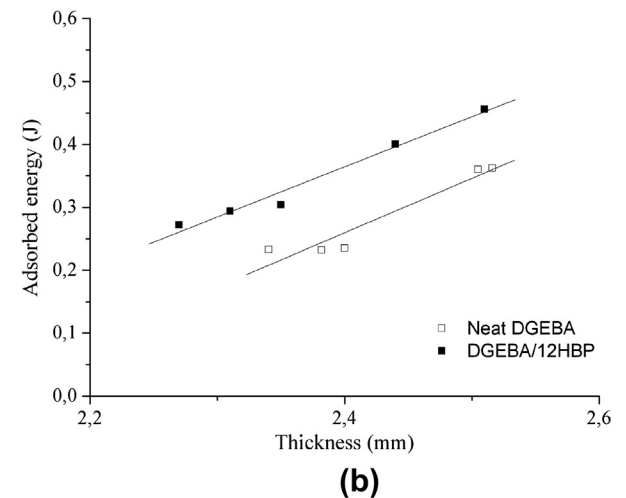
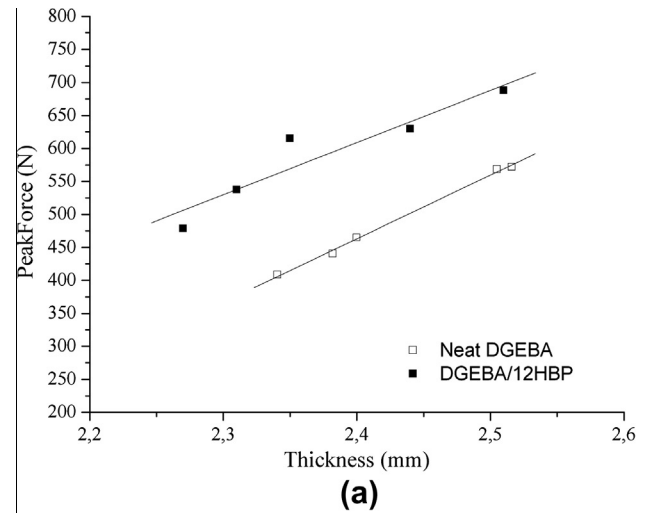


Fig. 5. Peak force (a) and adsorbed energy (b) versus thickness plot for HBP/DGEBA blends containing 12 wt% HBP.

Tensile tests and lap-shear tests were performed by using an INSTRON 5566 testing system. Tensile tests were performed on dog-bone shaped type IV samples according to ASTM D-638 whereas lap-shear tests were performed on samples obtained according to ASTM D1002. Data represent the average value of tests conducted on six samples.

A scanning electron microscope (SEM) FEI Quanta 200FEG (Eindhoven, NL) was used to examine the fracture surface of the epoxy sample. Optical microscope Olympus BX-51M was utilized to observe the debonded specimens and the acquisition of image was made by Extended Focus Image (EFI) software. The EFI is built-up by the optical longitudinal mechanical scanning and by the acquisition of a sequence of images during the scanning, called “image stack”. To create an EFI, in each image of the “stack”, the in-focus parts are selected and then stitched together in a single image.

Impact tests were performed by drop tower with CEAST fractovis strikers (Torino, Italy) at ambient temperature [16]. The specimens ($d = 60$ mm) were clamped under a 40 mm diameter supporter and impacted by the striker having a hemispherical steel tip of diameter 12.7 mm. The height and weight of the striker were 114.7 mm and 4.9 kg, respectively, leading to an impact velocity of 1.50 m/s. The specimens were subjected to an incident energy of 5.542 J. The free-falling dart tip and supporting dimension for geometry FC were specified in ASTM D 5628 – 96 R01.

Liquid water uptake was evaluated by immersion tests according to ASTM D 570-98. Samples ($0.2 \times 0.2 \times 1.5$ cm³) were desiccated overnight at 50 °C and then cooled and weighed to determine their dry mass. The weighed samples were placed in closed beakers containing 30 mL of water (pH = 7) and stored immersed in water baths kept at constant temperatures ($T = 45, 60$ and 80 °C). The adsorption kinetics were evaluated by periodically measuring the weight increment of the samples with respect to dry films (using a balance accurate to 0.0001 g) after gently bottling

the surface with a tissue, until saturation was reached. The water gain (W.G.) was calculated as follows:

$$\text{Water gain (\%)} = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100$$

where m_{wet} and m_{dry} are the weight of the wet and dry samples, respectively.

3. Results and discussion

3.1. Synthesis and characterization of HBP

Polyesteramides were synthesized in melt polycondensation without solvent [17] that has been demonstrated to be a simple, efficient and versatile procedure to obtain these polymers. In this paper, hyperbranched polymer has been synthesized for the first time with the same procedure. This one-step reaction renders polymers with low viscosity in quite good yields. The intrinsic viscosities (η) of the synthesized HBP measured in DMSO is 4.4 mL/g, the molecular weight (M_w) is 3800 and the polydispersity is 3.7. From thermal analysis, glass transition temperature, the initial temperature of decomposition [T_{IDT} (°C)], where 5% weight loss occurred, and temperature at the maximum rate of weight loss [T_{max} (°C)] values of the synthesized HBP are 12, 322 and 349 °C, respectively.

3.2. Structure identification of the DGEBA/HBP systems

Fig. 1 shows the ATR spectra of neat HBP, neat epoxy resin and epoxy blends loaded with two different percentages of hyperbranched polymer. In spectrum A the peak intensities of ester groups (1730 cm⁻¹) and of amide groups (1641 cm⁻¹) characteristic bands of the hyperbranched poly(amide-ester)s can be observed. In spectra B, C and D typical bands of epoxy resin are

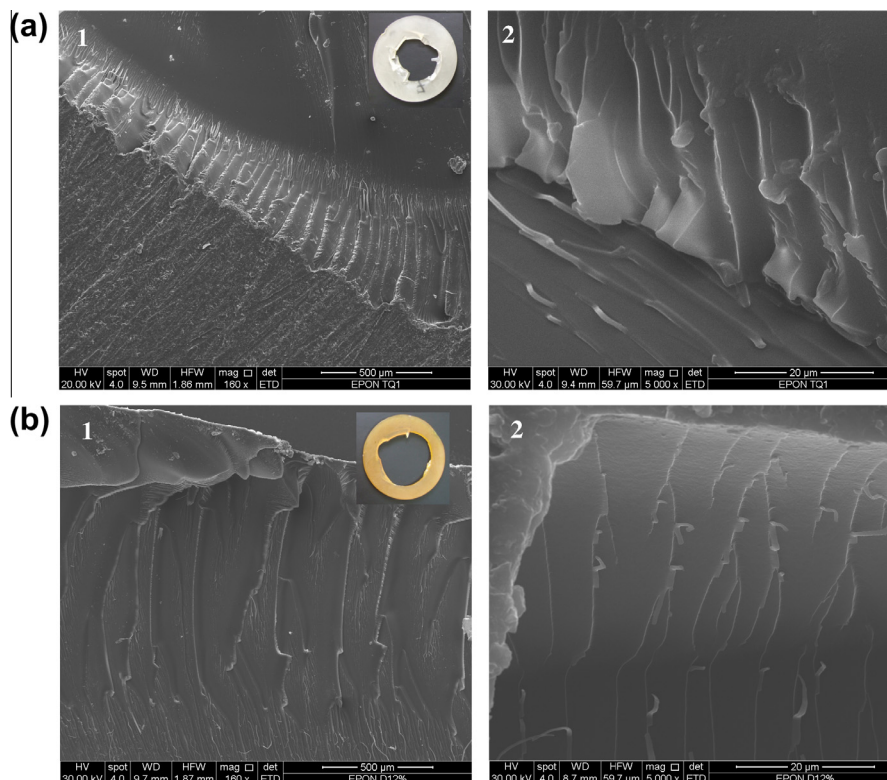


Fig. 6. SEM micrographs of fracture impact surfaces relative to (a.1,2) neat DGEBA and (b.1,2). DGEBA/HBP blends at 12 wt% of HBP at different magnitudes.

visible, in particular it is possible to identify the bands of ether groups at 1230, 1180, 1027 and 823 cm^{-1} and of the aromatic rings which correspond to stretching vibration bonds at 1504 cm^{-1} . In the spectra related to epoxy blends (C and D), the shoulder at approximately 1641 cm^{-1} is weakly visible, whereas the peak intensity at 1730 cm^{-1} increases as the amount of HBP added into the resin increases.

3.3. Thermal and mechanical properties of the DGEBA/HBP systems

The thermal stability of HBP, neat DGEBA epoxy resin and DGEBA/HBP blends (6% and 12% wt/wt) was evaluated by means of TGA analysis. From the TGA curves, T_{IDT} and T_{max} were determined. It can be observed that T_{IDT} (Table 1) slightly decreases as the HBP content increases whereas T_{max} remains constant at 358 °C.

All samples were examined by DMA analysis in order to study the relaxation and miscibility behavior of the investigated blends. In Fig. 2 the storage modulus and the loss tangent curve obtained for neat DGEBA and for all the DGEBA/HBP blends are reported.

In Fig. 2a, for the neat DGEBA sample, a single narrow and well-defined relaxation $\tan \delta$ peak at 127 °C, which is ascribed to its T_g , can be observed. Also DGEBA/HBP systems display a single and unimodal peak, thus indicating that HBP has good compatibility with the epoxy resin [10]. The $\tan \delta$ peaks shift to lower temperature in the cured blends with increasing HBP content (Table 1). This result can be attributed to the plasticizing effect of HBP which modifies the structure of the epoxy networks and enhances the movements of the chains [7]. The extent of the observed decrease is similar to that reported by Fu et al. who modified a DGEBA with a new epoxy-terminated low viscosity liquid thermosetting aromatic polyester hyperbranched epoxy resin (named HTTE).

Fig. 2b shows the storage modulus curves versus temperature for the DGEBA/HBP blends. No significant difference can be observed for the storage modulus of the blends at room temperature, whereas at higher temperatures, the modulus decreases as the HBP content increases due to a plasticization effect. Also in this case no differences can be evidenced among neat DGEBA and DGEBA/HBP systems in terms of both elastic modulus and tensile strength. This is most likely due to the fact that HBP is not involved in the curing reaction and thus no crosslinks are formed with the epoxy matrix. On the contrary, results obtained from nanoindentation tests (Table 1) show a decrease of elastic modulus and hardness of DGEBA/HBP systems respect to neat DGEBA, this can be attributed to the presence of HBP on the surface, as also proved by SEM picture, shown in Fig. 3. Then, the homogeneous blend of uncured DGEBA/HBP system undergoes phase separation during the curing process.

3.4. Impact properties of the DGEBA/HBP systems

The toughness behaviors of DGEBA and DGEBA/12%HBP has been studied by measuring their impact resistance. Peak force and adsorbed energy, obtained from the load–displacement and energy–displacement curves (Fig 4), are reported in Fig. 5a and b as function of sample thickness.

It can be observed that the addition of HBP leads to an improvement of about 25% on impact strength with respect to neat DGEBA (Fig. 5a). This result is confirmed by SEM analysis. Fig. 6a and b reports the SEM photographs of fracture impact surface for specimens of neat epoxy resin and DGEBA/12%HBP respectively. As shown in Fig. 6a, the neat epoxy network appears as smooth, glassy, fractured surface with cracks in different planes and this accounts for its poor impact strength. In contrast, micrographs of the blends at 12% content of HBP (Fig. 6b) show a rougher surface appearance and shear deformation. When cracks occur, shear deformation are induced to absorb energy, thus the toughness of DGEBA/12%HBP is significantly improved. Moreover, blends show

a single phase that can account for the good compatibility between the DGEBA and HBP. This is consistent with the results of DMA which shows a single peak representing a single phase [10].

3.5. Water uptake behavior of the DGEBA/HBP systems

Water adsorption of the prepared materials has been studied in order to verify the extent of resin degradation due to hygrothermal exposure. The water sorption profile at different temperatures (45, 60 and 80 °C) are reported in Fig. 7a and b for neat DGEBA and DGEBA/12%HBP respectively. Full saturation value was reached for all hygrothermal conditions after about 43 and 25 days of immersion in water, for DGEBA and DGEBA/12%HBP respectively. In addition, it has been proved that for both materials, the saturation water content is the same irrespective of the immersion temperature as also reported by Zhou and Lucas [18] for an epoxy system consisting of DGEBA and metaphenylene diamine as hardener. Moreover, at each investigated temperature, the incorporation of HBP leads to an increase in the amount of water absorbed at equilibrium mainly due to the higher polarity of the thermosets containing the aliphatic polyesteramide compared with neat DGEBA. In particular, the addition of the HBP synthesized in the present work leads to an increase in water content of about 34%. This value is lower than that observed by Morell et al. [12] for a DGEBA/MTHPA resin added with a commercial hyperbranched

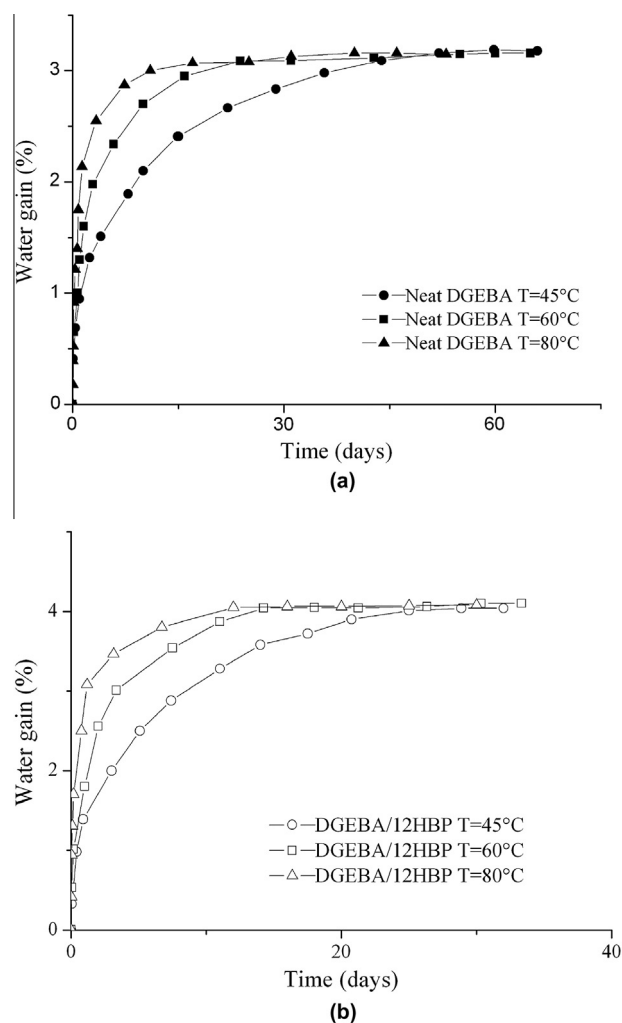


Fig. 7. Adsorption kinetics of (a) neat DGEBA and (b) DGEBA/HBP 12 wt% blend at $T = 45$ (●), 60 (■) and 80 °C.

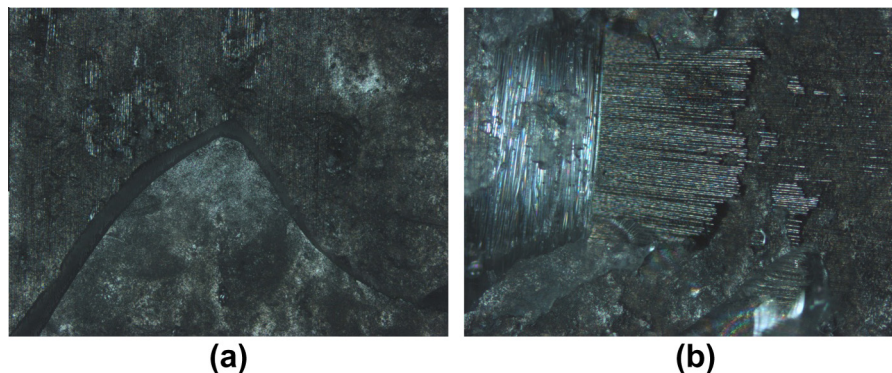


Fig. 8. Optical images of adhesive–adherend interface (a) neat DGEBA and (b) DGEBA/HBP blends (12%wt/wt) with 5× magnification in reflection geometry.

poly(ester-amide) Hybrane S1200. In similar experimental conditions, they found an increase in water content of about 90%. This can be attributed to the lower hydrophilicity of our HBP with respect to Hybrane S1200 due to the presence of longer aliphatic chains.

3.6. Adhesive behavior of the DGEBA/HBP systems

Adhesive properties of neat and loaded epoxy resins have been evaluated in terms of the lap-shear strength using composite adherends. Obtained results show that the shear strength value of composite joints bonded using neat DGEBA and DGEBA/12%HBP are 3.01 ± 0.1 MPa and 3.84 ± 0.1 MPa respectively, thus showing a significant improvement in shear strength of DGEBA/HBP systems. The fractured surfaces have been observed by optical microscope. The fracture seems macroscopically cohesive in the case neat DGEBA (Fig. 8a) thus showing a lack of mechanical resistance of the adhesive itself. Whereas, in the case of DGEBA/12%HBP (Fig. 8b), the breakage occurs in the adhesive–adherend interface, thus showing a macroscopically adhesive fracture. Moreover, the microscopic observation of the debonded specimens show that there exists rests of composite carbon fibers in the adhesive surface which must have been pulled away during the breakage of the tested specimen. This demonstrate the better adhesive behavior of DGEBA/12%HBP resins mainly due to the chemical interactions between the peripheral end group of the loaded HBP and the composite adherend.

4. Conclusion

In this work we introduced a novel hyperbranched poly(amide-ester)s, synthesized in one-step polycondensation without solvents, in an epoxy resin based adhesive in order to improve the impact resistance of the epoxy system without losing the thermomechanical properties. The homogeneous system of uncured epoxy resin/hyperbranched system undergoes phase separation during the curing process necessary for a good load transfer from the epoxy to the modifiers. Moreover, the amount of HBPs present at the interface between the toughened adhesive and the adherend could positively contribute to the adhesion because of the presence of numerous branches with suitable functional groups.

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