NANOSTRUCTURED EPOXY ADHESIVES MODIFIED WITH SELF-ASSEMBLING BLOCK COPOLYMERS FOR JOINING FIBER CARBON EPOXY COMPOSITES

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Keywords: epoxy adhesives, carbon fiber composites, nanostructured resin, block copolymer

Abstract

The application of an epoxy resin modified with a three blocks copolymer as adhesive of carbon fiber/epoxy matrix composites has been investigated. The used copolymer is a new developed one of the Nanostrength® family (E41 - Arkema) constituted of polystyrene, 1,4-polybutadiene and syndiotactic polymethyl methacrylate (SBM). Because of repulsive interactions among these three blocks, the SBM copolymer self-organizes at the nanometer scale. In the case of its addition to an epoxy resin, which is compatible with one of the blocks (methacrylate), suitable dispersions can be reached and copolymer imposes a nanostructuration to the host matrix.

The research has evaluated the adhesion capability and the mechanical properties of an epoxy based resin (DGEBA-DDM) modified with several contents of the SBM copolymer (0, 2.5, 5 and 10 wt. % of E41). Both single shear lap (SSL) and double cantilever beam (DCB) joined specimens have been tested to determine the influence of the SBM addition on their shear strength and the mode-I fracture toughness. Obtained results showed an increase of both properties, specially the last one, reaching increases higher than 50 % in relation with the G_{IC} measured for the pristine DGEBA.

1 Introduction

Thermoplastic polymers and particularly epoxy resins have been widely used as composite matrices, protective coatings and adhesives, due to their outstand mechanical, thermal and chemical properties. However, it is also well known its high brittleness, in comparison with other polymeric materials, which limits the potential application in uses which require toughness and damage tolerance [1].

Since several decades, epoxy resins are been matter of research with the main objective to increase their toughness. For this, there are several alternatives, such as the modification of their chemical formulation, using epoxy precursor of high molecular weights and low stiffness, or using crossing agents which allow reaching moderate conversion rates, providing resins with low cross linking degrees and, therefore higher plastic behavior. The most of the

obtained results following theses routes are worse than expected ones, implying the decreases of other interesting properties such as the reduction of glass transition temperature (T_g) and the decrease in strength and stiffness.

Other more interesting alternatives consist on the incorporation of a second phase in the thermosetting matrix to difficult the crack growth and, then providing a toughening effect. Although the nature of the second phase can be quite different, one of the more used methods is to add small amounts of non thermosetting polymers, such as thermoplastic or elastomeric ones, with are segregated into the epoxy matrix forming a differenced second phase. There are many industrial formulations based in this alternative to develop both structural adhesives and composites matrices [1-3].

The addition of elastomeric polymers provides outstanding improvements of the epoxy resin toughness. One of the most used additives is acronitile and butadiene copolymers. To reach materials with high mechanical properties is necessary a suitable interaction between both polymeric phases: for it, added polymers are usually partially functionalized with reactive groups, such as amine or carboxyl ones. The principal limitation of these systems comes from the unsaturated structure of the elastomeric network, which limits its thermal oxidative stability [1].

Another alternative is the addition of low amounts of thermoplastic polymers [2,3] as toughness modifiers for the epoxy resins. Some examples of these polymers are conventional ones, such as polymethylmethacrylate (PMMA), polybutadiene (PB) or polystyrene (PS); or technical ones, such as: polyeterimide (PSU), polyeterimide (PEI), etc. The conventional modifiers provide ductility to the epoxy resins but show some limitations, such as a decrease of the T_g which is also associated with a reduction of the service temperature. On the other hand, the technical thermoplastic polymers have higher T_g but limit the flexibility of the modified resins at low and moderate temperatures. These thermoplastic additives must have functional active groups to favor the interaction with the epoxy matrix.

Because of the limitations of the previous modifiers, one of the most interesting alternatives in the modification of thermosetting resins is to use block coplolymers, which combine the advantages of different thermoplastic and elastomeric polymers [2-5]. Recently, Arkema (France) has commercialized a family of these copolymers (diblock and triblock copolymers) constituted by miscible and compatible blocks with epoxy, such as PMMA, PB and PS. The different parts of the copolymer chain will have different tendency to dissolve in the epoxy resin, giving a special microstructure depending of the length of each block [6].

In general, the production of modified epoxy resins using thermoplastic copolymer follows a mechanism named Reaction-Induced Phase Separation, where the miscible polymer is the epoxy precursor and when the reaction progresses, the modifier polymer turns insoluble in the cross-linked network. So, using thermoplastic homopolymers, the morphology of the modified epoxy resins consists on a continuous epoxy matrix with small particles of the modifier polymer. The interface nature between both constituents is conditioned by the reactive groups and being crucial to ensure toughness improvements in the epoxy.

An especial case is the modification of epoxy resins using, for example, three blocks copolymer type SBM which is constituted of polystyrene, 1,4-polybutadiene and syndiotactic poly(methyl methacrylate). Because the PMMA block is miscible with epoxy, PB is partially compatible, being PS immiscible, the repulsive interactions between the three blocks, self-

organize at the nanometer scale. The size and distribution of the dispersed phase are mainly determined by the block lengths (figure 1) [6].
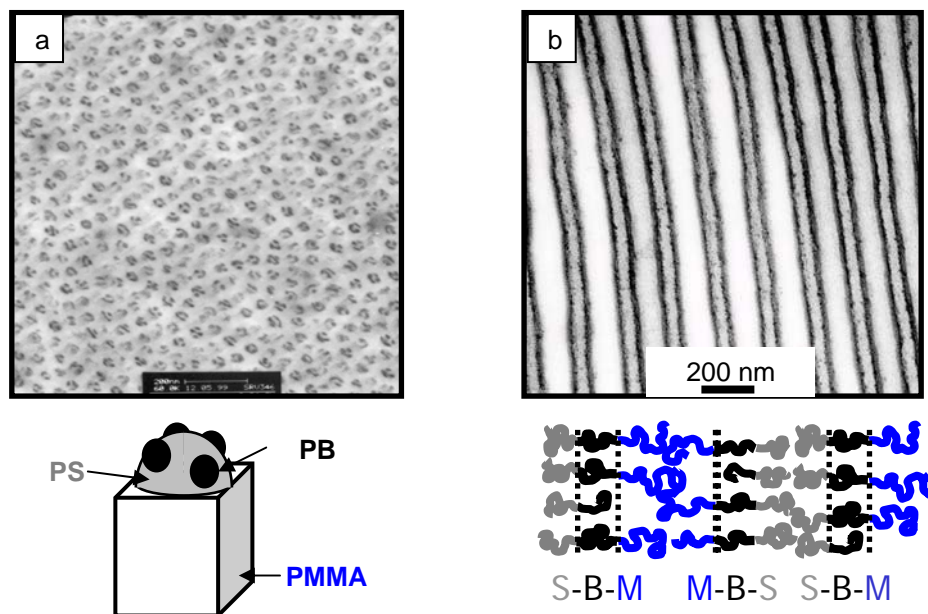

Figure 1: Morphology of modified epoxy resins using different SBM copolymers:
a) S15B5M80, b) S35B5M80 [6].

Properties given by the suppliers of these additives for modified epoxy resins using SBM copolymers in the range of 2.5 to 10 weight % ensure an increase of toughness up to 35% higher than the unmodified resin. On the other hand, the rest of the mechanical properties (stiffness, strength and ductility) maintain the original values.

In the present study, the adhesion capability and the mechanical properties of an epoxy based resin (DGEBA-DDM) modified with several contents of the SBM copolymer (0, 2.5, 5 and 10 wt. % of SBM) have been evaluated using carbon fiber reinforced polymers as adherends. Both single shear lap (SSL) and double cantilever beam (DCB) joined specimens have been tested to determine the influence of the SBM addition on their shear strength and the mode-I fracture toughness.

2 Materials and testing methods

The unidirectional carbon fiber/epoxy laminates ($[0]_{10}$) used as adherends were manufactured by the *Instituto Nacional de Técnica Aeroespacial* (Spain) from unidirectional prepregs (Hexply 8552/34%/UD134/AS4-12K) supplied by *Hexcel* (Stamford, USA). Laminates were made by vacuum bag molding laid up and then cured in an autoclave.

Adhesives were synthesized using as epoxy monomer, the diglycidyl ether of bisphenol A (DGEBA), with 178 g/epoxy equivalent. The curing agent was 4,4'-diaminodiphenylmethane (DDM). Both components of the epoxy adhesive were supplied by *Sigma–Aldrich*. The SBM copolymer was supplied by *Arkema* (France) with the commercial name of *E41*. Contents of 0, 2.5, 5.0 y 10 % respect on the monomer weight were tested. The manufacture procedure consisted on the addition of the SBM copolymer to the DGEBA monomer at 120 ºC, stirring

during 30 min to obtain a homogeneous mixture (magnetic stirrer, Agimatic-E, *Selecta*, Spain). Next, the epoxy precursor was added. A stoichiometric amount of DDM was added to the epoxy/SBM mixtures, followed by stirring at 120 ºC during 5 min to dissolve the hardener. This mixture was used as adhesive by its direct application on the treated laminate surfaces or poured into a mold, previously treated with a semi-permanent release agent (*Frekote®* by *Henkel*), for the fabrication of massive specimens.

Before applying the adhesive on the adherends, their surfaces were prepared by grit blasting which was carried out in a *Guyson* (mod. Jetstream 22, England) grit blaster using 220 grit alumina. Three passes were made with the gun at a distance of 10–15 cm from the specimen surface. The grit blasted surfaces were swabbed with acetone.

The joint strength was determined by single lap shear tests according to the ASTM standard D5868. The adherends were 100 mm long, 25 mm wide and 2.5mm thick. The area of the overlap was 25x25 mm^2, and the adhesive thickness was 0.7 mm. Five tests were done for each adhesive composition. Double cantilever beam (DCB) tests were performed to determine the mode-I adhesive fracture energy of the adhesive joints, following the protocol defined in the standard ASTM D 3433. In this case, the adherends were 150mm long, 25 mm wide and 3.3mm thick. A 75 mm thick polyethylene terephthalate (PTFE) film was inserted at one end of the specimen to act as a crack initiator. To perform the test, a precrack was generated from then on adhesive insert, and then the DCB test was performed. The thickness of the adhesive was 0.4mm

The adhesive microstructure and failure modes were characterized with a Nova Nano SEM230 Field Emission Gun Scanning Electron Microscope (FEG-SEM) from Philips (USA). All surfaces were coated by Au-Pd sputtering. Beside, flexure tests were carried out using massive specimens of the modified DGEB-SBM-DDM cured resins, according to ASTM D790 (B procedure). Additionally, dynamo thermo mechanical tests were also done on these cured epoxy resins, using a flexure mode and applying a deformation of 1 % with a frequency of 1 Hz, between 25 and 130 ºC and a heating rate of 2 ºC/min.

3 Results

Figure 2 shows the mechanical properties obtained by flexure tests for the net epoxy resin and when different amounts of SBM copolymer were added. Low additions produce light increases in strength and stiffness; but increasing the SBM concentrations, the fracture elongation increases and strength and stiffness maintain similar values to the net epoxy. These differences could be justified because the different morphology of the segregated phase as a function of the added copolymer amount. The best combination of mechanical properties which could provide the higher toughness would be close to 10 wt. % in SBM.
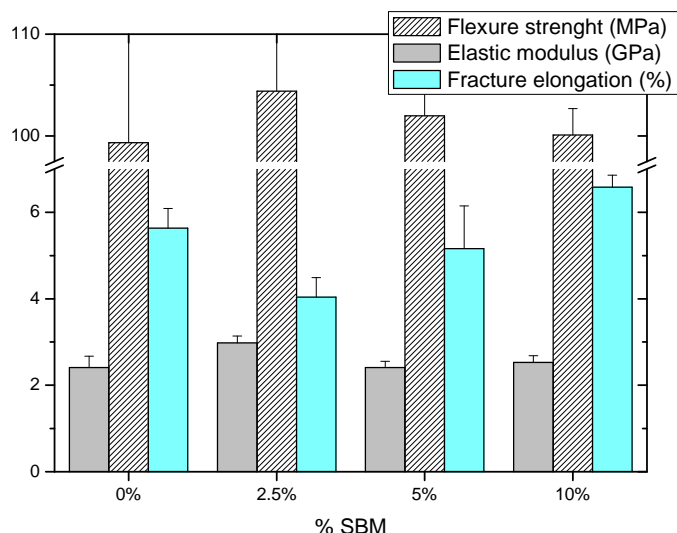
Figure 2: Mechanical properties of the DGBEA-SBM-DDM materials obtained by flexure tests.

Other potential effect of the addition of thermoplastic copolymers to the epoxy resins is the modification of the T_g and them of the service temperature. Figure 3 shows the storage modulus (E') and *tan* δ versus temperature obtained from the DTMA tests of the modified epoxy resins. Table 1 collets the T_g and E' values (both in glass, E'$_G$ and rubbery, E'$_R$ states) determined by this study.
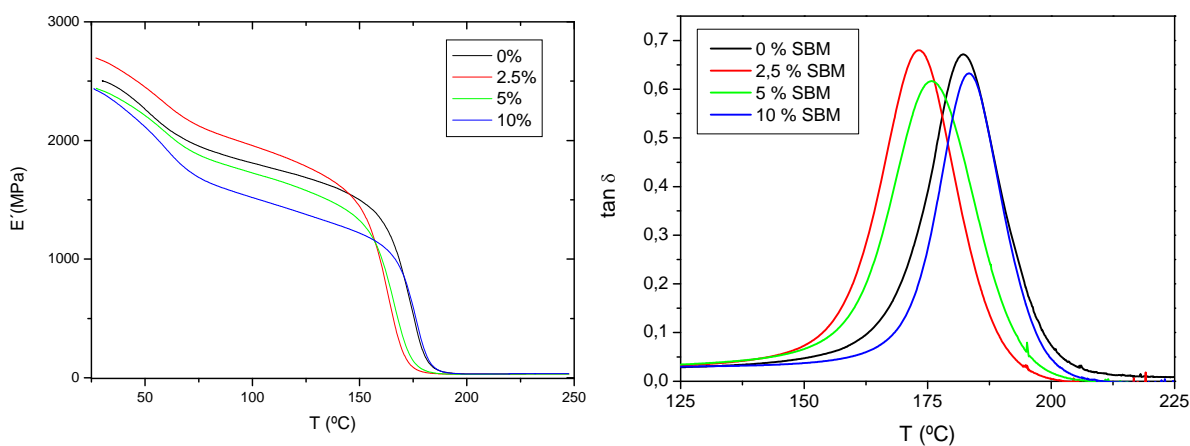

Figure 2. Change of storage modulus and tan δ with temperature for the tested materials

% SBM	T_g (ºC)	E'$_G$ (GPa) at 30 ºC	E'$_R$ (MPa) at 215 ºC
0	182.3	2.50	33.5
2.5	173.1	2.67	32.5
5	175.6	2.41	31.0
10	183.4	2.38	34.0

Table 1. Dynamo thermo mechanical properties of the tested materials

The nanostructured resins show a small maximum of *tan δ* at 67 ºC which intensity increases with the SBM content, being related with one transition of one of the SBM polymeric blocks. The other two blocks have their T_g down to 25 ºC and they have not been detected in these tests. The effect of the addition of SBM on the T_g of the epoxy resin depends again of the morphology of the segregated phase, and two different tendencies have been distinguished. At low SBM contents, the T_g decreases but when a 10 wt. % of SBM is added, this property suffers a light increase. This behaviour is coincident with the observed for the mechanical properties. Beside the glassy storage modulus is higher for the epoxy modified with 2.5 % of SBM, maintaining or decreasing its value respect on the net epoxy one, at higher SBM additions. On the other hand, the elastomeric storage modulus does not depend on the amount of SBM which can be considered as an indication that the cross-linking degree is similar in all tested materials.

Figure 3 shows the shear strengths (LSS) obtained using single over-lap adhesive joints of the grit blasted carbon fiber laminates, applying epoxy adhesives with different amounts of SBM copolymer. In all cases, the addition of SBM provides an improvement of the adhesive strength, especially in the cases of the 10 wt % SBM modified material (> 40 %).
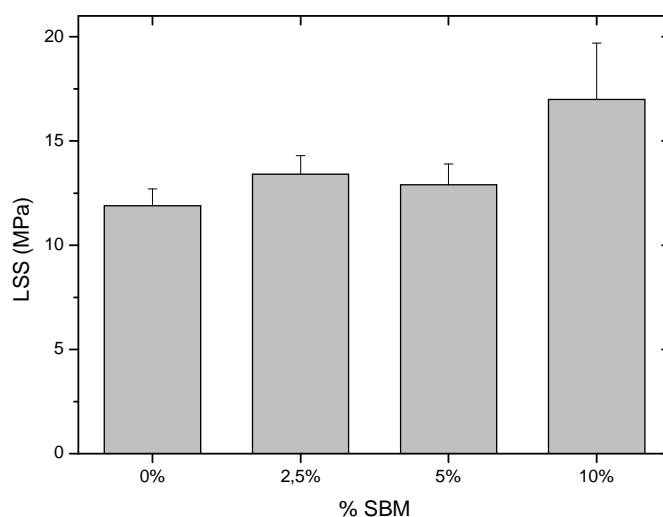

Figure 3. Shear strength of adhesive joints using epoxy resins with different amounts of SBM copolymer

The addition of SBM also favors an increase of the adhesive fracture energy G_{IC} obtaining, for this case, the maximum value when a 5 % in SBM was added to the DGBEA monomer. The increase in toughness can be evaluated in close of 100 % respect on the net epoxy resin (figure 4). The study of the fracture surfaces (figure 5) shows the effectiveness of the nanostructuration to modify the failure mode during the crack propagation, being this the main effect of the SBM addition on the mechanical properties of the epoxy resin when it is used as adhesive.
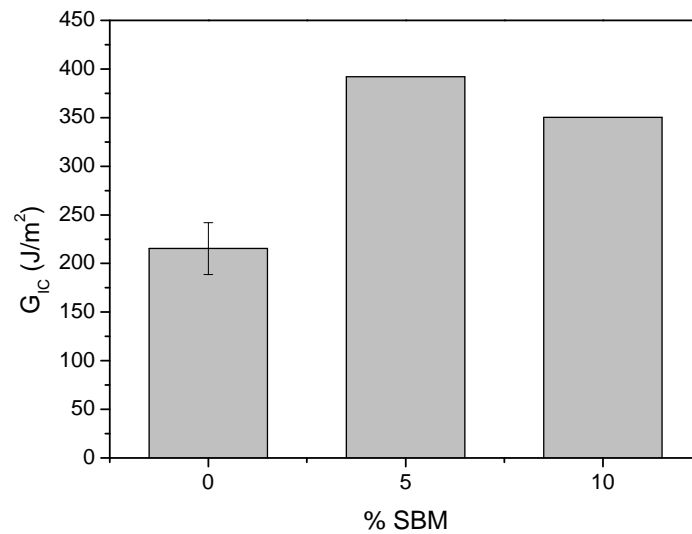
Figure 4. Adhesive fracture energy (G_{IC}) of CFRC with epoxy adhesives modified with different amounts of SBM copolymer
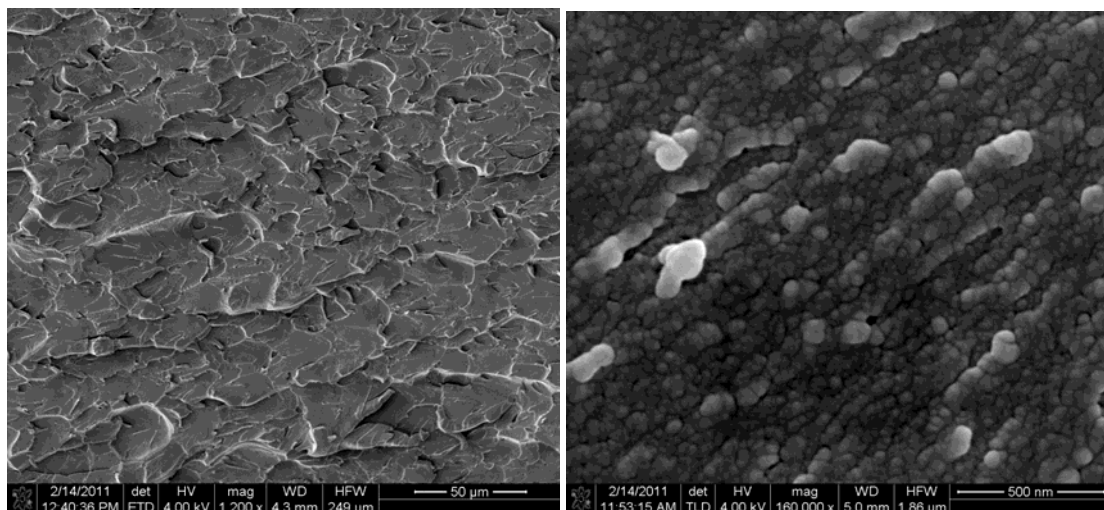

Figure 5. Fracture surfaces of an epoxy adhesive modified with a 2.5 wt % of SBM copolymer

Conclusions

This research have shown that the addition of low content of SBM copolymer (2.5 wt. %) to an epoxy adhesive provides an increase in strength and stiffness, but it is associated to a decrease of the T_g. For this low amount, the contribution of the SBM to the adhesive properties is not important. However, the modification of the DGBEA-DDM resins with concentration of SBM higher than 5 wt % induces important increases of the fracture elongation (13 %), keeping the strength, stiffness and T_g values respect on the net resin ones. The mechanical characterization of adhesive joints with these modified adhesives, using carbon fiber epoxy laminates as adherends, has provide outstanding increases of shear strength (> 40 %) and of adhesive fracture energy (100 %).

Acknowledgements

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