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Morphology and fracture properties of toughened highly crosslinked epoxy composites: A comparative study between high and low T_g tougheners

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ABSTRACT

The mechanical properties of an unmodified reference composite panel based on a highly crosslinked epoxy resin are compared with several corresponding toughened versions, all containing the same amount of representative hard or soft tougheners. The panels are prepared and tested under identical conditions. In terms of tougheners, soft MAM block copolymers and CTBN rubber are compared with two high glass transition temperature (T_g) amorphous thermoplastics, PES and phenoxy. The high T_g thermoplastic tougheners yield considerable improvements of the composites mechanical properties, especially the interlaminar fracture toughness, as compared to the reference panel. On the contrary, MAM and CTBN modification are much less effective. The analysis of the morphology strongly suggests that effective toughening of composite panels based on densely crosslinked epoxy resins requires the combination of at least two key factors: (i) a fine dispersion of the toughener and (ii) strong matrix-toughener and matrix-carbon fibers interfaces. The study provides valuable insights for the choice of suitable tougheners for high performance epoxy systems, based on the link with the physical toughening mechanisms.

1. Introduction

Highly crosslinked epoxy resins typically used in high performance automotive and aerospace applications lack molecular relaxation mechanisms making them inherently brittle. This lack of ductility and the resulting low fracture toughness limit applications in areas requiring high impact resistance and tensile strength. Therefore, many efforts to toughen epoxies have been reported in the past three decades. The most common strategy however consists in dispersing a second phase in the epoxy matrix, in order to delay crack initiation and to slow down crack propagation through various toughening mechanisms [1–4]. Typical secondary phases include reactive rubbers or preformed rubber particles, engineering thermoplastics as well as block copolymers made of hard and soft blocks. Hence the various toughening strategies can roughly be sorted between hard and soft, or high and low glass transition temperature (T_g), tougheners. The rubber systems that have attracted the most attention are copolymers of amino-terminated and vinyl-terminated butadiene-acrylonitrile (ATBN) or carboxyl-terminated butadiene-acrylonitrile (CTBN). The addition of CTBN has been shown to significantly improve the toughness of epoxy resins [5–13]. However, mainly epoxies with low T_g, involving low crosslinking density as liquid diglycidyl ether of bisphenol-A (DGEBA), benefit from rubber modification because the improved fracture toughness is only observed if the matrix is able to undergo shear yielding. This is a significant limitation to the use of rubbers for improvement of epoxy toughness. Moreover, rubber modification reduces the elastic modulus, the tensile strength and the T_g of the cured epoxy system due to the incomplete phase separation leading to the plasticization of the epoxy matrix. An alternative method of toughening with rubber is by directly mixing preformed rubber particles such as core-shell rubber. Such particles have

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predetermined sizes ranging from 0.2 to 0.4 μm [14–16] and can also efficiently improve the toughness of weakly crosslinked epoxies through several toughening mechanisms, mainly rubber particle cavitation [13]. However, for high performance tetrafunctional epoxy resins, high T_g thermoplastics such as polyetherimide (PEI) polyethersuflone (PES) or phenoxy, often represent the best option, as the latter do not only improve the fracture toughness, but are not detrimental and can even be beneficial to the modulus and the heat resistance, depending on the selected thermoplastic [17–26]. Finally, the addition of a block copolymer is another promising route to epoxy toughening [27–30]. Indeed, the various microstructures formed after reaction induced phase separation (RIPS) from the matrix can improve the properties of the resin. However, many parameters have to be taken into account to predict the resulting structure responsible for the toughness improvement, such as the nature and the relative length of the blocks used as well as the miscibility of these blocks with both resin precursors and hardener.

Each of the modifiers mentioned above has its own advantages and drawbacks. Therefore a systematic comparison of the various routes to toughening of a given epoxy resin of interest is highly desirable. Unfortunately, a direct comparison between results described in the literature is not straightforward because the fraction and the nature of the toughener, the thermosetting system, the curing cycle, the manufacturing process as well as the mechanical tests are almost always changing when looking at different investigations.

The overall objective of this work is provide such a systematic comparison for a representative high performance epoxy resin based on N, N, N′, N′-tetraglycidyl-4, 4′-diaminodiphenylmethane (TGDDM) and 4, 4′-diaminodiphenylsulfone (DDS), widely used in aeronautical applications, by evaluating the influence of various tougheners on the delamination toughness properties of autoclaved composite panels processed under the same conditions. Representative tougheners of the main classes cited above (block copolymer, rubber phase and thermoplastics) with contrasting T_g and compatibility have been selected. All tougheners have been incorporated at the same concentration of 10% in weight, as this was shown in a preliminary study to provide a good compromise between toughness, stiffness and processability. The relationship between the microstructure resulting from RIPS and the mechanical properties of the toughened composite panels, in particular the delamination toughness (G_{Ic}), has been established and compared with the unmodified reference panel. Moreover, the compression after impact (CAI) and the interlaminar shear strength (ILSS) have also been characterized and compared. To our knowledge, no comparative study has been reported on the influence of several tougheners in a single high performance matrix prepared and tested under identical controlled conditions. The present results can provide valuable insights to the scientific as well as the industrial communities for the choice of suitable tougheners for high performance epoxy systems and to make a link with the key mechanical performances.

2. Materials and experimental details

2.1. Materials

The epoxy resin used in this study is N, N, N′, N′-tetraglycidyl-4, 4′-diaminodiphenylmethane (TGDDM), Araldite MY721, crosslinked with a high temperature curing agent 4, 4′-diaminodiphenylsulfone (DDS), Aradure 9664-1, both from Huntsman Advanced Materials.

The selected tougheners for the epoxy matrix are (i) a symmetric triblock copolymer commercially designated by Arkema as Nanostrength™ M52 N NP (MAM), (ii) a carboxyl-terminated butadiene-acrylonitrile copolymer rubber (CTBN), Fortegra 100 supplied by Dow, (iii) a polyethersulfone with hydroxyl end-groups (PESOH), Ultrason E2020 P SR from BASF, which is an amorphous thermoplastic with a T_g of 225 °C, and finally (iv) an amorphous phenoxy thermoplastic (PKHH) with a T_g of 92 °C provided by InChem Corporation.

The carbon fiber (CF) reinforcement fabric used for the composite laminates production is HexForce® G0926 (HTA 6k) with a 5 harness satin weave (375 g/m^2) manufactured by Hexcel Composites.

2.2. Fabrication methods

2.2.1. Blends preparation

A preliminary study has shown that a high concentration (>10 wt%) of toughener will not only increase the viscosity of the prepreg resin itself and, hence, complicate the system preparation and handling, but it will also affect the desired properties such as the elastic modulus and T_g depending on the toughener. As a good compromise, blends of TGDDM/DDS with 10 wt% of toughener as well as unmodified TGDDM/DDS blends have been prepared using a melt-mixing method. The toughener in the form of powder (MAM, PESOH and PKHH) or as liquid (CTBN) were first added with TGDDM at 110 °C and mixed using a propeller stirrer until a visually homogenous mixture is obtained. DDS was then incorporated in the mixture under continuous stirring at the same temperature. The mixtures were next degassed in a vacuum oven at 120 °C for 20 min.

2.2.2. Laminates manufacturing

Prepregs based on carbon fiber fabrics containing unmodified or modified epoxy mixtures have been produced using a CGMI prepregger. The temperature of the impregnation table, the gap of the nip rollers and the running speed were adapted to provide a resin content of about 20–25% by weight in the cured laminates. The reference and the modified composite panels were manufactured by autoclave. Uncured prepregs were placed under a vacuum bag and a pressure of 7 bars was applied to minimize porosity. The curing cycle recommended by Huntsman and used in this work consisted of an isotherm at 80 °C for 2 h, followed by 1.5 °C/min ramp up to 100 °C, an isotherm for 1 h, followed by 1.5 °C/min ramp up to 150 °C and an isotherm for 4 h. Moreover, all composite panels have been post-cured at 200 °C for 7 h. The laminates contained 12 plies of carbon fiber fabrics having 300 × 300 mm size with a quasi-isotropic stacking sequence $[(+45/-45)/(0/90)]_{3S}$ and a thickness of about 4 mm after curing. Two composite panels were produced for the reference and for each of the modified mixtures. A polyimide (PI) insert acting as a crack initiation site for double cantilever beam (DCB) measurements was incorporated in the midplane of one of the two laminates. Ultrasonic inspections were performed on all composite panels to validate their quality. The composition of the polymer phase for all the composite panels is listed in Table 1.

2.3. Characterization techniques

2.3.1. Dynamical mechanical thermal analysis (DMTA)

Glass transition temperature (T_g), defined as tan-delta peak values, of reference and modified composites specimens were determined using a dynamic mechanical analyser DMTA/SDTA861e from Mettler Toledo. Rectangular specimens of 50 × 10 mm size were heated from 30 to 300 °C at 3 °C/min and analysed at a frequency of 1 Hz in a dual cantilever bending mode.

Table 1
Composition of polymer phase in the composite panels.

Modified epoxy based formulations	TGDDM/DDS content (wt%)	Toughener content (wt%)
REF	100	–
+MAM	90	10
+CTBN	90	10
+PESOH	90	10
+PKHH	90	10

2.3.2. Mode I interlaminar fracture toughness and fracture surface observations

The mode I interlaminar energy release rate (G_{Ic}) was measured using the double cantilever beam test (DCB) configuration according to the ASTM D-5528 standard (G_{Ic} associated to propagation is calculated using the modified compliance calibration). Specimens were cut to 150 × 25 mm, including two round notches at the end of the sample in order to attach piano hinges with small screws. Samples were loaded in tension using a Zwick Universal testing machine equipped with a 50 kN load cell, at 1 mm/min crosshead displacement speed. Crack growth was observed using a magnifying lens and measurements of load and displacement at the corresponding crack length were recorded. Moreover, the fracture surfaces of the specimens were examined after DCB tests by scanning electron microscopy (SEM) using a Jeol 7600F microscope. The samples were coated with a thin layer (8 nm) of chromium by sputtering in a Cressington 280HR chamber.

2.3.3. Interlaminar shear strength (ILSS)

The interlaminar shear strength tests were performed according to the EN 2563 standard. Rectangular specimens of 30 × 10 mm were tested with a rigid 3 points bending fixture on a Zwick Z250 Universal testing machine operating at room temperature under a constant crosshead displacement speed of 1 mm/min. The gap between the support cylinders was 20 mm.

2.3.4. Compression

Compression tests were performed according to the ASTM D-6641 standard. Rectangular specimens of 140 × 12 mm were tested on a Zwick Z250 Universal testing machine equipped with a 250 kN load cell. The specimens were clamped into the appropriate combined loading compression test fixture (WTF) with 3 Nm torque. The crosshead speed was 1.3 mm/min. A strain gage (EA-06-125EP-350 by Vishay) was glued on each side of the specimen with M-Bond 200 adhesive system (Vishay). The compression modulus was calculated between strain values of 1000 and 3000 μStr, and rejected if bending at 2000 μStr was superior to 10%. Accordingly, the failure stress was rejected if the bending at failure was superior to 10%.

2.3.5. Compression after impact (CAI)

Compression after impact specimens were cut to 100 × 150 mm and were subjected to a transverse impact (30 J) using an Instron Dynatup 9250HV impactor according to the AITM1-0010 standard. The size of the internal damage zone was determined by ultrasonic C-scan inspection. The damaged specimens were then loaded in a Zwick Z250 Universal testing machine equipped with a load cell of 250 kN and tested using an in-plane compression fixture (WTF) in order to determine the residual strength.

3. Results and discussion

3.1. Dynamical mechanical evaluation

The Young's modulus (E') of the unmodified and modified composites measured at room temperature and at high temperature (150 °C) as well as the corresponding T_g of the epoxy-rich phase are listed in Table 2. DMTA results show that the flexural storage modulus measured at room temperature of the modified epoxy matrix is preserved upon the addition of the polymer phase. However, a slight drop of the flexural modulus (less than 10%) is observed at 150 °C, depending on the selected toughener. Furthermore, no reduction in the dry glass transition temperature of the epoxy-rich phase is observed indicating that the second polymer phase has been completely phase separated. Otherwise, it may act as a plasticizer lowering the T_g of the cured matrix, which is typically the case in conventional rubber modified epoxies. Nevertheless, no reduction in T_g is observed in the case of CTBN modification. On the contrary, T_g of the CTBN modified epoxy composite appears to be even slightly higher than the one of the reference.

3.2. Mode I fracture toughness of composite panels

Typical load-displacement curves for the DCB test performed on unmodified and toughened composites are presented in Fig. 1. The curves show the usual serrated shape suggesting that the cracks propagate by small jumps through different microstructure arrangements as suggested by Aravand et al. [18]. Regardless of the shape of the curves, three groups of load-displacement curves can be distinguished: (i) the unmodified composite showing the lowest resistance to crack propagation, (ii) the MAM- and CTBN-modified composites both in between brittle and ductile material behavior and (iii) the PKHH- and PESOH-modified composites with a more ductile response. Moreover, Fig. 2 illustrates the resistance to delamination (R-curve) behavior of all composites as a function of crack advance. The addition of a ductile phase increases the resistance to crack propagation in all cases. Although the R-curve of the PKHH-modified composite shows an unstable crack propagation baseline, despite the presence of PKHH phases which should deflect the crack propagation path, it exhibits a higher average value of the interlaminar fracture toughness. The influence of the toughening agents on the strain energy release rate (G_{Ic}) of the composite samples based on the resin formulations described in Table 1 is summarized in Table 3. The incorporation of PESOH and PKHH significantly enhances G_{Ic} by 66% and 81.5% respectively, compared to the reference. The mechanisms responsible for the toughness improvement of PESOH- or PKHH-modified epoxy composites suggested in the literature are associated to the energy dissipated into plastic void growth and shear yielding as well as ductility improvement caused by the plasticizing effect resulting from the incorporation of PESOH or PKHH [17]. The presence of hydroxyl reactive groups located either at the end-chains (PESOH) or on the

Table 2
Thermo-mechanical properties of unmodified and modified composites.

Composite specimen name	Flexural storage modulus (MPa) at 23 °C	Flexural storage modulus (MPa) at 150 °C	T_g (°C)
Reference	11,500 ± 200	11,400 ± 200	257 ± 3
MAM-modified	12,550 ± 100	11,500 ± 250	251 ± 4
CTBN-modified	13,100 ± 29	12,900 ± 85	266 ± 3
PESOH-modified	10,800 ± 250	11,500 ± 225	257 ± 3
PKHH-modified	12,500 ± 75	11,100 ± 100	259 ± 2

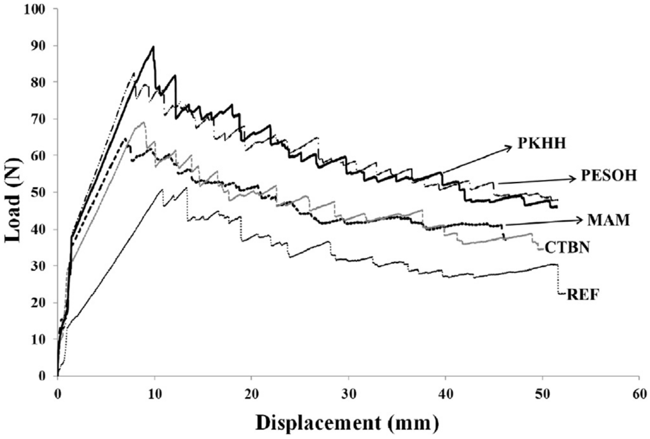

Fig. 1. Typical load vs. displacement curves obtained from DCB test for unmodified and modified composites.

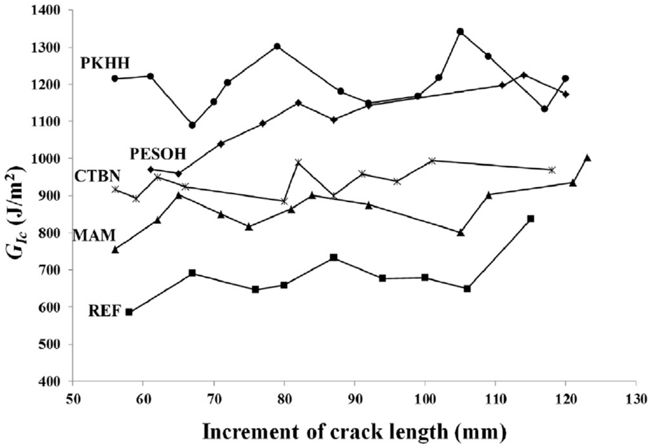

Fig. 2. Mode I interlaminar fracture toughness (G_{Ic}) vs delamination length for unmodified and modified composites.

backbone of the repetitive unit (PKHH) constitutes an explanation for the better affinity and/or reactivity with the epoxy matrix. Moreover, the hydroxyl reactive groups of these two tougheners may also increase the fiber-resin bonding and thus enhance the mode I propagation values. On the other hand, for MAM and CTBN rubber, the improvement is only around 30%. This result confirms that rubber modification [18] is not very effective to improve the fracture toughness of high T_g epoxy matrices due to their low plastic deformability which limits plastic void growth as well as shear yielding. For MAM-modified epoxy composites, Chen et al. [29] attribute the origin of the toughening to the cavitation of MAM particles as well as to the plastic growth of the voids for samples containing up to 7 wt% of MAM. For higher MAM concentrations (around 10 wt%), they observe a co-continuous microstructure after reaction induced phase separation responsible then for a drastic increase in the measured toughness.

Table 3
Mode I interlaminar fracture toughness (G_{Ic}) of the composite samples.

Composite sample name	Mean G_{Ic} (J/m^2)	%
REF	651 ± 50	–
+MAM	847 ± 54	30
+CTBN	898 ± 53	38
+PESOH	1084 ± 100	66
+PKHH	1183 ± 90	81.5

The morphologies of the DCB fracture surfaces of the reference composite compared to modified epoxy composite samples are illustrated in Fig. 3. For the unmodified composite (Fig. 3a), the failure surface morphology shows river cracks typical of the brittle behavior of unmodified epoxy, while the composite modified with PESOH exhibits a rougher surface (Fig. 3b) reflecting an increased ductility of the matrix. However, the corresponding modified epoxy matrix does not exhibit any nodular PESOH domains large enough to be resolved by SEM as described by Bucknall et al. [20]. SEM micrographs of the fracture surface of the PKHH-modified epoxy composite show a continuous epoxy-rich phase with homogenously dispersed PKHH nodules surrounding carbon fibers. The average size of the nodules is in the range 0.6–1.0 μm. On the one hand, the presence of a PKHH-rich phase increases the resistance to crack propagation through various mechanisms such as crack arrest, crack path deviation or crack bridging [17] and, on the other hand, the good affinity of PKHH with TGDDM leads to strong interface between the two, which participates to the toughness improvement of the PKHH-modified composite. Fig. 3d shows the fracture surface of the CTBN-modified epoxy composite, which contains large particles (identified by the white arrows) around 10–15 μm in diameter. Some welts located on the surface may indicate the occurrence of micro-cracking which can contribute to a modest toughening effect. The fracture surface morphology of the MAM-modified composite presented in Fig. 3e shows the heterogeneous dispersion of the copolymer in the modified epoxy matrix. The MAM-rich areas are responsible for cavitation and plastic void growth toughening, which explains the observed moderate improvement in the fracture toughness. From Fig. 3, we can extract major differences between the high T_g thermoplastic-modified and the soft copolymer or rubber toughened systems. In the latter case, interfaces (both matrix-CF and matrix-dispersed toughener) are much weaker and the dispersion significantly worse (heterogeneous and/or coarse). This strongly correlates with the degree of cracking resistance of improvement. Strong interfaces and finely dispersed toughener are needed to raise G_{Ic}.

3.3. Interlaminar shear strength (ILSS)

Fig. 4 summarizes the ILSS results of the reference and modified epoxy composites. PESOH as well as PKHH-modified epoxy based composites show a significant increase of the apparent interlaminar shear strength by about 32% and 35%, respectively, as compared to the unmodified specimens. The presence of reactive hydroxyl groups in both thermoplastics promotes a better affinity with the epoxy matrix and is presumably responsible for this improvement. This assumption is backed by the results of Fernandez et al. [26] who demonstrated that the ILSS of a tetrafunctional epoxy matrix (TGDDM) modified with an unreactive PES was identical to the value of the unmodified laminate. Conversely, the addition of MAM or CTBN rubber is either neutral or even detrimental to ILSS. The weak interfaces generated in these systems are most presumably at the origin of this behavior.

3.4. Compression

Fig. 5 summarizes the compression strength of the unmodified and modified epoxy composites. On the one hand, PESOH and PKHH-modified epoxy based composites show a significant increase of the compression strength by about 27% and 20% respectively compared to the unmodified specimen. On the other hand, the compression strength significantly decreases for the MAM

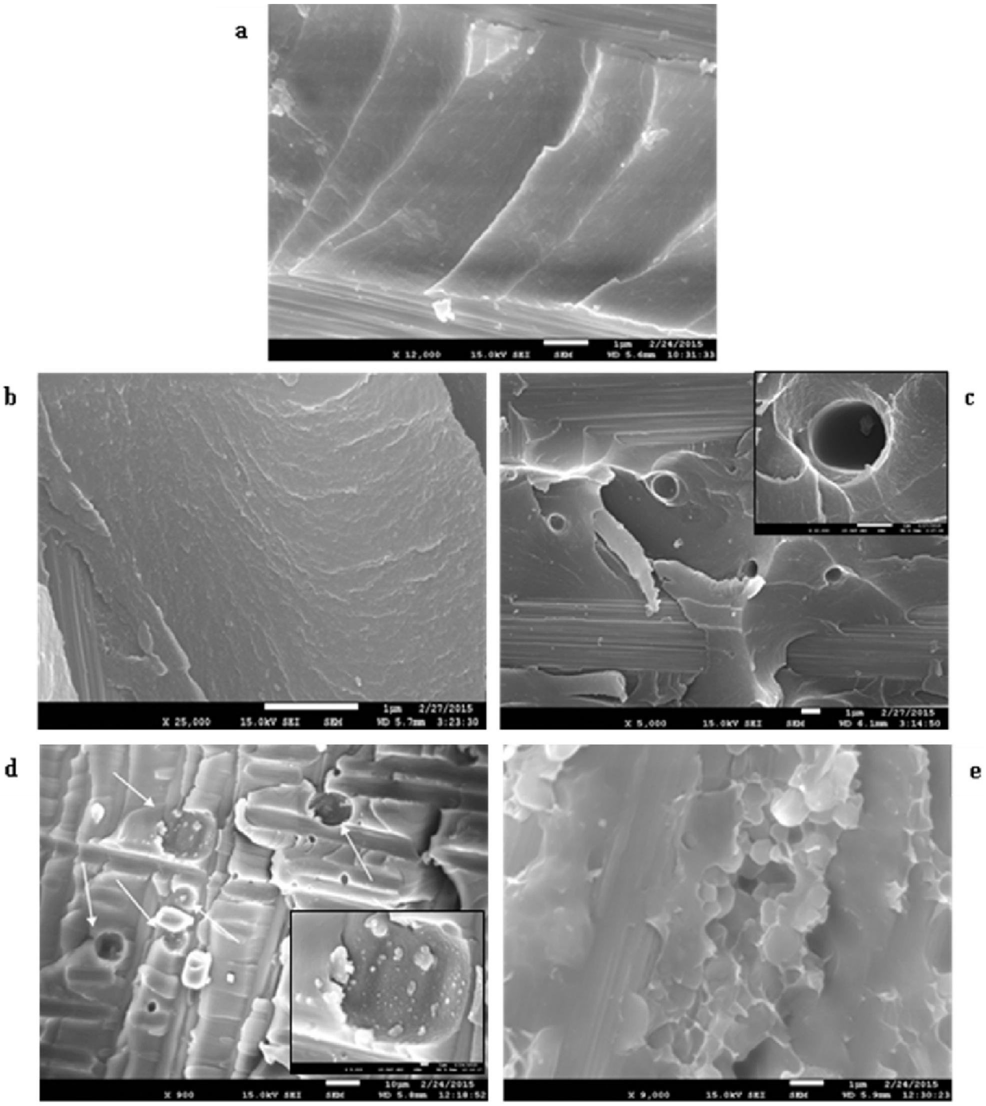

Fig. 3. SEM micrographs of DCB failure surface of (a) the reference sample, (b) PESOH-modified epoxy composite, (c) PKHH-modified epoxy composite, (d) CTBN-modified epoxy composite and (e) MAM-modified epoxy composite.

modified epoxy composite with respect to the reference (−23%) and is unchanged for the CTBN sample. These contrasting results are the consequence of the large differences between the moduli of the soft and hard tougheners.

The fracture strain of unmodified and modified epoxy composites under compression is illustrated in Fig. 6. PESOH as well as PKHH-modified epoxy based composites show a significant increase of the fracture strain by about 45% compared to the

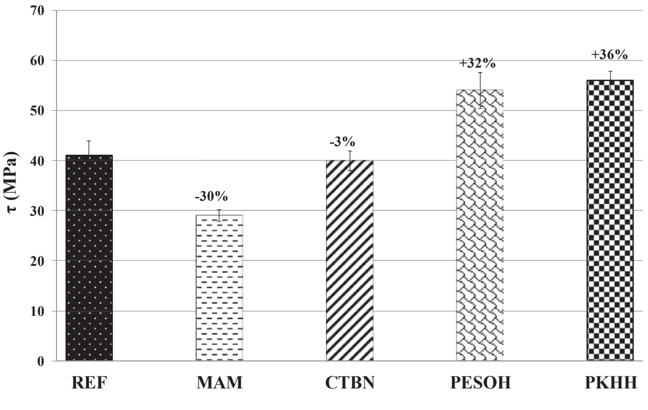

Fig. 4. ILSS values for the reference and modified epoxy composite.

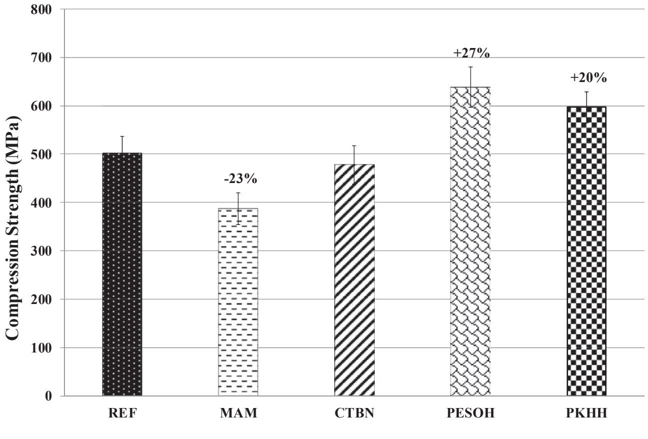

Fig. 5. Compression strength of unmodified and modified epoxy composites.

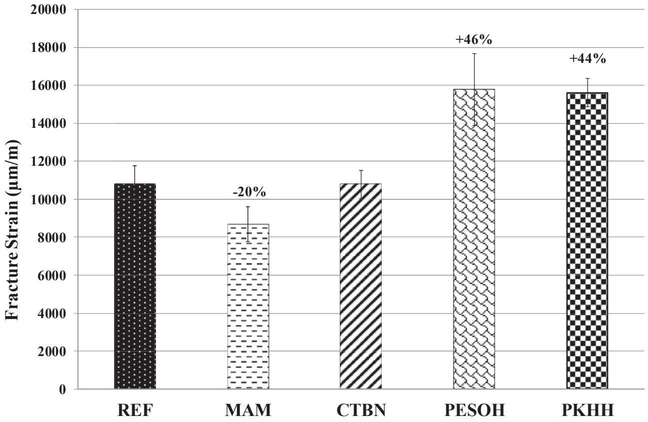

Fig. 6. Fracture strain of unmodified and modified epoxy composites.

Table 4
Evaluation of the delamination areas after impact for unmodified and modified composites.

Composite sample name	Damaged area (mm^2)	%
REF	973	–
+MAM	2067	112
+CTBN	1094	12.5
+PESOH	733	–25
+PKHH	704	–28

unmodified specimen. On the other hand, the fracture strain significantly decreases for the MAM modified epoxy matrix with respect to the reference (−20%) indicating a more brittle behavior of the system. Again, the CTBN-based composite gives performances which are similar to the reference. Fig. 7 shows a decrease of the compression elastic modulus for all the toughened systems as compared to the reference system. Indeed, the presence of the toughener phase always reduces the stiffness of the matrix since the highly crosslinked epoxy has a modulus higher than even the high T_g thermoplastics. This decrease is directly related to the volume fraction and the respective moduli of the polymers [31] but depends also on complex details of the microstructure, which explains why the reduction is not simply proportional to the modulus contrast between the epoxy and toughener phases.

3.5. Compression after impact (CAI)

Unmodified and modified epoxy composite samples were impacted at a static incident energy of 30 J. The delaminated areas for all samples were evaluated by C-scan measurement and the results are listed in Table 4. The damaged areas for the PESOH- and PKHH-modified epoxy composite samples are significantly smaller than for the reference, corresponding to a reduction of the delaminated surface by 25% and 28%, respectively. A comparison between the compression strengths after impact of the reference and all modified composite samples is given in Fig. 8. PESOH- and PKHH-modified epoxy composites show an improvement of the residual compression strength after impact by 10.5% and 14.5% respectively compared to the reference sample. This result is in agreement with the delaminated area after impact, indicating that the two high T_g thermoplastics effectively enhance the impact damage resistance of the corresponding composite panels. Although the impact properties are mainly dominated by the fiber architecture and there is only a limited contribution of the matrix, PESOH and PKHH effectively improve the impact resistance of the composite panels while this is not the case for MAM and CTBN rubber.

3.6. Summary

A spider chart summarizing the influence of the tougheners on the key mechanical properties of all composite panels is presented in Fig. 9. The high T_g thermoplastic modifiers provide improvements to all relevant mechanical properties of the composites except the compression modulus.

4. Conclusion

The mechanical properties of an unmodified reference composite panel based on a highly crosslinked epoxy resin were compared to the performances of the corresponding toughened versions, all containing the same content of representative hard or soft polymer phases. All panels were prepared and tested under identical conditions. As tougheners, soft MAM block copolymers and CTBN rubber were compared with two high T_g amorphous thermoplastics, PES and phenoxy. The high T_g thermoplastic tougheners provide considerable improvements of the composites mechanical properties, especially interlaminar fracture toughness (G_{Ic}) with an increase of 80% and 66% respectively, as compared to the reference panel. In contrast, MAM and CTBN modification are much less effective. Fracture surface micrographs reveal the

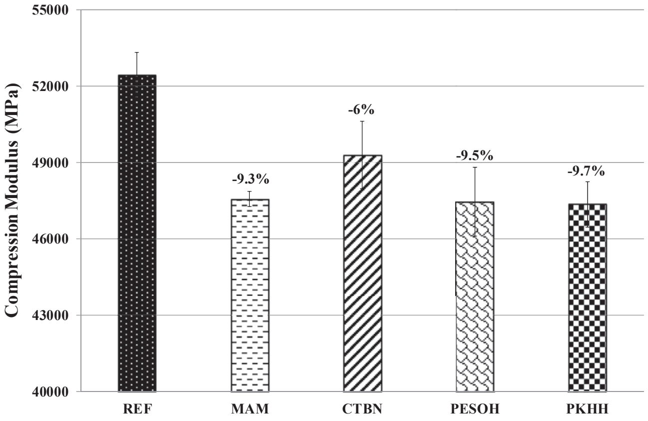

Fig. 7. Compression modulus evaluation of the reference and modified epoxy composites.

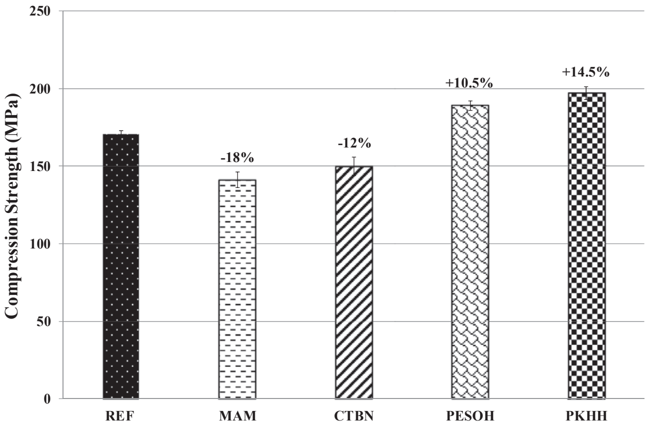

Fig. 8. Residual compression after impact strength of the reference and modified epoxy composites.

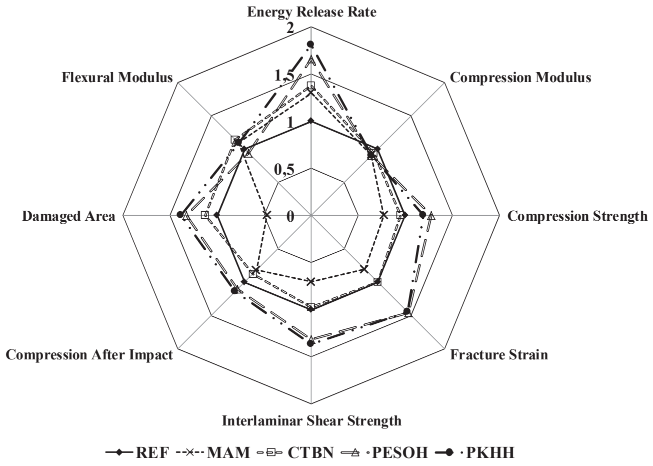

Fig. 9. Comparative plot of the main mechanical properties of the modified epoxy composites relative to the values for the reference material.

presence of well-dispersed and strongly adhering phenoxy nodules in the modified epoxy matrix. In the case of PES, the very finely dispersed thermoplastic domains can hardly be resolved by SEM. By contrast, CTBN domains are large and poorly adhering to the matrix. These results strongly suggest that effective toughening of composite panels based on densely crosslinked epoxy resins requires the combination of at least two key factors: (i) a fine dispersion of the toughener and (ii) strong matrix-toughener and matrix-CF interfaces. Both characteristics are found in phenoxy and PES-modified systems and promote the resistance of the resin to crack propagation (through various mechanisms), hence improving the impact damage resistance of the composite panels. On the contrary, soft and, poorly adhering particles as in the case of CTBN are less effective. The superior effect of the high T_g thermoplastics further suggests that the intrinsic ductility of the matrix, caused by partial thermoplastic-epoxy miscibility, probably plays an additional role which is not the case for the soft tested tougheners.

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