

Polystyrene cellulose fiber composites: effect of the processing conditions on mechanical and dynamic mechanical properties

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ABSTRACT

The usage of natural fibers on the composites development has grown rapidly in the recent years due to the fibers plentiful availability, renewable source, low density and biodegradability. However, there are some drawbacks, for instance, the fiber dispersion on a polyolefin matrix. In this work, the influence of processing speed on the mechanical and dynamic mechanical properties of polystyrene (PS) filled with cellulose fiber composites was investigated. The composites were processed on a twin-screw co-rotating extruder, using screw speeds of 200 rpm, 400 rpm and 600 rpm. The dynamic mechanical properties and the mechanical properties were investigated as a function of fiber content. The composites processed on a screw speed of 400 rpm had presented an increase on flexural and impact strength, compared to the composites processed at 200 rpm. The flexural and storage modulus had increased when increasing the fiber content, as well as increasing the processing speed. The greater fiber dispersion obtained at a screw speed of 400 rpm hinders the agglomeration arrangement and distributes the fibers more equally on the matrix. The increase on processing speed probably generates a fiber size reduction, increasing the fiber superficial area and generating a greater contact with the matrix as well. Therefore, the efforts transference of matrix to fibers is improved, originating an increase on the evaluated properties.

Keywords: Polystyrene, cellulose, composites, extrusion, screw speed.

1. INTRODUCTION

Natural fibers (e.g. cellulose, sisal, wood fibers, pine, bamboo, jute, palm, henequen and others) have gained rapid growth in the recent years due to a number of advantages they offer over conventional reinforcing materials (e.g. glass and carbon fibers), such as, abundance, renewability, low density, high specific strength and stiffness, almost no health hazards, and relatively low cost. [1-3]

Many studies have been done on thermoplastics-based and natural fiber composites, which have successfully proven their applicability to various fields of technical application [2-4]. However, one difficulty that have prevented a more extended utilization of natural fibers, and it is a challenge for cellulose fiber reinforced thermoplastic composites, is a lack of good interfacial bonding between the hydrophilic nature of fibers to a hydrophobic matrix [5-7]. The lack of adhesion between cellulose fibers and the matrix and poor dispersion of the fibers in the matrix leads to unsatisfactory composite mechanical properties [3].

Several works can be found concerning to the effect of coupling agents or lubricants to improve interfacial bonding and others concerning to the effect of processing conditions [2-7]. Bengtsson et al. evaluated highly filled cellulose/polypropylene composites, and they reported an increase of stiffness by adding fibers to the composites but a decrease on impact strength [3]. Zhang et al. investigated the effect of screw configuration, screw speed and different material compositions in order to achieve a uniformity improvement of wood/HDPE composites [8]. The results showed that the screw speed should be controlled to achieve efficient mixing without thermal degradation [8].

Mano et al. prepared composites of polypropylene (PP) and high density polyethylene (HDPE) reinforced with 20 wt% of curaua fibers using a twin-screw extruder and the effect of screw rotation speed was evaluated [9]. They concluded that fiber dimensions decrease with the increase in screw rotation speed because higher shear forces cause fiber breakage and fibrillation, as well as the aspect ratio. The morphology

showed that the dispersion of the fibers was higher for composites processed at 500 rpm, due to increased fibrillation, however, at 300 rpm the aspect ratio of the fibers is higher and the final mechanical properties are better [9].

Mohanty et al. investigated the variations on mechanical strength, storage modulus (E'), loss modulus (E''), and damping parameter ($\tan \delta$) with the addition of fibers and coupling agents on jute/HDPE composites [10]. They observed that the tensile, flexural and impact strength increased with increasing fiber loading up to 30%, as well as adding coupling agents [10]. $\tan \delta$ spectra presented a strong influence of fiber content and coupling agent on the α and γ relaxation process of HDPE [10]. Huang and Zhang investigated the effects of filler–filler and polymer–filler interactions on dynamic rheological and mechanical properties of HDPE/wood composites [11]. The results demonstrated that enhanced filler–filler interaction induced the agglomeration of wood particles, which increased the storage modulus and complex viscosity of composites and decreased their tensile strength, elongation at break, and notched impact strength because of the stress concentration [11].

In fact, a considerable amount of work has been reported on the effects of coupling agents on mechanical properties of composite materials. However, the literature lacks works on the effect of processing conditions on mechanical and mainly dynamic mechanical properties of polymer composites reinforced with natural fibers. On this context, this study aims to evaluate the effect of screw speed used during the extrusion process on the mechanical and dynamic mechanical properties of PS/cellulose fiber composites.

2. MATERIALS AND METHODS

Cristal polystyrene (N1921) supplied by Innova S/A (Triunfo, RS-Brazil) with melt form index of 20 g/10 min (200°C/5 kg, ASTM D1238) was used as composite matrix. Pure bleached cellulose fibers from *Pinus taeda* supplied by Cambará S/A (Cambará, RS-Brazil) with particle size distribution of 150-400 μm (ASTM D1921) were used as composite reinforcement.

The cellulose fibers were dried in an oven at 80°C for 24h, before being used in composite formulations. Samples with 0, 10, 20, 30 wt% of cellulose fibers were processed in a corotating twin-screw extruder COR-20-32-LAB MH Equipment, with L/D ration of 32, at screw speed of 200 rpm, 400 rpm and 600 rpm. The nine-barrel temperature zones were controlled between 160 and 190°C. After extrusion the samples were dried in an oven at 80°C for 24 h. Specimens for mechanical and dynamic mechanical tests were injection molded with a barrel temperature range of 170-180°C using a preheated mold at 60°C \pm 2°C.

The flexural tests were performed according to ASTM D790 using a universal test equipment EMIC DL 2000. The test speed was 1.5 mm/min. The unnotched IZOD impact strength tests were performed according to ASTM D256 in a CEAST equipment with a 1J pendulum. Rectangular specimens with dimensions of 50 mm x 12.7 mm x 3.5 mm were subjected to dynamic mechanical testing using an Anton Paar Physica MCR 101 oscillatory rheometer operating in DMA mode. The measurements were carried out in the torsion mode and the corresponding viscoelastic properties were determined as a function of temperature. The temperature used in the experiment was 25-120°C, with a heating rate of 3°C/min, under nitrogen flow. The samples were scanned at a fixed frequency of 1Hz and a dynamic strain of 0.1%. Studies on the composites morphology were carried out using a SHIMADZU Superscan SS-550, scanning electron microscope, with an acceleration tension of 15kV.

3. RESULTS AND DISCUSSIONS

3.1 Mechanical properties

The composite flexural strength and flexural modulus as a function of cellulose fiber content are shown in Figure 1. As shown in Figure 1(a) the addition of cellulose fibers increased the flexural strength for composites with 10 wt% and 20 wt% of cellulose content when compared with the matrix for screw speed of 400 rpm. However, the property decreased when 30 wt% of fibers were used. Higher cellulose content might result in fiber agglomeration and thus can result in a decrease of flexural strength. On the other hand, from Figure 1 (b) it can be seen that there is an almost linear increase on the flexural modulus with fiber loading. This behavior may be related to the fact that the cellulose fibers present a greater modulus than the polymer matrix [12-13].

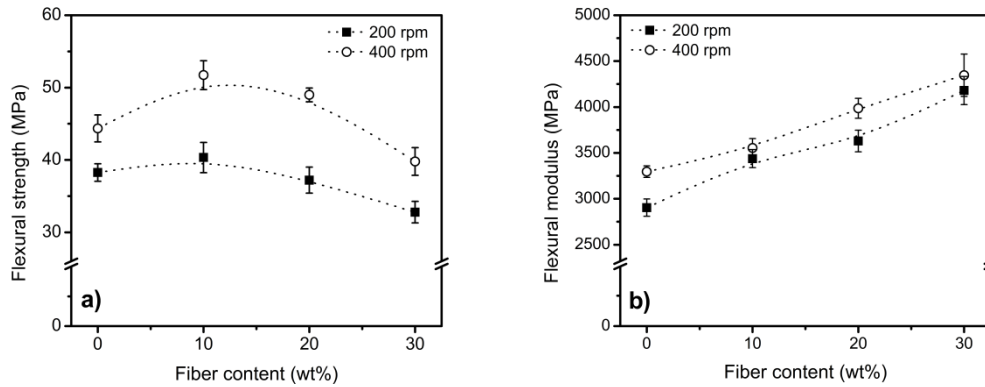


Figure 1: Flexural strength (a) and flexural modulus (b) of the composites processed at 200 and 400 rpm.

The strain at break decreased with increasing fiber content, as shown in Figure 2 (a). When the screw speed is increased it also generated an increase on strain at break of the composites. This result may indicate that the dispersion of cellulose fibers into polystyrene matrix had increased when increasing screw speed. In addition the increase of fiber content may be restricting the polymer molecular mobility, which may lead to an increase in stiffness, making the composite more brittle and reducing the strain at break with the fiber loading. Figure 2(b) presented the impact strength of the composites study as a function of fiber content. Better results are obtained for composites extruded at 400 rpm, which might indicate a better dispersion of the fibers using this screw speed. However, the cellulose fiber loading reduces the molecular mobility of matrix which reduces the energy absorption on impact, causing a reduction in composite impact strength with higher cellulose fiber content [12].

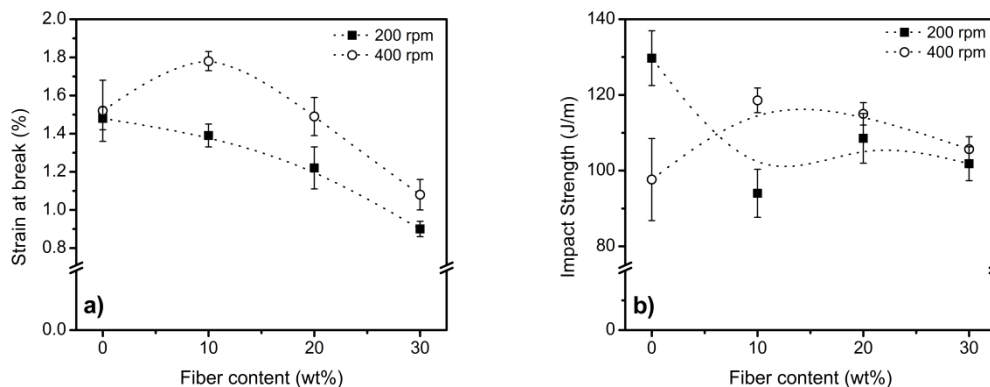


Figure 2: Strain at break (a) and impact strength (b) of the composites studied.

The screw speed is one of the important parameters that influence the mixing ability [8] between matrix and reinforcement in a composite material. Three screw speeds (200, 400 and 600 rpm) were used to study the effects of screw speeds on the dispersion of cellulose fibers. The results shown in Figure 1 and Figure 2, indicate that the dispersion of cellulose fibers into the polymer matrix had increased when the screw speed increased from 200 to 400 rpm. The SEM micrograph of composites with 20 wt% of cellulose fibers processed at 200 rpm and 400 rpm are shown in Figure 3.

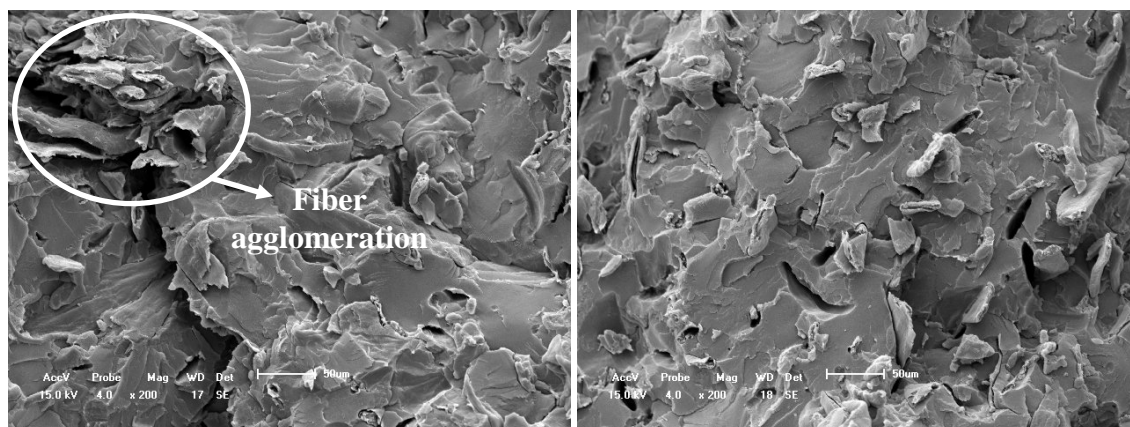


Figure 3: SEM micrograph with magnification of 200x for composites with 20 wt% of cellulose fibers processed at 200 (a) and 400 rpm (b).

The existence of cellulose fiber agglomeration for the composite processed at 200 rpm is obvious in the SEM micrograph. This indicates that the screw speed of 200 rpm is not so effective in breaking down the cellulose fiber agglomeration, which can result in lower flexural properties when compared with those processed at 400 rpm. Increasing the screw speed to 400 rpm increases the average shear rate, which may enhance the dispersive mixing and, thereby, helps in the uniform dispersion of cellulose fibers in the composite melt, which may result in higher mechanical properties corroborating the results observed in Figure 1. The flexural strength for composites processed at 400 rpm is approximately 30% higher than those processed at 200 rpm. The cellulose fibers tend to form agglomerates as a result of the intermolecular hydrogen bond between neighbor fibers [12]. The presence of agglomerates promote incompatibility with a hydrophobic polymer matrix reducing the composite mechanical properties [12,13], as verified in Figure 1 and Figure 2 for composites processed at 200 rpm. When the screw speed is increased the fiber breakage occurs as consequence of the higher shear rates caused by the extrusion process, and according to literature is expected that the mechanical properties decreased [9,13]. However, the higher shear rates obtained when the screw speed is increased may also promote better fiber dispersion into the matrix, even promoting the reduction in fiber length, which can probably reduce both the number and the size of agglomerates [13], as observed in Figure 3. The reduction in the number and size of cellulose fiber agglomerates might increase the interactions between fiber and matrix leading to higher mechanical properties for composites processed at 400 rpm. In addition, the higher screw speed promote fiber breakage reducing the length of the cellulose fibers, increasing the fiber superficial area and generating a greater contact with the matrix [9] as well, which might contribute to increase the mechanical properties.

However, when the screw speed was further increased to 600 rpm, the composites were severely deteriorated and the results were not showed in this study. The reason is that the increase of screw speed also increases the shear heating, resulting in higher melt temperatures [8]. As cellulose fibers and polystyrene are temperature-sensitive materials, both materials may have degraded due to the higher temperatures generated when the screw speed increased to 600 rpm. The dark appearance of composites processed at 600 rpm was observed during the extrusion and these composites were disregarded from the study of mechanical and dynamic mechanical properties.

3.2 Dynamic mechanical properties

The variation in storage modulus of the composites as a function of temperature can be observed in Figure 4. There is an increase in the storage modulus of the PS matrix with the incorporation of cellulose fibers over the entire region study for both screw speeds used, in agreement with the results observed for flexural modulus. This can be probably associated with the increase in the stiffness of the polymer matrix due the reinforcement effect imparted by the fibers, which allowed a greater degree of stress transfer at the interface [14-15]. As the temperature increases, storage modulus decreases and thus there is a sharp decline in the values of storage modulus in the glass transition region, near to 100°C. This behaviour can be attributed to the increase in the molecular mobility of the polymer chains above glass transition temperature (T_g) [14,15]. The drop in the storage modulus on passing through the T_g is lower for the reinforced composites compared with polymer matrix for both screw speed study. So, the difference between the modulus in the glassy state and rubbery state is smaller in the composites than in the matrix, which clearly indicates the reinforcing effect caused by

the cellulose fibers [14-16].

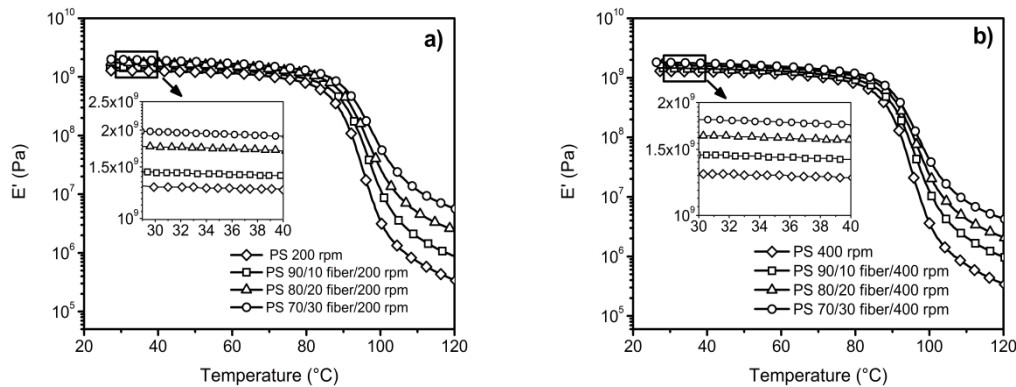


Figure 4: Variation of storage modulus as a function of temperature for composites processed at 200 (a) and 400 rpm (b).

The influence of cellulose fiber loading and dispersion into the polystyrene matrix using different screw speeds can be better understood by evaluating the coefficient C [14, 17]. The effectiveness of fillers on the storage modulus of the composites can be represented by a coefficient C given in the following equation [14, 17-18]:

$$C = \frac{(E'_g/E'_r)_{comp}}{(E'_g/E'_r)_{matrix}} \quad (1)$$

where E'_g and E'_r are the storage modulus values in the glassy and rubbery regions, respectively. The E' values measured at 35 $^{\circ}\text{C}$ and 120 $^{\circ}\text{C}$ were employed as the E'_g and E'_r , respectively. A high C value indicated that the filler is less effective [17-18]. The values obtained for composites processed at 200 and 400 rpm are given in Table 1. It can be observed that the C value decreases with cellulose fiber loading. This result indicates that the addition of the cellulose fibers promotes an increase in the composite strength and more stress can be transferred from the matrix to cellulose fibers, increasing the mechanical properties of the composites, as observed in mechanical tests. When the screw speeds were compared the composites processed at 400 rpm presented lower C values, indicating that the maximum stress transfer between matrix and fibers takes place as a result of better fiber dispersion along the polymer matrix.

Table 1: The coefficient C for the composites processed at different screw speed.

SAMPLE	C	SAMPLE	C
PS90/10Fiber/200rpm	0.440	PS90/10Fiber/400rpm	0.376
PS80/20Fiber/200rpm	0.208	PS80/20Fiber/400rpm	0.189
PS70/30Fiber/200rpm	0.105	PS70/30Fiber/400rpm	0.101

Figure 5 shows the variation in loss modulus as a function of temperature for the composites study. The incorporation of cellulose fibers caused broadening of the loss modulus peak when compared to the polymer matrix for both screw speeds studied. The peak broadening is an indication of a change in relaxation mechanisms [19-20]. This can be attributed to the increase in relaxation time caused by the larger concentration of cellulose fibers. The values for the loss modulus of the composites also increased with increasing cellulose fiber content, and composites with 30 wt% of cellulose fibers showed the highest loss modulus values. This higher value is due to the increase in internal friction, which enhances the dissipation of energy [15]. In addition, the presence of cellulose fibers with a high modulus value reduces the flexibility of the composite material by introducing constraints on the segmental mobility of the polymeric molecules which result in higher loss modulus values as the fiber content increases [14,17].

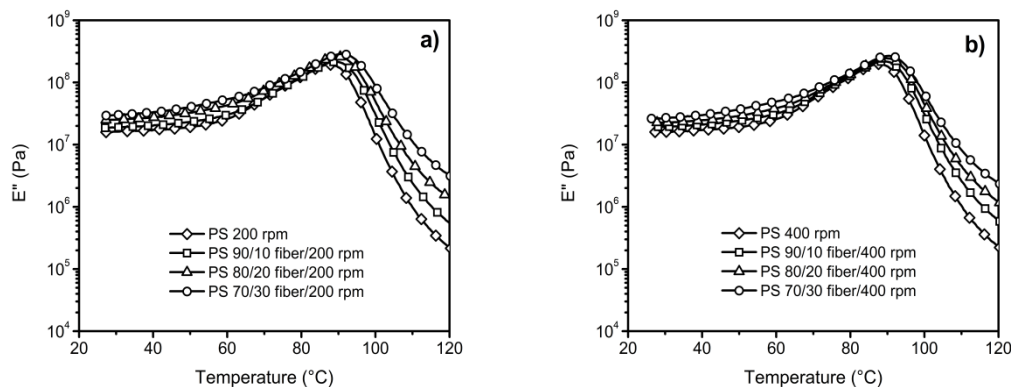


Figure 5: Variation of loss modulus as a function of temperature for composites processed at 200 (a) and 400 rpm (b).

The damping properties of the material give the balance between the elastic phase and viscous phase in a polymeric structure [14,17]. In composites, damping is influenced by the incorporation of fibers [17, 21-23]. The mechanical damping values for composites are lower than those of polystyrene matrix, as can be seen in Figure 6. It was observed that as the amount of cellulose fibers in the composite increases, the tan delta values decreases. The incorporation of cellulose fibers reduces the height of the tan delta peak. As the cellulose fiber content increases, the composite becomes more rigid. As a result, the restriction of the polymer chains increases and the peak height becomes lower.

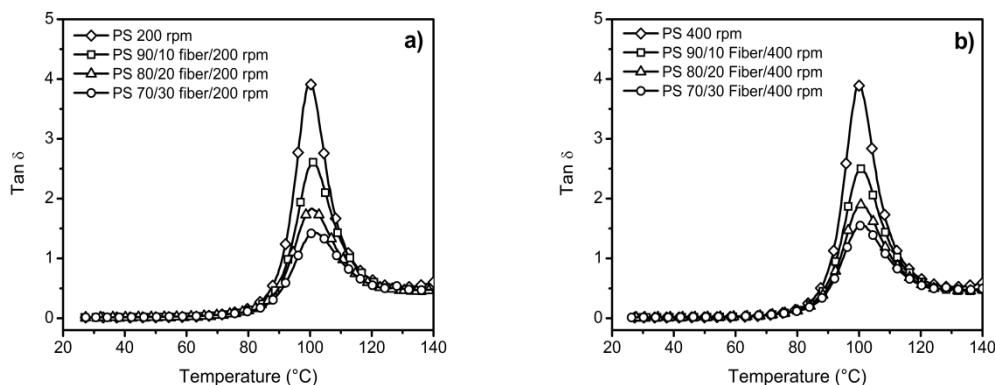


Figure 6: Variation of tan delta as a function of temperature for composites processed at 200 (a) and 400 rpm (b).

The peak height (PH) and peak width at half-height (PWHM) values were obtained from the tan delta curves and are presented in Table 2.

Table 2: The peak height and peak width at half-height for the composites processed at different screw speed.

COMPOSITE (wt%)	PH	PWHM	COMPOSITE (wt%)	PH	PWHM
PS90/10Fiber/200rpm	2.30	25.09	PS90/10Fiber/400rpm	2.20	24.64
PS80/20Fiber/200rpm	1.54	20.40	PS80/20Fiber/400rpm	1.51	20.27
PS70/30Fiber/200rpm	1.14	17.11	PS70/30Fiber/400rpm	1.24	17.69

The peak height is an indicative of the interactions on the interface between polymer and fiber [14, 22]. Since, a lower peak height indicates a good interfacial adhesion [22, 24]. In general, the composites processed at 400 rpm presented lower peak height values when compared with those processed at 200 rpm, which could indicate that weak interactions between cellulose fiber and polystyrene matrix could occur at the interface. On the other hand, the peak height at half-maximum is a criterion used to indicate the composite

heterogeneity [17]. A broader peak height at half-maximum indicates heterogeneity between the two phases that formed the composite material [17, 24]. So, for the composites with 10 wt% and 20 wt% of cellulose fibers processed at 400 rpm is probably that the higher screw speed could improve the fiber dispersion into the polymer matrix due the higher shear rates when compared with the composites processed at 200 rpm which results in higher mechanical and dynamic mechanical properties.

4. CONCLUSION

The effect of screw speed on mechanical and dynamic mechanical properties of polymer composites reinforced with cellulose fibers was evaluated. The results showed that composites processed at 400 rpm presented higher mechanical properties and better dispersion of the fibers than those obtained at 200 rpm. In general the flexural strength is 30% higher for composites development at 400 rpm. The dynamic mechanical analysis provides valuable information about the dispersion on the cellulose fibers into the polystyrene matrix and demonstrates that composites processed at 400 rpm presented a more effective distribution of the reinforcement into the matrix, as observed in SEM analysis. The results also demonstrates that the screw speed can be controlled to achieve efficient mixing without promoting thermal degradation of cellulose fibers resulting in composites with higher mechanical and dynamic mechanical properties.

5. ACKNOWLEDGEMENTS

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