

Polystyrene Composites Prepared with Polystyrene Grafted-fibers of Sugarcane Bagasse as Reinforcing Material

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Abstract. Bagasse Fibers of sugarcane were modified with dichloromethylvinylsilane and consecutively grafted with polystyrene. For unmodified fibers, TGA showed two maximum decomposition peaks at 320°C and at 370°C. For silanized fibers, the most stable stage was shifted to a higher temperature of 470°C and to 510°C for silanized and polystyrene grafted fibers. Young moduli of composites increased from 1.9 GPa for non-treated fibers to 3.3 GPa for silanized and polystyrene grafted fibers.

Keywords: Recycling; polystyrene; natural fibers; sugarcane bagasse; composites.

Resumen. Las fibras de bagazo de caña se modificaron con diclorometilvinilsilano y se injertaron con poliestireno. Las fibras sin modificar mostraron en TGA dos picos máximos de descomposición a 320°C, y a 370°C. Para las fibras silanizadas, se observó un desplazamiento de la última etapa hacia mayores temperaturas a 470°C y hasta 510°C para las fibras injertadas con PS. Para los materiales compuestos, los módulos de Young se incrementaron desde 1.9 GPa para las fibras sin tratamiento hasta 3.3 GPa para las fibras silanizadas e injertadas.

Palabras clave: Reciclado; poliestireno; fibra natural; bagazo de caña; materiales compuestos.

Introduction

There is a great interest for the development of new materials using recycled plastics as well as renewable resources from agroindustrial residues. Natural fibers, due to their reinforcing properties and biodegradability, are good candidates for use in new composites materials, since they are economic, have a low density, have high mechanical resistance and for their abundance in nature. In the last years, some thermoplastics or thermosetting composites have been developed using different sources of natural fibers like: henequen [1], coconut [2], sisal [3], bamboo [4], wood [5] and bagasse [6]. However, composites that contain natural fibers without modification show usually poor mechanical properties; this is normally a result of the poor adhesion between interfaces of hydrophilic fiber with hydrophobic matrix. To improve properties, some studies have been focused mainly improving the adhesion of fiber-matrix interface with coupling agents [5, 7, 8]. Polymeric matrices and fiber surfaces have been modified in this way, and show small improvements in mechanical properties.

Recycling of plastic materials results in partial degradation of the materials due to environmental conditions like sunlight, humidity and temperature, and subsequently they show a lost of mechanical properties. In order to reuse plastic waste, the incorporation of natural fibers in those plastics represents a possibility to improve their reduced properties [9, 10]. However, due to the hydrophilic character of fibers and the hydrophobic character of most polymer matrices, it is necessary to modify

the components to achieve a stronger adhesion. In a previous study using virgin polystyrene as matrix, it was demonstrated that a graft-polymerization onto the surface of sugarcane bagasse fibers improved interfacial fiber-matrix properties as revealed by micromechanics analysis [11].

With a purpose of using two waste products, we present now our results on the preparation of composites with recycled polystyrene reinforced with residues of natural fibers from sugarcane agro-industry to obtain a material with competitive mechanical properties to those prepared using virgin materials.

Results and discussion

Chemical characterization of fibers

Chemical modification of fiber surface was characterized by FTIR spectroscopy. Spectrum of alkalized bagasse fiber is shown in Figure 1, curve 1, while spectrum of silanized fiber is shown in Figure 1, curve 2. Absorption bands at 1599 and 1405 cm^{-1} shows clearly the presence of vinyl-Si group, while methyl-Si group is identified through absorption band at 1259 cm^{-1} (curve 2). Further features show a C-H aliphatic bond at 2942 and 2867 cm^{-1} , and a wide absorption band at 1000-1100 cm^{-1} for both Si-O and C-O bonds. In Figure 1, Curve 3 shows spectrum of fibers after grafting reaction. As can be seen, absorptions bands for vinyl-Si group disappear (1599 and 1405 cm^{-1}) and the same occurs in general with all other

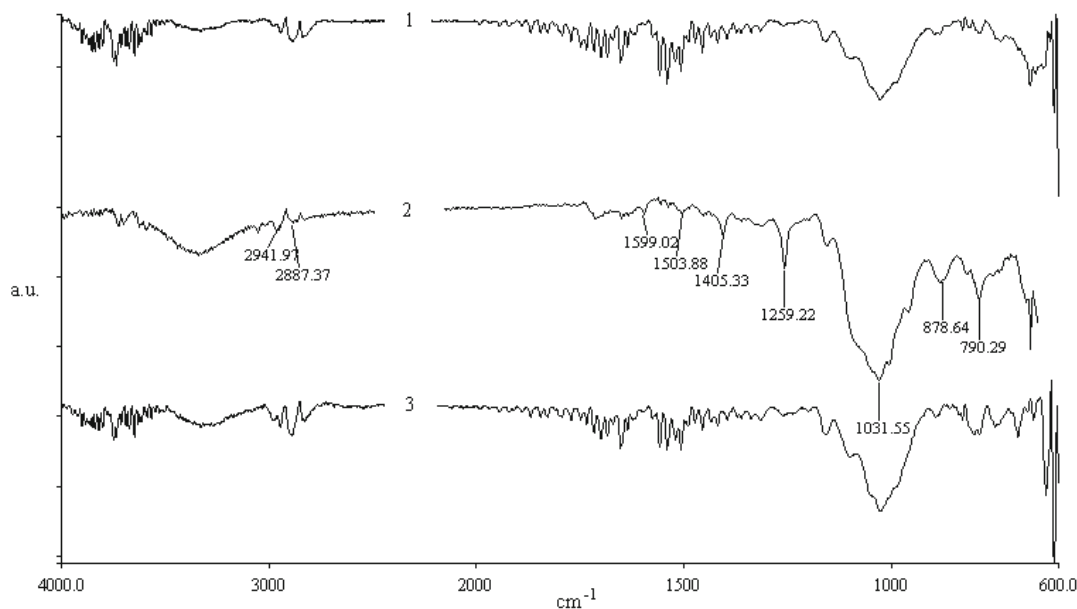


Figure 1. FT-IR Spectra of sugarcane bagasse fibers: 1. alkalinized fibers (AF), 2. alkalinized and vinylsilanized fibers (ASF). 3. Alkalinized, vinylsilanized and PS grafted fibers (ASGF).

absorption bands related to silane coupling agent, this could be a consequence of the fiber-surface being covered with polystyrene-grafts, however signals of polystyrene (PS) were masked by those of bagasse fibers.

Thermogravimetric analysis (TGA) of modified fibers confirmed silanization and grafting onto the surface of bagasse fibers. Figure 2 shows that decomposition of alkalinized fibers (AF) occurs in three steps, the first corresponds to a water loss with a maximum peak ($dw\%/dT$) at approximately 100°C, the other two steps can be assigned to decomposition of hemicelluloses at 320°C and cellulose and lignin at 370°C. The same steps were observed by Ouesanga A. and Picard C. [12] where hemicelluloses were less stable and lignin was more stable when analyses were carried out using a heating rate of 5 °C/min. The TGA of silanized fiber (ASF) also shows three decomposition steps, but the last step occurs at 470°C as a consequence of the presence of silicon-oxygen bonds that impart to fiber a higher thermal stability. This is confirmed by the weight

of residual material after analysis. It is greater for silanized fibers (32 weight%) than for alkalinized fibers (12 weight%). This could be due to the fact that silicon materials produce thermal stable substances at high temperatures like SiC [13] and SiO₂. PS grafted fibers (ASGF) showed a slight thermal stability increment for the decomposition step at higher temperature (510°C) due to the chemical bond between silanized fiber and polystyrene. The thermal stability increment was confirmed with a physical mixture of polystyrene and alkalinized fiber (PSAF) that is shown in the same figure. This curve shows the decomposition of polystyrene and bagasse fiber in only one step at 370 °C, which is more stable than the first decomposition step of alkalinized fibers (320°C).

Mechanical characterization of composites

Composite samples for mechanical testing were prepared according to Table 1.

Table 1. Composites of polystyrene-sugarcane bagasse fibers.

| Samples | Polystyrene, % | | | Fiber, % | | |
|------------|----------------|----------|---------|-------------|-----------|------------|
| | Virgin | Recycled | Natural | Alkalinized | Silanized | PS-grafted |
| VPS0F | 100 | — | — | — | — | — |
| VPS10NF | 90 | — | 10 | — | — | — |
| VPS10AF | 90 | — | — | 10 | — | — |
| VPS10ASF | 90 | — | — | — | 10 | — |
| VPS10ASGF | 90 | — | — | — | — | 10 |
| VPS5ASGF | 95 | — | — | — | — | 5 |
| RPS10ASGF | — | 90 | — | — | — | 10 |
| RPS7.5ASGF | — | 92.5 | — | — | — | 7.5 |
| RPS5ASGF | — | 95 | — | — | — | 5 |

Melted rheology in polystyrene and PS-fiber composites

After fibers were treated, virgin and recycled PS-fiber composites were prepared in a rheometer and torque was measured. Figure 3 show that virgin polystyrene without fiber (VPS0F) presents a defined melting peak with a shoulder between 1 and 2 minutes. When fibers were added to melt chamber, two peaks were observed, one corresponds to melting of polystyrene (1 to 2 min) and the other corresponds to interaction or humectation of fibers surface with melted polystyrene. Torque increased toward

the end of the blending as a result of matrix-fiber interaction. The time for humectation-peak (Peak at longer times) decreased with the treatment: Natural fibers without modification (VPS10NF) show that peak at 3.5 to 4 min, alkalinized fibers (VPS10AF) at 2.7 to 3.2 min; while for alkalinized, silanized and grafted fibers (VPS10ASGF) that peak was observed at 2.2-2.7 min. This behavior results from the better interaction between fibers and matrix after treatment of fibers. Blends of polystyrene with alkalinized and silanized fibers (VPS10ASF) produced a peak at 1.0-2.0 min corresponding to melt of polystyrene and another

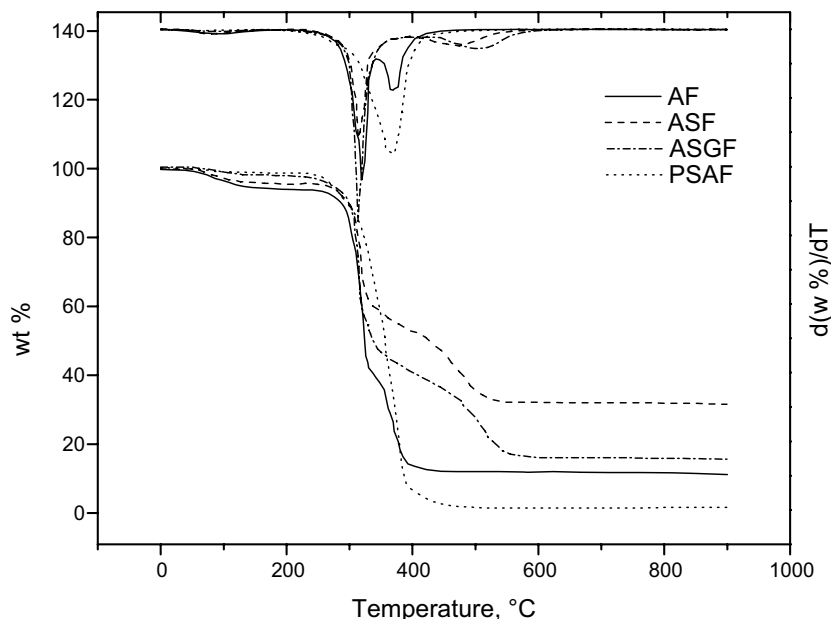


Fig. 2. Thermogram of fibers: Alkalinized fibers (AF), alkalinized and vinylsilanized fibers(ASF), alkalinized, vinylsilanized and PS grafted fibers (ASGF), physical mixture of polystyrene with the alkalinized fibers (PSAF).

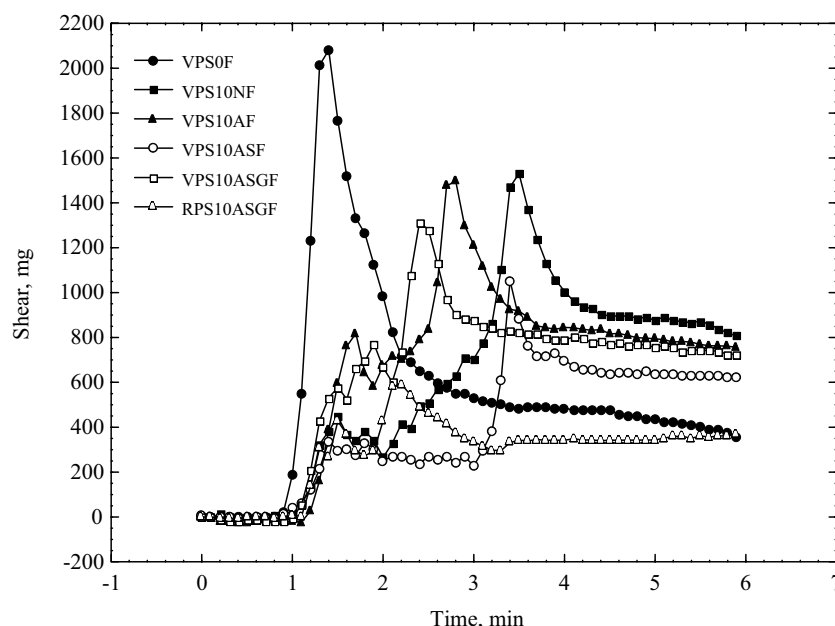


Fig. 3. Rheological diagram for blends of modified fibers with polystyrene.

for fiber humectation at 3.2-3.7 min, this last change in humectation time could be due to thermal reaction of vinyl-silane, evidenced by a darker coloring of the composites blend.

In Figure 4, it can be seen that composites prepared with virgin polystyrene had a higher torque than those prepared with recycled polystyrene. This could be due to material property loss as degradation consequence of reprocessing. Rheological behavior of composites using recycled polystyrene with an

increasing amount of fiber practically did not changed. This is because the fibers used have the same treatment, only a slight change in the melt peak for PS was observed.

Tensile properties of composites

Young moduli are presented in Figure 5. Modulus of virgin polystyrene (VPS0F) is approximately 1900 MPa, and this modulus

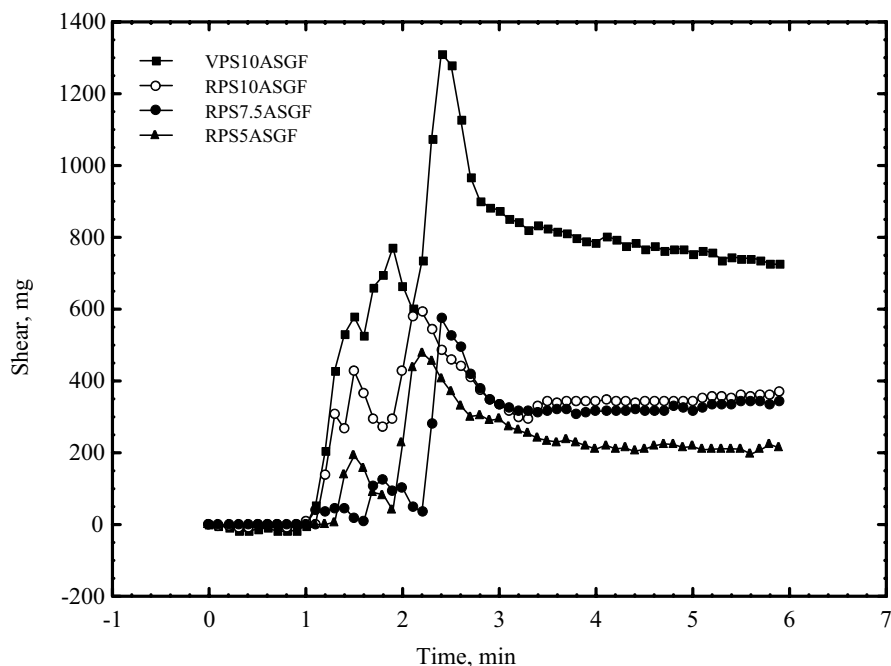


Fig. 4. Rheological diagram for composites. Effect of virgin and recycled polystyrene in composites and quantity of fibers in composites using recycled polystyrene.

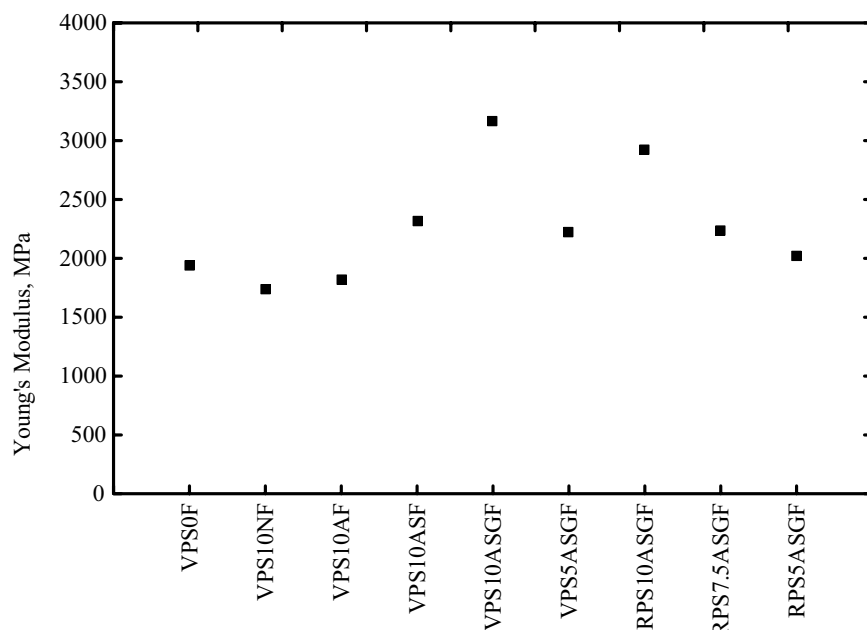


Fig. 5. Young's moduli for composites using polystyrene and bagasse fibers after different treatment methods.

decreased with the incorporation of natural fibers (VPS10NF) to 1750 MPa. This may be due to a low mechanical adhesion of hydrophilic surface of the fiber with hydrophobic matrix. When alkaline fibers (VPS10AF) were used, they have more surface exposed due to hemicelluloses and lignin extraction so that mechanical physical adhesion was increased more than for the natural fiber composite (1800 MPa). When fiber treatment was alkalization and silanization (VPS10ASF), the surface of fibers become more hydrophobic, and the adhesion between fibers and matrix increased so that Young modulus increased to 2300 MPa. These results demonstrate a better compatibility between the fiber-matrix. Young modulus increased up to 3300 MPa when fibers were further treated with grafting-polymerization (VPS10ASGF). This occurred because there is a better mechanical and chemical adhesion between fibers and matrix as a result of the entanglement of grafted polystyrene chains with chains of virgin polystyrene matrix. When the quantity of fibers in the composites decreased to 5% (VPS5ASGF), the modulus decreased in accordance to the smaller area of interaction between fibers and matrix. The same can also be observed in the last three cases of the graph where modulus decreased with fiber concentration when recycled polystyrene is used (RPS10ASGF). These results show clearly that silanized and PS grafting onto bagasse fibers as a treatment method is a good alternative for an improvement of mechanical properties of composites using recycled PS matrices. In fact, moduli of composites prepared with recycled polystyrene were improved using PS-grafted fibers (RPS10ASGF), over virgin polystyrene (VPS0F) and those composites prepared with virgin PS with either alkalized fibers (VPS10AF), or alkalized and silanized fibers (VPS10ASF).

Figure 6 shows tensile strength at break properties of virgin and recycled polystyrene composites. For composites with

modified and non-modified fibers tensile strength is slightly lower than that of virgin polystyrene. This could be a result to the fragile nature of bagasse fiber and its size reduction by shear stress deformation during thermal processing.

Elongation at break shown in Figure 7 also shows a similar behavior due to the rigidity properties of polystyrene and bagasse fibers. Deformation was independent of surface treatment of fibers, quantity of fibers and kind of polystyrene used in the range studied.

Interface characterization with Scanning Electron Microscopy

The surfaces of tension-fractured composites were analyzed by scanning electron microscopy (SEM). Figure 8 shows a micrograph of natural fiber-virgin polystyrene composite (VPS10NF). The surface shows a poor adhesion, as seen by the separation of the fibers.

Figure 9a shows a composite prepared with alkalized fibers and virgin PS. A pull-out fiber can be observed, this is an indication of poor interfacial adhesion due to differences in hydrophilic/hydrophobic properties. Figure 9b shows better behavior in adhesion because fibers were kept on the matrix, this happened perhaps due to vinylsilane treatment, since fiber surface is more hydrophobic. In Figure 9c, surface of a composite prepared with vinylsilanized and PS-grafted fibers is shown. In this micrograph, all fibers are perfectly embedded in the polystyrene matrix. Evidently, the wetting of fibers is a consequence of a better interfacial adhesion between fibers and the matrix. This is due to chemical modification and PS grafting of the surface of fibers. Figure 9d, shows a micrograph of a composite prepared with vinylsilanized and PS-grafted fibers and recycled polystyrene. The wetting of fibers is evidently improved due to

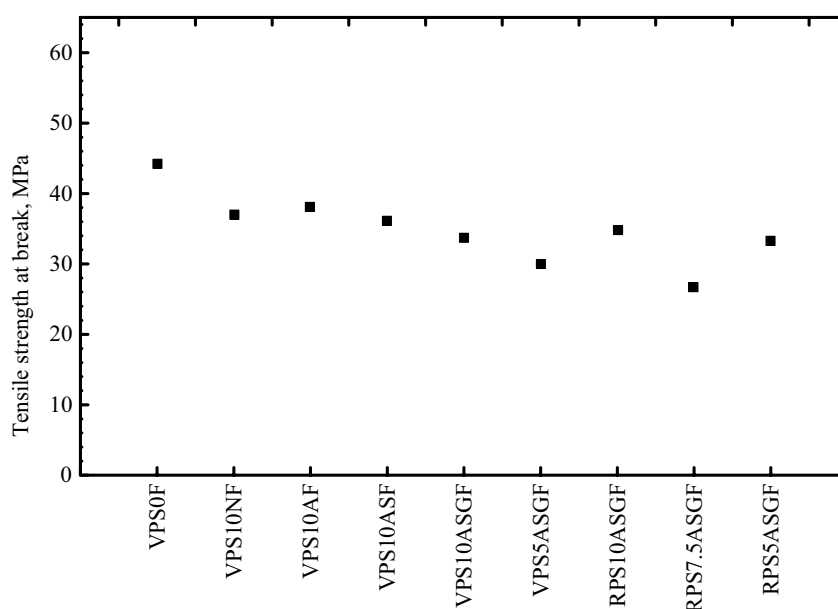


Fig. 6. Tensile stress at break for composites using polystyrene and bagasse fibers after different treatment methods.

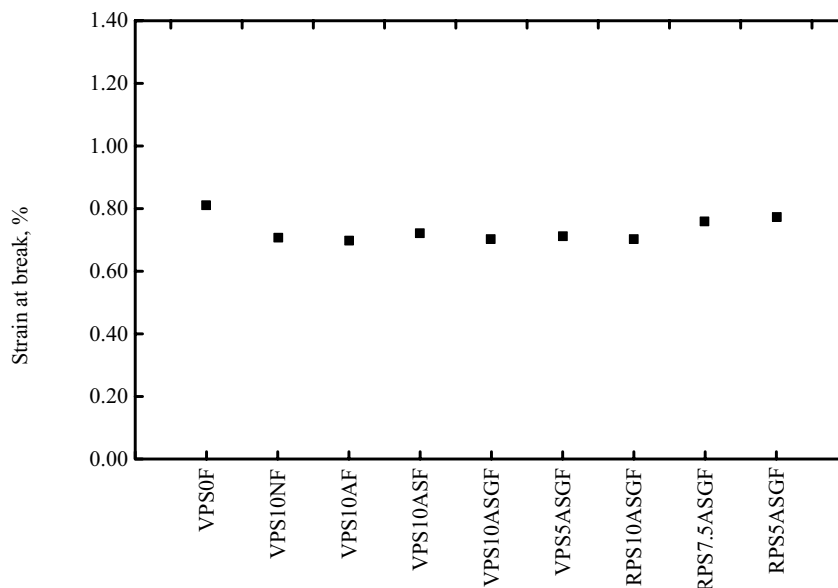


Fig. 7. Elongation at break for composites using polystyrene and bagasse fibers after different treatment methods.

better interfacial adhesion between matrix and fibers; however, recycled polystyrene matrix shows a lower homogeneity from matrix material as a consequence of reprocessing.

Size-analysis of fibers in composites is shown in Figure 10; the size of modified fibers is smaller than that of fibers without treatment. This shows that the increase in mechanical properties is due to the interaction at the interface as a consequence of structural changes in fiber surface and is not related to fiber size-change.

Conclusion

The interfacial adhesion between sugarcane bagasse fibers and polystyrene matrix was improved when fibers were treated consecutively with dichloromethylvinylsilane following with PS grafting. The silanized and polystyrene grafted fibers showed

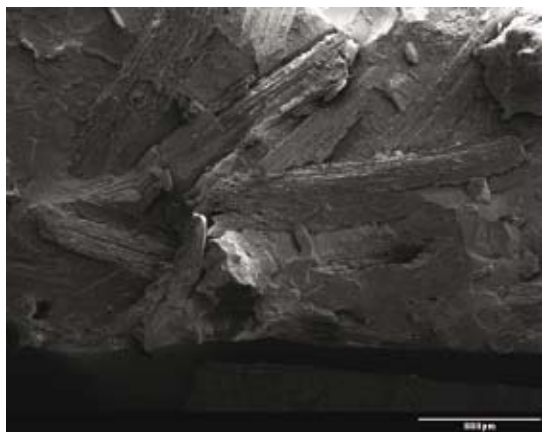


Fig. 8. Micrograph of the surface of the composites prepared with virgin polystyrene and natural fiber without treatment (VPS10NF).

a higher thermal stability than those non treated fibers. The mechanical properties like Young modulus were improved with just a slightly lost of tensile strength. SEM microcopies and size distribution analysis for the fibers showed that improvement of the mechanical properties for composites were due to better interfacial adhesion between fibers and polymer matrix. Finally, results show that PS-grafted sugarcane bagasse fibers are useful reinforcing additives to increase mechanical behavior of recycled PS composites.

Experimental

Materials

Sugarcane bagasse as reinforcing material was kindly supplied by sugar agro-industrial plant “Emiliano Zapata” in Zacatepec, Morelos, Mexico. Raw fibers were sieved in a standard Tyler mesh and only mesh 8/30 was used for experiments. Fibers were modified using: subsequently: alkalization, vinylsilanization, and grafting polymerization of styrene. Dichloromethylvinylsilane (97%, Aldrich) was used as coupling agent for the silanization step and toluene (ACS, Fermont) as a solvent; styrene (99%, Aldrich) was used for graft polymerization and benzoyl peroxide (97%, Aldrich) as initiator. Composites were prepared using treated and non-treated bagasse fibers and virgin polystyrene ($M_n=107,000$ g/mol, BASF Mexicana) or recycled PS ($M_n=103,000$ g/mol, from a compressed waste PS-foam), as matrices.

Characterization

Fibers were characterized by using a Fourier Transform Infrared Spectrometer (FTIR) Perkin Elmer 1600 using an at-

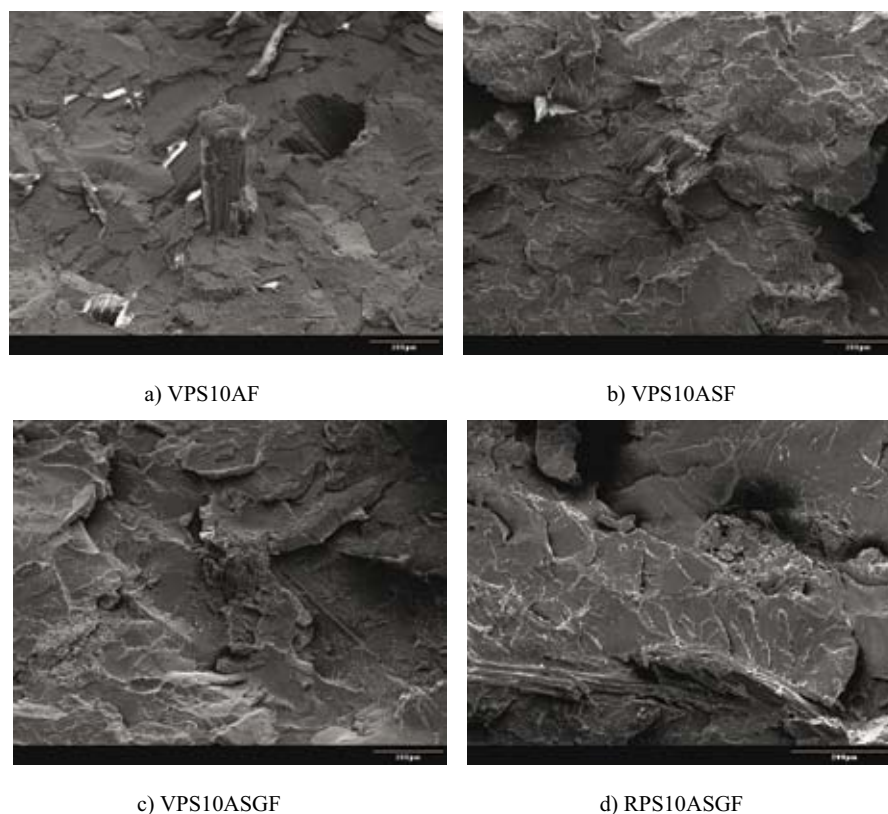


Fig. 9. Micrographs of the surface of composites prepared with virgin polystyrene: a) alkalized fibers (VPS10AF), b) alkalized fibers modified with vinylsilane (VPS10ASF), c) alkalized, vinylsilanized fibers grafted with styrene (VPS10ASGF) and recycled PS: d) alkalized, vinylsilanized fibers and grafted with styrene (RPS10ASGF).

tenuated total reflectance (ATR) accessory. Thermogravimetric analyses (TGA) were performed on Stanton-Redcroft model STA-780 equipment, samples were heated from 20 to 600°C under a dry nitrogen flux. A Haake buchler system 40 torque Rheometer was used for melting preparation of composites. A manual hot press Carver (3851CE) was used for preparation of samples for mechanical testing. A universal mechanical tester (Instron, 4465) was used for mechanical characterization. The SEM analysis was carried out on the surface of the fractured tensile samples recovered with a thin layer of gold using a JEOL microscopy model JSM-5300 at 10 KeV.

Modification of natural fiber surface

First, bagasse fibers were washed with hot water; then lignin was partially eliminated by shaking in a 1 M NaOH solution at room temperature. Oil and wax were removed by soxhlet extraction from alkalized fiber with methyl alcohol. Dried fibers were then reacted with 6 weight% of dichloromethylvinylsilane in a THF solution by refluxing. After silanization, fibers were filtered, washed with ethyl alcohol and finally fibers were dried in a vacuum oven at 90 °C. The percentage of silanization of fiber was determined gravimetrically.

Styrene grafting onto vinylsilanized fibers

Grafting polymerization of styrene onto vinylsilanized fiber was carried out in a round bottom flask with mechanical stirring (100 rpm) containing 10 weight% of styrene in toluene and 1 weight% of benzoyl peroxide as initiator, grafting temperature was 70 °C and the reaction was performed under nitrogen atmosphere for 2 hrs. At the end of the reaction, fibers were washed twice with hot toluene, and dried in a vacuum oven for 4 hrs.

Preparation of composites

Treated and non-treated fibers were incorporated to virgin and recycled polystyrene by the following preparation method: Mixtures were blended in a Haake rheometer at 190°C for approximately 6 minutes, until the polymer melted and the applied torque stayed constant.

Preparation of sample specimens for mechanical testing

The prepared mixtures were cut in pellets and molded by compression at 200°C using a Carver press according to ASTM D638 norm. The molding pressure was 10 Tons during 5 minutes then mould was cooled and specimens were removed. Test

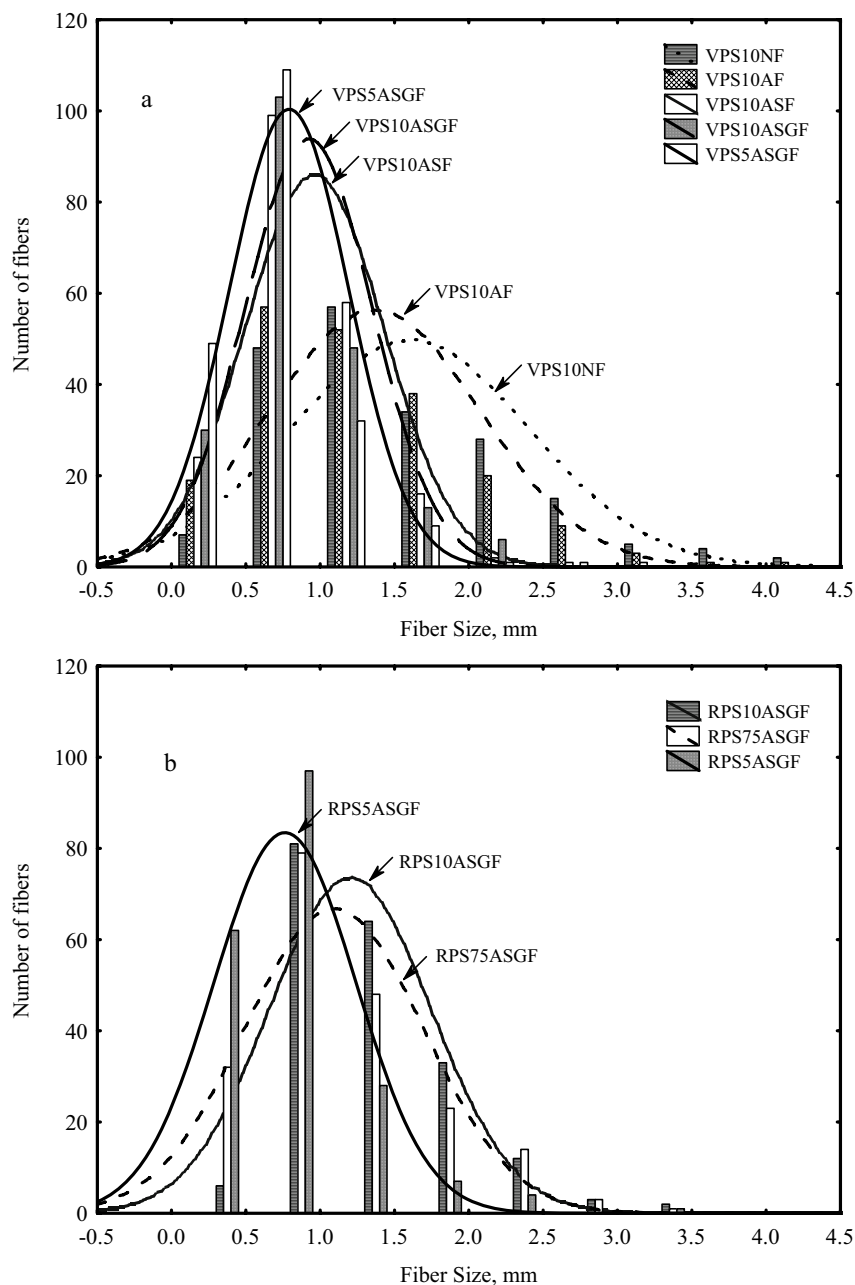


Fig. 10. Size of Fibers. a) Virgin Polystyrene as Matrix. b) Recycled Polystyrene as Matrix.

specimens were tested by using a universal mechanical tester (Instron, 4465) according to ASTM D638 norm.

For fiber size measurements, a random area (4 cm²) of flat transparent specimen from molding residue was analyzed using a Javelin CCD-Camera model JE3542 and the fiber lengths counted and averaged.

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