

Bio-Based Silica Reinforced Aliphatic Bio-Epoxy Composites

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Abstract– Composites of bio-based aliphatic poly-functional epoxy resin reinforced with high concentration of bio-silica were prepared by a solvent free method. The unmodified bio-silica (BS) was obtained from rice husk. Two amine hardeners were used: one was based on polyethylene oxide (PEO) and the other on polypropylene oxide (PPO). The epoxy-amine systems were reinforced with 10, 20, 30 and 40% weight fraction to the unreinforced epoxy resin. The structure and morphology of the BS was analyzed by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM), respectively. These techniques were also used to determine the silica dispersion degree in the polymer matrix. Thermal characterization was carried out using a Differential Scanning Calorimetry (DSC) and Thermogravimetric Analyses (TGA). The glass transition temperature, T_g, increased significantly for both polyetheramine cured systems incorporating 10 wt% and 20 wt% of the BS; nevertheless, the best performance was observed in PEO networks. The thermal stability at 5% of weight loss temperature increased consistently with reinforcement concentration up to ~ 21% and ~ 10% compared to neat PEO and PPO cured networks, respectively. Tensile strength and Young modulus for PEO systems showed similar results up to 30 wt% of BS, whereas for PPO networks they decreased relentlessly at 20 wt% of BS. PEO composites showed an overall increase in the Shore D hardness testing. Water swelling experiment illustrated greater hydrophilicity of PEO compared to filled and unfilled PPO systems. The water absorption remains unaltered up to 20 wt% of BS, revealing a good interaction between both networks and filler. It was clearly illustrated the difference in the effect of hydrophilicity (PEO) and the hydrophobicity (PPO) in the epoxy composite results. A better compatibility and good correlation between mechanical and thermal properties were observed in 10 wt% of BS in both polyetheramine cured networks.

Keywords- Rice husk silica, bio-silica reinforced polymers, bio based thermosets, aliphatic bio-epoxy composites, polymer composites.

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silica powder in industrial applications such as foundry, concrete blocks or as polymer reinforcement additive [2, 3]. The use of rice husk causes an environmental problem and it is habitually avoided in many countries. In some countries the husk is used as a by-product for the development of biomass and energy generation [4].

Researchers have studied several variables to improve the properties of epoxy-silica composites. Some authors have focused on improving the silica surface treatments to increase their compatibility with epoxy resins [5]. Different mixing processing, such as use of solvents [6], temperature increase mixing [7, 8] or the use of ultrasound [9] have also been explored to improve the dispersion of silica. Furthermore, some studies have focused on increasing wear resistance in paints [10], thermal stability, dielectric properties for electronic devices or packing applications [11]. Epoxy resins based on aromatic substances such as bisphenol A and diglycidyl ether (DGEBA), trifunctional triglycidyl p-amino phenol (TGAP), and tetrafunctional tetraglycidyl diamino diphenylmethane (TGDDM) have been traditionally used in high performance applications [12, 13]. However, the bisphenols are chemical compounds that can interfere with the human endocrine system and their use has recently been questioned [14]. Therefore, the present study uses a polyfunctional aliphatic epoxy resin. This epoxy resin can potentially replace aromatic epoxy resins in the development of filled composites for several industrial applications [15]. Additionally, these composites were prepared via a solvent free method, which makes this process environment-friendly. The current research was carried out to assess the effect of high concentration of untreated rice husk on the thermal, mechanical and swelling properties of this new class of bio-epoxy/amine networks.

I. INTRODUCTION

Epoxy resins are the most commonly used thermosetting polymers due to their excellent chemical and heat resistance, mechanical stress or toughness, electrical and anticorrosive properties [1]. Additionally, due to their chemical compatibility, minerals reinforcement has been added to epoxy resins for many years to improve their performance and applications use. The use of bio-silica from rice husk has been recently of noticeable interest, whether as an alternative for

II. EXPERIMENTAL SECTION

A. Materials

Sorbitol Glycidyl Ether (SGE) - Polyfunctional Epoxy Resin GE-60 (Mw~1065 g/mol) was provided by CVC Materials Company. Curing agents, Polyethylene Oxide diamine (PEO), Jeffamine EDR-148 (Mw~148 g/mol) and Polypropylene Oxide triamine (PPO), Jeffamine T-403 (Mw~403 g/mol) were used in this study. Bio-silica (BS) was

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obtained from rice husk [16]. Fig.1 shows the chemical structure of epoxy resins and curing agents.

B. Preparation of Silica and Epoxy-Silica Composites

The rice husk was pretreated with 1N of hydrochloric acid (HCl) for 3 hours and then washed with distilled water and dried at 60 °C for 24 hours to finally be calcined in an electrical furnace at 640 °C for 3 hours. Such procedures have been efficient to obtain amorphous silica [16].

Table I shows a summary of the composites prepared by dispersing the different concentrations of silica in the epoxy resin using Flacktek DAC 400.1 FVZ speed mixer operated at 2,500 RPM for 2 minutes. A stoichiometric amount of the amine was added to the epoxy / silica mixture. The mixture was then agitated again at 2,500RPM for 40 seconds to obtain a homogeneous mixture. All formulations of bio-epoxy resin and aliphatic amines were prepared with and without silica for comparison purposes. Mixing procedures were performed at room temperature without solvent, keeping the relative humidity under 50%. Before curing, the mixtures were subjected to vacuum and poured into a different silicone mold features for characterization and testing methodology. All the systems were cured for 1 hour at 80 °C and then, post-cured for 2 hours at 120 °C.

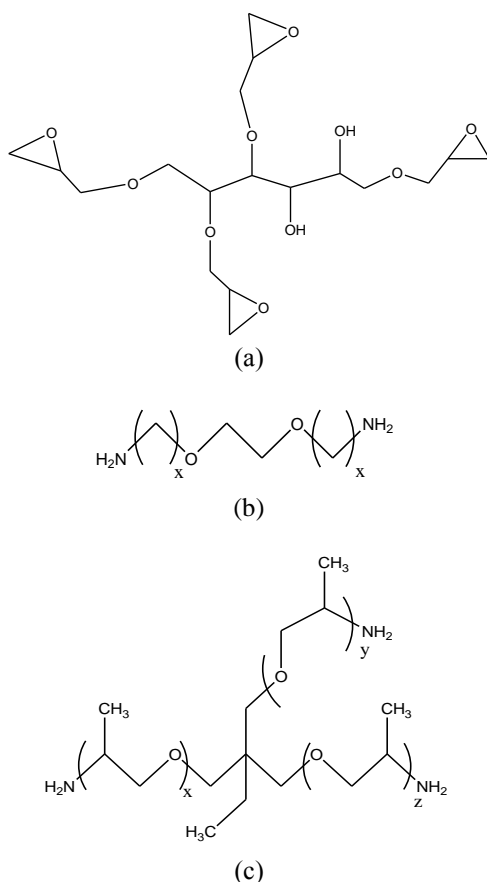


Fig. 1 Chemical Structures of the resins (a) GE-60, (b) EDR-148, x=2 and (c) T-403, x+y+z=5-6

TABLE I
COMPOUND CONCENTRATION

CODE	MIX DESIGNS OF SGE (GE-60) COMPOSITES
PEO	EDR-148
PEO 10	EDR-148/10% bio-silica
PEO 20	EDR-148/20% bio-silica
PEO 30	EDR-148/30% bio-silica
PEO 40	EDR-148/40% bio-silica
PPO	T-403
PPO 10	T-403/10% bio-silica
PPO 20	T-403/20% bio-silica
PPO 30	T-403/30% bio-silica
PPO 40	T-403/40% bio-silica

III. CHARACTERIZATION METHODS

A. X-Ray Diffractometry (XRD)

Cured samples were placed in a stainless-steel sample holder. X-Ray diffractograms were obtained using Phillip model PA equipped with Cu K α ($\lambda=1.54060$ Å) radiation, operating at 40KV and 45mA with an Incident Slit of 1/8" and detector Slit 1/16". The scanning conditions were: step size 0.05°, setup time 20 secs, angle span from 2° to 60° (2 θ). Diffractograms were analyzed with X'Pert HighScore Plus (version 2.2.3).

B. Scanning Electronic Microscopy (SEM)

Micrographs were obtained using an FEI Inspect S50 scanning electron microscope (SEM) in high vacuum mode in the sample chamber. Reinforced samples were cut with a razor blade after keeping in an oven at 120°C for ~20 minutes. Images were taken using an acceleration voltage of 7-10 kV, a backscattering electron detector (BSED) and a large-field detector (LFD). No conductive coating was used for the SEM samples examination.

C. Thermogravimetric Analysis (TGA)

TGA analyses were determined using TA instruments model Q600 SDT (TGA/DSC). Approximately 10 mg of the sample was placed in alumina crucible and heated from room temperature to 600°C, at a heating rate of 10°C/min in nitrogen atmosphere. TGA curves were analyzed using TA Universal Analysis 2000 Software (version 4.5A).

D. Differential Scanning Calorimetry (DSC)

DSC was used to determine the glass transition temperature (T_g) of the cured compounds using the equipment TA instruments Inc. SDT model DSC Q200. Approximately 10 mg of the sample was heated from -10°C to 100°C at 10°C/min heating rate, keeping it at 100 °C for 5 minutes. Then, the samples were cooled down to -10°C applying the same rate. The heating and cooling processes were repeated using the same parameters. A high purity nitrogen atmosphere was used at about 100 mL/min flow rate.

E. Tensile Test Strength

Tensile Strength tests were performed using Shimadzu AG-1S 10kN equipment, operating at 1 mm/min at room temperature ($25 \pm 2^\circ\text{C}$) and humidity below 50%. Five samples were used in each system. The tests were performed using a modification of the ASTM D638-14 Type IV standard.

F. Hardness Test

The D Shore hardness test was carried out on a Qualitest HPE-II equipment. Samples of 9.84 cubic millimeter were obtained by pouring the mixture into the silicone mold. The D Shore test was a modification of the ASTM D2240 standard using five samples per system and taking 3 readings in the different sides of the cube.

G. Swelling tests

Swelling tests were performed with samples of $9.74 \times 9.74 \times 2.24$ mm manufactured in silicon molds. Four samples of each series were submerged in water at room temperature using a glass flask of 20 mL. For each measured series, the samples were dried and weighted until they reached equilibrium. The weight was determined with an analytical balance Sartorius model BL210S with 0.0001 g precision. The swelling percentage was determined using the following equation:

$$M_t(\%) = \frac{w_t - w_o}{w_o} \times 100 \quad (1)$$

where t represents time, w_o is the initial weight and w_t is the weight at a specific time.

IV. RESULTS AND DISCUSSIONS

A. Morphology Assessment

1) *XRD*: Fig. 2 shows the diffractograms of bottom surfaces of the SGE cured samples with PEO (a) and PPO (b) amine hardeners. The top faces (not showed here) presented similar results. The amorphous peak around $2\theta = 20\text{--}22^\circ$ corresponds to silica in amorphous phase and its intercalation in the structure of the epoxy matrix [16–18]. No difference in the amorphous peak was observed, which implies a homogeneous structure in all samples with different concentrations of bio-silica. That homogeneity is possible due to the interaction of oxygen and hydroxide groups present in the epoxy resin and those formed during the epoxy-amine reaction occurring together with hydroxide groups present in the bio-silica. The hydrogen bonding interactions have been noticed in neat and filled epoxy-polyetheramine networks [15,19–21]. No difference was observed in the diffractograms of the SGE/PEO and SGE/PPO cured networks. In addition, there was no observable change in the different molecular weight of curing agents for the XRD analysis.

2) *SEM*: Fig. 3 shows micrographs of the calcined BS silica, using LFD detector with different magnifications. The material is highly porous and has a great surface area. Those

roughness microstructure characteristics play an important role in the interface BS/polymer matrix system.

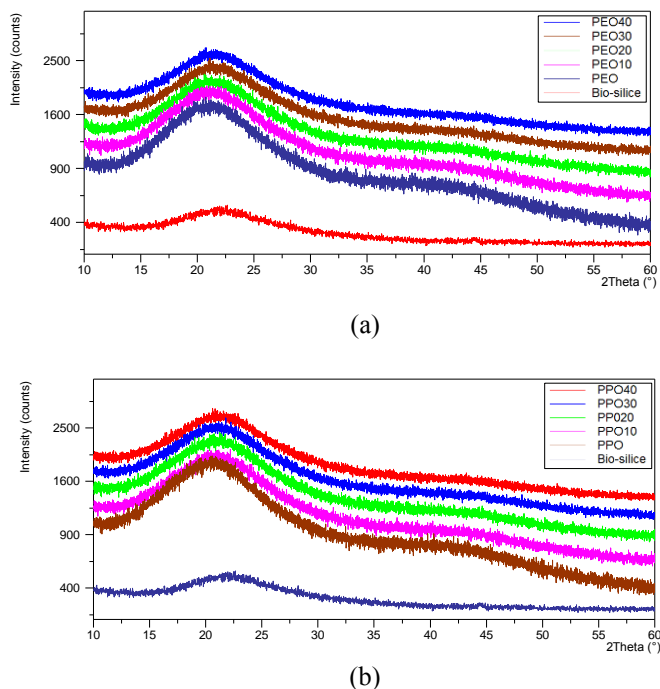


Fig. 2 X-Ray Diffractograms of the inferior phases of the SGE cured with PEO and PPO at different concentrations of bio-based silica.

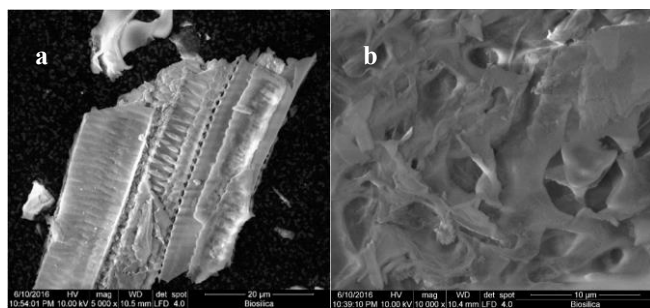


Fig. 3 Micrographs of the (a) calcined bio-silica and, (b) the calcined milled bio-silica.

Fig. 4 shows a close up of the bio-silica skeleton immersed in the PEO10 (a) and PPO10 (b) cured samples. Taking advantage of the atomic number (Z) difference between silica and carbon, it was possible to differentiate the BS into the polymer matrix using BSE detector. BS heterogeneous powder size is observed in the 700 nm to 11 μm range. It is to be noted that the resin diffuses around the silica showing good compatibility as indicated by the white circle in Fig. 4b. The micrographs at 20 wt% of silica concentration show a good and homogeneous dispersion in both systems. Good interfacial interactions are occurring manifest between this unmodified bio-silica with these networks.

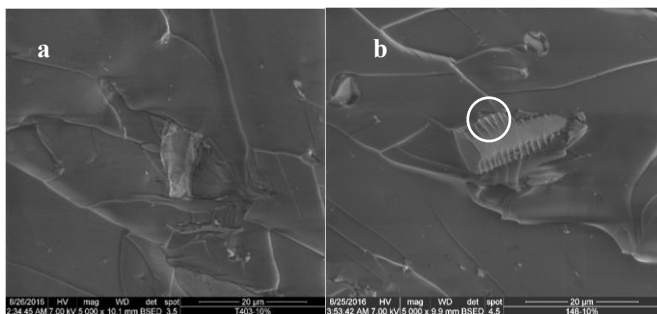


Fig. 4 Micrographs of the composites (a) PEO10 and (b) PPO10.

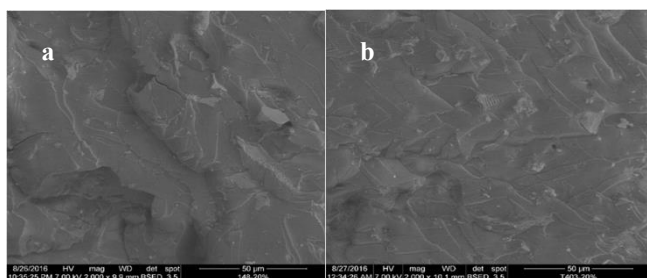
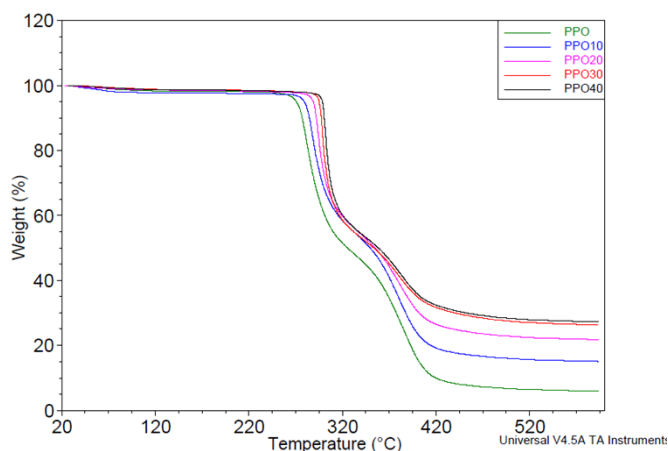
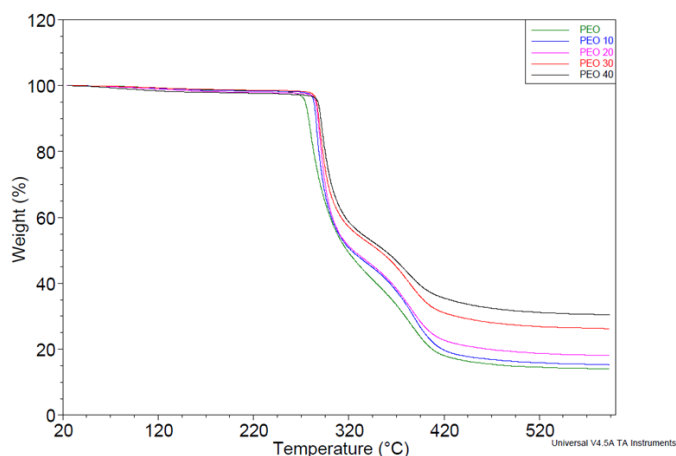


Fig. 5 Micrographs of the composites (a) PEO20 and (b) PPO20.

3) *Thermal Properties:* Fig. 6 shows the TGA thermograms of different compounds using an epoxy resin with 10, 20, 30 and 40 wt% of bio-silica. Fig.6 displays a consistent increase in the thermal stability of epoxy systems as the weight percentage of silica increases. That is due to a strong interaction between the matrix and the surface of the unmodified bio-silica. The SGE/PEO systems presented a greater increase than the SGE/PPO networks. Such result was expected because the SGE/PEO networks are more hydrophilic than the SGE/PPO networks so the interaction with the bio-silica is greater. Results presented in Tables II and III show greater stability in neat SGE/PPO network compared to SGE/PEO network in mass loss temperature at 5% and 50% ($^{\circ}\text{C}$), due to the higher molecular weight of PPO. However, both systems showed a more substantial increment in thermal stability compared to its corresponding neat system. The glass transition temperatures increase considerably when 10 wt% of silica is incorporated in both systems. However, for higher silica wt%, the T_g values decrease considerably. Other studies have demonstrated that a poor interaction between micro-silica and epoxy-amine networks does not help improve the thermal stability of neat systems [22], as opposed to the case in which there is a good interaction between the silica and epoxy networks [23]. The curing agent PPO, being more hydrophobic due to the methyl groups, decreases the interaction at the SGE/PPO/BS interface. In addition, PPO has less concentration of amine groups, therefore the hydrogen bonding interaction should be affected.



(a)



(b)

Fig. 6 Thermograms of the cured SGE systems with different bio-silica concentrations (a) PEO and (b) PPO.

TABLE II
THERMAL PROPERTIES OF THE SGE/PEO/BS SYSTEMS.

Sample	T_g ($^{\circ}\text{C}$)	5% Weight loss ($^{\circ}\text{C}$)	50% Weight loss ($^{\circ}\text{C}$)
PEO	34	225	319
PEO 10	49	270	329
PEO 20	46	271	348
PEO 30	25	283	354
PEO 40	21	285	359

TABLE III
THERMAL PROPERTIES OF THE SGE/PPO/BS SYSTEMS.

Sample	T_g ($^{\circ}\text{C}$)	5% Weight loss ($^{\circ}\text{C}$)	50% Weight loss ($^{\circ}\text{C}$)
PPO	42	271	325
PPO 10	50	279	348
PPO 20	40	289	353
PPO 30	32	295	352
PPO 40	29	299	358

4) *Mechanical Properties:* Tables IV and V show the mechanical properties of the SGE/PEO and SGE/PPO bio-silica composites. Mechanical properties have been related to 1) the structure of the network precursors, 2) the degree of conversion

following network formation and 3) the intermolecular interactions of groups within the network [20]. In this study, unfilled systems with expected high degree of crosslinking [15] in both SGE/PEO and SGE/PPO cured networks showed similar Young's moduli in the ~1.3-1.5 GPa range. These results represent a lower level of stiffness compared to conventional aromatic epoxy/amine networks in glassy state [21] due to the inherent flexibility of such fully aliphatic networks. Similar values of Young's modulus were observed in the SGE/PEO systems with 10 and 20 wt% of bio-silica contents. However, Young's modulus in the SGE/PPO systems decreases consistently with the addition of silica, despite the high molecular weight of PPO. Tensile strength increases or remains constant if there is a strong interaction between the filler and the resin [8]. A change in the crosslinking degree at higher concentration of bio-silica is possible, so the network formation and structure should be different. The maximum tensile stress remains in the same range for the different contents of silica for the SGE/PEO systems, except for 40 wt% of BS, in contrast with the SGE/PPO system that considerably reduces the tension strength at 20, 30 and 40 wt% of reinforced BS. The Shore D hardness shows mostly a superficial effect of silica in the matrix, with a slight observable increase in the SGE/PEO systems, and decrease in the SGE/PPO systems with 40 wt% of BS resin mixture. The incorporation of fillers usually increases the surface hardness in composites [24] and coating applications [10].

TABLE IV

MECHANICAL PROPERTIES OF THE PEO/BS SYSTEMS

Sample	Young Modulus (GPa)	Tensile Strength (MPa)	Hardness (Shore D)
PEO	1.3 ± 0.2	32.7 ± 0.4	77.9 ± 0.2
PEO 10	1.3 ± 0.1	33.0 ± 3.5	79.7 ± 0.1
PEO 20	1.3 ± 0.1	28.8 ± 2.6	79.8 ± 0.9
PEO 30	1.1 ± 0.1	30.5 ± 2.0	81.2 ± 0.9
PEO 40	0.6 ± 0.1	21.7 ± 1.2	81.7 ± 0.6

TABLE V

MECHANICAL PROPERTIES OF THE PPO/BS SYSTEMS

Sample	Young Modulus (GPa)	Tensile Strength (MPa)	Hardness (Shore D)
PPO	1.5 ± 0.1	36.4 ± 2.0	76.1 ± 0.7
PPO 10	1.4 ± 0.2	37.3 ± 2.7	78.9 ± 0.4
PPO 20	0.6 ± 0.1	17.9 ± 1.4	77.3 ± 0.9
PPO 30	0.5 ± 0.0	13.9 ± 2.1	76.2 ± 0.9
PPO 40	0.4 ± 0.1	12.7 ± 2.0	53.0 ± 0.6

5) *Swelling Properties*: Among physical properties, solvent swelling is a useful approach for assessing network properties at the macromolecular level, and can be used to describe the hydrophilicity/hydrophobicity of epoxy/amine networks [25, 26]. In this study, water swelling properties allowed us to determine the superficial interaction between the silica and the

network, as illustrated in Fig.7. Even though the silica and epoxy resin are hydrophilic, a strong interaction of the silica and SGE/PEO systems is observed as the water absorption initially decreases in the systems with 10 wt% of BS; once the systems are in equilibrium, the water absorption does not increase with the additions of 10 or 20 wt%. There is a possibility that the molecular structure of the system is not equal when the concentration of silica is higher due to a lower surface interaction. However, the SGE/PPO systems showed a lower water absorption in equilibrium compared to SGE/PEO systems. The polarity of the resin is determinant in the water absorption equilibrium [27]. In this case, a hydrophobic effect of the oxypropylene chain in the curing agent is observed in neat and filled systems and this effects appears to be remarkable in the swelling properties for these systems.

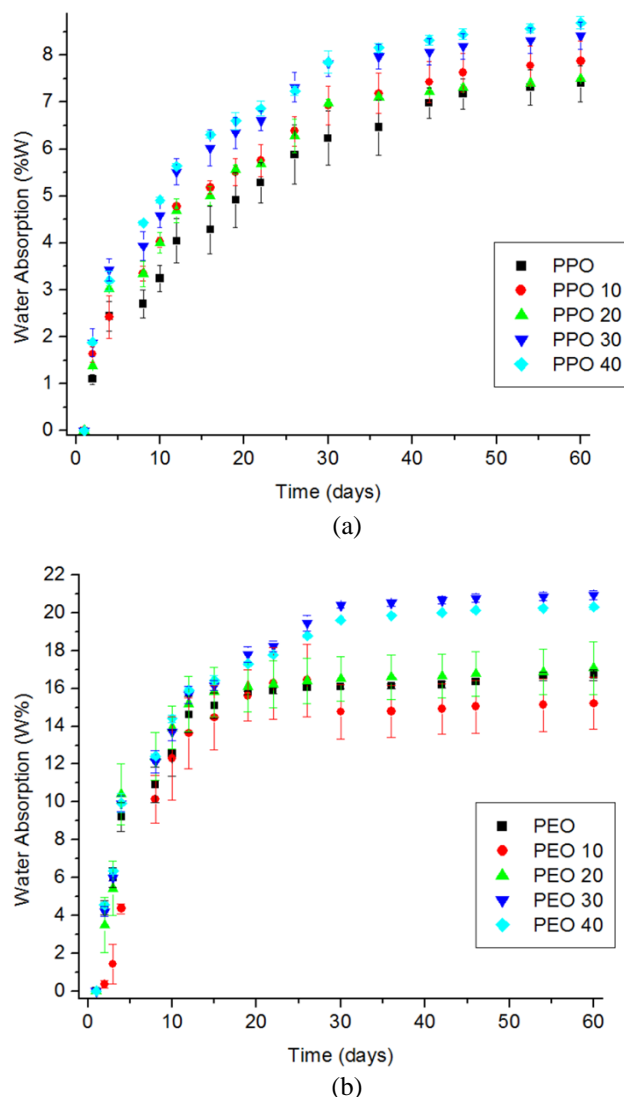


Fig. 7 Water absorption for the (a) PPO and (b) PEO networks.

V. CONCLUSIONS

Bio-epoxy resin cured with polyetheramines and bio-silica improved the physical properties as the concentration of the silica mixture increased. The bio-silica was dispersed throughout the different epoxy-amine systems via a solvent-free method. T_g values improved considerably at silica concentration of 10 wt% in both cured systems, but this improvement was greater in the SGE/PEO networks systems. The thermal stability increased consistently with the addition of bio-silica. In SGE/PPO systems, as the filler concentration increases, the tensile strength and rupture energy decrease due to a low surface interaction between the hydrophilic bio-silica and the hydrophobic characteristic of the curing agent. The swelling experiment determined the affinity of the network to the bio-silica and was also sensitive to hydrophobicity or hydrophilicity in the case of PPO and PEO hardener, respectively. The feasible preparation of these bio-silica reinforced composites without additional chemical surface treatments of silica, solvents or high temperatures for processing make these bio-epoxy composites suitable for several industrial applications.

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