

Benefits of Low Kenaf Loading in Biobased Composites of Poly(L-lactide) and Kenaf Fiber

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Received 14 May 2008; accepted 15 October 2008

DOI 10.1002/app.29519

Published online 30 January 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Bast fibers from stems of kenaf (*Hibiscus cannabinus*, L.), a warm-season tropical herbaceous annual plant, were dispersed into poly-L-lactide (PLLA) matrix by melt-mixing followed by compression molding. Low fiber fractions (1–5%) were investigated. The composites showed a slight lowering of thermal stability when evaluated by thermogravimetric analysis. X-ray diffraction and differential scanning calorimetry indicated an influence of kenaf on the crystallization of PLLA. The fiber dispersion in the polymer matrix was established by

polarized optical microscopy. Scanning electron microscopy showed good fiber–matrix adhesion as revealed by the combination of dispersion, interaction, and crystallinity, which enabled an increase in the mechanical properties of the composite that scaled with concentration. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1294–1301, 2009

Key words: poly-L-lactide (PLLA); renewable resources; green and biocomposites; kenaf; crystallization; dynamic mechanical analysis

INTRODUCTION

The need to replace fossil-based materials has led to an increased interest in biopolymer composites. Reinforcement of polymers with natural fibers has also been of interest.^{1–6} A primary benefit is the improvement in mechanical properties. Kenaf (*Hibiscus cannabinus*, L.; family Malvaceae) is a tropical-season herbaceous annual plant, related to cotton, okra, and hibiscus that can be produced across a large range of cultural conditions and locations, and has excellent potential as a commercial crop for industrial applications.^{7–9} It is grown widely for cordage in Asia. Products from kenaf have many uses that include animal litter, a fiberglass substitute, animal forage, cellulose fiber, potting mix, pulp and paper making, sacs, canvasses, and carpets.^{7,10–14} Applications of kenaf fibers have received renewed attention because of their lightweight, low combustibility, nontoxicity, biodegradability, and low cost.^{15–17} In the past few decades, increased use of fiber-reinforced composites for various structural and semi-structural applications has resulted in the development of synthetic fibers for such applications.^{18–25} In the automobile industry, an increased need to replace fossil-based materials with renewable resources has led to the interest in reinforcing

polymers with natural fibers.^{4,26} For example, Toyota Motor Corporation recently used some of these properties in their production of door panels from polypropylene/kenaf blends.^{26–29} Incorporating kenaf in the manufacture of automobiles not only increased their biodegradability but also reduced their weight and enhanced their noise absorbent ability. Parikh et al.³⁰ found that nonwovens made of retted kenaf blended with cotton fibers, recycled polyester, and off-quality polypropylene could meet industry specifications of flammability, odor, mildew, and strength. Mueller and Krobjilowski³¹ have studied the formation of composites by using flax fibers and biodegradable melt-blown polymeric materials as the matrix. It was observed that the natural fiber-based composites possessed many of the required properties that are comparable with the polypropylene-based composites.

Poly-L-lactide (PLLA) is one of the most important biodegradable polymers and has been the focus of many studies in recent years.^{32–37} PLLA has a melting temperature of 160°C and good tensile properties.³⁸ As such, PLLA possesses wide applications as a raw material in industrial applications³⁹ and in medical applications^{36,40} (suture materials and orthopedic fixation devices). Serizawa et al.^{39,41} investigated the development of fiber-reinforced polylactic acid for use in electronic products. In their studies, high-performance biomass-based plastics consisting of polylactic acid were added to kenaf, which fixes carbon dioxide efficiently. They discovered that the

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heat resistance, crystallization, and molding properties were significantly improved. In addition, the impact resistance properties were greatly improved. There was also an improvement in tensile strength by adding a flexibilizer to the composite. The major problem often raised in the natural fiber-reinforced material is the low adhesion between the surface of the natural fiber and the matrix. Feng et al.⁴² found that using maleated polypropylene was effective in improving the compatibility between kenaf and the polypropylene matrix. Various chemical modifications have been carried out with kenaf to improve the fiber-polymer compatibility. In this regard, Edeerozey et al.¹⁵ treated kenaf with different concentrations of sodium hydroxide and determined that the optimum amount of NaOH for kenaf was a 6% NaOH concentration, resulting in a higher tensile strength, whereas a 9% concentration resulted in a lower tensile strength for the modified fibers. In a related study, Hude et al.⁴³ found that silane-treated, fiber-reinforced composites and alkali-treated, fiber-reinforced composites offered superior mechanical properties when compared with unmodified fiber-reinforced composites.

Pan et al.⁴⁴ investigated the crystallization and mechanical properties of biobased "green" composites based on PLLA and kenaf containing 10, 20, and 30 wt % fibers. They found that the crystallization and mechanical properties of composites were significantly improved. We note, however, the recent growth in the field of polymer nanocomposites where increased interfacial area and consequently low volume fractions of additives can be harnessed to provide significant benefits. We examine this concept in the kenaf-PLLA composite where we utilize just 1, 3, and 5 wt % kenaf fiber. Crystallization, thermal, and mechanical properties are determined.

EXPERIMENTAL

Materials

The PLLA used had a M_n : 98,600; M_w : 194,799 and was supplied by NatureWorks (MN, USA). Kenaf bast fiber was obtained from the International Kenaf Association. It was grown and retted during the 2007 growing season. The plants were grown at the Philippine island of Marinduque near the city of Boac. The plants were harvested, the bark was manually stripped from the plants, and the bark ribbons were bundled together and placed in ocean water for 12 days. After 12 days in the ocean water, they were placed in fresh water to clean the ribbons and remove the salt and salt water. Then, the fibers were dried and brushed. The diameter was in the range of 67–100 μm . Lengths of 1 mm were cut from this fiber.

Preparation of PLLA + kenaf composites

The dried kenaf was blended with PLLA in the concentration of 1, 3, and 5 wt % in a Brabender using a speed of 80 rpm at 200°C for 3 min. The Carver press was preheated to 160°C, and a total of 5 metric tons of pressure was applied at a rate of 0.5 metric tons per minute.

X-ray diffraction

The powder X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima III X-ray diffractometer. Each pattern was scanned from 2° to 50° (2 θ), with a step size of 0.05° and a dwell time of 1.34 s, using Cu K α radiation ($\lambda = 1.540 \text{ \AA}$).

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) of the neat polymers and composites were measured on a Rheometric Scientific Analyzer 3, operating in the three-point bending mode. A minimum of three samples of 25 \times 8 \times 1.94 mm³ were used to ensure reproducibility. An initial strain sweep was conducted to determine the linear viscoelastic region. The linear strain was determined to be 0.1% from a strain sweep. All tests were conducted at a frequency of 1 Hz.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was measured using a Perkin-Elmer DSC6 apparatus. The system was calibrated using elemental indium. The sample was run from 5 to 200°C at a heating rate of 10°C/min and at a cooling rate of 5°C/min. Isothermal measurements were conducted by heating the samples to 200°C at 10°C/min, and then cooling the samples to 120°C at a rate of 5°C/min.

Polarized optical microscopy

A Nikon polarized optical microscope (POM) equipped with an Instec STC200 hot stage was used to investigate the superstructure of the nanocomposites. Thin films of pure PLLA and PLLA/kenaf nanocomposites (about 100 μm thick) were sandwiched between two thin glass slides and heated using the hot-stage to 200 °C at a rate of 10 °C min⁻¹. The samples were then held at 200 °C for 2 min before quenching to the desired temperature.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGA6. A 20–25 mg sample was pyrolyzed under nitrogen gas in a ceramic

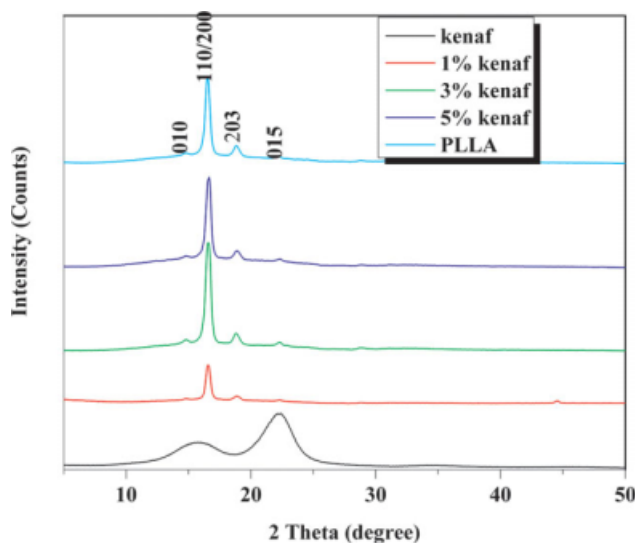


Figure 1 XRD patterns of PLLA and the kenaf composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sample pan from 30 to 600°C at a heating rate of 5°C/min under or nitrogen.

RESULTS AND DISCUSSION

X-ray diffraction

Figure 1 shows the XRD patterns of the kenaf and the blends. The morphology and the structural properties of PLLA have been previously investigated by Miyata

and Masuko.⁴⁵ All of the reflections were indexed as (*hkl*) reflections based on the orthorhombic unit cell with dimensions $a = 1.078$ nm and $b = 0.604$ nm. The X-ray diffractogram of the neat PLLA show noticeable peaks in the region $2\theta = 15^\circ\text{--}22.3^\circ$ because of the diffraction planes (Fig. 1 and Table I). Kenaf shows two broad peaks in these regions indicating cellulose structural peaks. The crystal structure of naturally occurring cellulose is known as cellulose 1. Plant fibers are composite themselves designed by nature, composed of cellulose, hemicelluloses, lignin, waxes, and some water-soluble compounds.⁴⁶ In the case of the composites, the peaks are present in the 1, 3, and 5% kenaf, indicating that the integrity of the composition as a whole is well preserved in the composites.

Thermogravimetric analysis

Figure 2(a,b) shows the TGA results and the corresponding derivative plot. For the kenaf, weight loss occurs from the start of the TGA experiment, suggesting the possible loss of water. Two peaks in the DTGA curve corresponding to 350 and 375°C with onsets around 100 and 250°C could likely correspond to water and lignin or cellulose degradation. Lignin⁴⁷ and cellulose⁴⁸ have been found to degrade significantly above 250 and 200°C. Hydrolysis would be expected to lead to decreased thermal stability of the PLLA. As the TGA and DTGA curves indicate, for low-weight fraction kenaf (1%) no change is observed when compared with the base PLLA. However, with increased kenaf (3 and 5% by

TABLE I
XRD of PLLA and Composites with Kenaf Fiber

Sample	<i>hkl</i>	2θ (°) ^a	<i>H</i> (%) ^b	<i>d</i> (Å) ^c	<i>XS</i> (Å) ^d	FWHM ^e
PLLA	(010)	14.7	2.6	5.99	223	0.411
	(110/200)	16.5	100.0	5.36	211	0.413
	(203)	18.8	13.5	4.70	185	0.483
	(015)	22.2	2.2	4.00	196	0.463
1% kenaf	(010)	14.7	3.1	5.98	339	0.294
	(110/200)	16.5	100.0	5.35	220	0.416
	(203)	18.8	11.3	4.70	182	0.491
	(015)	22.3	4.2	3.97	230	0.404
3% kenaf	(010)	14.7	3.1	5.98	279	0.342
	(110/200)	16.6	100.0	5.33	188	0.475
	(203)	18.8	10.6	4.71	177	0.504
	(015)	22.3	3.8	3.97	188	0.480
5% kenaf	(010)	14.7	2.9	5.99	245	0.379
	(110/200)	16.6	100.0	5.32	202	0.447
	(203)	18.8	10.7	4.69	180	0.495
	(015)	22.3	3.2	3.97	196	0.462

^a 2-theta degree.

^b Relative intensity %.

^c Interlayer spacing.

^d Crystallite size.

^e Full-width half-maximum.

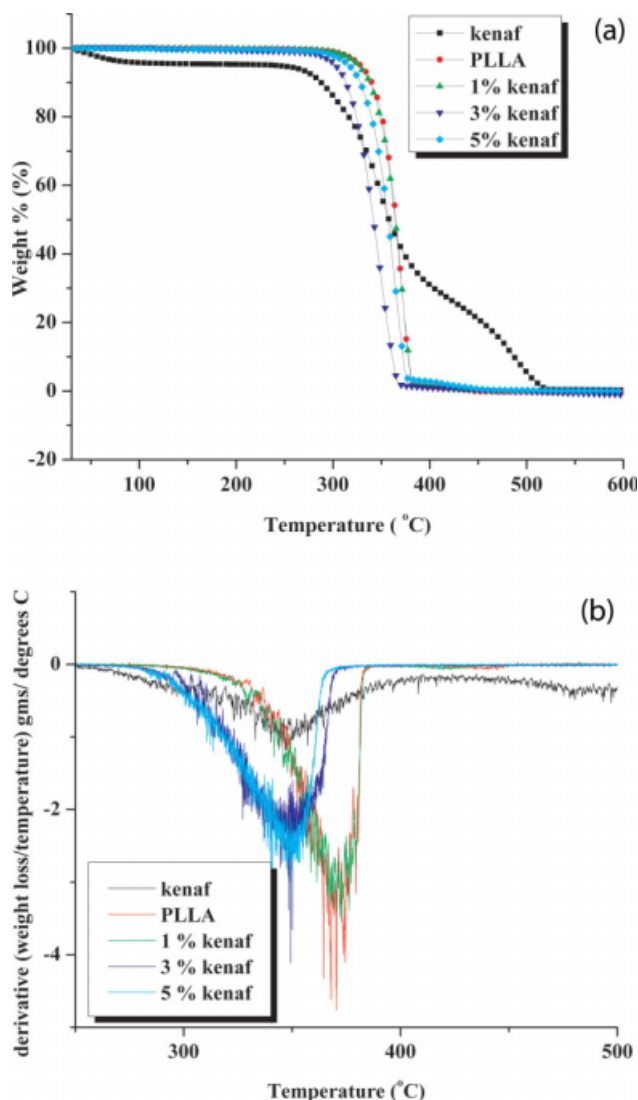


Figure 2 (a) TGA traces of PLLA and composites showing low impact of kenaf at 1% loading but decreased degradation onset for the 3 and 5% kenaf composites and (b) DTGA results showing that the maximum weight loss in kenaf occurs at significantly lower temperatures than in PLLA and this influences the 3 and 5% kenaf containing PLLA composites more than the 1% kenaf composite. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

weight), the release of water from the kenaf leads to decreased thermal stability in the PLLA.

The decreased thermal stability due to hydrolysis is consistent with that obtained by Kirwan et al.⁴⁹ in their investigation of polyvinylalcohol modified with *Miscanthus giganteus*. The final weight loss increases with kenaf loading, indicating char formation.

Differential scanning calorimetry

Figure 3 shows the DSC nonisothermal melting curve for PLLA and its composites. As can be seen,

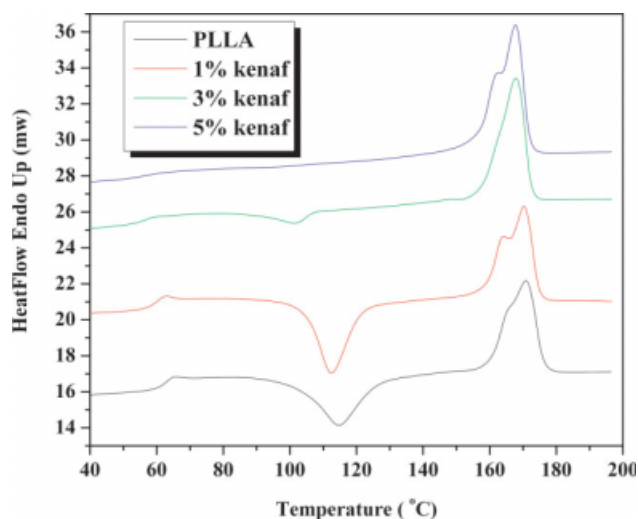


Figure 3 DSC curves of second heating of PLLA composites run at 10°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the glass transition temperature (T_g) occurred at ca. 59°C; this did not change for the composites as well. The cold crystallization peak temperature appear at ca. 114°C. As the %kenaf increased, the cold crystallization temperature dropped to 112 and 101, and finally at 5% by weight kenaf, the cold crystallization peak was eliminated. A decrease in the cold crystallization temperature indicates an enhancement in crystallinity. This enhancement is not apparent in the melting points, which remained unchanged. However, the enthalpy of melting showed an increase with the increasing %kenaf. The effectiveness of kenaf as a crystallization nucleator⁴⁴ is evident in the DSC plots of the cooling scans shown in

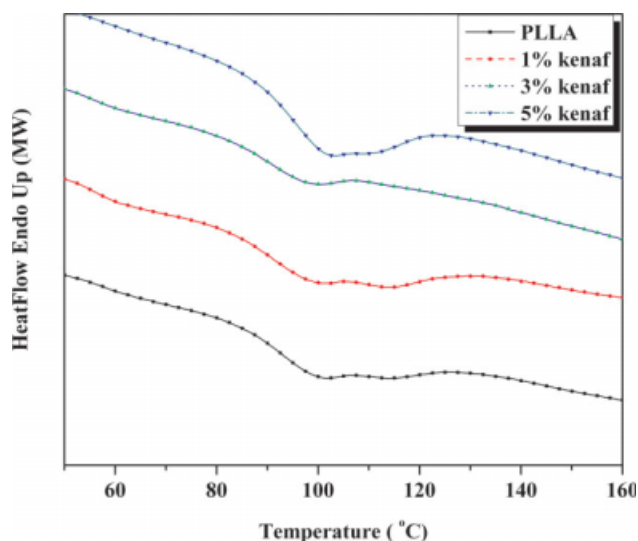


Figure 4 DSC cooling scans for PLLA and composites run at 5°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
DSC of Pure Kenaf and Its Composites

Sample	T_g (°C)	T_{cc} (°C)	T_c (°C)	T_m (°C)	ΔH_m (J/g)	ΔH_c (J/g)	X_c (%)
PLLA	59.1	114.7	99.3	168.1	45.5	-34.1	55.9
1% kenaf	59.3	112.8	100.3	169.5	51.9	-38.6	63.8
3% kenaf	59.1	101.4	105.9	168.2	51.4	-39.6	63.2
5% kenaf	-	-	104.5	168.0	48.1	-39.3	59.1

Figure 4. As can be seen, the crystallization temperature (T_c) for the PLLA occurred at ca. 100°C, but this temperature increases for the composites. Corresponding enthalpies of recrystallization also increased. As shown in Table II, the percent crystallinity increased with the increasing %kenaf in the composite. The value of the enthalpy of melting for an infinitely large PLLA crystal is taken as 81.3 J/g⁴⁴ value denoted as ΔH_f , when compared with our experimentally determined enthalpy ΔH_m , we calculated the percentage crystallinity (X_c)

$$\% \text{ Crystallinity} = \frac{\Delta H_m}{\Delta H_f} \times 100$$

Isothermal crystallization results support the determination that kenaf is an effective crystallite nucleator. Figure 5 and Table III shows the results for the PLLA and its composites. As the kenaf content increases, the time for recrystallization decreases from 5 to 3 min.

Dynamic mechanical analysis

Figure 6(a,b) shows the results of DMA illustrating the storage and loss modulus (E' and E'' , respec-

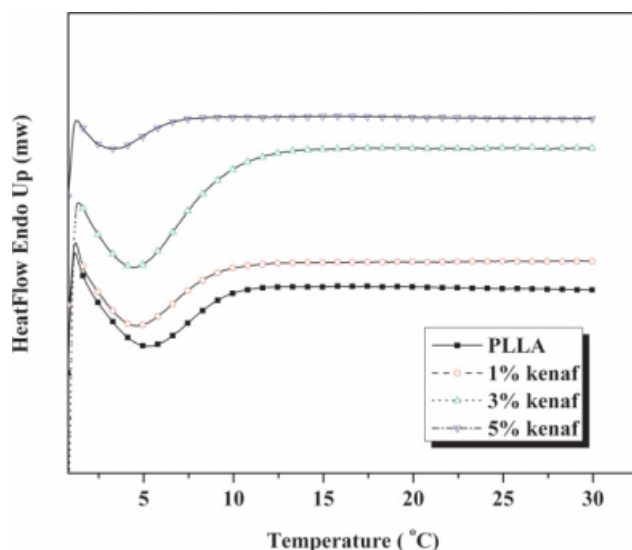


Figure 5 Isothermal melt-crystallization curves at 120°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

tively) for the PLLA, kenaf, and composites. The respective data were plotted against temperature. As seen in Figure 6(a), the storage modulus shows an increase in the E' value for the 1% kenaf when compared with the neat PLLA, and a further increase for the 3 and 5% kenaf when compared with the 1% kenaf was observed. The storage modulus is higher than the PLLA matrix. These results are due to the strong interaction that exists between the PLLA and kenaf, which indicates reinforcement potential. The glass transition, as indicated by the peaks in the E'' -temperature curve [Fig. 6(b)], shows a modest increase with increased kenaf concentration. The pure PLLA has a glass transition at 61°C, whereas the composites show peaks at 62, 63, 64°C for 1, 3, and 5% kenaf composites. Interestingly, the E' peak also increases with the concentration indicating a higher energy absorption capability in the composites when compared with the pure PLLA.

Fiber dispersion

The fiber dispersion of the composite samples was investigated by polarized optical microscopy. Figure 7 shows optical microscopy of the 1, 3, and 5% kenaf composites. The photographs of the molded sample were taken at room temperature. As seen in the figure, the dispersed nature of the kenaf in the PLLA matrix is clearly visible under the microscope in the presence of tiny strands indicating the fiber. With increased concentration of kenaf, high fiber bundling occurs.

Figure 8 shows the scanning electron microscopy (SEM) of kenaf and the composites. From the SEM studies of kenaf surface topography, we can obtain vital information regarding the level of interfacial adhesion that exists between kenaf and the matrix. In our studies and from the results of the SEM micrographs [Fig. 8 (a)], the kenaf morphology

TABLE III
Isothermal DSC Curves of Pure Kenaf and Its Composites at 120°C

Sample	t_c (min)
PLLA	5.05
1% kenaf	4.55
3% kenaf	4.46
5% kenaf	3.33

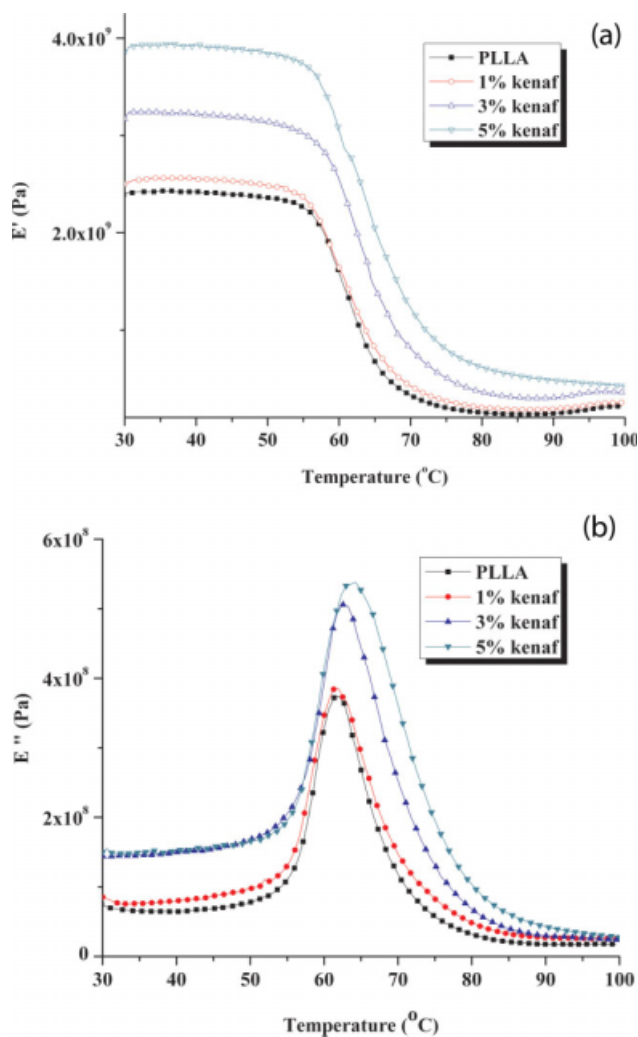


Figure 6 (a) Storage modulus of PLLA and kenaf composites showing enhanced glassy plateau moduli with kenaf concentration and (b) loss modulus as a function of temperature for PLLA and kenaf composites showing slight increase in glass transition and E'' maxima with kenaf concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

shows variations in diameter at a range of about 67–100 μm . Figure 8(b) shows fiber pull-out bundles of kenaf showing PLLA coating around the fiber bundle indicating good adhesion, whereas Figure 8(c–e) shows the SEM of 1, 3, and 5% kenaf composites, respectively, with fractured surface. The micrographs show fiber bundling with the matrix adhered to the fiber surface indicating enhanced fiber–matrix adhesion. In comparing these results with those of Kirwan et al.,⁴⁹ we note that hydrolysis at the fiber–matrix interface during processing is likely to result in a strong fiber–matrix interface. Similar to their results we note that the composites experienced 200°C for 3 min, which likely limited the drying of the kenaf fiber interface to the point of leading to a weak interface.

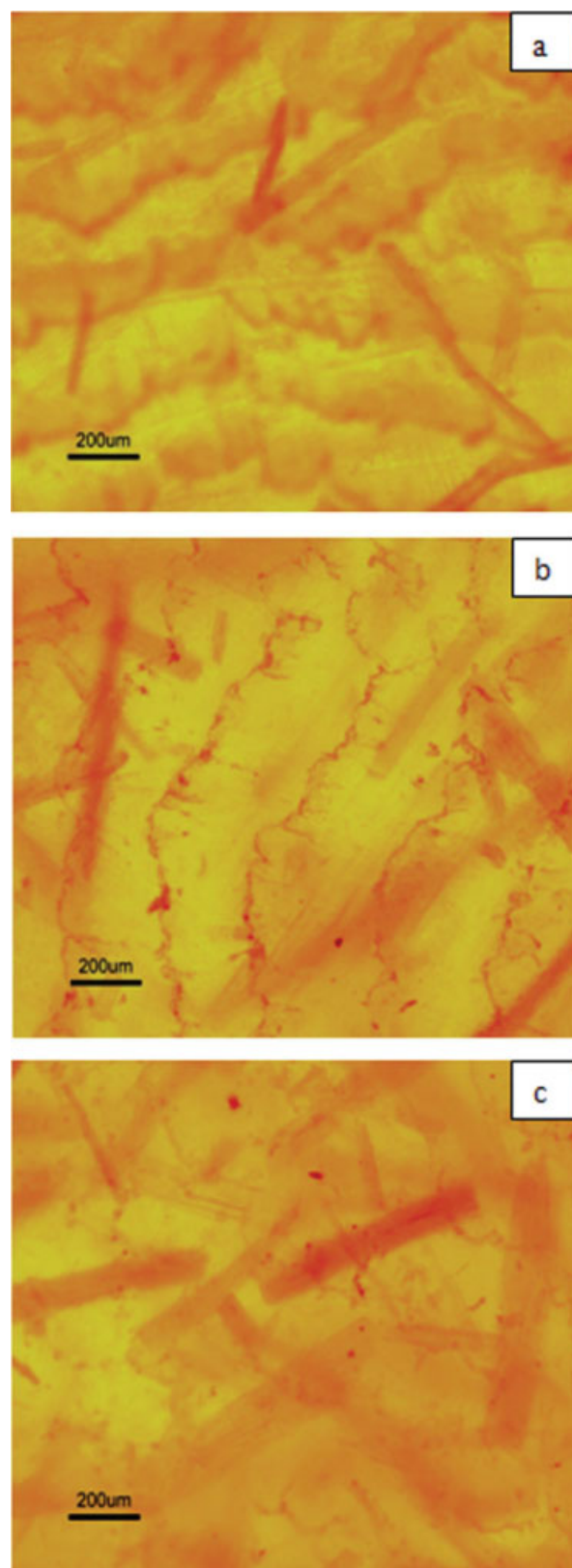


Figure 7 Optical microscopy of a, b, and c (1, 3, and 5% kenaf–PLLA composites), respectively, showing increased fiber bundling with concentration. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

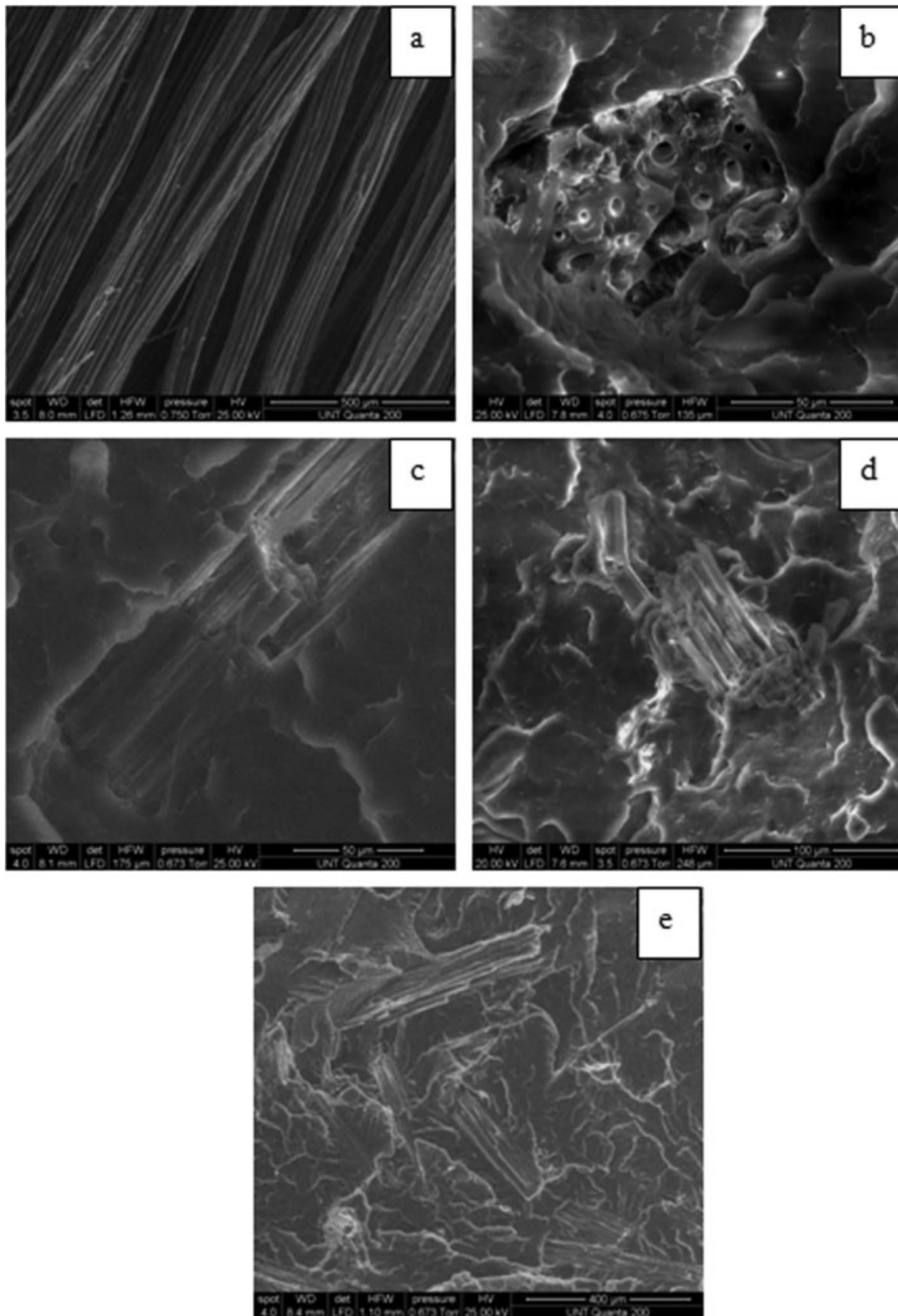


Figure 8 (a) Kenaf fibers prior to insertion in PLLA, (b) fiber pull-out bundles of kenaf showed PLLA coating around the fiber bundle indicating good adhesion, and (c–e) fracture surface SEM photomicrographs of the kenaf, 1, 3, and 5% kenaf, respectively.

CONCLUSIONS

This study establishes the feasibility of successfully fabricating PLLA–kenaf natural fiber composites with very low kenaf loading (1–5%). The enhancement in stiffness and crystallization rates when compared with the literature reported results in 10, 20, 30% kenaf-containing composites. The addition of kenaf to PLLA increased the storage modulus and the thermal properties, thereby improving the crystallization rate even at low kenaf loading. Increased fiber bundling occurred as the weight fraction of kenaf increased. Good fiber wetting by the PLLA was indicated by SEM. These results are significant as we compare the conventional-based filler with natural-based filler fibers. Similarly, we envision an increased movement to (or “development of”) safer, green, environmentally friendlier, and cheaper materials with a resulting improvement in mechanical properties.

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