

SIMULTANEOUSLY TOUGHENED AND ELECTRICALLY CONDUCTIVE EPOXY RESIN FORMULATIONS. THE EFFECT OF TOUGHENER ON THE MECHANICAL AND ELECTRICAL PROPERTIES

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Abstract

Nowadays, multifunctionality become highly desired in the field of fiber reinforced polymer composites for aerospace industry. Within the scope of this research, electrically conductive and tough epoxy resin formulations were investigated, with specific focus on the morphology, additive distribution and resulting macro-scale properties. As electrically conductive additive, carbon black (CB, 1.5 wt%, fixed concentration) is used to modify diglycidylether of bisphenol A (DGEBA) – 4,4'-diaminodiphenyl sulfone (4,4'-DDS) system. In addition to CB, various organic tougheners including core-shell particles (CS) and two different grades of tri-block copolymers of PMMA-b-PBA-b-PMMA are used up to 10 wt% (M22N and M52N). The M52N having higher soft phase compared to M22N increased the fracture toughness of the DGEBA-4,4'-DDS resin system at most, from 0.55 to 1.26 MPa·√m at 10 wt% concentration. Core-shell and M22N tougheners induced cavitation and promoted plastic deformation of the matrix. However, M52N showed cavitation, crack bridging and increased plastic deformation of the matrix as micro-mechanical toughening mechanisms. Besides fracture toughness, organic tougheners showed enormous effect on the electrical conductivity by affecting the network formation of CB. The addition of core shell and M52N tougheners increased the electrical conductivity by promoting stronger CB network. However, M22N inhibited strongly the CB network formation.

1. Introduction

In last two decades, fiber reinforced polymer composites are used extensively in commercial aircraft industry as structural materials due to their specific stiffness and strength, chemical and thermal resistances, etc. For primary structures such as fuselage and wings, besides very high mechanical and thermal performance of the polymeric composite, a certain level of electrical conductivity is as well desired to provide electrostatic dissipation and/or lightning strike protection.

It is well known in the literature that epoxy rich interlayers of the epoxy fiber reinforced composites especially with highly interlayer toughened aerospace grade composites have very poor transverse electrical conductivity ($E_{dc-interlayers}$: 10^{-13} S/m) [1]. One of the strategies to achieve electrical conductivity in z-direction of a composite is to modify the polymer matrix with conducting additives. For this aim, carbon based additives such as carbon black, carbon nanotubes and graphene [2-6], metal based additives such as copper [7], silver nanowires and nanoparticles [8, 9] have been used often.

To produce a conducting polymer formulation, conductive additive should possess a 3-dimensional network providing pathways of electron transport through the whole polymer. On the other hand, it is well known that the better fracture toughness can be achieved by the homogeneous dispersion and distribution of the toughening additives. As a result, to achieve toughness and electrical conductivity simultaneously, a novel morphology possessing homogeneous toughener dispersion with aggregated conductive additive network formation is expected to be necessary.

In this research, diglycidylether of bisphenol A (DGEBA) cured with 4,4'-DDS is chosen as the reference high T_g epoxy system and modified with an industrially available conducting additive and various types of tougheners simultaneously. Highly conducting carbon black (fixed concentration of 1.5 wt% for all composites) is used to improve the conductivity of the epoxy matrix. To simultaneously increase the toughness, core-shell particles and two different grades of functionalized tri-block copolymer of PMMA-b-PBA-b-PMMA (named as M22N and M52N) are used up to 10 wt%. M22N has higher molecular weight, higher polarity but a smaller soft-phase (polybutyl acrylate comonomer) compared to the M52N. Cured nanocomposites are then characterized with dynamical mechanical thermal analysis (DMTA), direct current electrical resistance measurement (R_{dc}) and fracture toughness (K_{Ic} and G_{Ic}) testing.

2. Materials

The epoxy resin used in this study is the diglycidylether of bisphenol A (DGEBA) resin, Baxxores 2200[®] (epoxy equivalent weight: 182 g mol⁻¹ provided by BASF). As hardener, the 4,4'-diaminodiphenyl sulfone (4,4'-DDS) ORGANICA[®] (amine equivalent weight: 62.075 g mol⁻¹ provided by Feinchemie GmbH) is chosen. The chemical structures of the DGEBA and 4,4'-DDS is shown below in figure 1.

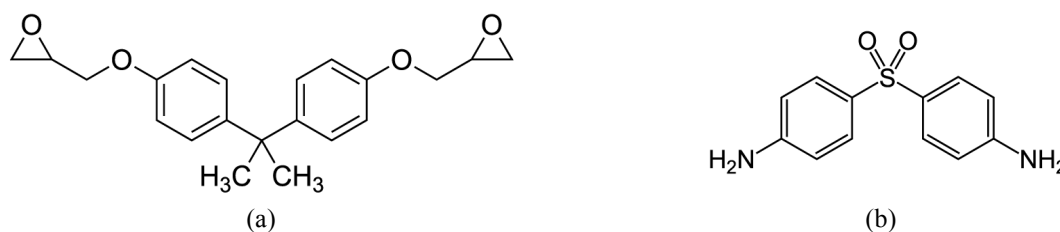


Figure 1. (a) DGEBA resin, (b) 4,4'- DDS hardener

Carbon black, Printex XE-2B (primary particle size: 20 nm, provided by Orion Engineered Carbons GmbH) with highly branched aggregate structure called *high structure* is used as conductive filler. As tougheners, core-shell particles, Albidur EP 2240-A (cross-linked polysiloxane core with stiff-epoxy compatible shell, SLS: 2 μ m average particle size, provided as 40 wt% masterbatch in DGEBA by Evonik AG) and two different grades of functionalized tri-block copolymer of PMMA-b-PBA-b-PMMA (MAM), Nanostrength[®] (provided by ARKEMA) are used which are called as M52N and M22N. M22N has higher molecular weight, higher polarity but lower soft phase content compared to the M52N. The molecular structure of the tri-block copolymers are shown schematically in fig. 2 below.

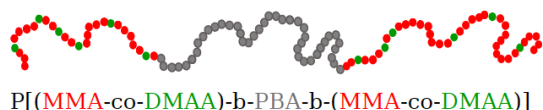


Figure 2. Molecular structure of the functionalized tri-block copolymers.

3. Composite production and experimental methods

3.1. Composite production

Within the scope of this work, except the neat resin, the amount of the carbon black (CB) is fixed for every composite which is 1.5 wt%. Following, the amount of the organic tougheners (core shell, M22N and M52N) are increased from 2.5 wt% up to 10 wt%. In case of tri-block copolymer M22N, it was only possible to produce mentioned testing samples up to 7.5 wt% toughener content due to lack of degassing for higher toughener content.

3.1.1. Production of carbon black – core shell epoxy composites

The calculated amount of DGEBA, carbon black and core shell – DGEBA masterbatch (40 wt% core shell) were weighted, and mixed at 90 °C in an oil bath with a laboratory mixer for 15 minutes. Following, the mixture was dispersed further with a three-roll-mill (EXAKT 120 EH-450, Germany). 3-roll milling was done in one cycle with 15 µm and 5 µm gap distance in between rolls. Following, stoichiometric amount of 4,4'- DDS was weighted and mixed with laboratory mixer at 140 °C for 40 minutes to dissolve the hardener. The final mixture was then degassed at < 10 mbar vacuum environment for minimum 10 minutes. At last, degassed batch was cured isothermally in an aluminium mold at 180 °C for 150 minutes.

3.1.2. Production of carbon black – tri-block copolymer epoxy composites

Tri-block copolymers M52N and M22N are solid pellets which are soluble in DGEBA resin before curing reaction and form a phase separated morphology during curing. First of all, weighted amount of CB and DGEBA resin is mixed with three-roll mill using the production parameters mentioned above. Following, the tri-block copolymer is added to CB-DGEBA mixture and mixed at 140 °C for 20 minutes to dissolve the tri-block copolymer completely. The stoichiometric amount of 4,4'- DDS is calculated, weighted and added to the mixture at 140 °C and the final mixture is further mixed for another 40 minutes with laboratory mixer to dissolve the hardener. The final mixture was then degassed and cured as same as core shell carbon black epoxy composites.

3.2. Dynamical mechanical thermal analysis (DMTA)

Dynamical mechanical thermal analysis (DMTA) was performed according to DIN EN ISO 6721-7 using an Advanced Rheometric Expansion System (ARES RDAIII, Rheometrics Scientific) in torsional mode. An elastic deformation of 0.1 % with a frequency of 1 Hz was applied, from 25 to 250 °C at a heating rate of 3 K/min. According to the standard, rectangular samples were used (50-10-2 mm³). The glass transition temperature (T_g) of the epoxy composites was determined as the maximum of the loss factor, $\tan.\delta$.

3.3. Fracture toughness (K_{Ic} and G_{Ic}) testing

Fracture toughness of nanocomposites was determined according to ISO 13586 using CT specimens. The specimen length was $1.25w = 41.25$ mm and the thickness $d = 4$ mm. For each sample, a sharp crack was generated by tapping a sharp razor blade into the machined V-notch. The tests were carried out using a universal testing machine Zwick BZ2.5/TN1S (Zwick GmbH & Co. KG, Ulm, Germany). The crack opening displacement (COD) was measured using a clip extensometer (632.29F-30, MTS, Germany). The critical stress intensity factor at the crack tip (K_{Ic}) was calculated using eq. (1) which is written below. The critical strain energy release rate (G_{Ic}) of the neat epoxy and nanocomposites were calculated according to the eq. (2).

$$K_{Ic} = \frac{F_{max}}{d\sqrt{w}} aY(a/w) \quad (1)$$

F_{max} represents the maximum force required for unstable crack propagation, a the crack length, w sample length from loading point (33 mm), d sample thickness and $Y(a/w)$ is a geometrical term.

$$G_{Ic} = \frac{K_{Ic}^2}{E_{SH}} \quad (2)$$

E_{SH} is the elastic modulus calculated according to theory of Saxena and Hudak from the material compliance during unstable crack propagation.

3.4. Direct current electrical resistance testing

The electrical resistance of the nanocomposites are measured according to the ASTM D257 with a multimeter Keithley 2100. To achieve an excellent contact in between the modified polymer and the electrodes, composites were cured in between of two round electrodes at the distance of 1 mm in a rheometer. During curing, 1 mm sample thickness was kept constant. The effective electrode diameter was 4 cm.

4. Results and discussions

First of all, the effect of addition of CB and various organic tougheners on the T_g of the DGEBA – 4,4'-DDS system is investigated. *Tan.delta* is used to evaluate and compare the glass transition temperature of the composites. The results are shown below in fig.3.

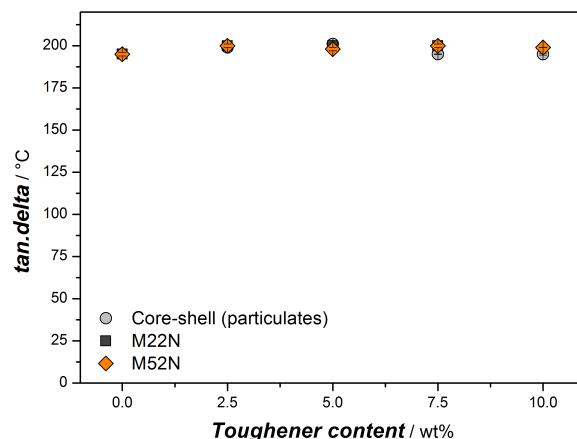


Figure 3. Glass transition temperature of the composites. Except neat system, all composites have fixed amount (1.5 wt%) of carbon black. Organic toughener content is varied up to 10 wt%.

As it can be seen above in fig. 3, the addition of the organic tougheners with fixed 1.5 wt% CB did not significantly affect the T_g of the neat resin system.

Composites are then characterized with fracture toughness tests according to ISO 13586 and results are presented below in figure 4.

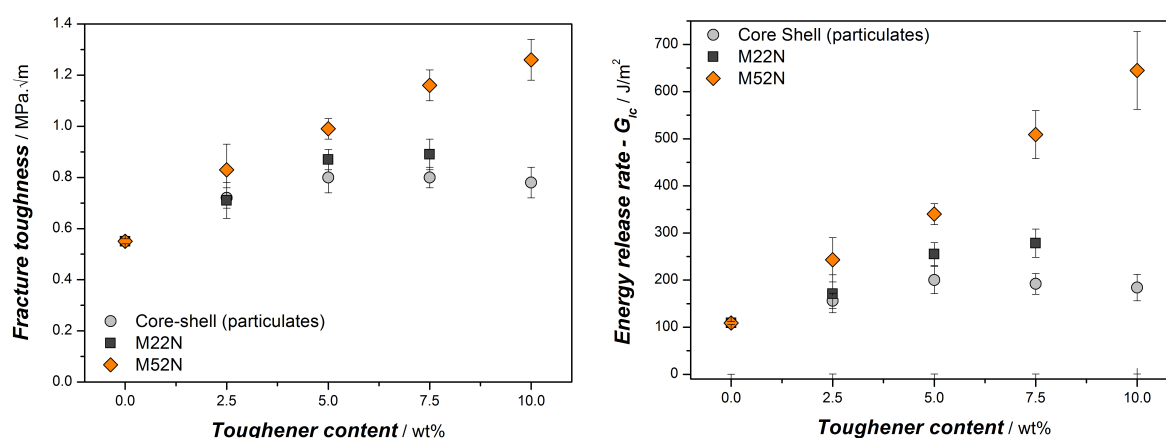


Figure 4. Fracture toughness (K_{1c}) and strain energy release rate (G_{1c}) of the composites versus organic toughener content up to 10 wt%.

As it can be seen from the figure 4, addition of all types of tougheners increased the fracture toughness and strain energy release rate of neat epoxy. Neat DGEBA – 4,4'-DDS has K_{1c} of 0.55 ± 0.01 MPa.√m. The addition of core shell particles up to 5 wt% increased the toughness almost linearly which is followed by a plateau region. Highest fracture toughness achieved with CS addition was 0.8 ± 0.06 MPa.√m at 5 wt% CS content. In case of M22N tri-block copolymer, the highest fracture toughness achieved was 0.89 ± 0.06 at 7.5 wt% filler loading. On the other hand, the highest toughness was achieved by the addition of M52N triblock copolymer. Fracture toughness of neat epoxy increased linearly by the addition of M52N which reaches to 1.26 ± 0.08 MPa.√m at 10 wt% of filler content.

Below in fig. 5, the fracture surfaces of multifunctional composites having 7.5 wt% organic toughener content and 1.5 wt% fixed CB content are shown. As it can be seen in fig.5-a above, the neat DGEBA

4,4'-DDS system shows very smooth fracture surface indicating the lack of plastic deformation during the unstable crack propagation. On the other hand, core-shell particles resulted in cavitation and increased surface roughness indicating higher plastic deformation of the matrix (fig.5-b). In case of M22N triblock copolymer (fig.5-c), nanophase separation of the toughener was seen. As micromechanical toughening mechanisms, homogeneously distributed 30 nm cavitates and increased roughness indicating higher matrix deformation are observed. Finally, as it is shown in fig.5-d, M52N triblock copolymer showed rather elongated cavitates (<100 nm) and very rough fracture surface indicating high plastic deformation during crack propagation. In addition, at very high magnifications of SEM (100 kX) crack bridging was as well observed which is expected to increase the strain energy release rate during crack propagation even further.

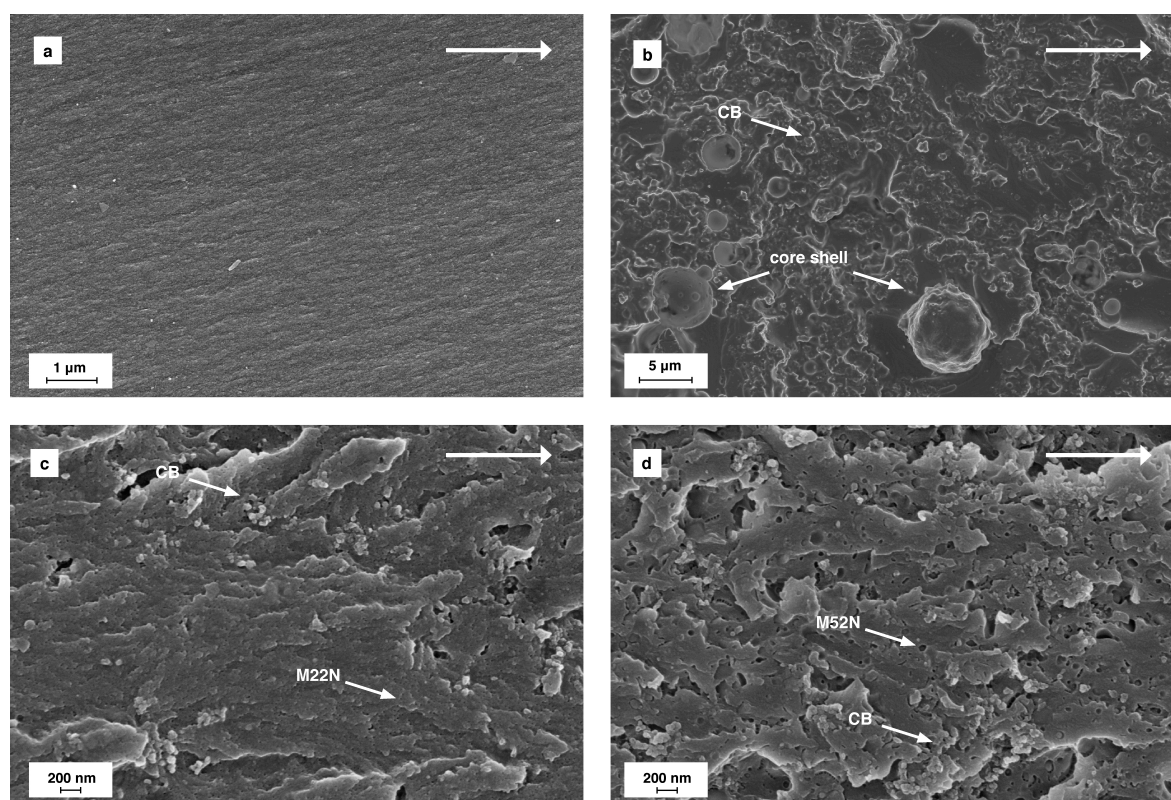


Figure 5. SEM micrographs of the fracture surfaces of the composites. Crack propagation direction is from left to right. a) neat resin, b) core-shell - carbon black, c) M22N - carbon black and d) M52N - carbon black epoxy composites. Toughener and carbon black content is 7.5 wt% and 1.5 wt%, respectively.

The electrical resistance of the multifunctional composites are measured according to the ASTM D257. From the measured resistance of composites, the calculated electrical conductivity results are shown in fig.6 below.

Addition of only 1.5 wt% carbon black increased the conductivity of the neat system up to $1.3 \pm 0.3 \cdot 10^{-4}$ S/m. As it can be seen in fig.6, addition of organic non-conductive tougheners showed dramatical effect on the conductivity of composites. Addition of 7.5 wt% CS and M52N to the 1.5 wt% CB – DGEBA-4,4'-DDS system increased the conductivity further to 0.019 ± 0.005 S/m and 0.017 ± 0.01 S/m respectively. On the other hand, deteriorating effect of triblock copolymer M22N was clearly observed especially above 2.5 wt% M22N content. The addition of 7.5 wt% M22N into the 1.5 wt%

CB loaded epoxy system resulted in 10^{-7} S/m conductivity which is almost 1000 times lower compared to the only 1.5 wt% CB modified epoxy.

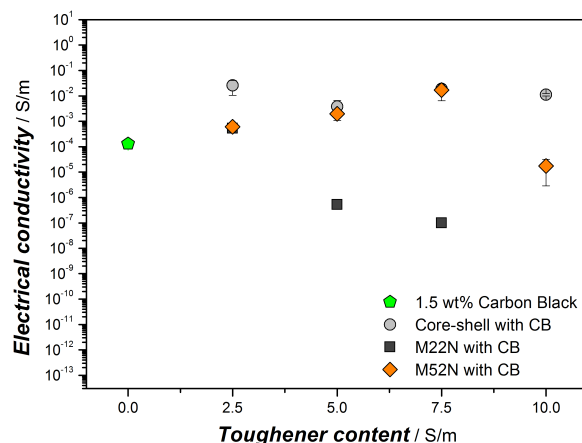


Figure 6. Electrical conductivity results of multifunctional composites. The carbon black content of all the nanocomposites are fixed at 1.5 wt%. Toughener content is increased up to 10 wt%.

5. Conclusions

As a summary, synergistic effects in between the organic tougheners and carbon black conductive filler were studied by focusing on fracture toughness and electrical conductivity. Addition of the all the toughening agents increased the critical stress intensity factor (K_{Ic}) and as well energy release rate (G_{Ic}) compared to the neat epoxy. Triblock copolymer M52N with higher soft phase content increased the K_{Ic} of the neat DGEBA-4,4'-DDS up to $1.26 \text{ MPa}\cdot\sqrt{\text{m}}$ which is 230% of the toughness of neat epoxy. In addition, tougheners CS and M52N having good dispersion with relatively localized distribution supported the carbon black conductive network formation during curing process which led to higher conductivities compared to the epoxy with only carbon black. The tri-block copolymer M22N on the other hand inhibited strongly the carbon black agglomeration due to the very homogeneous dispersion and distribution of the phase separated cavities leaving no free volume for carbon black to agglomerate during curing.

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