

EFFECT OF PEG-B-PPG-B-PEG COPOLYMER MASS FRACTION ON CARBON BLACK NANOCOMPOSITES

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ABSTRACT

The present research aims to evaluate the mass fraction of triblock copolymers to verify the dispersion of carbon black (CB). The polymer matrix was formed by an epoxy resin and a triblock copolymer consisting of poly(ethylene glycol)/poly(propylene glycol)/poly(ethylene glycol) (PEG-b-PPG-b-PEG) with a weight of 14,600 g /mol and 82.5% of PEG in its blocks dispersed in the epoxy resin by the fraction of 20% m/m and 10% m/m. Then, three different fractions of carbon black (CB) were added in the preparation of nanocomposites (1.5%, 3% and 6% w/w). The methodology chosen for this study was the "in situ" preparation of the compositions: the samples were cured at 60° C for 24 hours and then placed at a temperature of 100° C for 1 hour for the post-curing step. To proceed the characterization, morphological and thermal properties of the composite were carried out. In order to evaluate the dispersion of nanoparticles in the matrix, transmission optical microscopy (MOT) and field effect scanning electron microscope (FEG) analysis were performed. To evaluate the thermal properties, differential scanning calorimetry (DSC) test was performed. The study showed that 10% of copolymer (COP) presented a better dispersion of carbon black (CB) nanoparticles.

Keywords: Epoxy, Copolymer, Carbon Black, FEG.

INTRODUCTION

Epoxy resins are thermosetting polymeric materials and have a range of applications including automotive, aeronautical, construction, sports equipment, electronics and so on due to their excellent adhesion, low density, good durability, chemical, thermal and mechanical resistance ⁽¹⁾. The cured epoxy has high performance properties, but its structure is highly crosslinked, presenting high fragility, causing in some cases limitations of its application ⁽²⁾.

In recent decades, investigations have been carried out to reach better understanding of the behavior of thermoset systems modified by the addition of block copolymers ^(2, 3-4), so that there is a better toughening of thermosets. However, when there is an increase in fracture toughness, it has a consequent loss in the Young modulus and in the glass transition temperature (Tg) ⁽³⁾. To minimize the plasticizing effect of the copolymer and increase Young's modulus, nanoparticles were used.

Because nanoparticles have a high surface/volume ratio, which increases the number of particle-matrix interactions ⁽⁵⁾, they can act as a desirable interface for stress transfer, but they

can also act disadvantageously such as inducing strong forces between them, leading to an excessive agglomeration behavior ⁽⁶⁾.

There are studies $^{(6,7-8)}$ on the use of block copolymer as dispersing agents for nanoparticles. The authors reported that there was a better dispersion of these nanoparticles with the addition of the block copolymer, evidencing the increase in mechanical properties. Thus, it is intended to study which of the 10% and 20% block copolymer fractions can obtain a better dispersion of carbon black nanoparticles (1.5%, 3% and 6% w/w) in order to obtain improvements of the properties as a whole.

MATERIALS AND METHODS

In order to carry out the copolymer/epoxy mixture, the copolymer was first placed under magnetic stirring for approximately 100 °C and 2 minutes so that after being added to the epoxy resin, complete homogenization could be reached. When the copolymer was homogeneous, the epoxy resin was added and mixed for approximately 2 minutes under magnetic stirring.

Carbon black (CB) nanoparticles were added to the copolymer/epoxy mixture at a temperature of 80 °C and initially mixed by magnetic stirring and later by sonication with high power ultrasound (Sonics VX750) to obtain a better dispersion of nanoparticles. The power used in the sonication was 20% and the energy added to the mixture was 400 J/g and the total amount of energy was used for each mixture.

As the last, the hardener was added and mixed only under magnetic stirring for 10 minutes and the specimens were released by casting in silicone molds, according to the standard of each test.

For the characterization of the composite, morphological and thermal analyzes were performed. Morphological analyzes were carried out using a transmission optical microscope (MOT) using the OLYMPUS UTV05XC-3 equipment. In this analysis, two coverslips were employed, in which a little of the epoxy/copolymer/nanoparticles mixture was placed in one of them and the curing process was accomplished normally, the samples for analysis are illustrated in Figure 1, the black squares indicate the area that was analyzed.

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1.5% NE	2% NE	6% NE	1.5% ME	2% NE	6% NE

Figure 1: Samples for MOT analysis, the letter A represents samples with 10% copolymer and the letter B with 20% copolymer (Author, 2022).

Another analysis carried out to evaluate the dispersion of nanoparticles in the field effect scanning electron microscope (FEG), the JEOL equipment, model JSM 6701F (UDESC – CCT). To perform the analysis of the nanocomposites, fractures were accomplished in the samples in order to obtain high resolution images of the fractured surface.

To determine the thermal properties, the differential scanning calorimetry (DSC) test was used, in the Maia-230 NETZSCH equipment (UDESC-CCT). To perform the analysis, the samples were scraped and subjected to two cycles of heating and cooling at a rate of approximately 10 °C/min maintained in a controlled atmosphere of nitrogen. The first heating started at 0°C up to approximately 250°C, followed by a cooling at a rate of 10 °C/min. The second heating cycle was from 0°C to approximately 250°C. The glass transitions (TG) were

obtained using the second heating cycle as a reference, since the first one was performed in order to eliminate residual stresses in the material.

RESULTS AND DISCUSSION

Dispersion Study

Figure 2 shows the transmission optical microscopy (MOT) analysis of the different proportions of epoxy/copolymer/nanoparticles. It is observed that in Figure 2 B, C, E and F it is possible to see areas of black color of different sizes as indicated by the white dotted circles. According to the literature, these darker areas represent rich zones in nanoparticle clusters and the lighter areas are regions with few clusters ⁽⁹⁾.

In Figure 2, the black arrows in A, B, C and D are indicating trapped air bubbles and the composite mixture ended up crosslinking in this air bubble. The white dotted circles show that the agglomerates of the nanoparticles increased with the growth of the amount of carbon black (CB). Although they were agglomerated, it can be observed that the sizes of the agglomerates are small, some studies have addressed that the role of the block copolymer would help in the dispersion of nanoparticles, since the copolymer may act as a dispersing agent for nanoparticles in the matrix ^(10, 11-12).

It was verified that the samples with a concentration of 10% of copolymer showed a better distribution of agglomerates than those with 20% copolymer for they did not have 100% cure and the nanoparticles had time to re-agglomerate. According to the literature ⁽¹³⁾, after the dispersion of nanoparticles it is possible to reassemble the nanoparticles that were not dispersed in the sonication. The incorporation of the hardener in the mixture can also cause re-agglomeration of the nanoparticles because the viscosity of the hardener is lower than the one of the resin ⁽¹⁴⁾. Another factor would be the rise in temperature during the curing process, which serves as a driving force to induce the nanoparticles to re-agglomerate ⁽¹⁵⁻¹⁶⁾.



Figure 2: MOT micrographs showing the dispersion state for the nanocomposites (A) 10%COP1.5%CB (B) 20%COP1.5%CB (C) 10%COP3%CB (D) 20%COP3%CB (E) 10% COP6%CB (F) 20%COP6%CB (Author, 2022).

Figure 3 illustrates the results of the FEG in which it is possible to verify that in both concentrations the nanoparticles are agglomerated, in the proportions of 10% copolymer + 1.5% carbon black and 10% copolymer + 6% carbon black obtained a better dispersion of the nanoparticles compared to the concentration of 3% carbon black that it is possible to visualize the rich concentration of agglomerates of the nanoparticles of carbon black (CB), as shown in Figure 3B with the black circles on the left. In this analysis, only the samples with 10% of block copolymer were performed (illustrated in Figure 3), because the samples with 20% of copolymer were not crosslinked. This increase in the copolymer from 10% to 20% could be preventing the coalescence of these materials and that is what happened with the 20% copolymer mixture.



Figure 3: FEG micrographs showing dispersion of nanoparticles in the epoxy/copolymer/nanoparticle system (A) 10%COP1.5%CB (B) 10%COP3%CB (C) 10%COP6%CB (Author, 2022).

DSC Analysis

Table 1 shows the Tg values found for the nanocomposites studied in this research, which were obtained from the inflection of the transition curves of the second heating of DSC (see Figure 4). The Tg found for pure epoxy agrees with the literature. Silva ⁽³⁾ used the same resin and hardener 4,4 Diaminodiphenylmethane (DDM)) and found a Tg of 180 °C.

While for the epoxy and copolymer samples there was a sudden drop in Tg of 50% and 62.4% compared to pure epoxy. In this way, it can be observed that the higher the percentage of copolymer in the samples, the lower the glass transition temperature. This is due to the

plasticization effect of the block copolymer, which ended up resulting in a reduction in the network crosslink density of the epoxy ⁽³⁻¹⁷⁾.

Analyzing the samples with the addition of carbon black, it was observed that the samples with 6% CB had a lower Tg compared to the other samples and had a small difference in Tg compared to the copolymer/epoxy samples. Silva ⁽³⁾ reported in his study that in relation to nanocomposites without block copolymer, it can be observed that the addition of the copolymer PPG-b-PEG-b-PPG obtained a decrease in Tg for both nanoparticles of carbon nanotubes, graphene and carbon black. These results suggest that the nanoparticle geometry did not interfere with the plasticization effect of this block copolymer.

With the addition of carbon black there was no drastic decrease in the glass transition temperature (Tg), it is noted that in the epoxy/10% copolymer/3% carbon black nanocomposites there was a decrease and then the Tg increased by 6% carbon black. Fiore ⁽¹⁸⁾ studied nanocomposites (polyester and carbon black) and reported that with the addition of 3% carbon black there was a decrease in Tg and the first signs of matrix percolation became evident. For the nanocomposites with 20% copolymer, the sample that had a decrease in Tg was with 6% carbon black, the other two samples had the same Tg.

2022).					
Samples	Tg (°C)	<u>Samples</u>	Tg (° C)		
Epoxy	178 ±2	Epoxy + 20%Cop + 1.5%CB	51 ±2		
Copolymer	-57 ±2	Epoxy + 20%Cop + 3%CB	51 ±2		
Epoxy + 10%Cop + 1.5%CB	87 ±2	Epoxy + 20%Cop + 6%CB	40 ±2		
Epoxy + 10%Cop + 3%CB	70 ±2	Epoxy + 10% Cop	90 ±2		
Epoxy + 10%Cop+ 6%CB	87 ±2	Epoxy + 20%Cop	67 ±2		

Table 1 - Glass transition temperature (Tg) obtained by the second heating of the DSC (Author, 2022).

CONCLUSIONS

In this research it can be observed that as the amount of carbon black (CB) in the matrix material increased, the agglomerates of the nanoparticles grew. However, even if there were these agglomerations, the sizes of the agglomerates were small, that is, the block copolymer served as a dispersing agent for nanoparticles in the matrix.

It was observed that as the fraction of the copolymer increased, it ended up avoiding the coalescence of these materials, thus, for the continuity of the study, the fraction of 10% of copolymer in block was chosen in order to analyze the study of the percolation threshold, and the percentages of carbon black remained the same.

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