

Influence of the incorporation of flexographic photopolymer plate residues on the mechanical properties of epoxy

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Abstract

A thermosetting epoxy polymer composed of diglycidyl ether of bisphenol A and triethylenetetramine (DGEBA/TETA) was modified by incorporating flexographic photopolymer plate residues (rubber microparticles). The photopolymer plate residues were processed in two ways: (a) by grinding and performing particle size classification (where the resulting samples were denoted PP) and (b) by polyester layer separation and grinding the elastomeric fraction by cryogenic grinding (where the resulting samples were denoted ER). Both residual particles were incorporated into the epoxy at concentrations of 2.5, 5 and 7.5 wt%. The main results indicate that PP was not efficient as a modifier of the epoxy system. A reduction in mechanical properties (maximum tensile strength and deformation) was observed in the samples produced with PP in different concentrations. But, when the ER is incorporated, an increase in tensile property and in the deformation capacity, as well as impact resistance was observed in samples produced with ER. Scanning electron microscopy analysis showed a greater presence of voids in formulations produced with PP, which corroborates the decrease in the tensile strength of these samples.

Keywords: epoxy, residues, elastomer residue, mechanical properties.

1. Introduction

The use of residues as reinforcement or fillers in polymeric compositions is a practice that has gained great prominence in recent years and continues to grow, since it contributes to the valorization and reuse of discarded materials. In addition, these materials also promote specific changes in the polymeric material, such as increasing stiffness, improving toughness or even reducing product costs. The recycling and valorization of residues produced in processes reduces costs and provides new opportunities for limiting the use of natural resources; as a direct consequence, there is a reduction in environmental impact and production costs (Beauson *et al.*, 2014).

One of the fastest growing sectors in recent years is polymer packaging. Among all polymeric materials, flexible films are becoming increasingly popular, mainly due to their versatility, light weight, strength and printability, among other properties (Hou *et al.*, 2018; Morris, 2016). However, as a result of this activity, one of the main residues generated from the production of flexible packaging is photopolymer plates used in the flexography step of polymeric film production. Photopolymer plate residues are essentially formed by two distinct materials: (I) a base polyester, which has the goals of supporting the photopolymer plate and guaranteeing its dimensional stability, and (II) a photopolymer elastomer. Photopolymers are light-sensitive materials (photosensitive) responsible for the formation of graphics and counter graphics. During exposure to UV radiation, photopolymer monomers polymerize (crosslinking the plate material), leaving these areas resistant to chemical action during the development process. No exposure areas are removed

during this process (Cordeiro *et al.*, 2010). These materials have a relatively short lifespan, and after that, they are usually sent to landfills.

Despite the large industrial consumption of these materials in the plastic packaging sector, there are few solutions or applications for their reuse or even relevant publications about the recycling or reuse of these plates used in flexographic printing. However, it is known that the use of recycled elastomers, when incorporated into other resins in small amounts, can modify the properties of the polymer matrix, such as toughness and impact resistance. In this context, Cordeiro *et al.* (2010) evaluated the use of flexographic photopolymer plate residues in thermoplastic matrices of polypropylene and ethylene-vinyl acetate copolymer and reported the technical feasibility of using this residue for small modifications of the constituent polymer (Cordeiro *et al.*, 2010).

For thermoset materials, one of the polymers that has been investigated with combinations of elastomer residues is epoxy. Epoxy-based resins are thermosetting polymers that are relatively easy to process and relatively inexpensive. This material is often used as a matrix in high-performance composites. However, although the vast majority of epoxy-based resins have high stiffness and specific strength, they are fragile due to their highly crosslinked network structure (Irez *et al.*, 2020; Zavarech & Vahdat, 2012). Thus, an undesirable property of epoxy is its low resistance to crack propagation, which makes it a fragile material. Several methods have been proposed to increase the strength of epoxy resins, One of the most successful methods is

the use of composite materials based on “epoxy-rubber” due to their low cost and easy fabrication, and their use is increasing due to their performance and wide range of functional properties (Irez *et al.*, 2020; Ramos *et al.*, 2005; Kim *et al.*, 1996). Among the different epoxy modifiers, rubber particles have good performance as a hard and tough modifier of polymer matrices (Quan & Ivankovic, 2015; Tsai *et al.*, 2009; Dadfar & Ghadami, 2013). Epoxy resins can be modified by incorporating a particulate elastomer, which will lead to the formation of a second phase in the material, altering the material’s morphology. The incorporation of an elastomeric phase in a thermoset matrix is a common means of increasing fracture toughness, as reported by Almeida *et al.* (1998), and according to Kaynak *et al.* (2003), the main advantage of this method is the control of particle size and volume fraction. According to Tang *et al.* (2012), the major toughening mechanisms involving rubber particles are debonding/cavitation, localized shear banding of matrix, as well as rubber particle bridging. However, with the improvement in fracture toughness and/or tensile strength, other desirable properties of rubber-epoxy resins, such as the elastic modulus and failure strength may decrease significantly (Tang *et al.*, 2012; Tang *et al.*, 2013; Sankar *et al.* 2010).

Thus, this study aims to evaluate the influence of the use of the residue of photopolymer plates discarded from the plastic packaging industry as a modifying agent of mechanical properties in an epoxy system composed of diglycidyl ether of bisphenol A and triethylenetetramine (DGEBA/TETA).

2. Materials and methods

2.1 Materials

The residue of useless photopolymer plates originating from the flexography process of polymeric packaging was kindly provided by Canguru Plásticos Ltd. located in Criciúma/SC,

Brazil. Bisphenol A diglycidyl ether epoxy resin (DGEBA), with the trade name Araldite F, and cold curing agent triethylenetetramine (TETA), with the trade name Aradur 951, were purchased

from Maxepoxi Industrial e Comercial Ltd. The toluene used to separate the components of the photopolymer plates was obtained from Dinâmica Química Contemporânea Ltd.

2.2 Methods

2.2.1 Recycling of flexographic photopolymer plates

In this study, two types of photopolymer plate residues used as modifiers of epoxy resin were evaluated: (I) residues in their natural form, by

which only mechanical processes of grinding and granulometric classification were applied, called photopolymer plates (PPs), and (II) residues

after phase separation (constituents), preferably achieved using the elastomeric fraction of the material, called elastomer residues (ERs). In condition

II, first, the components of the useless photopolymer plate were separated, in which a Soxhlet extractor was used by adopting the methodology described by Cordeiro *et al.* (2010).

Subsequently, the PPs and ERs were processed by mechanical grinding

using a Mecanofar MF160 knife mill with a \varnothing 10 mm sieve. After this step, the natural plates were micronized by a mechanical process using a knife mill and particle size classification, while the ER was again micronized by a cryogenic process using a Netzsch Attritor high-

energy mill operated at 1400 rpm for a grinding time of 3 h in a cryogenic atmosphere with liquid nitrogen. In the end, particles with particle sizes smaller than 24 mesh (0.5 mm) were obtained in both processes. Figure 1 shows the stages of the ER recycling process.

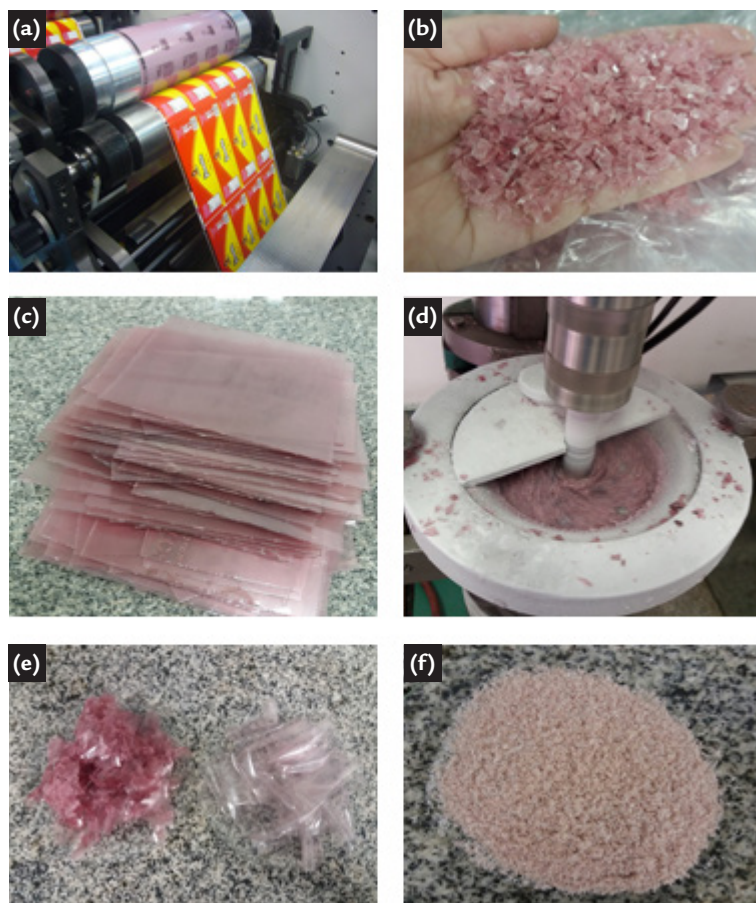


Figure 1 - Photographic images of (a) the photopolymer plate used in the flexography process, (b) photopolymer plate residues, (c) photopolymer plate residues after phase separation, (d) mechanical grinding of residues, (e) cryomilling of elastomeric residues and (f) particulate elastomer residue to be incorporated into the epoxy.

2.2.2 Preparation and characterization of PP or ER/epoxy and characterization

The stoichiometric ratio of the epoxy resin (DGEBA) to the TETA curing agent used in the mixture was 0.67; the resulting sample was denoted 13 PHR (13 grams per 100 parts of resin). Both residues (PP and ER) were added at percentages of 0 (no modifier), 2.5, 5 and 7.5 wt% to the epoxy/DGEBA system. First, the resin was weighed and manually mixed with the curing agent (TETA), PPs and ERs in a beaker (50 mL) for approximately 1 minute in the proportions described with the aid of a glass rod. The mixtures were placed under vacuum for 15 minutes to remove the bubbles and then poured into a stainless-steel cast previously coated with aluminum film and release agent to facilitate extraction. The specimens were cured at room temperature and

characterized after 10 days of production. The specimens were prepared for mechanical tests based on the ASTM D638 standard.

The ER and PPs were characterized by Fourier transform infrared spectroscopy using a Shimadzu IR- Prestige 21 spectrometer in the spectrum range from 4000 to 500 cm^{-1} at room temperature.

Thermal analysis of the PP and ER was performed by thermogravimetry (TG) with a Netzsch-Bruker STA 449 F3 analyzer in a nitrogen atmosphere with a flow of 40 mLmin^{-1} , a maximum temperature of 600 $^{\circ}\text{C}$ and a heating rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$.

Morphological analysis of the ER, PP residue and epoxy was performed by scanning electron microscopy (SEM) using a JEOL JSM-6390 instrument.

Due to the need to obtain a conductive surface, the samples were covered with a thin film of gold applied by sputtering a Denton Desck IV vacuum metallizer.

The mechanical properties of epoxy with and without modifiers were determined by measuring tensile strength with Emic DL10000 equipment using a 10 kN load cell and speed of 1 $\text{mm}\cdot\text{min}^{-1}$ according to the ASTM D638 standard. All tests were conducted at $25 \pm 2^{\circ}\text{C}$. Five specimens were used to determine the tensile strength property of each sample.

Izod impact strength testing was performed with a CEAST Resil 25 pendulum. Unnotched specimens were used according to ASTM D256. Each test value was calculated as the average of at least seven independent measurements.

3. Results and discussion

3.1 Characterization of photopolymer plates and elastomer residues

Figure 2 shows the FTIR spectra of the loads (PP and ER) after processing. The bands observed at 2922 cm^{-1} and 2886 cm^{-1} , present in both spectra, represent vibrations of the CH and CH_2 groups. The bands at 1724 and 1729 cm^{-1} , also observed in both spectra, can be attributed to the stretching of the C=O (carbonyl) bond, which can be explained by the presence of methacrylate groups in the photopolymer

and carbonyl compounds (Cordeiro *et al.*, 2010). The presence of the representative carbonyl band in the elastomer residue sample suggests that this sample has undergone oxidation processes or even contamination with a polyester base, as described by some authors; this material is commonly produced in styrene butadiene rubber (SBR) or ethylene propylene diene monomer (EPDM) rubber (Cordeiro *et*

al., 2010; Tomašegović *et al.*, 2020). The 1448 cm^{-1} band is assigned to the C–H vibration of the CH_2 group. The bands at 1104 cm^{-1} and 1008 cm^{-1} correspond to the O=C–O–C group (Elnagar *et al.*, 2014). The 700 cm^{-1} band corresponds to the deformation of C=C in the styrene or butadiene present in the elastomer. Gunasekaran *et al.* (2007) reported an analogous band located at 704 cm^{-1} for SBR.

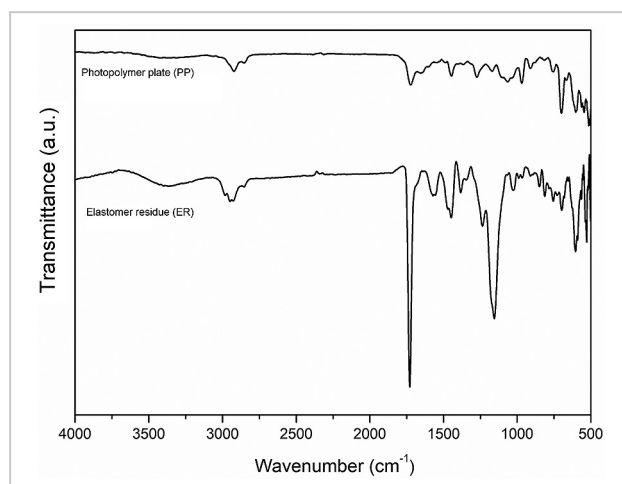


Figure 2 - FTIR spectra of residues from PPs and the ER.

Figure 3 shows the degradation thermograms of the processed loads of the photopolymer and elastomer. The degradation temperature of both samples presented similar behaviors. The decomposition of the photopolymer sample starts at approxi-

mately $360\text{ }^{\circ}\text{C}$, while that of the elastomer starts at $350\text{ }^{\circ}\text{C}$, with a higher reaction intensity at $470\text{ }^{\circ}\text{C}$ for PPs and $480\text{ }^{\circ}\text{C}$ for ERs. This small variation in the thermal stability of the samples can be attributed to the fraction of the polyester layer being

small in relation to the total mass in the plate, with the largest constituent being the elastomer. Despite the presence of at least 2 components in the PP sample (polyester base and elastomer), two degradation events in the analysis performed were not observed.

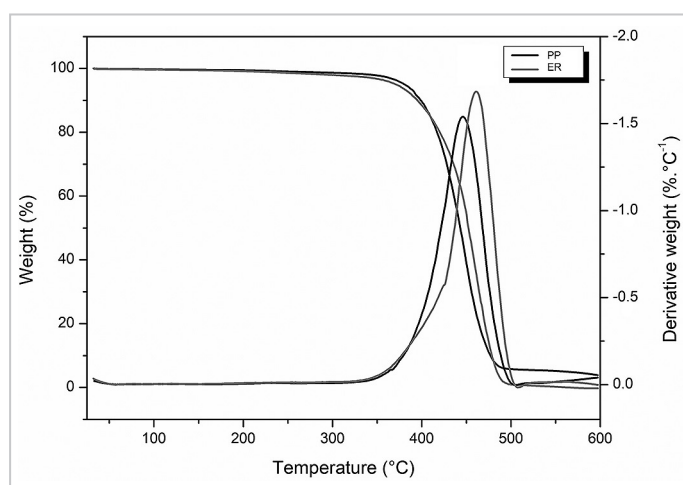


Figure 3 - Thermogravimetric analysis of the photopolymer and elastomer residues after processing.

Figure 4 shows the micrographs obtained by performing SEM on the PPs and ER after processing. The milling method interfered with the morphology of the particles. The

plate milled by a mechanical process only (and particle size classification) resulted in more irregular particles with great variation in particle size and morphology. In the rubber particles

ground by a high-energy cryogenic process, the size and morphology of this material were uniform. The mean size observed in the ER particles was $250 \pm 53\text{ }\mu\text{m}$.

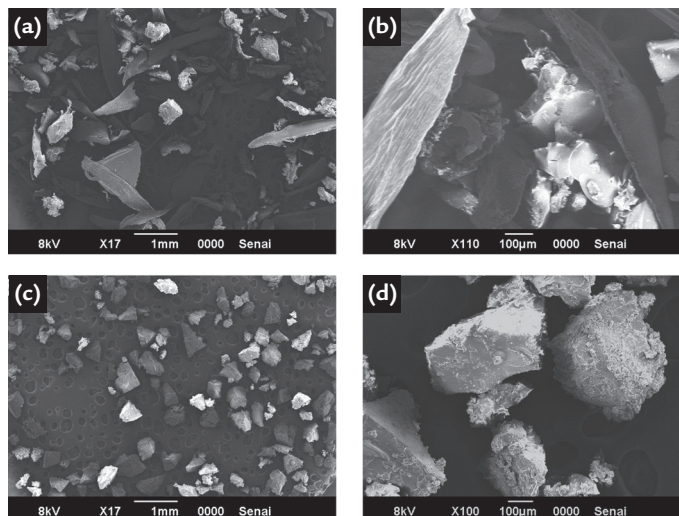


Figure 4 - SEM micrographs of the PPs (a and b) and ER (c and d) after processing.

3.2 Characterization of the epoxy system with the PPs and ER

Table 1 shows the tensile strength and impact strength results obtained from the mechanical tests performed on the epoxy and epoxy modified with PPs and ER. It was observed that the PP particles did not bring significant variation in the impact strength of the epoxy. The ER particle increased the impact strength by up to 21.3% (Epoxy/ER5 sample) when compared to unfilled epoxy. Although and within experimental errors, 5 wt% of ER seems to be sufficient to bring a significant

change in impact property compared to neat epoxy resin. The presence of the PP modifier, when compared to unfilled epoxy, tends to reduce the tensile strength of the epoxy and considerably reduce the deformation capacity of these samples with the 3 evaluated contents. The ER modifier, on the other hand, increases the tensile strength at contents of 2.5 and 5 wt% and does not significantly change the deformation of materials modified with ER compared to pure epoxy, with

the exception of the epoxy/ER 2.5 sample, which showed a significant improvement in deformation capacity. This fact may be associated with the shape of the ER being more regular than that of the PP, as well as the removal of impurities from the photopolymer plate and the presence of voids in the epoxy matrix, as will be shown below. A similar ultimate tensile strength reduction behavior of epoxy with rubber particles was also reported by Manjunatha *et al.* (2010).

Table 1 – Tensile properties of epoxy with and without PP and ER modifiers.

Sample	Tensile strength (MPa)	Strain at Break (mm/mm)	Elastic Modulus (GPa)	Izod Impact strength (kJ/m ²)
Epoxy	22.93 ± 1.69	0.10 ± 0.01	3.18 ± 0.34	16.4 ± 1.1
Epoxy/PP2.5	13.88 ± 1.41	0.04 ± 0.01	5.02 ± 1.53	16.7 ± 1.2
Epoxy/PP5	20.08 ± 2.62	0.02 ± 0.01	4.34 ± 1.15	14.5 ± 3.7
Epoxy/PP7.5	15.28 ± 2.28	0.02 ± 0.01	7.13 ± 0.46	15.2 ± 2.6
Epoxy/ER2.5	29.12 ± 2.22	0.20 ± 0.02	3.99 ± 1.63	16.1 ± 3.2
Epoxy/ER5	29.07 ± 2.92	0.14 ± 0.09	5.48 ± 1.49	22.8 ± 1.1
Epoxy/ER7.5	21.66 ± 1.81	0.10 ± 0.05	4.66 ± 1.28	19.9 ± 3.5

Many authors attribute the decrease in the elastic modulus and increase in the deformation capacity of the epoxy system to the incorporation of rubber particles (Irez *et al.*, 2020; Tsai *et al.*, 2009; Manjunatha *et al.*, 2010; Abadyan *et al.*, 2012), a fact not observed in the samples with ER and PP particles, which suggests that these particles presented a reinforcing and non-toughening character. Interestingly, the sample reinforced with PP showed a decrease in tensile strength, but an increase in the elastic modulus, which is possibly associated with a decrease in the deformation capacity of the sample. Samples reinforced with ER particles

showed an increase in tensile strength and an increase in modulus, when compared to pure epoxy, but lower when compared to samples reinforced with PP. This fact may be associated with the greater deformation capacity of these samples. PP particles probably cannot transmit the same characteristics observed using conventional rubbers, which suggests that PPs are more rigid than ER or conventional rubbers.

To understand the failure mechanism associated with the inclusion of PP and ER particles, the failure surfaces of the specimens were examined using SEM. Figure 5 shows the SEM micrographs obtained for the fracture

region of the samples after the tensile strength test. The absence of holes and voids in pure epoxy was observed, and all samples modified with PPs and ER showed voids. Comparatively, the epoxy samples with the PP residue seem to have more bubbles than the samples with ER. This may be because PPs contain residue of paints and solvents, which during processing can volatilize and generate these bubbles. When ER undergoes the phase separation, cryogenic grinding and drying process, this component is reduced by the extraction of the solvents used in the process.

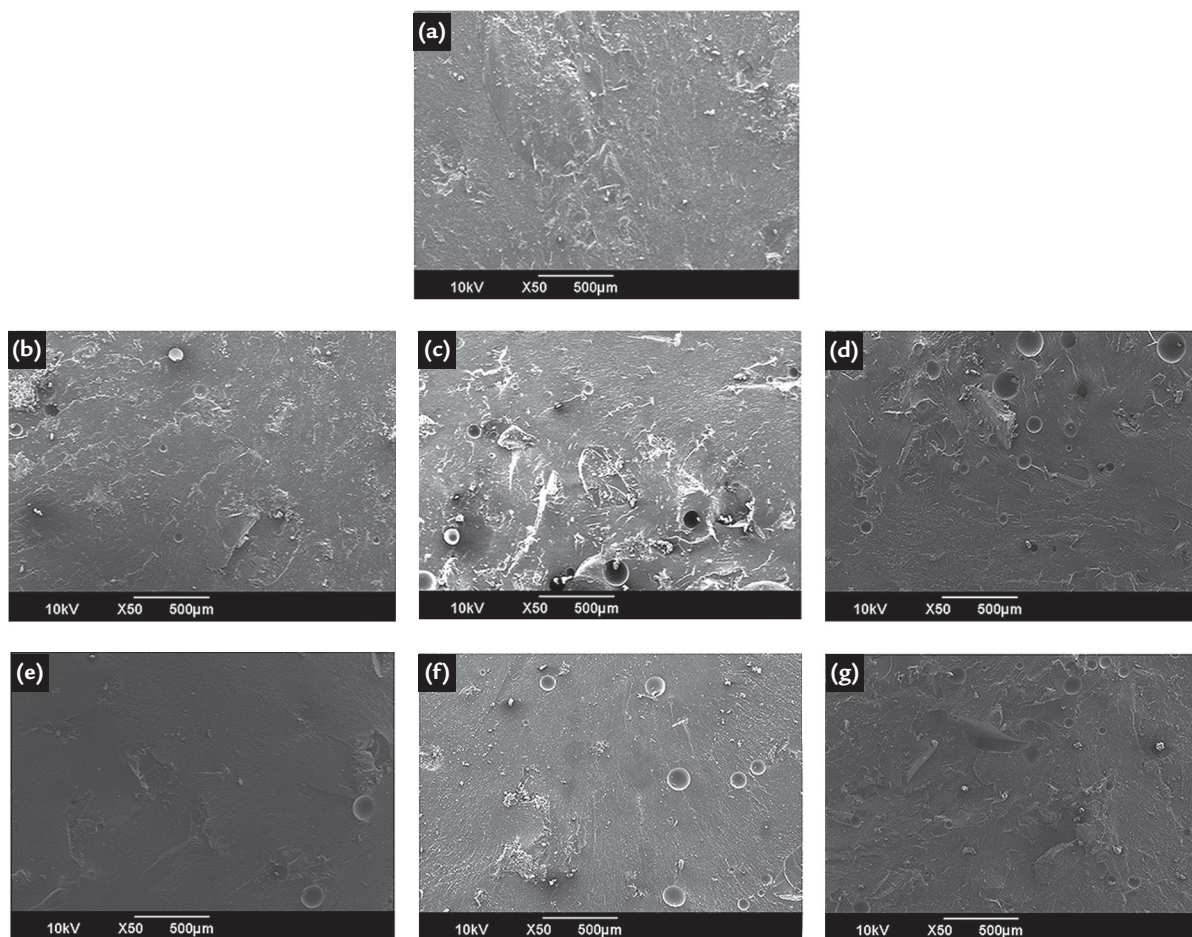


Figure 5 - SEM micrograph of (a) pure epoxy, (b) EP/PP 2.5; (c) EP/PP 5; (d) EP/PP 7.5; (e) EP/ER 2.5; (f) EP/ER 5; and (g) EP/ER 7.5.

According to Irez *et al.* 2020, in a study on epoxy modification using EPDM residues as the elastomeric phase, a reduction in the tensile strength was also observed with the addition of the elastomer. The authors credit this reduction to the low interfacial adhesion between the elastomer and the epoxy causing the formation of voids. Crosslinked elastomers provide few active sites on the surface of rubber particles, which makes it difficult to form chemical bonds with epoxy. Additionally, due to this low compatibility, voids can form in the epoxy matrix, which gives rise to low tension transfer from the matrix to

the rubber particles, reducing the overall stiffness of the compounds. During solidification, different concentrations of rubber and epoxy can bring some inequalities in the balance of internal tensions, which leads to void formation at the existing interfaces. Furthermore, with the increase in the content of recycled rubber particles, the possibility of observing agglomerations increases. Therefore, these agglomerations could create weak parts (weak points) in the composite. Consequently, when the composites are subjected to loading, these voids and agglomerates mentioned above constitute the weak points of the composite where

cracks can start/occur. This state results in premature failure. This mechanism may be associated with the low tensile strength response of samples reinforced with PP.

Figure 6 shows SEM micrographs of the epoxy/ER5 sample, with emphasis on the particle-fiber interface region. The particles show moderate interaction with epoxy, with regions with good wettability and interaction (Figure 6a) and regions of voids (Figure 6b) caused both by the presence of agglomerates, by the volatilization of particle components such as moisture or residues of paints or by changing the viscosity of the resin.

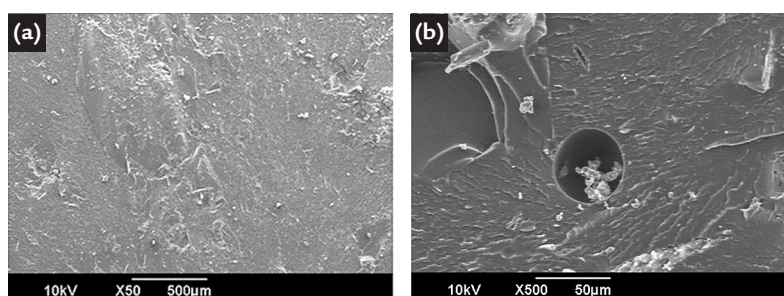


Figure 6 - SEM micrograph showing the interface region in the epoxy/ER composite with (a) good interaction and (b) weak interaction in the interface region.

4. Conclusion

The DGEBA/TETA epoxy system was modified by two different residues from flexographic photopolymer plates in different mass fractions, and the impact of incorporating these two types of particles from photopolymer plate residues on the mechanical properties of epoxy was analyzed. The processing and separation of the polyester fraction contributes to the production of an epoxy system with superior mechanical properties

(tensile and impact strength). The incorporation of PP particles was not effective in improving the deformation/elongation capacity of the epoxy when subjected to mechanical tensile action, which suggests that the incorporation of this material brings a reinforcing and non-toughening characteristic to the epoxy. However, after beneficiation and phase separation, the epoxy samples modified with ER particles showed an improvement in

their maximum stress and deformation properties. By morphological analysis of the fracture region, voids were observed in all samples containing PPs and ER, a fact not observed in pure epoxy. The processing of the residue of photopolymer plates, with the separation of the polyester fraction, contributes to the production of more homogeneous particles, which makes this material more applicable for epoxy modification.

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