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# Experimental investigation on the effect of nanostructuring on the adherence properties of epoxy adhesives by a probe tack test

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## ABSTRACT

In this work, we aimed to characterize the energy of adherence of nanoscale structured epoxy adhesives Diglycidyl ether of bisphenol-A/Methylene-diethylaniline (DGEBA/MDEA) induced by phase separation triblock copolymers Poly (Methacrylate de Methyl)-b-Poly (Butyl Acrylate)-b-Poly (Methyl Methacrylate) (PMMA-b-PBA-b-PMMA) at gel state by a probe tack test, which is an original use of this kind of test for thermoset adhesives. For a set of mechanical parameters (probe's roughness, contact time, contact pressure and debonding velocity), we measured the energy of adherence for both neat and filled adhesives. The probe tack test was performed at different steps of gelation. We compared the behavior of the adhesives and evaluated the dissipation contribution to the energy of adherence of the adhesives during the test. We finally discussed the nanoparticles' influence on the competition between cavitation and fibrillation. We report that the addition of nanoparticles leads to an overall improvement of the energy of adherence, with a significant increase of the dissipation contribution to the energy measured.

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## 1. Introduction

Epoxy resins are widely used as adhesives for structural bonding. Improving the resilience (i.e., the toughness) of those adhesives would be one way to reduce their brittleness while keeping a structural bonding. A compromise between the improvement of the resilience and the upkeep of other properties may be achieved by adding micro- or nano-particles to the adhesives.

Many approaches exist to achieve an improved resilience. Djilali et al. [1] and others [2,3] used micro particles (siloxane oligomers) in epoxy-amine systems to increase their flexibility. Several works [4–6] used epoxy resins modified with various functionalized butadiene-acrylonitrile rubbers (CTBN, HTBN, ATBN...). In other approaches [7–9], thermoplastics such as polyethersulfones, polyetherimides or polyetheresters were used as fillers.

A general trend observed is a significant improvement in toughening but a strong decrease of the glass transition temperature ( $T_g$ ). The decrease of the  $T_g$  is generally attributed to a poor miscibility of the fillers with the epoxy-amine system.

Increasing the miscibility between the fillers and the epoxy resin is a key point to keep the  $T_g$  constant, and the addition of antiplasticizers [10,11] may be one way to achieve it.

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Thermoplastic polymer used as nanoparticles is another way to improve the flexibility of an epoxy network, thus improve its toughness, without depreciating the  $T_g$ . Indeed, it has been shown that nanostructured epoxy has the same  $T_g$  as the neat epoxy it was obtained from [12–15]. Nanostructuring by thermoplastic polymers is often achieved by having block copolymers, with at least one block being miscible within the epoxy-amine matrix [13,16], which creates a nanoscale phase separation. Several authors reported by transmission electron microscopy (TEM) [13,17,18], scanning electron microscope (SEM) [12,18] or atomic force microscopy (AFM) [19], that this kind of fillers lead to a regular distribution of nanodomains. It was also shown that the nanoparticles filled epoxy had their toughness improved [20], as well as their impact resistance [21].

We chose thermoplastic triblock copolymer to design our nanoparticles filled adhesives. This choice was made after the study of Brethous et al. [22]. They demonstrated that triblock copolymers (named M52 and M22N, supplied by Arkema) was a suitable solution to improve epoxy toughness without strongly depreciate the  $T_g$ . The nanoparticles filled adhesives (referred to as LTA in the following) are obtained by adding the copolymers to the neat adhesive (referred to as HTA in the following). Two of the three blocks of the nanoparticles have a good thermodynamical compatibility with the epoxy resin, which is a necessary condition to achieve nanostructuring of the epoxy resin [13], as reviewed earlier. The third block being insoluble, it is rejected out of the

matrix. Therefore, the nanostructured adhesive has 2 phases, and the insoluble phase presents a nodular shape, with domains of a few nanometer, as reported for similar epoxy toughened by thermoplastic copolymer in the literature [13,23–25].

In order to be effective, an adhesive must wet the surface when the bond is formed and get solid cohesive properties to sustain a certain level of stress during the process of debonding. Structural epoxy-amine adhesives accomplish this by cross-linking.

This kind of adhesives exhibit a debonding energy higher than the thermodynamic work of adhesion  $W_a$  characterizing the formation of chemical bonds at the interface [26]. Toughened epoxy-amine adhesives exhibit an even higher debonding energy [21], mainly due to an increase of viscoelastic dissipation. Many adhesive tests, classified in three categories following the solicitation mode (I, II or III) are used to quantify the total debonding energy [27]. Amongst others, cleavage tests (Boeing wedge test, Double Cantilever Beam), peel tests, shear tests, pull out tests (traction tests) are widely used to quantify this energy. An extensive review of mechanical tests can be found in [28]. For fully cross-linked adhesives, it is known that bulk energy losses are coupled to the thermodynamic work of adhesion,  $W_a$  [26]. However, when the adhesives are weakly cross-linked, it is possible to study one or another contribution to the debonding energy. Probe tack tests are usually used to evaluate the contribution of the dissipative energy of lightly cross-linked adhesives [29]. Indeed, tacky materials are often close to a nearly uncross-linked network, which is a suitable molecular structure to exhibit high tack energy (i.e., a high debonding energy) [30].

This paper brings a contribution to the field by studying the dissipative behavior of thermoset adhesives, and the impact of the addition of nanoparticles on this dissipation. We perform tack tests at different gelation steps for weak conversion rates, which is an original use of this method to measure the adherence of thermoset adhesives.

Firstly, a rheological study is carried out to determine the gelation span (i.e., the interval within which the thermoset adhesives can be tested by a probe tack test) for both filled and neat adhesives. Secondly, we perform probe tack tests at different gelation steps. For each adhesives, we study the evolution of the energy of adherence as a function of the cross-linking time. Finally, we discuss the impact of the addition of nanoparticles on the dissipative behavior of thermoset adhesives.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Adhesives

Diglycidyl ether of bisphenol-A (DGEBA) (DERR332, Sigma Aldrich, functionality of 2) is used as the epoxy resin. The epoxy resin is mixed to a tri-amine hardener (MDEA, Lonzacure, functionality of 4), with a stoichiometrical ratio of 1:0.31. This adhesive can be filled with two kinds of copolymers: M52 and M22N, supplied as powders, by Arkema [22]. M52 and M22N are triblock copolymers made of Poly (Methacrylate de Methyl)-b-Poly (Butyl Acrylate)-b-Poly (Methyl Methacrylate) (PMMA-b-PBA-b-PMMA). The suffix N indicates that dimethylacrylamide (DMA) is incorporated into the PMMA block to increase the miscibility of the PMMA blocks with epoxies. The M22N has a lower Poly (Butyl Acrylate) soft block fraction content than the M52 [31].

The neat adhesive is obtained by first heating up the DGEBA to 160 °C, then adding the MDEA hardener. The mixture is then stirred vigorously for 5 min at 160 °C. The nanostructured adhesives are obtained by first heating up the DGEBA to 160 °C. Then the nanoparticles (either M52 or M22N) are added by step of 0.1 g to avoid

**Table 1**  
Properties of the epoxy resins [22].

Uncured systems	DER 332-MDEA	DER 332-MDEA + 10% M52	DER 332-MDEA + 10% M22N
Viscosity at 25 °C (Pa.s)	0.9 ± 0.2	9.2 ± 0.8	19.6 ± 1.5
Fully cured systems	DER 332-MDEA	DER 332-MDEA + 10% M52	DER 332-MDEA + 10% M22N
$T_g$ (°C)	167 ± 3	170 ± 3	164 ± 3
$E$ (GPa)	2.73 ± 0.03	2.55 ± 0.03	2.61 ± 0.03
$K_{IC}$ (MPa.m <sup>1/2</sup> )	0.89 ± 0.04	1.24 ± 0.12	0.98 ± 0.05

agglomeration of the powder. After putting the first 0.1 g, the mixture is vigorously stirred until complete dissolution of the powder in the epoxy resin. Then the next 0.1 g are added, and so on until the whole weight is completely mixed. The temperature is kept constant and equal to 160 °C during the copolymer incorporation to ensure phase inversion. Finally, the MDEA hardener is added as for the neat adhesive. In this study, we prepared three formulations: the first formulation is the neat adhesive, referred to as HTA. Both nanoparticles filled adhesives are filled with 10 wt% of nanoparticles. The adhesive filled with the M52 is referred to as LTA M52, while the adhesive filled with the M22N is referred to as LTA M22N.

The nature of the copolymers and their influence on the epoxy network have been reported elsewhere [22]. They are briefly summarized in Table 1. The most important trend is that filling the neat adhesive with 10 wt% of nanoparticles (either M52 or M22N) does not change the  $T_g$  nor Young's modulus, while increasing the toughness.

#### 2.1.2. Substrates and probe preparation

Transparent glass slides (50 × 50 × 1 mm<sup>3</sup>) were used as the substrates. The probe is machined from a commercial steel tube to a final diameter of 6 mm. The surface of the probe is polished to a mirror-like roughness ( $R_a \sim 33 \pm 7$  nm).

### 2.2. Methods

A probe tack test is used to characterize the energy of adherence of the thermoset adhesives. The probe tack test has been extensively used to characterize *Pressure Sensitive Adhesives* (PSA) [32–34]. A PSA (which is commonly made of thermoplastic polymers) is usually considered as good if it can form a strong bond with a substrate over a short time, and dissipate a large amount of energy during debonding. Many variables are relevant in such a test: contact force, contact time, debonding speed as well as interfacial free energy between the adhesives and the probe, and the rheological properties of the polymer. The relevant parameter is the tack energy (i.e., the energy of adherence), which is estimated as the area under the curve Force versus Time during the debonding step (or equivalently on the Force versus Displacement curve, since a *constant speed* is applied during debonding). Study of the shape of the curve during debonding [35] and of the deformation behavior during debonding [36] give additional insight on the energy measured, by splitting the total energy into cavitation and fibrillation contributions, as shown on Fig. 1. Besides measurement of the force over time, optical video imaging has also been extensively used to explain the viscoelastic dissipation. It has been observed that a high tack adhesive exhibits cavitation during the early stage of debonding, followed by extensive fibrillation [36]. Depending on the rheological parameters of the adhesive, several cases can be observed during debonding (here, we consider a constant arbitrary debonding speed):

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