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Reinforcement of Polyester with Renewable Ramie Fibers

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Ramie (*Boehmeria nivea*) fiber is one of several lignocellulosic fibers with superior strength, but the least investigated, particularly as reinforcement in strong, tough polymeric composites. This paper presents mechanical properties for polyester reinforced with aligned ramie fibers up to 30% by volume. It was found that adding 30 vol% of ramie fibers increases the flexural strength of polyester about three times (212 ± 12 MPa vs. 63 ± 7 MPa) and tensile strength by a factor of two (89 ± 9 MPa vs. 53 ± 3 MPa). Polyester-ramie fiber composites also displayed a significant improvement in toughness. The impact energy values, as measured by Charpy and Izod impact tests, increased nearly two orders of magnitude for 30 vol% ramie fiber composite as compared to neat polyester. Additionally, fractographic studies revealed reasonable wetting of fibers by the polyester resin, and FTIR analysis confirmed a hydrophilic nature of ramie fibers. In spite of weak adhesion between hydrophilic fibers and hydrophobic matrix, composites of improved strength and toughness were demonstrated in this study. Limited fiber-matrix adhesion was reflected in preferential longitudinal propagation of cracks along the fiber/polyester interfaces, indicating also that most of the fracture area is associated with the fiber surface.

Keywords: *Ramie fiber, Biofibers, Polyester, Thermal Molding, Flexural Properties, Fracture, Impact Strength, Toughness*

1. Introduction

Natural fibers extracted from plants, generally termed as ‘lignocellulosic fibers’, are presently considered engineering materials[1] that also constitute an environmentally appropriate alternative to replace more expensive, non-recyclable and energy-intensive synthetic fibers[2,3]. This is due to the recognition of various attractive attributes such as abundance, availability, renewability and low cost, together with increasing environmental concerns for the use of synthetic nonrenewable fibers. As a consequence, several lignocellulosic fibers have been investigated in recent years and are already being applied as reinforcement for polymer composites, owing to the attributes listed above[4-15]. Other attractive features of lignocellulosic fibers include reduced damage to tooling and molding equipment, as well as relatively better surface finishes and lower abrasiveness of composite part surfaces[11].

Lignocellulosic fibers are typical of tropical regions and, in principle, their application in industrialized composites would represent job opportunities and income for developing countries in Africa, South Asia and Latin America[16]. In fact, composites reinforced with coconut, sisal, jute, and hemp are already on the market as substitutes for more common fiberglass automobile components[17-19]. Alternative reinforcements have found use in components such as interior panels and seat cushions made of fiberglass or polymeric foams[20]. Among the lignocellulosic fibers with potential as composite reinforcement, that extracted from the stem of ramie (*Boehmeria nivea*), and shown in Fig. 1 is now investigated. The tensile strength of non-selected ramie fibers with diameters 60-140 µm varies from 400 to 938 MPa[7,13,16], and is comparable to those of other strong natural fibers such as flax, jute, sisal, kenaf, hemp, pineapple and curaua[13,16]. Selected smaller diameter (25 µm) of ramie fibers demonstrated tensile strength of about 1,500 MPa[1].

Despite attractive strength properties and numerous studies on reinforced composites[21-43], little has been reported on the use of ramie fibers in polyester composites. These limited ramie/polyester composite studies were carried out on Brazilian ramie fibers, mostly by the authors’ group[22,38,39,41,43].

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Figure 1. The typical ramie plant (a), bunch of ramie fibers (b) and separated ramie fibers (c).

Indeed, Brazil was the third world producer of the ramie fiber during 1990s, with about 10 thousand tons annual production, primarily for use in textiles[16]. However, the ramie plant cultivation and fiber processing have been declining in Brazil in the past decade. A possibility to revitalize the production of ramie fibers could be related to their use in new industrial composite materials. With favorable mechanical properties, ramie fiber composites are attractive structural materials for doors, panels, and furniture. They could also compete with other traditional lignocellulosic fiber composites for automobile components[17-20].

Novel polyester composites reinforced with ramie fibers were formulated in the present work and characterized for their flexural, tensile and impact properties. From 10 to 30 vol% of aligned fibers were added to polyester without involvement of compatibilizing agents or treatment of the fiber surfaces that would increase costs. The composites were formulated using press molding technology. Fiber infrared analysis and composites SEM fractographs disclosed the effectiveness of the fiber/matrix interaction.

2. Experimental

2.1. Materials

Ramie fibers used in this study were received from Brazilian firm SISALSUL (São Paulo, Brazil) which commercializes various natural fibers. These fibers were minimally processed with only water cleaning and air drying at room temperature. Moisture content was determined, after drying at 60ºC in a stove, to be around 8 wt%. The matrix polymer used was a fluid orthophthalic polyester resin with methyl-ethyl-ketone as catalyst provided by Dow Chemical and supplied by Resinpoxy, Brazil.

2.2. Methods

The characteristics of the lot of ramie fibers used in this investigation were statistically evaluated based on the analysis of 100 ramie fibers. Each ramie fiber had its length and diameter measured. The diameter was measured at seven points by a profile projector and then rotated 90 degrees to a second set of measurements, assuming the fibers have approximately circular cross section. Double measurements were taken at each point. The fibers were then weighed on a precise balance. Using the Weibull method the mean density of ramie fibers was determined.

Composites with continuous and aligned ramie fibers (10, 20 and 30 vol%) were formulated by press molding in a DIPAMAK (Model 30T) hydraulic press. Fibers were impregnated with fluid orthophthalic polyester resin and 0.5 wt% methyl-ethyl-ketone catalyst. The mixture was set to cure at room temperature for 24 h inside a 152 x 122 x 10 mm rectangular mold under 0.53 MPa of pressure. The ramie fibers were aligned along the 122 mm width of the mold. Six rectangular 122 x 25 x 10 mm flexure specimens were cut from each composite plate after 24h curing. These specimens were subjected to room temperature (RT) three points bend tests, according to ASTM D790 standard, in an Instron machine (Model 5582) with load cell of 1kN at a strain rate of 1.6 x 10^{-2} $s^{-1}$and a span-to-depth ratio of 9.

Tensile test specimens were prepared individually by arranging the fibers in silicone dogbone-shaped mold with 5.8 x 4.5 mm reduced cross section and 35 mm length. The volume fraction up to 30 vol.% ramie fibers were aligned continuously along the mold. The resin was poured over the fibers inside the mold and cured for 24 hours at RT. Seven specimens for each amount of ramie fibers were prepared for the test. These specimens were subjected to RT tensile test in an INSTRON machine (Model 5582) with load cell of 1kN at a strain rate of 10^{-2} s^{-1}.

For Charpy impact tests, following the ASTM D6110 standard, notched specimens (122 x 12.7 x 10 mm) were cut from the composite plates along the direction of alignment of the fibers. The notch with 2.54 mm depth, angle of 45º and a tip curvature radius of 0.25 was machined according to DIN 847 norm. For each condition, 14 specimens were tested to ensure statistical validation. The specimens were RT impact tested using a Charpy hammer pendulum in an EMIC machine (model AIC). The impact energy was obtained with a 2.7 J hammer for the pure polyester specimens and with a 5.4 J hammer for their ramie fiber composites.

In the Izod impact tests, also following the ASTM D256 standard, notched specimens (61 x 12.7 x 10 mm) were cut from the composite plates along the direction of alignment of the fibers. For each condition, 14 specimens were tested to ensure statistical validation. The specimens were RT impact tested using an Izod hammer pendulum in the same aforementioned EMIC machine. The impact energy was obtained with a 2.7 J hammer for the pure polyester and 5.4 J for their ramie fiber composites.

The Fourier Transform Infrared (FTIR) spectrum of ramie fibers was obtained using a Prestige 21 SHIMADZU spectrometer. Individual ramie fibers, and fractured specimens of pure matrix and their composites were imaged using a JEOL scanning electron microscope (Model JSM-6460 LV) operating at either 10 or 15 kV.

3. Results and Discussion

3.1. Density and Size Distribution

The average density of the ramie fiber used was found to be 1.49 ± 0.11 g/cm^3, which agrees with reported 1.5 g/cm^3 [16]. The distribution of length and diameter for a range of statistical groups is shown in Fig. 2. A comparison between the average length of the ramie fibers in this work (L = 158 ± 69 mm) with its critical length ℓ_c = 1.6 mm, obtained from pullout tests[39] indicates that these fibers should be considered as continuous (L > 15 ℓ_c) [44] for composite reinforcement. Since the fibers used are much longer than the critical length, in all the following discussions, they are referred to as ‘long’.

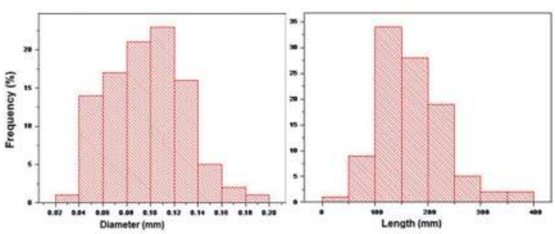

Figure 2. Statistical distribution of length and diameter of the lot of ramie fibers used in this work.

3.2. Ramie Fiber FTIR

Figure 3 shows the FTIR transmittance spectrum of the investigated Brazilian ramie fiber. This spectrum is very similar to that reported by Garside and Wyeth[45] for a distinct ramie fiber (the origin of that fiber was not disclosed). The prominent absorbance band around 3,400 cm^{-1} in Fig. 3 can be assigned to OH stretching and associated with adsorbed water on the fiber surface. Other bands, such as those at 1740, 1630, 1050 and 620 cm^{-1} can be related to C=O, C-O, and C-H stretching associated with aliphatic, aromatic and acid constituents of the fiber lignin and waxes [45]. Bands in Fig. 3 indicate a strong tendency of the ramie fiber to retain water as well as an active participation of lignin and waxes in possible surface interactions. These results suggest a predominantly hydrophilic nature and a difficulty of ramie fiber adhesion onto hydrophobic polyester. Consequently, a weak ramie fiber/polyester matrix interface is expected.

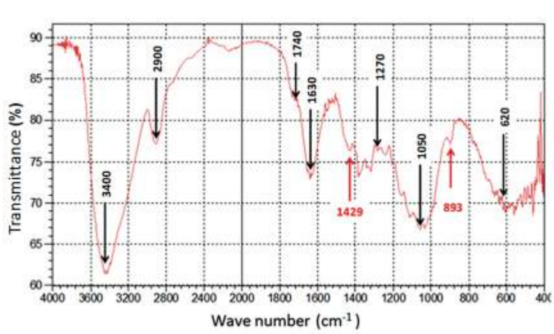

Figure 3. FTIR spectrum of the ramie fiber.

Figure 4 schematically illustrates a suggested model for the molecular structures at the ramie fiber surface facing a polyester macromolecule in the matrix. Not only the adsorbed water on the fiber surface but also the molecular structures of the cellulose, lignin and wax are not able to establish effective bonds with the polyester. In fact, strongly polarized cellulose fibers are inherently incompatible with hydrophobic polymers [46]. Interaction at the fiber/matrix interface in Fig. 4 would be mainly accomplished by van der Waals forces, with some possibility of hydrogen bonding between OH groups of ramie surface and C=O groups of polyester. Thus, a relatively weak interfacial shear stress is to be expected between the ramie fiber and the polyester matrix [12, 36]. As further discussed, the weak interactions do not exclude from formulation of ramie fiber/polyester composites with improved strength and toughness.

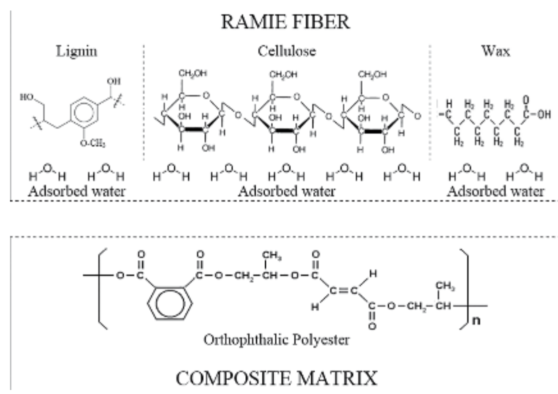

Figure 4. Schematic model of the molecular structure at ramie fiber/polyester matrix interface.

3.3. Mechanical properties

Figure 5 shows the variation of the flexural strength of the polyester composites, together with snapshots of broken specimens. Within the precision bars (standard deviation) the flexural strength increased exponentially from 63 ± 7 MPa for neat polyester to 212 ± 12 MPa for the 30 vol% ramie fiber polyester composite, Fig. 5(a). The research results with other lignocellulosic fibers such as jute[47], piassava[48] and curaua[22] also demonstrated improved flexural strength of formulated polymeric composites.

The significant improvement in flexural strength can be explained on the basis of the fiber-matrix interaction and the rupture behavior, common for polymers reinforced with fibers. For the pure polyester, fracture in flexure occurred by transverse brittle rupture at the center region of the specimen where the test machine compressed the specimen. For the ramie fiber composite, though the rupture was also transverse, Fig. 5(b), the long fibers acted as an obstacle for crack propagation through the polyester matrix, resulting in increased resistance to rupture. The effort to break the composite forced the relatively weak fiber/matrix interface to

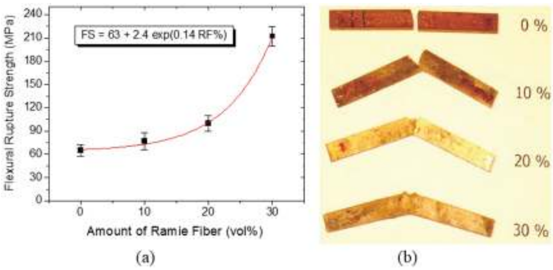

Figure 5. Variation of the flexural strength (FS) with ramie fiber content (RF%) in polyester matrix (a) and the macrostructure appearance of the flexural specimens (b).

fail. The rupture may not necessarily nucleate at the center, since much higher fiber/matrix interface area tend to allow cracks to nucleate at interfaces and then propagate between the fiber surface and the polyester matrix. This contributes to an extensive bending deflection and unbroken specimens, Fig. 5(b), regardless of machine crosshead displacement. Such a scenario, characteristic to many fiber-based composites, is supported by fractographs of the pure matrix and the composites.

Figure 6(a) shows the typical fracture surface of a transverse rupture in pure polyester, revealing brittle fracture with some defects. In ramie fiber composites, the transversally fractured polyester matrix with embedded fibers and voids corresponding to fiber pull-out can be seen in Fig. 7(a). Figure 8(a) is a higher magnification of Fig. 7(a), revealing discontinuous interface between the ramie fiber and the polyester matrix. In fact, most of the interfaces presented evidence of debonding in the form of a separation of the fiber surface from the polyester matrix. This can be certainly attributed to the low interfacial shear stress of 6.2 ± 2.3 MPa found for this type of composite [39]. A weak ramie fiber/polyester matrix interface is also supported by the FTIR spectrum discussed in Section 3.2. The large difference with respect to the fractures in the 0 and 30 vol% fiber composites is the greater participation of the fiber surface in the process of rupture. This is associated with a larger area of rupture, running parallel to the direction of fiber alignment, as well as a higher absorbed mechanical energy.

Figure 9 presents the variation in the tensile strength of the polyester composites containing from 0 to 30 vol% of ramie fiber, along with a photograph of the ruptured specimens. The tensile strength increased from 53 ± 4 MPa (0 vol%) to 89 ± 9 MPa (30 vol%), reflecting a similar exponential behavior as the flexural strength. Indeed, in the case of neat polyester, fracture occurred by transverse brittle rupture at the center point. The rupture is also transverse in the composites, with fiber acting as an obstacle for crack propagation through the matrix. This is supported by fractographic analysis. Figure 6(b) shows typical transverse surface of fractured pure polyester specimen. A transverse fracture is particularly distinguishable from Fig. 7(b), showing the matrix with embedded fibers and voids corresponding

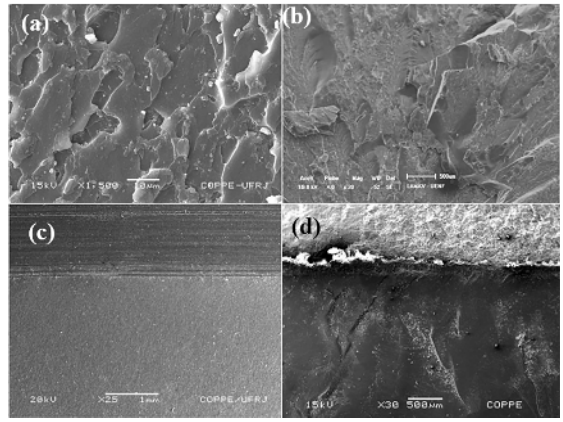

Figure 6. Fractographs of the neat polyester; (a) flexural test (b) tensile test (c) Charpy impact test (d) Izod impact test.

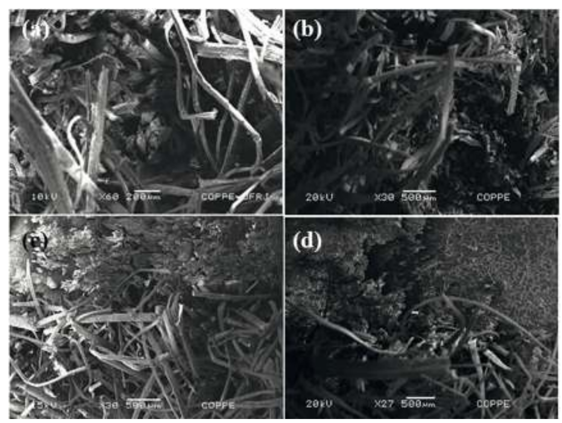

Figure 7. Fractographs of polyester/30 vol% ramie fiber composite with low magnification: (a) flexural test (b) tensile test (c) Charpy impact test (d) Izod impact test.

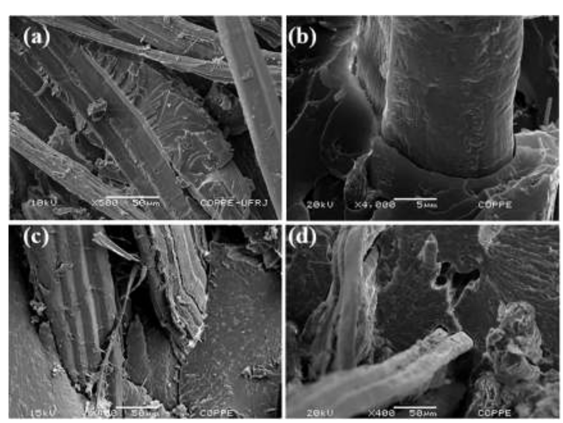

Figure 8. Fractographs of polyester/30 vol% ramie fiber composite with high magnification; (a) flexural test (b) tensile test (c) Charpy impact test (d) Izod impact test.

to pull out of fibers. A discontinuous interface between the ramie fiber and the matrix is shown in Fig. 8(b), presenting evidence of debonding in the form of a separation of the fiber surface from the polyester matrix. This is expected due to the already mentioned low interfacial shear stress found for this type of composite[39].

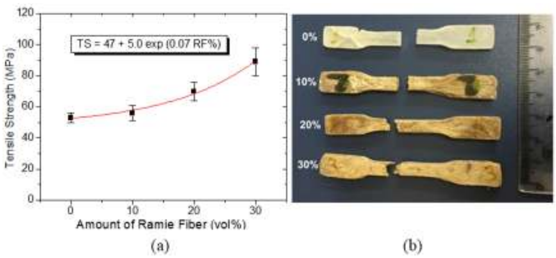

Figure 9. Variation of the tensile strength (TS) with ramie fiber content (RF%) in polyester matrix (a) and the macrostructure appearance of the tensile specimens (b).

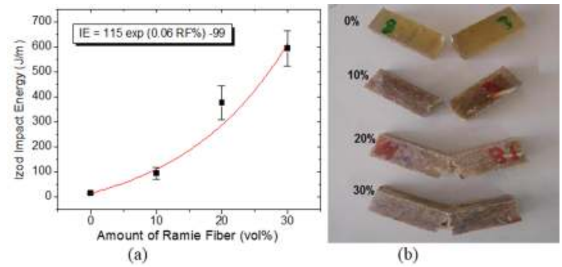

Figure 10. Variation of Izod impact (IE) energy with ramie fiber content (RF%) in polyester matrix (a) and the macrostructure appearance of the impact specimens (b).

It is also important to discuss the implications of the rupture modes to the mechanical response of both flexure and tensile tests. The rupture that initiates inside the polyester matrix propagates transversally to the fiber alignment. The arrest of this initial transverse rupture by the ramie fibers, Fig. 7(b), corresponds to a mechanism of effective reinforcement. This fracture mode allows an improvement in the composite flexural and tensile strengths. Additionally, a rupture that initiates at the fiber/matrix interface propagates longitudinally between the fiber surface and the polyester matrix, Fig. 8(b), corresponding to a mechanism of higher absorbed mechanical energy[49]. This longitudinal rupture mode also causes reinforcement to the composite. The combined action of both modes provides an exponential improvement, as revealed by the observed results for flexure, Fig. 5(a), and tensile, Fig. 9(a), tests. In flexure tests, a longitudinal rupture markedly improves the deformation, measured by the total bending deflection at rupture. In fact, the 30 vol% of fiber composite specimens ,Fig. 5(b), did not break despite the extension of deformation.

3.4. Impact Properties

Figure 10 shows the variation of the Izod impact energy for pure polyester as well as ramie fiber/ polyester matrix composites. The ramie fiber incorporation into the polyester matrix significantly improved the impact toughness of the composite. Within the standard deviation, similar to the flexural and tensile strengths, this improvement can be considered as an exponential function with respect to the amount of ramie fiber. The Izod impact energy value (~0.59 kJ/m) increased 39 times for 30 vol% ramie fiber composite as compared to the pure polyester (~0.015 kJ/m). The relatively high variation in impact energy values, given by the standard deviation associated with the higher fiber percentage points in Fig. 10, is a well-known heterogeneous characteristic of the lignocellulosic fibers[1-16].

The values shown in Fig. 10 are significantly above those reported in the literature for other lignocellulosic fiber-polyester composites tested at low velocity impact[50] and in standard Izod impact tests[51,52]. Indeed, reinforced with 40 vol% of long and aligned coir fibers, the Izod impact energy of the composite increased 8 times that of the neat polyester[51]. With 10 wt% of weaves of peach palm fibers, the increase was 2.6 times the neat polyester impact energy[52].

The reinforcement of a polymeric matrix with both synthetic[53] and natural[13,50,51] fibers are known to increase the impact toughness of the composite. Table 1 compares values of Izod impact energy of polymeric composites with different natural fibers[51,54]. The use of long and aligned ramie fibers resulted in significantly higher impact toughness than those reported[54] for polypropylene composites reinforced with 50 vol% of short cut and randomly oriented lignocellulosic fibers. Higher impact resistance of the polyester compared to that of polypropylene matrix could be one of the reasons for the superior performance of the composites studied in this work. Long and aligned ramie fiber reinforced polyester composites are probably the main reason, which results in the toughest among the category of natural fiber polymer composites reported so far.

Figure 11 shows the variation of the Charpy impact energy for polyester and composites. The ramie fiber incorporation into the polyester matrix significantly improved the impact toughness of the composite. Within the standard deviation, this improvement can also be considered as an exponential function with respect to the amount of ramie fiber added. The impact energy value recorded for 30 vol% composite (~1 kJ/m) is 65 times higher than that for neat polyester (~0.015 kJ/m).

The relatively low interface strength between a hydrophilic natural fiber and a hydrophobic polymeric matrix, previously reported [39] and here discussed in Section 3.2, contributes to an ineffective load transfer from the matrix to a longer fiber. This would result in relatively greater fracture surface and higher impact energy needed for the rupture[49]. Another factor is the flexural compliance of a long fiber during the impact test, as discussed below.

The incorporation of long and aligned ramie fibers results in a marked change with respect to neat polyester (0% fiber), in which a totally transverse rupture occurs. Even with 10 vol% of fiber, the rupture is no longer completely transverse, as evident in Figs. 10(b) and 11(b). This indicates that the cracks nucleated at the notch will initially propagate transversally through the polyester matrix, as expected in a

Table 1. Impact toughness of polymeric composites reinforced with natural fibers.

Composite	Fiber Content (vol%)	Fiber Condition in the Composite	Izod Impact Toughness (J/m)	Reference
Ramie/polyester	30	Long and aligned	594	Present work
Jute/Polypropylene	50	Short-cut randomly oriented	39	(Leao et al. 1998)
Sisal/ Polypropylene	50	Short-cut randomly oriented	51	*ibid*
Flax/ Polypropylene	50	Short-cut randomly oriented	38	*ibid*
Wood/ Polypropylene	50	Short-cut randomly oriented	28	*ibid*
Curaua/ Polypropylene	50	Short-cut randomly oriented	54	*ibid*
Coir/ Polypropylene	50	Short-cut randomly oriented	46	*ibid*
Coir/polyester	40	Long and aligned	121	(Monteiro et al. 2008)

* Present work.

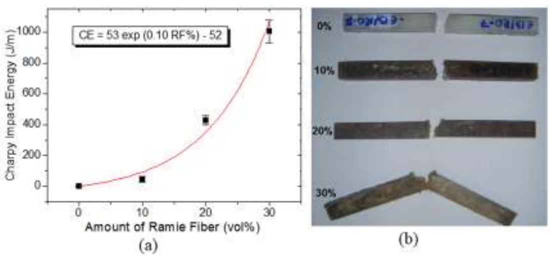

Figure 11. Variation of Charpy impact energy (CE) with ramie fiber content (RF%) in polyester matrix (a) and the macrostructure appearance of the impact specimens (b).

monolithic polymer. However, when the crack front reaches a fiber, the rupture proceeds through the fiber/matrix interface. As a consequence, after the Izod, Fig. 10, or Charpy, Fig. 11, hammer hits the specimen, some long fibers are pulled out from the matrix but, owing to their compliance, do not break but simply bend. In fact, few totally ruptured fibers were observed in the composites containing fibers above 20 vol%. For these amounts of long and aligned ramie fibers, part of the specimen was bent enough to allow the hammer to continue its trajectory, either by leaving the hit part still attached to the fixed part of the Izod specimen, Fig. 10(b), or carrying away the full Charpy specimen, Fig. 11(b), without complete separation. The value of the impact toughness in this case cannot be compared with others in which the specimen is totally split apart.

The fact that a specimen is not completely separated into two parts underestimates the impact toughness. In other words, had all the fibers been broken, the absorbed impact energy would have been still higher. The mechanism discussed above is better understood by the fractographic studies carried out on the tested samples. Figures 6(c) and 6(d) show the fracture surface of a pure polyester (0% fiber) specimen. The upper layer with distinct shades of gray in the fractographs corresponds to the notch in the specimen, revealing the horizontal marks from machining. The smoother and dissimilar gray layer underneath corresponds to the transversal fracture surface. Observed fracture suggests that a single crack was responsible for the rupture. The roughness is likely associated with voids and imperfections introduced during the matrix processing.

Figures 7(c) and 7(d) show details of the Charpy and Izod impact fracture surface of 30 vol% ramie fiber composite. They reveal a reasonable penetration (wetting) of polyester in between the fibers and the direction of preferential propagation of cracks. Some fibers were pulled out from the matrix and some broken fibers can also be seen. By contrast, the part of the specimen in which the preferential rupture occurred, longitudinally through the fiber/matrix interface, revealed that most of the fracture area is associated with the fiber surface. This behavior corroborates the rupture mechanism of cracks that propagate preferentially between the fiber surface and the polyester matrix, and could be due to low interfacial strength [39, 49]. The greater fracture area seen in Figs. 8(c) and 8(d) associated with long and aligned fibers acting as reinforcement for the composite justify the higher absorbed impact energy.

4. Final Comment on Fiber/Matrix Interactions

Based on the results presented in Figs. 3 to 11, it should be emphasized that a weak interaction between the polyester matrix and the strong ramie fibers acts as an effective mechanism to propagate longitudinal cracks along the fiber/matrix interface. This favors not only the pullout of some fibers but also the integrity of the composite until the complete rupture and/or pull-out of the long ramie fibers. The relatively high tensile strength of these fibers[1,39] prevents an earlier collapse of the composite structure, as depicted in Figs. 5(b), 9(b), 10(b) and 11(b) for fiber amounts above 20 vol%. Moreover, the combination of weak fiber matrix interface, which promotes longitudinal fracture, and a high strength reinforcing fiber contributes significantly to improve the composite flexural, Fig. 5(a), and tensile, Fig. 9(a), strengths as well as its impact resistance, Fig. 10(a) and Fig.11(a). Indeed, for the first time, it is shown that this combination results in exponential strength and toughness improvements shown for the first time in polyester composites.

5. Conclusion

Natural fibers from the ramie plant (*Boehmeria nivea*) were used in this study as reinforcement to polyester. Composites with up to 30 vol% of ramie fibers were formulated using a mold pressing technology. Flexural and tensile strengths as well as impact energies of formulated composites were measured. Fracture mechanisms were analyzed based on macroscopic view of broken specimens and SEM fractographs. The following conclusions were reached:

- Brazilian ramie fibers can be successfully incorporated as reinforcement to polyester composites without the use of surface modifying agents. Beyond 30 vol% fiber, the wetting with polyester becomes difficult and properties are impaired.
- The reinforcement of polyester with 30 vol% of ramie fibers increased its flexural strength about three times, from 63 ± 7 MPa to 212 ± 12 MPa, and tensile strength nearly two times, from 53 ± 4 MPa to 89 ± 9 MPa.
- Formulated composite also displayed a significant exponential improvement in toughness. The Charpy impact energy (~1 kJ/m) and Izod impact energy (~0.59 kJ/m) values increased two orders of magnitude for 30 vol% ramie fiber composite as compared to polyester (~0.015 kJ/m).
- The fractographic studies revealed that the rupture in composites initiates and propagates transversally (perpendicular to the fiber alignment) through the matrix. Ramie fibers act as obstacles to crack propagation, resulting in an effective improvement of the strength. Poor fiber-polyester adhesion is responsible for a longitudinal propagation of cracks throughout the interface, which generates larger rupture areas, as compared to a transverse fracture and increases the energy absorbed upon impact.
- Polyester composites with fiber content above 20 vol% showed incomplete rupture of the specimen owing to the bend flexibility, i.e., flexural compliance, of the ramie fibers. The combination of weak fiber/matrix interface with the strong ramie fiber results in exponential strength and toughness improvements for the polyester composites.

6. Acknowledgments

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