

Thermal Properties and Fire Resistance of Jute-Reinforced Composites

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Abstract

The thermal behaviour, fire resistance and mechanical properties of jute-reinforced composites with vinylester and resol matrix were studied. Organically modified clay was added to the polymeric matrix in order to enhance the properties of the composites. An inhomogeneous distribution of the nanoreinforcement in the polymer was observed by X-ray diffraction. Thermogravimetric analyses revealed that the addition of clay to the resol resin by sonication enhanced the thermal resistance of the jute-reinforced composite at temperatures higher than 300°C. The fire resistance of the composites was evaluated by means of a cone calorimeter. A diminution in the peak of the heat release rate was observed when clay was added to the polymeric matrix. On the other hand, neither the time to ignition nor the total heat evolved was significantly reduced by the clay addition. Additionally, an increment in the flexural modulus as well as in the flexural strength of the resol composites was observed when the clay was added to the matrix. The fiber–matrix interface of the composites was studied by scanning electron microscopy. It was observed that as the clay dispersion degree was increased the interface quality was diminished in the resol composites.

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Keywords

Clay, natural fiber, thermal degradation, fire resistance, mechanical properties

1. Introduction

In recent years, natural fiber reinforced composites have attracted substantial attention as potential structural materials for low cost applications. Natural fibers offer good opportunities as reinforcement materials for composites, because they are strong, light, cheap, abundant and renewable. Several researches have been made on the use of natural fibers as reinforcing agents in thermoset and thermoplastic poly-

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mers. In a previous work [1] we obtained natural fiber/thermoset composites with acceptable mechanical properties. But in other work [2] we observed that those materials had a significantly lower fire resistance than the glass fiber reinforced composites. The objective of the present work is to improve the fire resistance of natural fiber composites by using matrices with better thermal performance. Among the natural fibers, jute is of particular interest due to its easy availability, renewable character, low price and low density leading to high specific strength. Also, jute composites have shown better thermal and fire resistance than other natural fibers used in the previous work [2].

Phenolic resins have been widely used as glass fiber reinforced composite matrices due to their flame resistance, in addition to their excellent dimensional stability and chemical resistance. The drawback of this resin is its fragility. On the other hand, it was observed that the addition of inorganic nanoreinforcement to polymers enhanced their mechanical and barrier properties as well as thermal stability by promoting flame retardancy at very low filling levels [3–5]. It was reported recently that the addition of clay loadings as low as 1–5 wt% produces a substantial improvement in fire performance of different polymeric systems [6–11]. Low flammability in terms of heat release rate (HRR) in cone calorimeter experiments has been observed. The quality of clay dispersion that determines the existence of a microcomposite, an intercalated and/or exfoliated nanocomposite, is also an important factor in determining fire performance. However, there are mixed results in the literature regarding this topic.

Morgan *et al.* [12] reported that there was little effect upon fire performance whether the nanocomposite was exfoliated or intercalated. Samyn *et al.* [9] showed that PA-6 and PS nanocomposites exhibit significant reduction of the peak of HRR (PHRR) but the morphology (exfoliation, intercalation and presence of tactoids) does not play any significant role. However, if the nanodispersion is achieved, the polymer/clay nanocomposite should exhibit flame retardancy properties, at least in terms of PHRR. On other hand, Wang *et al.* [13] reported significant differences in the PHRR between nanocomposites and microcomposites. Similarly, Varley *et al.* [10] showed the importance of achieving true exfoliation compared to intercalation in optimizing fire performance of polymer nanocomposites containing 5% of clay. Superior fire performance for the exfoliated composites was attributed to the formation of a more thermal stable char layer. Corresponding results were obtained by other authors. Schartel [6] demonstrated that adding 5–7.5 wt% of clay to the PP-g-MA polymer system was sufficient to prepare nanocomposites with improved flame retardancy. He concluded that the quality of the nano-scaled structure significantly determines the magnitude of the fire retardancy effect. It was reported that small amounts of inert fillers fail to make a crucial impact either on the total heat evolved or in the time to ignition.

Nevertheless, the formation of inorganic residues can result in a kind of barrier, thus influencing other important characteristics such as the heat release rate. Ji and Li [11] showed that by adding only 1 wt% montmorillonite into a vinyl ester

resin, the elastic modulus was increased by about 18% while the mass loss measured by fire test could be reduced by almost 13%. They compared five types of mixing combinations and they concluded that intensive mixing improved exfoliation until certain optimum point. Tactoids and intercalated nanoclay morphology reduced all properties of the montmorillonite/vinylester system; partially exfoliated or nearly fully exfoliated nanoclay morphology increased all properties of that system as compared with pure vinylester resin.

Layered silicate nanocomposites exhibit some remarkable advantages such as an ecologically friendly character, low cost, availability and a potential industrial application, over other flame retardant systems. In addition, the mechanical performance of the polymer is not adversely impacted by the clay addition, which is typically the case with conventional flame retardants [14]. The improvement in the thermal properties with the addition of clay is caused by the formation of a thermal insulating and low permeability char layer from the polymer degradation. The char acts as a physical barrier between the bulk and the surface of the polymer where the combustion of the polymer takes place [15, 16]. Vinylester resins are commonly used with natural reinforcements because of their good compatibility with the fibers, their low viscosity and good mechanical properties.

Therefore, the aim of this work was to study the fire resistance, carbon dioxide and carbon monoxide evolution, thermal and flexural properties of jute-reinforced composites using different thermoset matrices. The performance of a jute-reinforced phenolic resin was characterized and compared with that of a composite with vinylester, which is the commonly used matrix. Additionally, clay was added to the matrices in order to enhance their properties.

2. Experimental

2.1. Materials

A commercial vinylester (VE) Derakane 411-350 (Dow) and a resol type phenolic resin were used as matrix of the composites reinforced with 30% vol of woven jute fibers (Casthanal, Brazil). The resol resin was synthesized with a formaldehyde/phenol molar ratio equal to 1.3 catalysed with sodium hydroxide [17].

Polymer/clay composites, obtained by adding 5 wt% of the montmorillonite Cloisite[®] 30B (C30B) to the resol and VE resin, were also used as matrix. The clay was dispersed in the resins by sonication in an ultrasonic bath during 30 min. The sonicated samples were named as follows: resol resin (REs) and vinylester (VEs). The C30B was also mixed with the resol resin by means of a mechanical stirrer during 2 h (REm), in order to compare the influence of the method of mixing on the properties of the material. The fiber-reinforced composites were obtained by compression moulding, pouring the resin over the fibers and then compressing in a stainless steel mould. The vinylester composite was cured in an oven at 110°C and postcured at 140°C. The resol composites were cured by maintaining them for 1 h at: 90, 110, 140 and 170°C.

2.2. Methods

X-ray diffraction analyses (XRD) of the composites were performed in a Philips PW 1710 diffractometer (45 kV and 30 mA) at $2^\circ/\text{min}$, with a radiation of $\text{Cu K}\alpha$ ($\lambda = 1.54 \text{ \AA}$).

Thermogravimetric analysis was carried out in a Shimadzu thermal analyser at $10^\circ\text{C}/\text{min}$ under air atmosphere. The weight of the samples was close to 20 mg.

An Atlas cone calorimeter was used to test the fire resistance of the composites (ISO 5660:1993), using horizontal configuration and a radiant heat flux of $35 \text{ kW}/\text{m}^2$. The exposed surface of the sample was $100 \text{ mm} \times 100 \text{ mm}$. The computed results were heat release rate (HRR), total heat evolved, time to ignition, CO and CO_2 evolution. The thickness of the sample was $4 \pm 0.2 \text{ mm}$.

Flexural tests were performed in an Instron 4467 at a crosshead speed of $2 \text{ mm}/\text{min}$ in a three-point bending configuration (ASTM D 790). An average value of at least five specimens was determined.

Scanning electronic microscopy (SEM) was performed on the fractured surfaces of the composites in order to analyse the interface fiber/polymer. The surface of the specimens was coated with a 300 \AA gold layer and observed in a scanning electron microscope (JEOL JSM-6460LV).

3. Results and Discussion

To investigate the dispersion of the C30B layers in the polymer, XRD analyses were performed on the composites. Figure 1 shows the XRD patterns obtained for the montmorillonite C30B and the jute-reinforced composites containing resol/clay

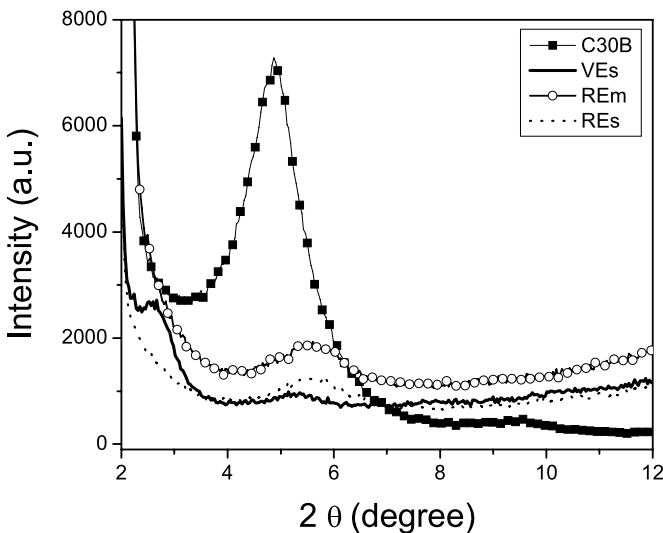


Figure 1. XRD patterns for the C30B and the jute-reinforced composites with VE/clay and resol/clay composites matrices.

and VE/clay matrices. The 001 diffraction peak of the C30B appeared at $2\theta = 4.86$. It was observed that this peak was shifted to lower angles for the VE/clay matrix composite. A shift in the basal peak provides strong evidence that there was an increment in the spacing between the clay layers and an increase in the degree of intercalation. However, in the pattern of the resol/clay composites, REs and RE_m, the peak shifted only slightly to higher angles compared to the basal peak of the clay. This could be due to a gallery contraction because of the higher quantity of ions present in the resol resin compared to the VE. This behaviour was also observed in epoxy and resol nanocomposite systems and was explained as a consequence of different rates of intra- and extra-gallery polymerization during curing [18–20]. In the lower angles region, a broader band appeared in the pattern of the RE_m with respect to the REs one. Then, the clay presented an inhomogeneous distribution in the polymer but it seems that sonication provided a better dispersion of the clay in the polymer than the mechanical mixing.

Regarding the thermal degradation of natural fibers, it is well known that under nitrogen atmosphere, there are two decomposition steps at 290°C and 360°C. The first step corresponds to de-polymerization of hemicellulose and glucosidic bondings, while the second one is due to the thermal destruction of the α -cellulose. Lignin degrades in a broad range overlapped with the hemicellulose and cellulose decomposition [21, 22]. Figure 2 shows the percentage of residual mass as a function of the temperature for the jute fibers, VE matrix and its composites under air atmosphere. The lower degradation step of jute fibers (degradation of hemicellulose) remained unchanged with respect to the test made under nitrogen. But the main degradation process is shifted to lower temperature (326°C) due to the oxidative degradation of the cellulose [23–25]. On the other hand, VE resin showed

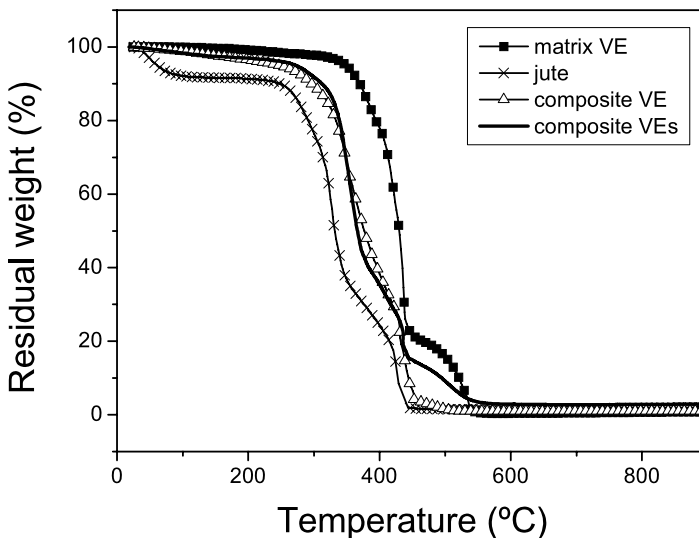


Figure 2. Thermogravimetric curves at 10°C/min of jute, VE matrix and its composites.

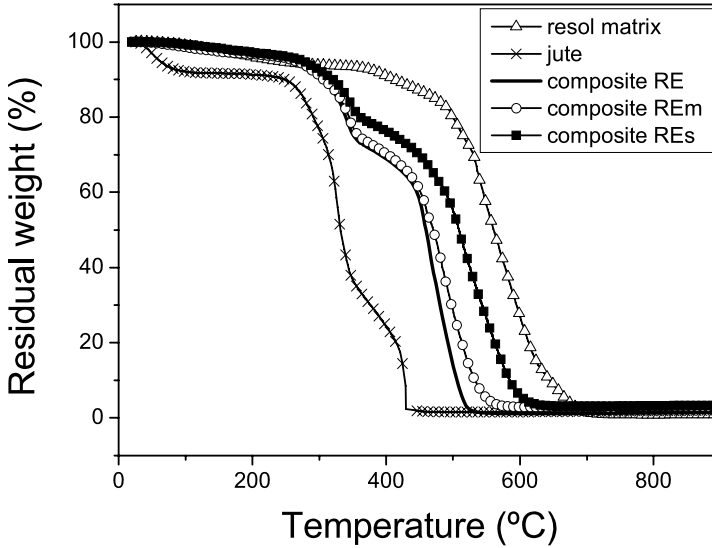


Figure 3. Thermogravimetric curves at 10°C/min of jute, resol matrix and its composites.

one main decomposition step at 430°C and another one at 524°C. The composites showed an intermediate behaviour between the matrix and the jute fibers. It was also observed from the thermogravimetric analysis that the addition of clay slightly reduced the thermal degradation of the composites at temperatures higher than 450°C.

The residual mass curves obtained for the resol matrix and its composites are shown in Fig. 3. The resol resin showed the better resistance to temperature between the two matrices studied. Its higher rate of weight loss was observed in the range of temperatures between 400 and 600°C where oxidative reactions take place. The thermal oxidative process leads to the evolution of carbon monoxide, carbon dioxide, and benzaldehyde, while thermal fragmentation reactions form methane, phenol and phenol homologues [26]. The composites curves are intermediate between that of the fibers and the matrix, as in the case of the VE composites. It was observed that the dispersion of the clay in the resol matrix by sonication enhances the thermal resistance of the composite at temperatures higher than 300°C. This should be due to the fact that the better dispersed clay acted as a heat barrier enhancing the overall thermal resistance of the system [4].

The heat release rate, described as the driving force of the fire, is the single most important parameter in a fire. Figure 4 shows the curves of the heat release rate (HRR) as a function of time for the resol and VE matrices and its composites, obtained in the cone calorimeter. All the curves showed a first peak, which indicates the start of burning and after this peak, the HRR dropped due to the formation of an insulating char layer. At the beginning, this mechanism was not present in the RE_m-jute composite. The peak of HRR is an essential factor for flame spread and

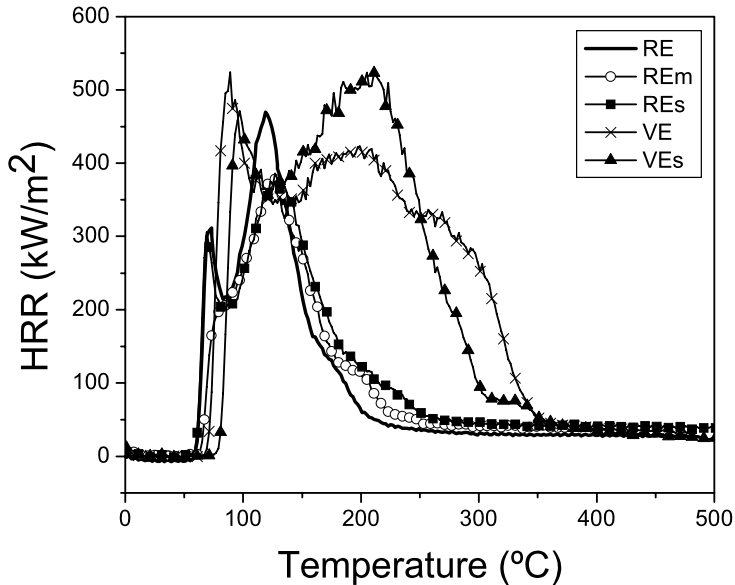


Figure 4. Heat release rate for the jute-reinforced composites with resol, VE and polymer/clay matrices.

Table 1.

Cone calorimeter results of the jute composites with resol and VE matrices

Matrix of the jute-reinforced composites	Time to ignition (s)	Total heat evolved (MJ/m ²)	CO _{average} (kg/kg)	CO _{2 average} (kg/kg)
VE	75.8	93.1	0.043	1.79
VE + clay sonicated (VEs)	86.7	90.2	0.045	1.89
RE	68.1	45.7	0.018	1.51
RE + clay mixed (REEm)	64.5	39.7	0.019	1.46
RE + clay sonicated (REs)	65.0	50.7	0.019	1.36

fire development. A lower value of the peak of HRR in clay/resol jute composites was observed compared with the pure resol composites. A reduction in the peak of heat release rate was also observed in other polymeric systems [6, 7, 27] but these decreases were not proportional to the amount of clay added. This reduction in the flame spread was attributed to the accumulation of layered silicate at the surface of the condensed phase acting as a barrier for pyrolysis gases.

The total heat evolved measured in the cone calorimeter represents the total fire load that a material provides. It was observed that the total heat evolved is higher for the VE composites than for the resol composites (Table 1). However, the time to ignition is lower for the resol composites. This could be due to the presence of fibers exposed on the specimen surface, which began to degrade earlier. However, neither

the time to ignition nor the fire load (total heat evolved) was significantly influenced by the clay addition (Table 1). This is due to the fact that a physical barrier prolongs burning time without decreasing the total amount of combustible material [28]. It was reported that the reduction of total heat evolved was not significant in most of the polymer/clay systems and that there is no major influence on the time to ignition value [27, 29].

In addition, between the materials studied, the resol composites evolved the minor quantity of carbon monoxide and carbon dioxide. However, the addition of clay neither diminished the quantity of toxic smoke evolved nor increased its production, which is usual for other common fire retardants. One of the most important fire hazards is the evolution of toxic gases such as carbon monoxide (CO). More than 50% of the fire victims die due to toxic gas inhalation, not from direct fire or burns [30].

The fire risk (Fig. 5) gives the performance of a material against the fire. The *y*-axis indicates the propensity to cause a fire of long duration, and the *x*-axis illustrates the propensity to cause a quickly growing fire. The resol matrix composites showed the best performance. Phenolic resins lead to the production of a char structure, which results in low flame spread rate compared with other polymers. The addition of clay by sonication to both resol and VE matrices reduced the rate of growing of the fire. It was observed that the fire retardancy efficiency was strongly dependent on irradiance, decreasing the fire retardancy provided by the clay reinforced composites from irradiance of 70 to 30 kW/m² [6, 27]. Then, probably performing the cone calorimeter test at higher irradiance a better performance of the clay containing composites over the polymer should be obtained.

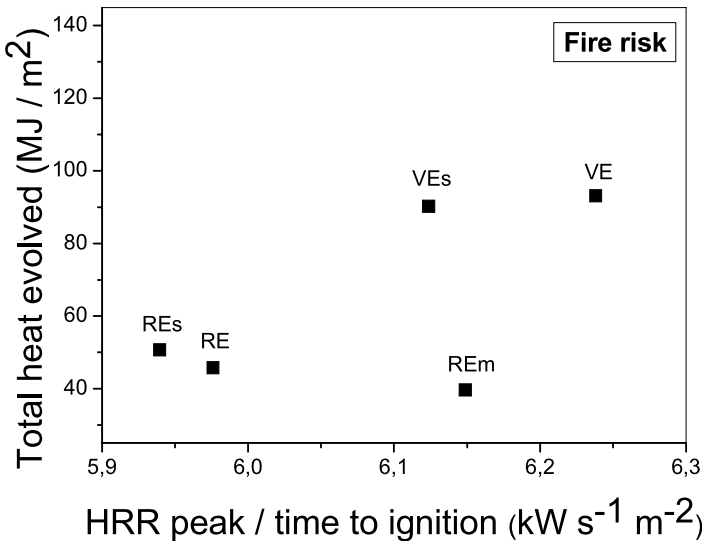


Figure 5. Fire risk evaluated for the jute-reinforced composites with resol, VE and polymer/clay matrices.

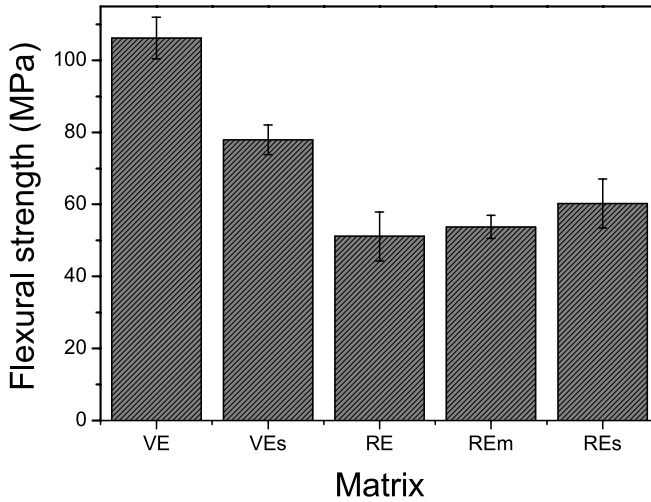


Figure 6. Flexural strength for the jute-reinforced composites with resol, VE and polymer/clay matrices.

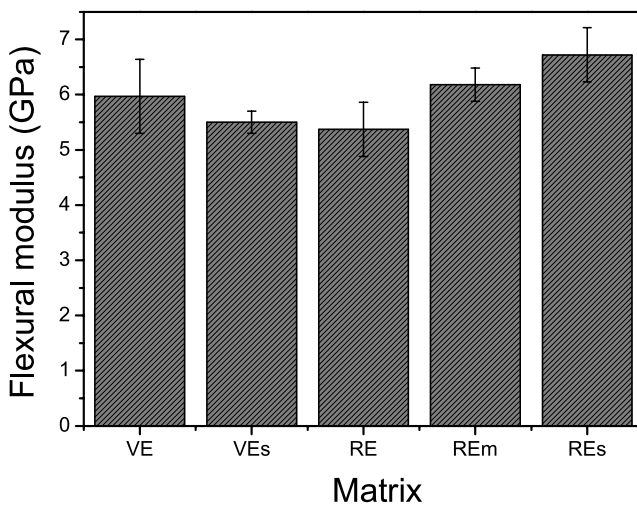


Figure 7. Flexural modulus for the jute-reinforced composites with resol, VE and polymer/clay matrices.

Flexural properties of the composites are shown in Figs 6 and 7. The flexural modulus as well as the flexural strength of the resol composites showed a higher increment when the clay was added by sonication. Flexural modulus showed an increment of 25% while the flexural strength increased by 17% when the clay was added by sonication to the matrix of the jute-reinforced composite. In general, an important increment in the modulus of thermoplastic polymers and rubbers was observed by the addition of clay, but the increment observed was not so high in

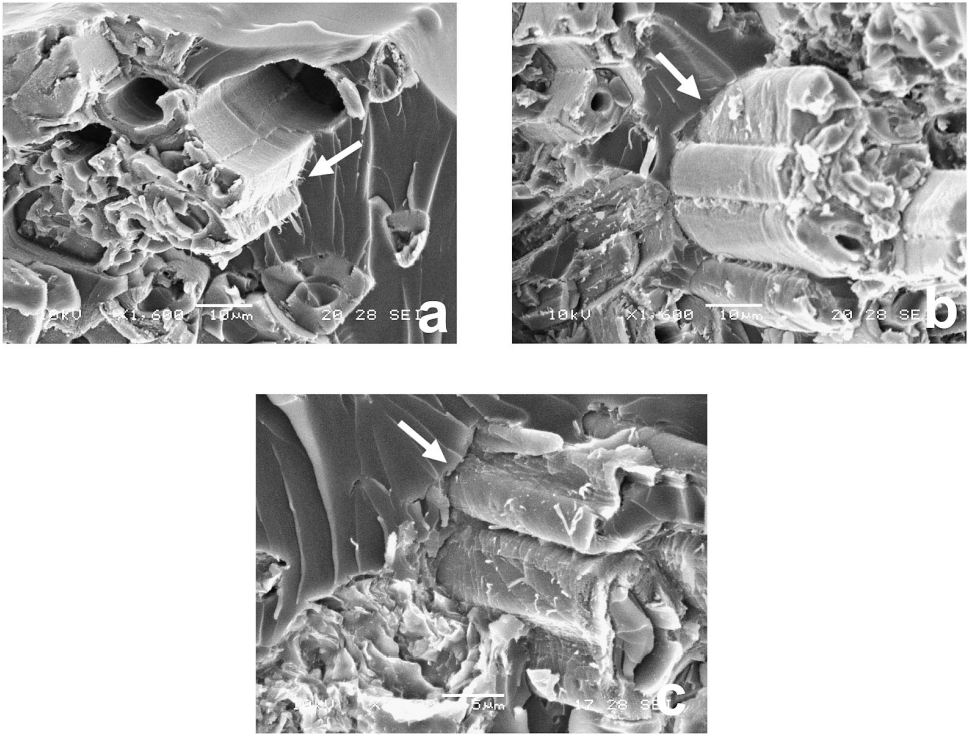


Figure 8. SEM microphotographs of the fractured surfaces of the jute-reinforced composites containing the matrices: (a) resol, (b) resol + 5% C30B (mechanical mixing), (c) resol + 5% C30B (sonicated).

thermoset polymers [31]. VE composite showed the best flexural strength, and there was no contribution of the clay to these properties (Fig. 6).

SEM images were obtained in order to analyze the effect of the clay on the quality of the fiber–matrix interface. Figure 8(a) shows the fracture surface of the resol-jute composite. It could be observed that there is good adhesion between the fibers and the resol matrix due to their hydrophilic character, which leads to high chemical affinity (Fig. 8(a)). Figure 8(b) shows that the addition of clay by mechanical mixing produced no effect on the interfacial adhesion, but when the clay was mixed by sonication a poorer interface was observed (Fig. 8(c)). Therefore, as the clay dispersion degree is increased, the interface quality is diminished. It was observed in a previous work [32] that the presence of clay influences the resol resin polymerization reactions, thus reducing the affinity of the polymer to the fibers. However, flexural strength showed an opposite trend which can only be explained in terms of an increment in the resistance of the matrix. This is more evident in the case of the flexural modulus (which is not dependent of the fiber–matrix interface) where a higher increment is observed as the clay is dispersed better in the matrix (Fig. 7).

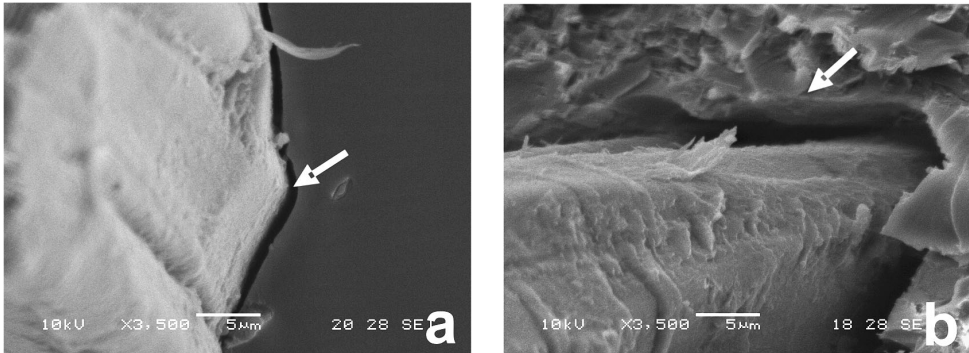


Figure 9. SEM microphotographs of the fractured surfaces of the jute-reinforced composites containing the matrices: (a) vinyl ester, (b) vinyl ester + 5% C30B (sonicated).

Similar analysis was performed on the fracture surface of the VE–jute composite. This interface was not as good as that observed in resol composites (Fig. 9(a)). The addition of clay produced the same detrimental effect on the interface observed in the resol composites (Fig. 9(b)). This caused a higher fall in the flexural resistance than in the flexural modulus. A decrease in the modulus of VE resin with the addition of clay was also observed by Ji and Li [11] when the montmorillonite was not exfoliated in the polymer matrix.

4. Conclusions

It was possible to obtain jute-reinforced composites using resol and clay/resol resins as matrices. Those composites showed an improvement in the fire performance in comparison with those obtained with vinyl ester resin, which is the commonly used matrix. Lower fire risk was observed as well as lower heat evolved. Additionally, the best results in thermal and mechanical properties were obtained when the clay was added to the matrix by sonication, allowing a better dispersion of the clay in the polymer. However, the addition of clay to both matrices by sonication produces a detrimental effect on the fiber–matrix interface.

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