Original Communication

Starch/polycaprolactone-containing composites reinforced with pre-treated sisal fibers

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ABSTRACT

Composites based on thermoplastic cornstarch (TPS) and polycaprolactone (PCL) were reinforced with 5, 10 and 20% (wt%) of pretreated sisal fiber. The impact of the addition of sisal fiber on the mechanical, thermal and morphological properties of composites was investigated. The addition of 5-10% fibers in composites exhibited improved mechanical and thermal properties attributed to more efficient dispersibility of fiber in the matrix and good compatibility between fibers and the matrix polymers, which also led to increased crystallinity and caused composite to be more rigid. The DSC and X-ray diffraction studies suggested interaction between polymers in the blend via carboxyl groups in thermoplastic starch-PCL and hydroxyl groups in fibers. An increase in storage energy was also observed from the DMTA studies, indicating mobility reduction in the polymer chains. Crystallization of PCL was apparent in the TPS/PCL blends but not in TPS/PCL composites with the added fibers, suggesting that sisal fibers hindered the crystallization of PCL in composites.

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1. INTRODUCTION

Lignocellulosic fibers have been used as reinforcement material in polymeric composites. There are several advantages for using natural fibers; they are low cost, renewable, non-toxic and low-density material that are available in abundance world-wide [1, 2]. One consistent drawback is the poor interfacial bonding between the hydrophilic lignocellulosic fibers and the hydrophobic polymers in composite, which leads to poor mechanical properties [2]. Efforts have been made to improve fiber-matrix interaction by modifying the surface and structural properties of fibers via variety of pretreatment methods, which include alkali treatment, bleaching, acetylation and steaming [2-4]. Recently, it has been shown that fiber pretreatment using an alkaline process (mercerization) effectively altered fiber property, leading to much improved mechanical property of composites reinforced with such fibers. Silane treatment of cellulosic fiber has also been reported to improve tensile strength and modulus in composites and to achieve better dispersion of fibers in the matrix [5]. Chemical bleaching of fibers with hydrogen peroxide is another method widely used in textile industry to induce surface modifications in fiber [3].

Though completely biodegradable, TPS offers poor mechanical properties and is susceptible to

moisture. However, both of these properties could be improved by blending TPS with synthetic polymers [6, 7]. On the other hand, PCL is synthetic polyester that is highly flexible, easy to process, totally biodegradable and is compatible with a wide variety of polymers including TPS, and has been used in the development of new materials [8]. Additionally, PCL is hydrophobic in nature and its crystallinity tends to decrease with increasing molecular weight [8-10]. The only shortcoming is the high-cost of PCL which is hampering its wide-scale use in bioplastics.

The blending of TPS and PCL was considered as a solution to improve TPS property and lower the cost of the PCL-based composite material [9, 11-13]. The mechanical and thermal properties of TPS/PCL with various moisture and glycerol contents have shown low compatibility between PCL and TPS based on DMA and DSC measurements [14]. Particularly, blends extruded with high glycerol content showed dual-phase continuity in the matrix and strong indication of a specific interaction between the PCL and TPS due to the hydrogen bonding interaction between carbonyl groups of PCL and hydroxyl groups on starch molecule [11].

The mechanical properties of natural fiber reinforce polymers are strongly influenced by the interfacial adhesion between the matrix and the fibers and any pre-treatment or chemical modification of fiber that improve the interfacial matrix-fiber bonding usually results in the enhancement of tensile properties of the composites [15]. Thus, chemically treated sisal fibers were incorporated into TPS/PCL composite blends to increase compatibility between the matrix polymers', improve composite properties, and also to lower the overall cost of the PCL based composites. In present study, the influence of the chemically treated (bleached) sisal fibers on mechanical, thermal and thermal-mechanical properties of extruded TPS/PCL blends were investigated along with any associated changes in the fiber-matrix interface.

2. MATERIALS AND METHODS

Materials

Sisal fibers were supplied by Embrapa /Algodão, PB, Brazil. All reagents for fibers treatment were reagent grade and used without any further purification. NaOH was purchased from Qhemis, Brazil, hydrogen peroxide (H_2O_2) solution was obtained from Nuclear, Brazil. Glycerol and stearic acid were purchased from Synth, Brazil. Cornstarch (70% amylose and 30% amylopectin) used was Amidex® 3001 supplied by the Corn Product Brazil and the polycaprolactone (CAPA® 6500, Mw 84500 ±1000) was purchased from Perstorp Quimica do Brazil, Ltda.

Fiber treatment

The sisal fibers were first subjected to treatment with NaOH followed by bleaching with H_2O_2 as described by Sun *et al.* [16]. For treatment with NaOH, previously ground (16 mesh) fibers were suspended in 200 mL of 5% NaOH (w/v) at 90°C under constant agitation for 60 minutes. The solution was brought to the room temperature (24°C), and subjected to vacuum filtration. Fibers were washed with distilled water until neutral pH was achieved. Fibers were dried in oven with air circulation at 50°C to constant weight. The recovered fibers were bleached with the H_2O_2 by suspending in a solution containing 16% H_2O_2 (v/v) and 5% NaOH and agitated for 90 min at 55°C. Preparation was cooled to the room temperature and fibers were filtered and washed with distilled water until the pH was neutral. Fibers were dried in oven with air circulation at 50°C.

Extrusion and blends

The TPS material was prepared by premixing cornstarch and glycerol (70:30) until a homogeneous material was obtained. Material was processed in a co-rotating twin-screw extruder (Coperion, Ltda, SP, Brazil) equipped with six heating zones and a ribbon dye. The screw rotating speed was 200 rpm and the temperature profile was 140, 140, 150, 150, 160 and 160°C. Ribbons were pelletized. To prepare the TPS/PCL blend (80:20), TPS pellets were mixed with PCL and extruded under similar conditions. TPS/PCL (80:20) composites containing 5, 10 and 20% (wt%) fiber were further processed in a single-screw extruder (AX Plasticos, Brazil, 150 rpm, and temperatures were set at 120, 125 and 130°C) to obtain films.

Scanning electron microscopy (SEM)

Specimens were mounted onto aluminum stubs using double-sided adhesive carbon tape (Ted Pella,

Redding, CA) for analyses. For obtaining fractured surfaces, composite were first submerged into liquid nitrogen and fractured with a pre-chilled razor blade held in a vice-grip (cross section) and stored in desiccators until further use. Samples were mounted with the cross-section surfaces facing up. All specimens were sputter-coated with Gold-Palladium for 45 s in a Denton Desk II sputter coating unit (Denton Vacuum USA, Moorestown, NJ). Specimens were analyzed using a Hitachi S4700 field emission scanning electron microscope (Hitachi HTA, Japan) at 2 kV.

Mechanical testing

Mechanical tests were performed on the EMIC Universal Testing Machine (PR, Brazil- Model, DL3000; speed, 5 mm/min; cell load, 50 kgf) following the ASTM protocol (ASTM D-882-09 2009).

Dynamic mechanical thermal analysis (DMTA)

About 46 x 1.5 x 1 mm specimens were subjected to a sinusoidal deformation in bending mode at three points, ramp of 3°C/min in the range of 100 to 50°C with fixed frequency of 1 Hz. Analyses were performed on the DMTA (TA Instruments, New Castle, DE, USA; Model - DMA Q800 V7.0). The conditions used were the dynamic force 0.12 N and range of 20 µm.

Thermogravimetric analysis (TGA)

Thermal degradation was evaluated using TA Q500 equipment (TA Instruments, New Castle, DE, USA) under following conditions: weight, 10.00 ± 0.50 mg; synthetic air flow, 60 mL min^{-1}; heating rate, 10°C min^{-1}; temperature range, 25°C to 600°C.

Differencial scanning calorimetry (DSC)

For DSC, Samples were analyzed on DSC-Q100 equipment (TA instruments, New Castle, DE, USA) under the following conditions: weight 6.00 ± 1 mg, nitrogen flow, 60 mL min^{-1}; heating rate, 10°C min^{-1}; temperature range, -80°C to 150°C, first ramp.

Determination of crystallinity in composites

The degree of crystalline (X_c) of PCL in the composites was determined from the melting peak area using the following equation described by Vertuccio *et al.* [12]:

$$X_c = \frac{\Delta H_m}{\Delta H^0_m f}$$

where ΔH_m is the enthalpy of fusion of the sample, ΔH^0_m is the heat of fusion for 100% crystalline PCL (taken to be 136 J/g) [17] and f is the weight fraction of PCL.

X-ray diffraction

The X-ray diffraction (XRD) patterns were measured for fibers using X-ray diffractometer (Lab X- XDR-6000- Shimadzu, Japan), employing CuKα radiation (wavelength = 1.5406 Å) at 30 kV and 30 mA. Samples were placed under 45% relative humidity conditions for at least 48 h before testing. Scattered radiation was detected in the angle range 2θ (5-40°) at a scan rate of 2°/min. The crystallinity (χ_{CR}) was calculated from the 200 peak (I_{200}, 2θ = 22.7) and the minimum between the 200 and 110 peaks, (I_{AM}, 2θ = 18°) by means of Segal method (Equation 1). I_{200} represents both crystalline and amorphous material while I_{AM} represents amorphous material only [18].

$$x_{CR} = \frac{I_{200} - I_{AM}}{I_{200}} \tag{1}$$

3. RESULTS AND DISCUSSIONS

Sisal fibers treated with the alkaline solution (NaOH/H$_2$O$_2$) revealed a distinctly altered surface morphology compared to the untreated raw fibers (Fig. 1). Samples viewed under the SEM clearly showed that the treatment process removed surface associated material yielding fibers that were much smoother than the untreated ones (Fig. 1A,B and 1C,D). Both TPS and PCL polymers when extruded alone exhibited relatively homogeneous surfaces (Fig. 2A and 2B). A cross-section of the extruded PCL alone (Fig. 2C), mostly indicated a homogenous polymeric phase. Interestingly, in a TPS/PCL blend, surface view also revealed rather smooth surfaces (Fig. 3A), however, a cross-section of the same sample at similar magnification showed two distinct phases (Fig. 3B), indicating immiscibility between the TPS and the PCL polymers. The extrusion of TPS/PCL blended with treated fibers at 5%, 10% and 20% (wt%) concentration was carried out. Samples fractured under liquid nitrogen and examined in the SEM,
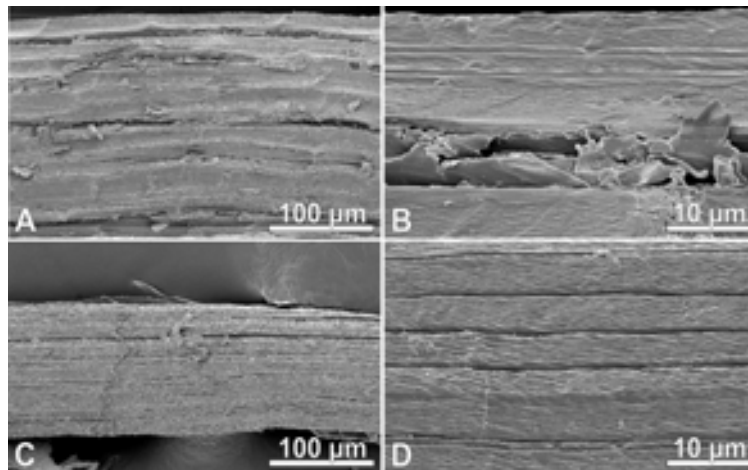
Fig. 1. SEM image of the surface view of raw sisal fibers (A and B) and sisal fibers treated with alkaline solution (C and D). B and D are the images of A and C at higher magnification, respectively.
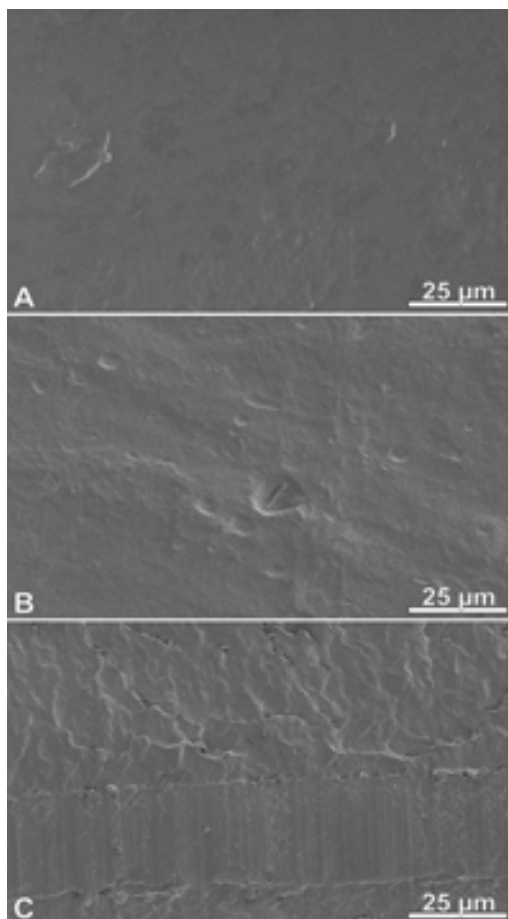
Fig. 2. SEM surface view of the extruded TPS (A), PCL (B) and an extruded fractured PCL sample (C).

showed reasonably good fiber dispersion in the matrix as well as good interfacial adhesion between the fibers and the matrix (Fig. 3). At 5% concentration, fibers were dispersed, but mostly covered by the matrix polymers (Fig. 3C and 3D). The fiber dispersion in the polymer matrix was much better when the fiber content was 10% (Fig. 3E and 3F). At this concentration fiber also appear to show some form of orientation. At 20% fiber concentration, fibers appeared to be well dispersed in the matrix, however, few domains containing aggregates of fibers were also observed (Fig. 3G and 3H) where fiber-matrix interfaces were clearly visible. This suggests that there may be a threshold concentration for fibers in order to be effectively dispersed and miscible with the matrix polymers. Exceeding this threshold may lead to deterioration in composite's properties.

The extruded blends of TPS/PCL with and without added fibers were prepared and tested for their mechanical properties. The data on tensile strength (TS), elongation at break (E) and Young's modulus (YM) for individual polymer, their blends, and blends containing 5, 10 and 20% treated fibers are provided in Table 1. TPS polymer offers reasonably good TS and YM. However, upon drying, TPS became brittle and exhibited poor TS. The extruded neat PCL polymer, on the other hand, exhibits good TS and
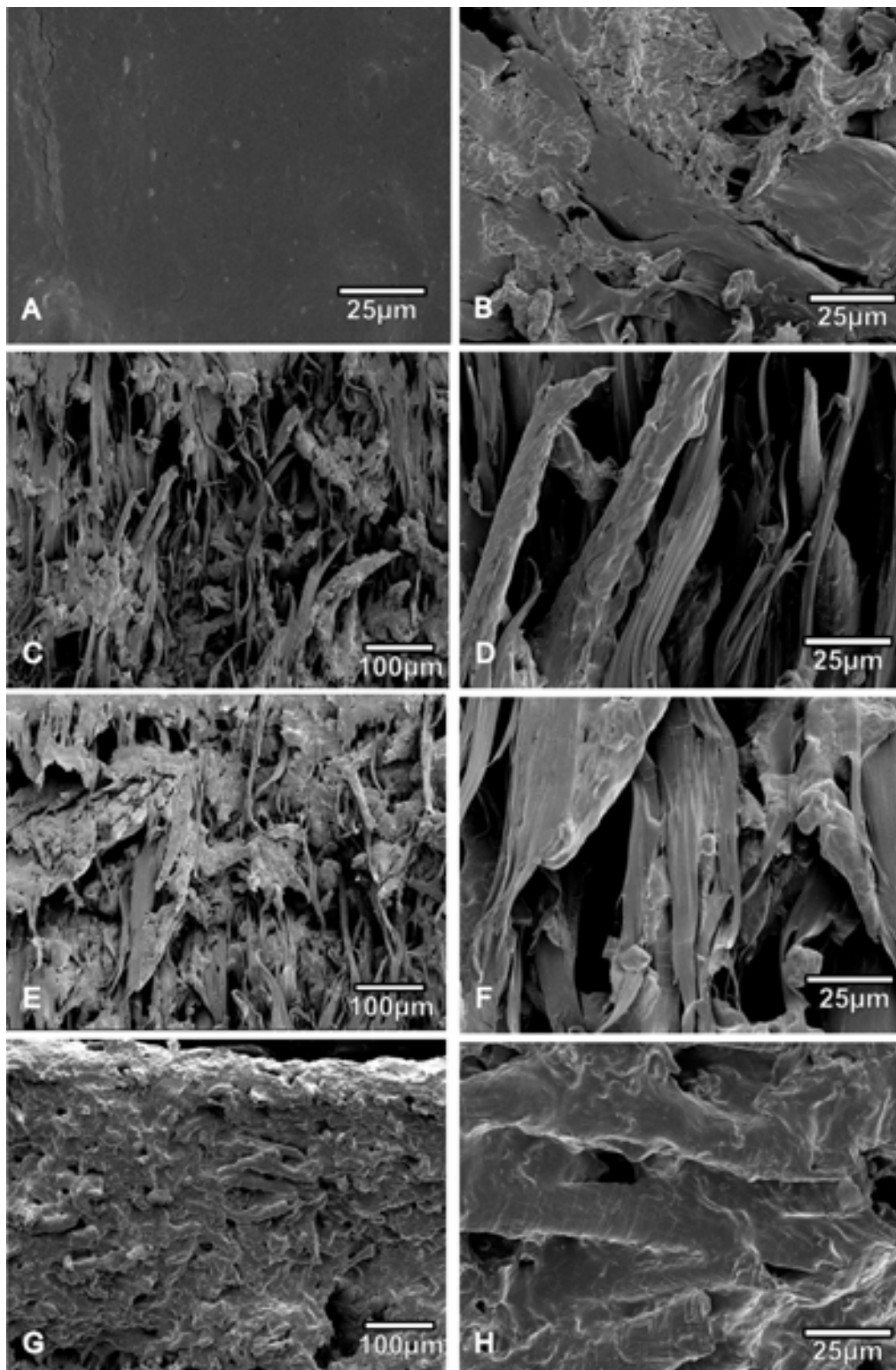
Fig. 3. A surface view of an extruded TPS/PCL blend (A) and view of its fractured surface (B). Fractured surfaces of TPS/PCL extruded blends with 5% (G, C and D), 10% (E and F) and 20% (G and H) treated fibers. D, F and H are the higher magnifications of samples C, E and G, respectively.

**Table 1.** Mechanical properties of polymers, blends and blends containing variable amount of fibers.

Samples	Tensile Strength (MPa)	Elongation at break (%)	Young's Modulus (MPa)
TPS	0.65 ± 0.07	63.89 ± 8.31	64.62 ± 2.39
PCL	4.3 ± 0.98	12.76 ± 2.28	115.12 ± 19.4
TPS/PCL	1.73 ± 0.25	13.11 ± 1.92	62.25 ± 1.83
TPS/PCL/Sisal 5%	3.25 ± 0.21	14.55 ± 1.22	68.5 ± 2.58
TPS/PCL/Sisal 10%	2.33 ± 0.11	19.53 ± 3.56	$63.43 \pm 1,13$
TPS/PCL/Sisal 20%	3.84 ± 0.48	8.93 ± 1.26	103.5 ± 7.06

had a remarkable YM but suffered from poor E. Blending PCL with TPS improved TS of the composite about two-fold, but YM remain quite similar to that of neat TPS. Interestingly, in terms of E, composite behaved more like the neat PCL polymer. The incorporation of sisal fibers generally increased TS, indicating a good interfacial adhesion between fibers and matrix polymers. For example, addition of 5% and 10% fiber generally showed some improvements in all three parameters tested (TS, E and YM) but the most dramatic impact was seen in blends with 20% fiber contents that showed over 2-fold increase in the TS and over 60% increase in the YM over TPS/PCL blends without fiber. However, a significant drop in the E was also observed in composites with 20% fiber content. As expected, the modulus in these composites also increased in value because of the rigid nature of the fibers that reduced the ductile behavior of the composites. Rosa *et al*. [3] observed a similar behavior in composites containing starch/ethylene vinyl alcohol/glycerol and coconut fibers, showing that the ductile behavior of the composites was reduced as a consequence of the rigid nature of the fibers. In this regard, Khoathane *et al*. [19] found that the TS and YM of composites reinforced with bleached hemp fibers increased incredibly with increasing fiber loading. Whereas, Ku *et al*. [15] reported that generally, the tensile strengths of the natural fiber reinforced polymer composites increase with fiber content, up to a maximum or certain threshold value beyond which mechanical properties of composite are compromised. This was also observed in composites with 20% fiber content which experienced

a significant loss in elongation at break. The reduction in interfacial adhesion between matrix polymer and a cellulosic filler owing to high amount of filler content in a composite has also been reported by other investigators [20]. The use of alkali and silane treated short hemp fibers in PLA composite promoted good fiber/matrix adhesion and increased matrix crystallinity, which led to improved tensile and impact properties in composites [21].

PCL is a ductile polymer with large deformations, but it has a relatively low modulus for use in application where high rigidity is required [22]. Chen *et al*. [22] has reported that the addition of PCL into thermoplastic starch matrix led to reduction of elasticity modulus. It was observed that the elongation at break in TPS/PCL blend decreased. According to Vertuccio [12], the starch particles in the PCL matrix prevented the cold drawing that result in orientation of PCL molecules. In the region of linear elasticity of the PCL matrix, the PCL chains could not move freely which then resulted in high rigidity [22].

The observed variations in the logarithm of storage modulus (normalized) and loss factor (tan δ) in composites (Fig. 4A and 4B) indicated that the moduli of all TPS/PCL composites generally decreased in value at the same rate over the experimental temperature range. In contrast, the neat PCL and TPS/PCL samples showed some PCL recrystallization with the neat PCL sample showing an increase in modulus at higher temperatures. Also, the neat TPS sample had a modulus that exhibited more temperature dependence, since its modulus decreased more
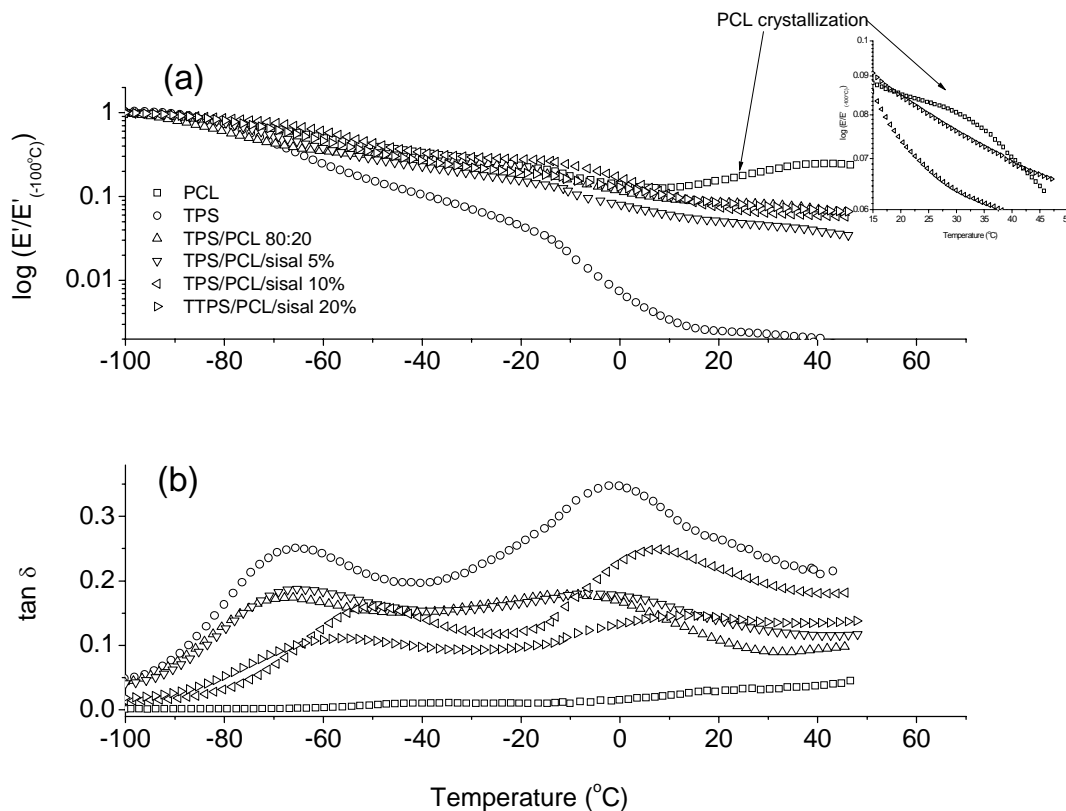
Fig. 4. (A) Logarithm of storage modulus (normalized) and (B) loss factor (tan δ) *versus* temperature for PCL, TPS, TPS/PCL blend and composites.

than the other samples. The addition of sisal fibers led to a slight increase in the T_g of starch components in the composites. This might indicate the fibers restricted the motion of starch chains, resulting in greater energy required to transition from glassy to rubbery materials [23, 24]. In addition, TPS/PCL samples containing fibers showed no PCL recrystallization, indicating that the fibers might have inhibited the PCL crystallization process. The glass transition temperatures (T_g) of starch polymer are often dictated by their amylose/amylopectin ratios, and Tg of a given starch-type was found to be directly proportional to the amylose content in the starch polymer [25]. However, it has been reported that when palm fiber is used as reinforcement in rice starch films, the thermal stability and glass temperature (T_g) shifted towards higher temperatures with increased reinforced fibers content, which restricted the mobility of starch chain due to the establishment of strong interactions between starch and the fibers [26, 27]. The

proposed mechanism for interactions between hydroxyl groups of bleached fibers with carboxyl groups of PCL and hydroxyl of TPS is depicted schematically in Figure 5.

Table 2 provides the values for the normalized log of storage modulus (E`) in the rubbery region at 25°C as well as the glass transition temperatures of blends and polymers. Blending PCL with TPS resulted in an increase of storage modulus, indicating that the material has become more rigid. Increase in storage modulus was also observed with the addition of fibers in TPS/PCL blends (Table 2) and the increase in storage modulus was proportional to the fiber content in the blend (Table 2). The addition of fiber in TPS/PCL blend causes composites to be more rigid, which also resulted in increased T_g values for starch (Table 2). Other investigators used wheat straw fibers as a reinforcing filler in polypropylene and showed that an increase in fiber content up to 20% (wt) led to an increase in
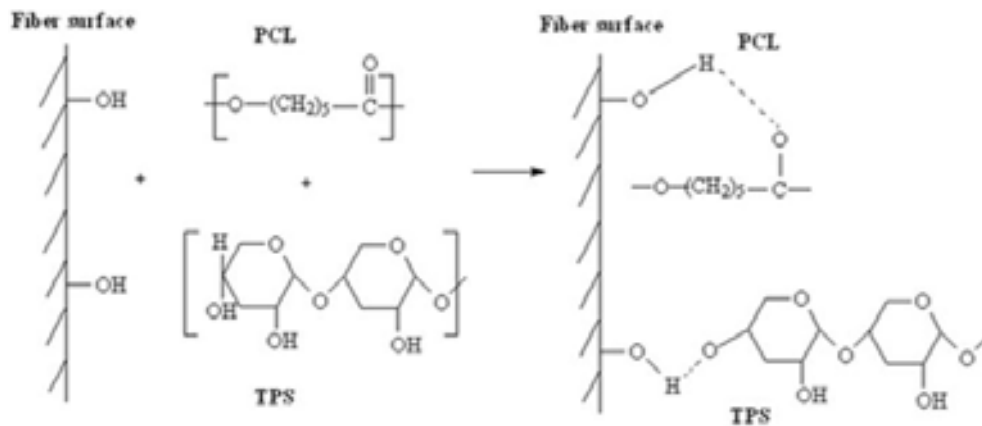
Fig. 5. Proposed mechanism for interaction between hydroxyl groups
of treated fibers with carboxyl groups of PCL and hydroxyl of TPS.

Table 2. log of E` normalized and glass transitions temperatures $(T_g)^{(*)}$ of polymers, blend and blends with fibers.

Sample	$\log(E`/E`_{(-100^oC)})$	$T_{g\ glycerol}$ (^oC)	$T_{g\ starch}$ (^oC)	$T_{g\ PCL}$ (^oC)
PCL	0.180	xxx	xxx	-40
TPS	0.002	-65	-1	n.d.
TPS/PCL	0.083	-66	-5	n.d.
TPS/PCL/sisal 5%	0.048	-65	-5	n.d.
TPS/PCL/sisal 10%	0.068	-50	7	n.d.
TPS/PCL/sisal 20%	0.080	-57	12	n.d.

(*) T_g are taken at maximum of tan δ peaks.
n.d.- not determined.

the tensile strength of the composite. However, beyond this amount, tensile strength decreased. On the other hand, the tensile modulus increased due to higher stiffness of the fibers. When fibers were treated with silane, both tensile strength and modulus increased, but the viscosity was reduced because of better dispersion of the treated fibers [5].

Thermogravimetric analysis was carried out to elucidate the thermal degradation behavior of blends. Fig. 6 provides the thermal degradation curves for fiber, polymers and blends. The TPS/PCL samples generally had higher T_{max} values compared to the neat TPS sample due to the presence of PCL. However, blend containing 20% fiber had a lower T_{max} value (287°C) because

of the higher fiber concentration. The neat PCL sample had the highest thermal stability (365°C), whereas the neat TPS sample had the lowest thermal stability (290°C) throughout most of the temperature range. Also, the TPS/PCL samples had similar TGA curves to the neat TPS sample, due to the high TPS concentrations in those samples, until approximately 325°C. After this point, the TPS/PCL samples became more thermally stable due to the presence of PCL and/or sisal fibers.

The heats of fusion (ΔH_m) and melt temperatures (T_m) for polymers and composites without and with fiber were determined from DSC heating thermograms (Fig. 7). The blending of TPS and sisal fibers with PCL had little effect on T_m of
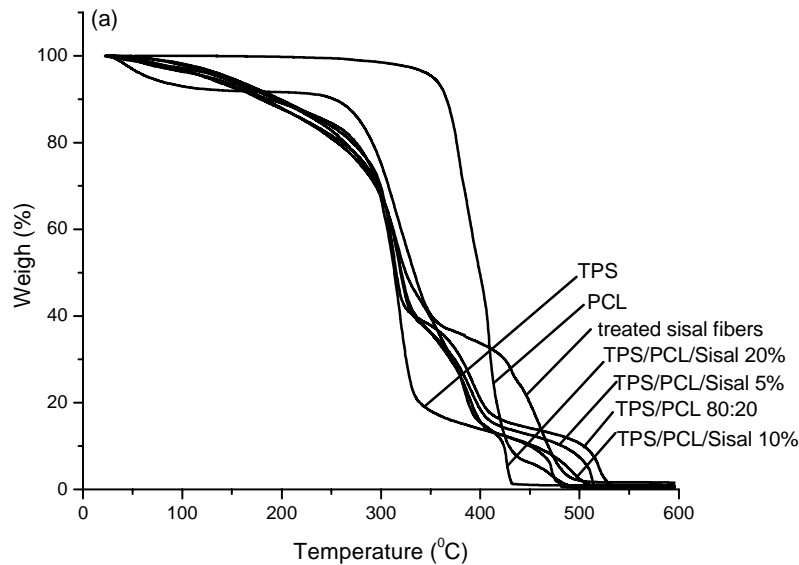
Fig. 6. TG curves of polymers and composites containing 5%, 10% and 20% fibers.
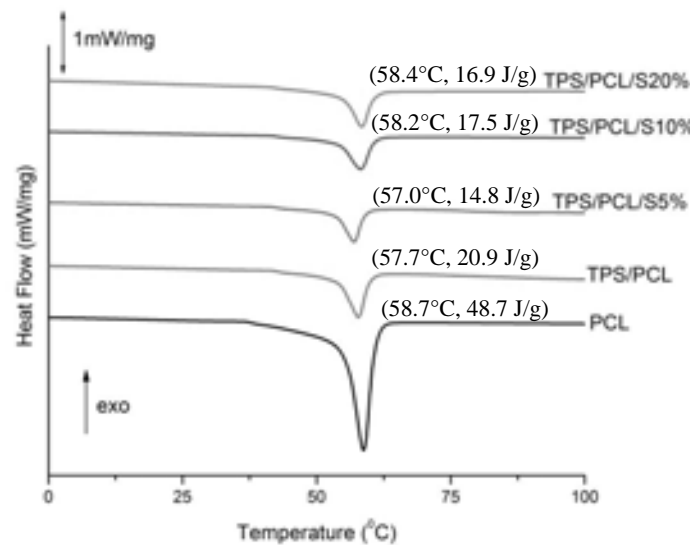

Fig. 7. DSC thermograms of PCL, TPS/PCL (80:20) and TPS/PCL composites containing 5%, 10% and 20% fibers.

each sample, indicating those components did not affect the crystalline structure of PCL. However the samples containing sisal fibers had lower crystalline content than the TPS/PCL sample. This was due to the fibers inhibiting PCL crystallization, which was consistent with the DMTA results (Fig. 4). The ΔH_m used as an indicator of crystallinity in composite [28] generally decreased with increased fiber content compared to TPS/PCL blend without fibers (Fig. 7). The only exception was the composite with 10% fiber where an increase in ΔH_m was observed, indicating a higher degree of crystallinity.

In the X-ray diffractograms (Fig. 8), neat starch samples showed a characteristic peak around 19° (2θ) attributed to processing-induced crystallinity of single helical amylose and has also been reported by other investigators [29]. Another,
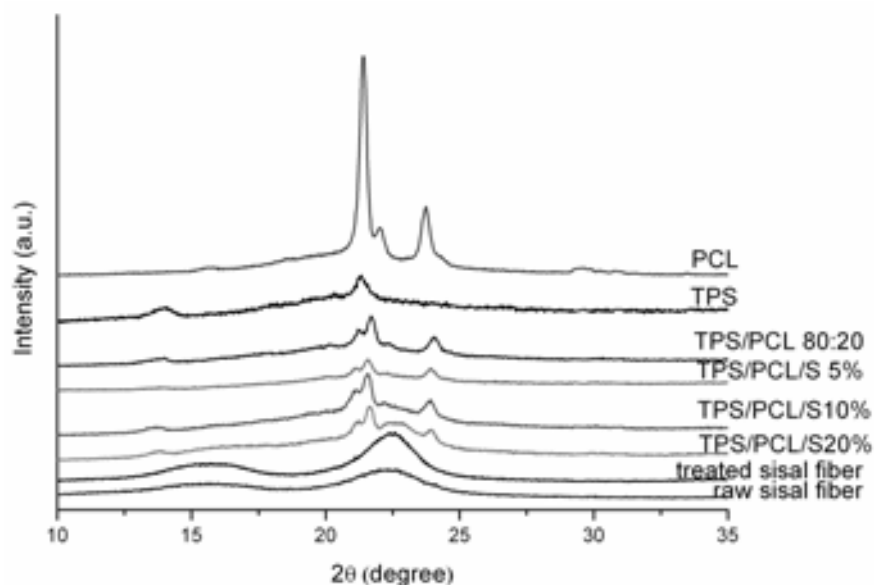
Fig. 8. X-ray diffraction of polymers and composites.

relatively small peak around 15.1°(2θ), represents a V-type exclusion complexes in starch form between amylose and lipids [30]. Such V-type complexes that are typical of the destructurized starch have also been reported to be highly resistant to starch-degrading enzymes [31, 32]. The diffractogram revealed a characteristic crystalline structure for PCL with peaks at 2θ = 21.3° and 23.7° (Fig. 8). The spectra of composites showed a well developed crystalline phase for PCL. Similar observations have also been reported by other investigators [12] in composites containing PCL/starch in combination with nanoclays. A characteristic cellulose peak around 2θ = 22.6° could be observed specially for the composite with 20% of fiber indicating the preservation of cellulose structure in this composite.

The TPS/PCL samples without added fiber had the same X-ray diffraction peaks as the neat PCL sample, indicating little change in PCL crystalline structure (Fig. 8). These results were consistent with the T_m data from the DSC experiments (Fig. 7). Treated sisal fibers had the highest crystallinity (85%) when compared with the raw sisal fibers (69%) showing that the amorphous phase was removed with the bleaching treatment Thus, from the data one could conclude that incorporation of 10%-20% treated sisal fibers in a TPS/PCL blend improved both the thermal and

the mechanical properties of the composite. A good dispersibility of the fiber in the matrix and interaction between fiber-matrix led to increased crystallinity that caused composite to be more rigid. The increase in fiber content tends to increase the PCL crystallinity in the blend.

Results presented here suggest creation of branched and cross-linked macromolecules via reactions between carboxyl groups in PCL-starch and hydroxyl groups in sisal fibers causing an increase in crystallinity as observed by DSC, X-Ray Diffraction and DMA analyses.

Crystallization of PCL that was apparent in the TPS/PCL blends but not in TPS/PCL composites with the added fibers, suggested that sisal fibers hindered the crystallization of PCL in composites.

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