Preparation and Characterization of Ramie-Glass Fiber Reinforced Polymer Matrix Hybrid Composites

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The use of ramie fibers as reinforcement in hybrid composites is justified considering their satisfactory mechanical properties if compared with other natural fibers. This study aims to verify changes in chemical composition and thermal stability of the ramie fibers after washing with distilled water. One additional goal is to study glass fiber and washed ramie fiber composites focusing on the effect of varying both the fiber length (25, 35, 45 and 55 mm) and the fiber composition. The overall fiber loading was maintained constant (21 vol.%). Based on the results obtained, the washed ramie fiber may be considered as an alternative for the production of these composites. The higher flexural strength presented being observed for 45 mm fiber length composite, although this difference is not significant for lower glass fiber volume fractions: (0:100) and (25:75). Also, by increasing the relative volume fraction of glass fiber until an upper limit of 75%, higher flexural and impact properties were obtained.

Keywords: natural fiber, glass fiber, hybrid composite, ramie

1. Introduction

The use of natural fibers as reinforcement in polymeric composites has increased due to their low cost, biodegradability and low specific weight that may even yield higher specific strength and stiffness than glass fiber. Also, production of fibers requires a small amount of energy at low CO2 emission and no abrasion during processing. A wide range of fibers can be applied as reinforcement, including cotton, flax, hemp, ramie, sisal, jute, banana, bamboo, curaua and buriti1-7.

Actually, ramie textile applications have been replaced by synthetic fibers, mainly in clothes8. So, the motivation of this work is to study ramie fiber as composite reinforcement, with the concern to, in the future, maintain the culture of the fiber in the country. Also, to attend the urgent need to develop environment-friendly materials, this study focused on to improve the fiber-matrix interaction without chemical treatments (washed ramie fiber) and to prepare the composites by the resin transfer molding (RTM) technique. RTM is used in the automobilist industry and have some advantages against conventional techniques, e.g. low capital investment, void content reduction, low cycle times, better process control with consequently waste reduction9.

China and the Philippines are the largest producers of ramie fiber. Nowadays, Brazil is the third global producer of ramie, a plant of the Urticaceae family, derived from the Boehmeria nivea and Boehmeria tenacissima, the fibers of which are long, ranging between 150 and 200 mm8. The chemical composition of the ramie fiber is: cellulose (68.6-76.2 wt. (%)); hemicellulose (13.1-16.7 wt. (%)); lignin (0.6-0.7 wt. (%)); pectin (1.9 wt. (%)); wax (0.3 wt. (%)); moisture content (7.5-17 wt. (%)). In relation to mechanical properties, Margem et al.2 reported that the exceptional tensile strength of ramie fiber (in comparison with other natural fibers) has motivated researches on its application in polymer composites.

There are some disadvantages in the use of the natural fibers in polymeric composites, including high moisture absorption, non uniformity and poor mechanical properties. The major disadvantage is the polar and hydrophilic nature of lignocellulosic fibers and the non-polar characteristics of thermosetting resins.7 This results in a poor interphase between fiber and matrix. To improve fiber-matrix interaction, the fiber surface can be treated (e.g. alkali treatment, isocyanate treatment, peroxide treatment, vinyl grafting, bleaching, acetylation, and treatment with coupling agents), but the cost and complexity of these treatments can make it rather expensive9.

Spinacé et al.11 submitted the curaua fiber to four different treatments: a) pristine curaua; b) curaua washed with water; c) curaua treated with sodium hypochlorite and d) curaua treated with cold oxygen plasma. The washed fibers showed lower moisture content values and an increasing in the crystallinity and surface roughness. For fibers treated with sodium hypochlorite, the behavior is very similar, while for fibers treated with cold oxygen plasma a decreasing of crystallinity was observed. Thus, to remove impurities and improve the fiber-matrix interaction without chemical treatments, fibers washed with water is a viable alternative.
The properties of natural fiber composites can be enhanced via hybridization with synthetic fibers (e.g., glass fiber), aiming to improve among other properties stiffness, strength and moisture resistance of the composites. The possibility of mixing different types of reinforcement is interesting: the natural reinforcement is recyclable and it allows that tailor made mechanical properties to be obtained. Thus, a balance between environmental impact and performance can be achieved.\textsuperscript{11-13}

Jawaid and Khalil\textsuperscript{11} cited recent relevant studies about polymer hybrid composites, and a limited number of studies related to hybridization of ramie with another natural or synthetic fiber. For instance, Paiva Júnior et al.\textsuperscript{14} studied polyester/hybrid ramie-cotton fabric composites, molded by compression. They concluded that ramie fibers have a great potential as fiber reinforcement in resin matrix composites materials, which showed an increase on the tensile strength over the neat resin of up to 338%.

This work aims to study changes in chemical composition and thermal stability of ramie fibers by washing them with distilled water. An additional goal is to study the incorporation of glass fiber and washed ramie fiber into a polyester matrix focusing on the effect of varying both the fiber length (25, 35, 45 and 55 mm) and the relative volume fraction between glass and ramie fibers. In all experiments the overall fiber loading was kept constant (21 vol.%).

2. Experimental Procedures

2.1. Materials

Ramie roving was purchased from Sisalsul Fibras Naturais (São Paulo, SP, Brazil), and glass fiber roving (EC 2400 P207 with density of 2.5 g.cm\textsuperscript{-3}) from Vetrotex (Cápivari, SP, Brazil). Modified unsaturated polyester resin UC EFLEX UC 5530-M was supplied by Elekeiroz S.A (Varzea Paulista, SP, Brazil). Mold-releasing agent poly(vinyl alcohol) (PVA), curing agent methyl ethyl ketone peroxide in diisobutyl phthalate (BUTANOX LPT) and the resin promoter dimethylaniline (DMA) were purchased from Disfibra (Caxias do Sul, RS, Brazil).

2.2. Preparation of fiber

In a previous study, it was defined the range of the fiber lengths: it was impracticable to prepare the mats with less than 25 mm fibers lengths by the difficulty to chop and separate the fibers; in lengths exceeding 55 mm it was evidenced a curvature of the fiber (bending) in the mat manufacturing. As already reported in the literature\textsuperscript{15}, this fact causes a decrease in mechanical properties of the composite. Then, glass and ramie fibers were chopped in different lengths: 25, 35, 45 and 55 mm. The natural fiber was immersed in distilled water for 10 minutes, then twisted and washed (with distilled water at 20-25 °C) for 50 minutes. It was then oven-dried at 105 °C with air circulation for 60 minutes. Finally, the ramie fibers were manually selected to eliminate wastes. The method was adapted by Ornaghi et al.\textsuperscript{16} studies.

2.3. Mat manufacturing

The glass and ramie fibers were mixed and manually arranged in a pre-mold of same shape of the mold in order to produce a hybrid mat. The overall fiber loading was kept constant (21 vol.%). This value was defined in accordance with the best results obtained in previous studies\textsuperscript{17} in the same mold. The glass fiber loading was varied from 0 to 75 vol.%. It was not possible to molding composites with 100% of glass fiber in this method due to the fiber dragging through the resin flow during the molding process. The relative volume fraction between glass fiber (GF) and washed ramie fibers (RF) is shown in Table 1.

For example, the 45 mm fiber length, 25% glass fiber and 75% of ramie fiber loading composite was designated by (45/25:75).

2.4. Preparation of composites

Before molding, the mat was pressed under the following conditions: 10 minutes, 49 kN and 80 °C. Also before molding a mold-releasing agent (PVA) was applied to the mold. The polyester resin used was manually mixed (for approximately 1 minute) with 0.5 wt. (%) of Butanox LPT and 0.1 wt. (%) of DMA, respectively. The process parameters used in the resin transfer molding (RTM) were: mold temperature between 20 and 25 °C, positive pressure of 0.5 bar. The resin preparation and process parameters were defined in a previous experiment, considering the resin gel time. The curing was carried out in situ at a temperature of 25 °C for 24 hours, followed by first post-curing at 80 °C for 6 hours and second post-curing at 120 °C for 2 hours\textsuperscript{18,19}.

2.5. Characterization

The fibers were investigated by Fourier Transform Infrared Spectroscopy (FTIR – Nicolet IS10 – Termo Scientific), using the Attenuated Total Reflectance (ATR) technique. Thermogravimetry (TGA – Shimadzu TGA-50) was performed in the temperature range from 25 to 900 °C at a heating rate of 10 °C.min\textsuperscript{-1}. Three samples were taken for FTIR and TGA analyses. The glass fiber density was confirmed (2.53 ± 0.03 g.cm\textsuperscript{-3}) using the pycnometry analysis, with water (solvent). The ramie fiber density was determined using a helium Picnometer (MVP-1 Quantachrome). Four analyses were taken and the average density value was reported.

The fiber diameter and surface cross-section of the hybrid composite (cryogenically fractured samples) were carried out using a Scanning Electron Microscope (SEM - JEOL JSM-6060). The average diameter of about 30 samples was determined. All specimens were sputtered with a layer of gold prior to SEM observations. Samples were

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<th>Table 1. Composition of the mat (% vol.)</th>
<th>Glass fiber content (%)</th>
<th>Ramie fiber content (%)</th>
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<td>(GF:RF)*</td>
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*GF = Glass Fiber; RF = Washed Ramie Fiber.
oven-dried at 70 °C with air circulation for 24 hours. After that, the fibers and composites were mounted on aluminum holders using double-sided electrically conducting carbon adhesive tabs prior to the analysis.

Unnotched Izod impact test was performed using a CEAST impact machine in accordance with ASTM D256-04\textsuperscript{[20]}. Specimens of 63.5 × 12.7 × 4 mm were prepared, and the maximum energy of the hammer used for hybrid composites, natural fiber composites and resin were 7.5, 2 and 1 J, respectively. An average value from ten replicates of each sample was taken. The flexural tests (three point bending configuration) were performed in the universal testing machine EMIC DL-3000, in accordance with the D7264M-07\textsuperscript{[21]} standard. Specimens of 128 × 13 × 4 were prepared, and the test was conducted using a load cell of 2 kN at 1.8 mm/min rate of loading. Seven specimens were tested in each case and the average values were reported. All tests were conducted at a temperature of 23 ± 2 °C and 50 ± 5% relative humidity.

3. Results and Discussion

3.1. Fiber characterization

The average density obtained for washed ramie fibers was 1.49 ± 0.04 g.cm\(^{-3}\), the values being comparable to those of the literature (1.50 g.cm\(^{-3}\))\textsuperscript{[13]}. The average diameter for in natura fibers was 77.7 ± 19.8 mm, and for washed fibers was 69.5 ± 19.6 mm. The fibrils are a constituent of the fiber, with an average diameter of 12 ± 4 mm. Thus, the ramie fibers presented values close to the range found in the literature: 18 to 80 mm\textsuperscript{[13]}. The absorption bands for characteristic chemical groups of the lignocellulosic fibers composition (cellulose, hemicellulose and lignin) can be observed in Figure 1. The spectra revealed a broad and intense peak at 3340 cm\(^{-1}\), characteristic of the hydroxyl groups present in the cellulose, water and lignin structures\textsuperscript{[22,23]}. The peaks at 2920 and 2850 cm\(^{-1}\) are characteristic bands of the C-H stretching vibration present in the cellulose and hemicellulose components. The characteristic 1730 cm\(^{-1}\) band corresponds to the carbonyl (C=O) stretching vibration in hemicellulose\textsuperscript{[23,24]}. Between 1320 and 1360 cm\(^{-1}\) the absorption peak refers to the bending vibration of C-H and C-O groups of the aromatic rings in polysaccharides\textsuperscript{[9]}. The band at 1238 cm\(^{-1}\) is relative to the (C-O) vibration of esters, ethers and phenolic groups attributed to the presence of wax on the fiber surface\textsuperscript{[25]}. The absorption peak at 1030 cm\(^{-1}\) is related to the (CO) and (O-H) stretching vibrations which belong to the polysaccharide in cellulose. Finally, the peak observed at 896 cm\(^{-1}\) is attributed to the presence of b-glycosidic linkages between the monosaccharides\textsuperscript{[9]}. Data obtained by FTIR analysis show differences in the intensities between in natura and washed ramie fiber in two main absorption cellulose bands (3340 and 1030 cm\(^{-1}\)). In the spectrum of the in natura fiber, these bands are more accentuated, and it can be an indicative of a larger exposition of cellulose and water on the fiber surface. It is known that more than 70 wt. (%) of the fiber structure is composed of cellulose and 7.5-17 wt. (%) of moisture content\textsuperscript{[9]}. Then, it is possible that part of water and cellulose present in the fiber surface could be removed by the method of fiber's preparation (washing, drying and selection processes).

The thermogravimetric curves of the in natura fiber (NF) and washed fiber (WF) can be seen in Figure 2. The thermogravimetric curve of ramie fiber shows three weight loss steps. The initial weight loss observed between 40 and 110 °C is attributed to the vaporization of the water from the fibers. The second weight loss with the maximum decomposition rates in 289 °C (NF) and 297 °C (WF), is associated to the thermal depolymerisation of hemicellulose, pectin and the cleavage of glycosidic linkages of cellulose, while the third weight loss (368.15 °C for NF and 372.8 °C for WF) corresponds to the degradation of α-cellulose present in the fiber. The decomposition of lignin occurs slowly within the whole temperature range, owing to its complex structure\textsuperscript{[9]}. The ramie fiber washing process promoted an increase in the thermal stability, shifting the degradation peaks to higher temperatures (289 to 297 °C and 368.15 to 372.8 °C). It was also observed a slight difference in the curves behavior below 220 °C, probably due to the more accentuated presence of water, wax and residues in the in natura fibers. The wasting removal during the washing process can also explained by differences in the mass residues that remains at 800 °C (16% for natural fibers and 10.5% for washed fibers). In this case, it should be responsible for the increasing of the thermal stability. From an earlier study realized by Spinacé et al.\textsuperscript{[9]} it is known that the water washed curaua fibers presented a 10 °C increase in the temperature of the maximum rate of the cellulose degradation process.

3.2. Influence of fiber length and hybridization

The analyses of the results obtained were realized by comparison of the experimental data. Flexural properties of the composites are shown in Figure 3. All composites showed higher flexural strength when compared to the neat resin. The flexural strength of neat resin is found to 36.4 ± 5 MPa. By the incorporation of ramie fiber (0:100 - 45 mm fibers length), the flexural strength increases by about 57%. It was also observed an increase in the flexural strength as the relative glass fiber volume fraction increases. Data from
Romanzini et al. indicate the tensile strength (2000-3500 MPa and 500 MPa) and the Young’s modulus (70 and 44 GPa) for E-glass and ramie fibers, respectively. Thus, this increasing is due to the stronger and stiffer characteristics of the glass fiber in comparison with the ramie fiber and also to the better adhesion of the synthetic fiber to the polyester resin in comparison with ramie fiber, with consequently higher degree of stress transfer to the former fibers upon loading.

It is important to mention that, in a three-point flexure test, failure occurs due to bending and shear failure, so by raising the glass fiber content the flexural strength will be improved due to increased shear resistance between fiber and matrix.

There was no significant influence of the fiber length on the flexural strength measurements of composites containing (0:100) and (25:75) fiber loading. The 45 mm fiber length composites showed better performance than other fiber lengths studied (50:50 and 75:25 fiber loading). The lower values found for the 55 mm fiber length composites may be due to the difficulty of adequately distributing and homogenizing the fibers in the mold.

Figure 3 shows the effects of different glass and ramie fiber ratios on the impact strength. All composites showed remarkably higher impact strength when compared to the neat resin. The impact strength of neat resin is found 48.6 ± 6 MPa. By the incorporation of ramie fiber (0:100 - 45 mm fibers length), the impact strength increases by approximately 309%. The important role of the fibers in the impact resistance can be explained on the basis that the fibers interact with the crack formation in the matrix acting as a stress transfer agent.

Moreover, it can be noted that the impact strength increased as a result of the glass fiber incorporation. The glass fiber enables better adhesion to the polyester resin than the ramie fiber, and this increase can be attributed to the better energy dissipation at the glass-matrix interface in order to detach the fibers from the matrix. The impact strength of the (45/50:50) composite increased 80.2% in comparison with the (45/25:75) composite. For the (45/75:25) composite, there was a relative increasing of 142.6% in comparison to the (45/25:75) composite.
Finally, it is expect that increasing the fiber length the impact strength increases due to the higher energy dissipation along the fiber length. Consequently, higher energy absorption is achieved\(^2\). As shown in Figure 3, considering the standard deviation, this tendency did not show a significant influence for all the glass/ramie fractions.

The influence of fiber length as well as the efficiency of the bonding between fiber and matrix is important to ensure high strength and stiffness to the composites. Therefore, there is a critical length that must be exceeded for the fiber to fracture without pullout. For values below the critical length, the failure usually occurs at the interface by fiber debonding\(^3\). Angelini et al.\(^4\) studied ramie fiber and obtained a critical length (\(l_c\)) of 0.47 mm. Thus, the range of lengths studied in this work exceeds the critical length found in the literature.

Figure 5 shows the fracture surface of 45 and 55 mm fiber length hybrid composites. The presence of short fractured fibers projecting out of the matrix can be indicative that, in general, there was no pullout failure.

Therefore, a good adhesion between fiber-matrix can be obtained for ramie fiber just by removing the fiber impurities with distilled water.

4. Conclusion

Washed ramie fibers may be considered an alternative for the manufacturing of the polymeric hybrid composites. FTIR analysis shows a slight difference between in natura and washed fibers, even as thermal analysis showed an increase in the thermal stability, shifting the degradation peaks to higher temperatures. The 45 mm fiber length composites showed better performance in flexural strength as compared with those of 25, 35 and 55 mm fiber length, although this difference is not significant for lower glass fiber volume fractions (0:100) and (25:75). The drawbacks encountered in the 55 mm length fiber processing lead out to the low values assessed for these composites. Furthermore, the ramie fiber promoted higher mechanical properties in the composites studied. With hybridization, an increasing in the relative volume fraction of glass fiber until an upper limit of 75% was observed as well higher flexural and impact properties. So, ramie fiber should be considered an alternative to substitute partially glass fibers in polymer composites.

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