Evaluation of Thermal and Mechanical Properties of Epoxy Resin/Aluminum Nanoparticle Composites

Simone de Souza Pinto[1,2,*], Felipe Silva Pinto[1], Magali Mayumi Ueno[1], and Fabio Roberto Passador[1]

[1]*Federal University of São Paulo (UNIFESP), Department of Science and Technology, Polymer and Biopolymer Technology Laboratory (TecPBio), 330 Talim St., São José dos Campos, SP, Brazil, 12231-280*

[2]*Serviço Social da Indústria, SESI-CE 240, Ferraz de Vasconcelos, São Paulo, Brazil*

Abstract: In this study, we explored the development of epoxy resin nanocomposites with 0.1, 0.3%, and 1.0% by weight of aluminum nanoparticles. These nanocomposites were evaluated for mechanical properties (tensile test and Izod strength test) and thermal properties (differential scanning calorimetry and thermogravimetric analyses), and their morphology was assessed using field emission gun scanning electron microscopy. Adding even small amounts of aluminum nanoparticles led to notable improvements in the mechanical and thermal resistance. Remarkably, composites with 1.0 wt% of aluminum nanoparticles presented a 25% increase in the elastic modulus, a 20 °C increase in the glass transition temperature, and a 30 °C increase in the degradation temperature. These findings hold significant promise for advancing the field of polymer-metal nanocomposites.

Keywords: Nanocomposites, Epoxy resin, Aluminum nanoparticles, Polymer-metal nanocomposites.

1. INTRODUCTION

Over the past decades, the scientific community has extensively explored the development of nanomaterials and nanocomposites, researching their synthesis, manufacturing, properties, and applications [1, 2]. Nanocomposites belong to a class of composite materials where the dispersed phase has at least one nanoscale dimension [3]. In the production of nanocomposites with polymeric matrices, different types of nanofillers can be used, such as nanoclays, carbon nanotubes, graphene, and metallic nanoparticles [4-6].

Powder metallurgy has proven to be a reliable method for manufacturing net-shape components, which requires less machining and leads to higher production rates, ultimately reducing total costs [7]. Due to their high-performance mechanical structures, they find applications in thermomechanical scenarios that require customized magnetic and electrical properties [8]. Aluminum stands out as one of the lightest engineering materials, and aluminum particles have been widely used in various areas of research due to their versatile applications, including energy storage, hydrogen production, surface coatings, chemical synthesis, catalysis, pigments for conventional inks or even in 3D printing [9, 10].

However, aluminum is a notorious metal due to its tendency to form a passivating layer, an undesirable effect for electrical applications as the oxide formation renders the material insulating. Specifically, nanocomposites with a polymeric matrix combined with the addition of metallic nanoparticles remain underexplored in the literature. The distinct chemical nature and different densities between these two classes of materials can pose challenges in processing and dispersing the metallic particles within the polymeric matrix. The addition of aluminum nanoparticles into epoxy resin has the potential to enhance both electrical and mechanical properties [11].

The use of aluminum is particularly attractive due to its low density, 2.7 g/cm^3, and its unique attributes, such as electrical and thermal conductivities, as well as good formability. In this context, this work investigates the morphological aspects of the nanoparticles and the mechanical and thermal behaviors of epoxy composites reinforced with different contents of aluminum nanoparticles (Al) (0.1, 0.5, and 1.0 wt%).

2. EXPERIMENTAL

2.1. Materials and Processing

An epoxy resin (EPOCAST® 50-A1) with a fast-curing system (Hardener 9816) supplied by Huntsman (USA) was selected as the polymeric matrix. The Al nanoparticles with purity of 99.99%, spherical morphology, and particle size between 70 - 80 nm were supplied by Nanostructured & Amorphous Materials Inc. (USA).

*Address correspondence to this author at the Federal University of São Paulo (UNIFESP), Department of Science and Technology, Polymer and Biopolymer Technology Laboratory (TecPBio), 330 Talim St., São José dos Campos, SP, Brazil, 12231-280; E-mail: simonesouza.pn@gmail.com

E-ISSN: 2410-4701/23

The preparation of the nanocomposites proceeded in the following steps: firstly, the Al nanoparticles were added into the epoxy resin precursors (100/14 epoxy resin/hardener) by mechanical mixing. Second, after the complete dispersion and removal of air retained in the resin during mixing, the nanocomposites were poured into previously prepared silicone molds with the standard dimensions for tensile and impact tests. The epoxy resin cure occurred for 72 h at a room temperature of (27 ± 1) ^{o}C.

Epoxy resin/Al nanocomposites were prepared with three different contents of Al nanoparticles: 0.1, 0.5, and 1.0% by weight. Additionally, a reference sample of neat epoxy resin without the addition of nanoparticles was also prepared.

2.2. Characterization of Al Nanoparticles

The morphological aspects of the Al nanoparticles were characterized by field-emission gun scanning electron microscopy (FEG-SEM) using a TESCAN - MIRA3 microscope, operating at 5 kV. The nanocomposite samples were fractured, mounted on stubs with carbon conductive tape, and covered with a thin gold layer by sputtering.

X-ray diffraction (XRD) analyses were performed in a Rigaku diffractometer (model Ultima IV), using CuK_{α} radiation, an acceleration tension of 40 kV, an electric current of 30 mA, and a nickel filter for K_{β}. The recording parameters were a 10° min^{-1} speed and 2θ range from 20° to 90°.

2.3. Characterization of the Epoxy Resin/Al Nanocomposites

The nanocomposites were characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), tensile test, Izod impact strength, FEG-SEM, and electromagnetic analyses.

The thermal stability of the nanocomposites was evaluated by TGA, using Netzsch equipment (model TG 209 F1 Iris®), under a nitrogen atmosphere, from room temperature up to 800 ºC with a heating rate of 20 ºC.min^{-1}.

DSC analyses were performed in TA Instruments equipment (model Q2000), with nitrogen as a carrier gas, at a constant flow rate of 50 mL.min^{-1}. The samples were submitted to a thermal cycle of heating from 0 to 200 °C, with a heating rate of 10 °C.min^{-1}.

An EMIC universal test machine (model GR048) with a crosshead speed of 5 mm/min and a load cell of 0.5 kN was used for the tensile tests of the specimens, according to ASTM D 638.

The impact strength Izod tests were performed on a CEAST/Instron Izod impactor test machine (model 9050), according to ASTM D256-06. The equipment was coupled with a hammer of 0.5 J. Ten specimens of each composition with a notch of 2.54 ± 0.1 mm depth (done with a manual notching machine CEAST/Instron) were tested.

3. RESULTS AND DISCUSSION

3.1. Al Nanoparticle Characterization

Figure **1** shows FEG-SEM images of the Al nanoparticles. Figure 1(a) shows the presence of many aggregates of Al particles, which explains the formation of Al particles in the microphase. Some particles are strongly linked together (microphase), producing a distinctive neck, with a true metal–metal inter-crystalline boundary [12]. Higher magnifications (Figure

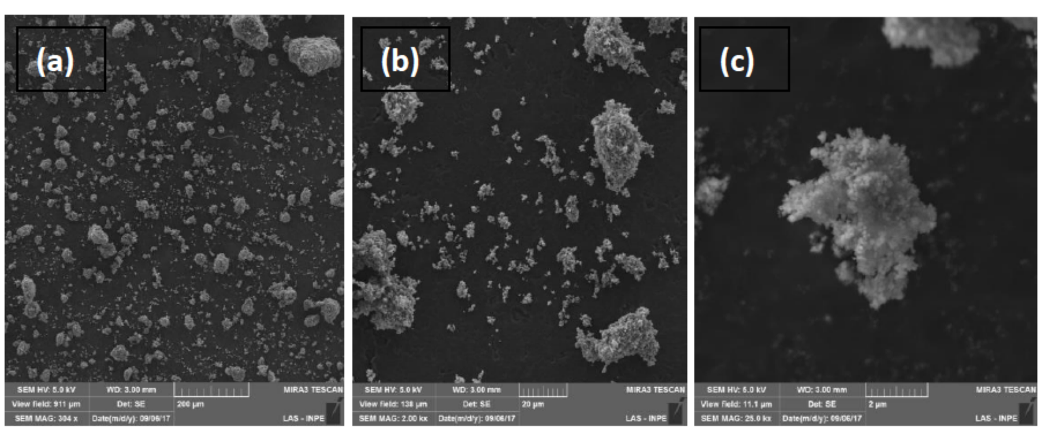

Figure 1: FEG-SEM of Al nanoparticles with different magnifications.

1(b,c)) show more details of the aggregates with the presence of individual spherical particles with sizes ranging from 30 nm or less.

Figure **2** shows the X-ray diffraction pattern of the Al nanoparticles. The characteristic peaks of both nano and bulk Al at 2θ = 38°, 44°, 65°, and 78°, 83°, corresponding to Miller indices (111), (200), (220), (311), and (222), can be seen in Figure **2**, which confirm the high degree of crystallinity for this nanomaterial [13].

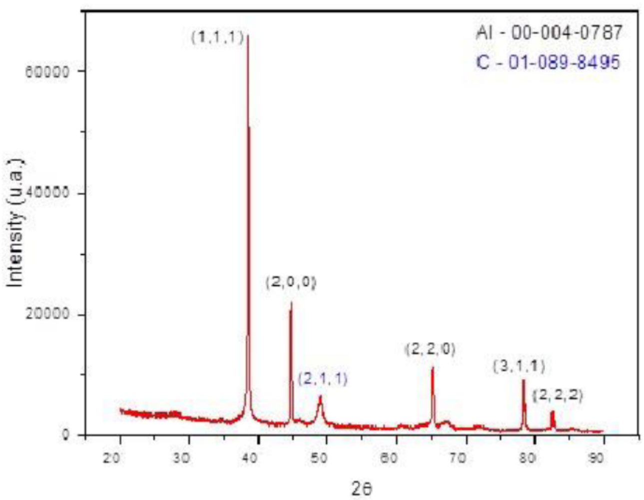

Figure 2: XRD pattern of the Al nanoparticles.

3.2. Characterization of Nanocomposites

Figure **3** shows the TGA curves of the epoxy resin and epoxy/Al nanocomposites. Table **1** reports the initial thermal decomposition temperatures (T_{onset}). TGA was used to verify behavior of aluminum powder at

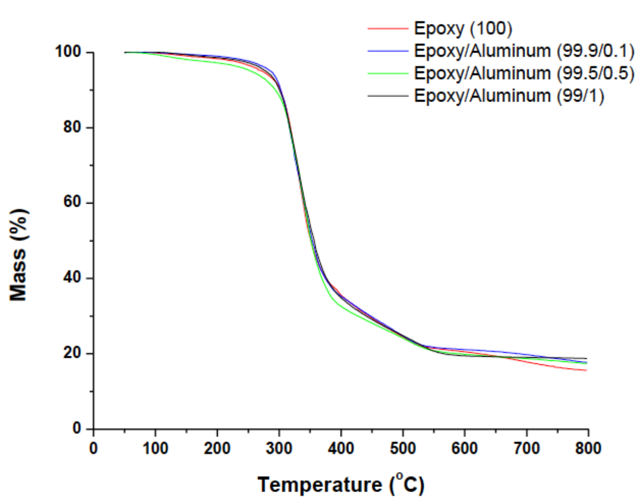

Figure 3: TGA curves under nitrogen atmosphere of epoxy resin and epoxy/Al nanocomposites with different contents of Al nanoparticles.

high temperatures [14]. It is observed that epoxy resin begins to decompose at a temperature of 300 ºC. The initial decomposition temperature of the nanocomposites increases to higher temperatures values with the addition of Al nanoparticles, reaching a maximum value of 330 ºC for the sample with 1.0 wt% of Al. A greater drop in the weight loss is observed between 300 ºC and 400 ºC. From 600 ºC the weight loss remains approximately constant, resulting in a residue content of around 20%, at 800 °C.

Table 1: T_{onset} Results Obtained by TGA and T_g Obtained by DSC for Epoxy and Epoxy/Al Nanocomposites with Different Contents of Al Nanoparticles

Samples	T_{onset}(ºC)	T_g (°C)
Epoxy (100)	300	71
Epoxy/Al (99.9/0.1)	304	85
Epoxy/Al (99.5/0.5)	327	87
Epoxy/Al (99.0/1)	330	90

Figure **4** shows the DSC curves of the epoxy resin and the epoxy/Al nanocomposites. The glass transition temperature (T_g) results are summarized in Table **1**.

The epoxy resin has a glass transition temperature of 71 °C. The addition of Al nanoparticles considerably increases the T_g values of the compositions. An increase of 14 ºC was observed with the addition of 0.1 wt% of Al nanoparticles, while the addition of 1.0 wt% resulted in an increase of approximately 20 °C in the T_g for this nanocomposite. These results are very positive and allow the use of these nanocomposites at higher working temperatures.

Table **2** presents the mechanical results for the epoxy resin and nanocomposites. An increase in the elastic modulus of 12% is observed with the addition of 0.1 wt% of Al nanoparticles to the epoxy resin. The Al nanoparticles acted positively by increasing the mechanical properties of the nanocomposites, even with the addition of small amounts (maximum of 1.0 wt%) acting as a reinforcing filler. This behavior may be related to the presence of particle aggregates, which hindered the movement of macromolecules, thus requiring greater uniaxial force, which resulted in a greater elastic modulus. The addition of 1.0 wt% Al nanoparticles increased the elastic modulus by about 25%. Regarding the ultimate tensile strength (UTS), an increase in UTS values is observed with the addition of

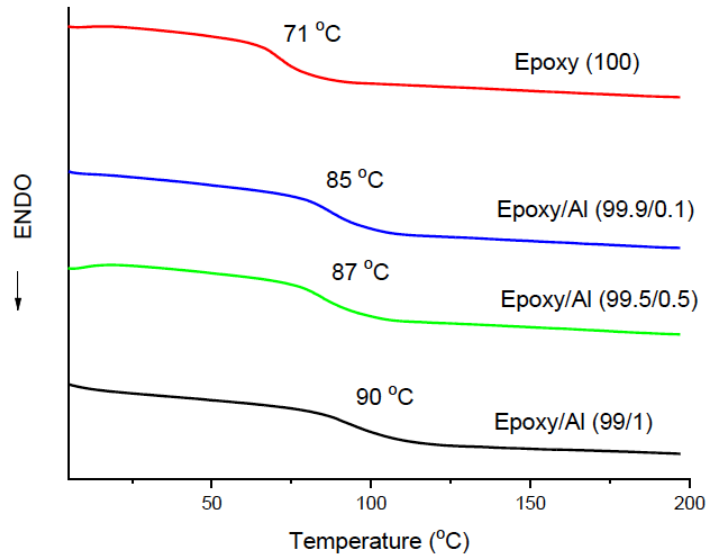

Figure 4: DSC curves for the epoxy resin and epoxy/Al nanocomposites with different contents of Al nanoparticles.

Al nanoparticles, with an increase of 25% for the epoxy/Al (99/1) nanocomposite when compared to the neat epoxy resin.

For Izod impact strength (IS), it was observed that the addition of 0.1 wt% of Al nanoparticles resulted in a 13.5% decrease in IS. Already 0.5 wt% of Al nanoparticles decreased the IS by 20%, and 1.0 wt% of Al nanoparticles decreased by 62% compared to the neat epoxy resin. This may be related to the difficulty in moving macromolecules. Aluminum nanoparticles, while making the material more rigid, significantly reduced impact resistance, as these particles act by hindering the movement of macromolecules, increasing mechanical resistance and making the material more fragile.

Figure **5**(**a**-**d**) shows the fracture behavior of specimens after the Izod impact test. Figure **5**(**e**-**g**) shows FEG-SEM images of the fractured surfaces of epoxy/Al nanocomposites with different Al nanoparticle contents.

Figure **5**(**a**) shows a typical fracture surface of a brittle material related to the neat epoxy resin without any plastic deformation. With the addition of Al nanoparticles (Figure **5**(**b-d**)), it is noted that the fracture surface becomes increasingly smooth, without the presence of any barrier that could hinder the crack propagation. FEG-SEM images of the nanocomposites (Figure **5**(**e-g**) show the presence of spherical-shaped aggregates of aluminum nanoparticles (highlighted by red circles). The Al nanoparticles form small clusters well dispersed throughout the polymer matrix, which probably contributed to the increase in mechanical (elastic modulus and UTS) and thermal properties.

4. CONCLUSION

Epoxy resin nanocomposites with different contents of aluminum nanoparticles were successfully prepared. The addition of small amounts of aluminum nanoparticles promoted improvements in thermal and mechanical properties. Notably, the 1.0 wt% increment of aluminum nanoparticles served as a reinforcing

Table 2: Ultimate Tensile Strength (UTS) and Elastic Modulus (E) Obtained by Tensile Test and Izod Impact Strength (IS) of Epoxy Resin and Epoxy/Al Nanocomposites

Samples	UTS (MPa)	E (MPa)	IS (J/m)
Epoxy resin	40.0 ± 1.7	206.7 ± 13.8	41.5 ± 7.1
Epoxy/Al (99.9/0.1)	42.5 ± 0.3	242.7± 5.1	35.9 ± 7.4
Epoxy/Al (99.5/0.5)	43.2 ± 0.6	246.7 ± 5.8	33.2 ± 1.4
Epoxy/Al (99.0/1)	50.0 ± 0.9	273.7 ± 8.9	15.7 ± 0.5

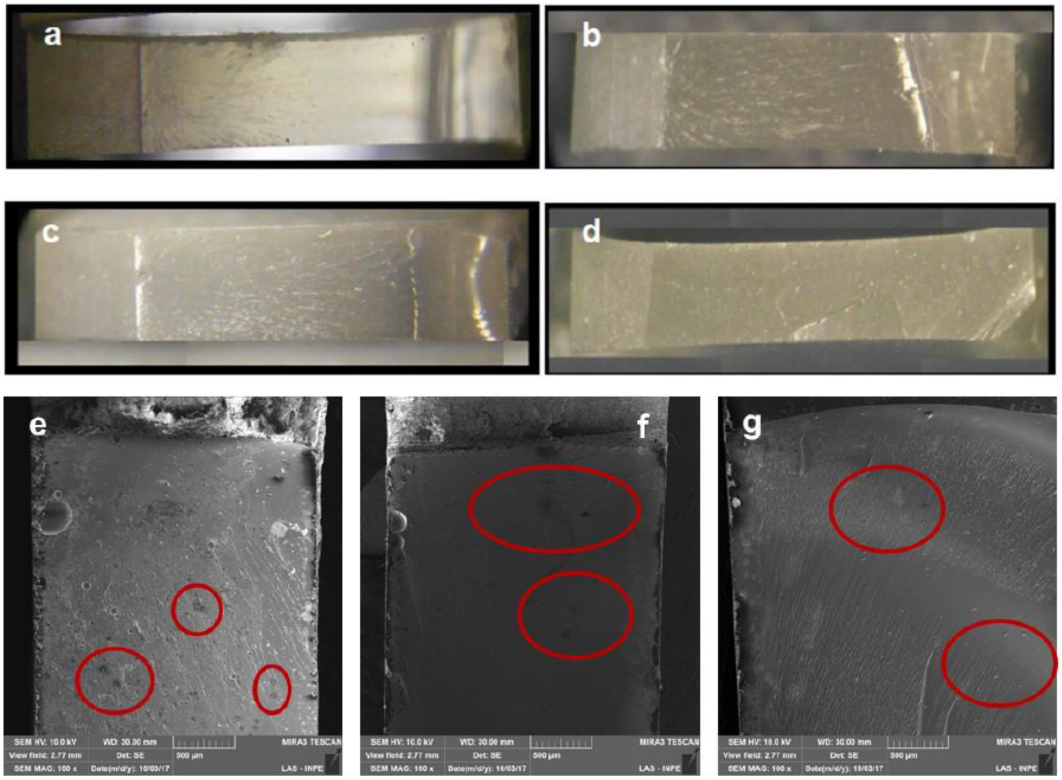

Figure 5: Image of the fracture surface after the impact resistance test: (**a**) neat epoxy resin, (**b**) epoxy/Al (99.9/0.1), (**c**) epoxy/Al (99.5/0.5), and (**d**) epoxy/Al (99/1). FEG-SEM of the fracture surfaces of the nanocomposites: (**e**) epoxy/Al (99.9/0.1), (**f**) epoxy/Al (99.5/0.5), and (**g**) epoxy/Al (99/1).

agent, resulting in a 25% increase in elastic modulus, an approximately 20 °C increase in glass transition temperature, and a 30 °C increase in T_{onset} of degradation temperature. The well-dispersed nature of the aluminum nanoparticle aggregates within the nanocomposite, as observed through FEG-SEM analyses, suggests that the chosen process holds great promise for the development of polymer-metal nanocomposites exhibiting favorable mechanical and thermal properties.

ACKNOWLEDGMENT

The authors are grateful to the financial support of CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico, processes 407288/2021-0, 440132/2021-3, 307933/2021-0).

REFERENCES

[1] Pinto S.S. *et al*., The influence of morphology, structure, and weight fraction of magnetic additives on the electromagnetic characteristics of composites, vol. 489, pp. 126-138, 2019. https://doi.org/10.1016/j.jmmm.2019.03.085

[2] Othman H.A. *et al*., Structural and luminescent properties of aluminum-based nanophosphors, vol. 47, pp. 27789-27802, 2021. https://doi.org/10.1016/j.ceramint.2021.06.206

[3] El-khatib, A.M. *et al*., Impact of micro and nano aluminum on the efficiency of photon detectors, Results in Physics, vol. 30, pp. 104908, 2021. https://doi.org/10.1016/j.rinp.2021.104908

[4] Shaih A.M., Kubade, Effect of nanofillers on rolled polymer nanocomposites: A review, Materials Today: Proceedings, 2023. In Press, Corrected Proof. https://doi.org/10.1016/j.matpr.2023.07.346

[5] Njuguna J., *et al*., Nanomaterials, nanofillers, and nanocomposites: types and properties, Composites Science and Engineering, pp. 3-37, 2021. https://doi.org/10.1016/B978-0-12-820505-1.00011-0

[6] Njuguna, J., *et al*., Nanomaterials, nanofillers, and nanocomposites: types and properties, Polymer Nancomposites and Other Materials Containing Nanoparticles, pp. 3-27, 2014. https://doi.org/10.1533/9780857096678.1.3

[7] Schubert A., *et al*., Developments in Powder Mixed EDM and its perspective Application for targeted Surface Modification, Procedia CIRP, vol. 113, pp. 100-119, 2022. https://doi.org/10.1016/j.procir.2022.09.134

[8] Elsayd A. *et al*., The effect of milling time on the preparation of an aluminum matrix composite reinforced with magnetic nanoparticles, Heliyon, vol. 9, pp. e16887, 2023. https://doi.org/10.1016/j.heliyon.2023.e16887

[9] Aliasker K.T., *et al*., Exploring the effects of self-lubricating MoS2 in magnesium metal matrix composite: Investigation on wear, corrosion, and mechanical properties, Colloids and Surfaces A: Physicochemical and Engineering Aspects, vol. 677, pp. 132362, 2023. https://doi.org/10.1016/j.colsurfa.2023.132362

[10] Devanathan R. *et al*., Influence in mechanical properties of stir cast aluminium (AA6061) hybrid metal matrix composite (HMMC) with silicon carbide, fly ash and coconut coir ash

reinforcement, Materials Today Proceedings, vol, 22 pp. 3136-3144, 2020. https://doi.org/10.1016/j.matpr.2020.03.450

[11] Meena P.L., Saini, K., Synthesis of polymer-metal oxide (PANI/ZnO/MnO2) ternary nanocomposite for effective removal of water pollutants, Results in Chemistry, vol. 5, pp. 100764, 2023. https://doi.org/10.1016/j.rechem.2023.100764

[12] El-khatib A.M., *et al*., Impact of micro and nano aluminum on the efficiency of photon detectors, Results in Physics, vol. 30, pp. 104908, 2021. https://doi.org/10.1016/j.rinp.2021.104908

[13] Satish K.V. *et al*., X-ray/gamma radiation shielding properties of Aluminum-Barium Zinc Oxide nanoparticles synthesized via low temperature solution combustion method, Nuclear Engineering and Technology, vol. 55, pp. 1519-1526, 2023. https://doi.org/10.1016/j.net.2023.02.001

[14] Mikhaylo T. *et al*., Effect of polymorphic phase transformations in Al2O3 film on oxidation kinetics of aluminum powders, Combustion and Flame, vol. 140, pp 310-318, 2005. https://doi.org/10.1016/j.combustflame.2004.10.010

Received on 15-10-2023 Accepted on 17-11-2023 Published on 22-11-2023

DOI: https://doi.org/10.31875/2410-4701.2023.10.11