

Kenaf Fiber/Poly(ϵ -caprolactone) Biocomposite with Enhanced Crystallization Rate and Mechanical Properties

Pengju Pan,¹ Bo Zhu,¹ Tungalag Dong,¹ Shin Serizawa,² Masatoshi Iji,² Yoshio Inoue¹

¹Department of Biomolecular Engineering, Tokyo Institute of Technology, Yokohama 226-8501, Japan

²Nano Electronics Research Laboratories, NEC Corporation, Ibaraki 305-8501, Japan

Received 16 August 2007; accepted 5 October 2007

DOI 10.1002/app.27470

Published online 3 December 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Plant-derived kenaf fiber (KF)-reinforced poly(ϵ -caprolactone) (PCL) biocomposites were successfully fabricated by the melt mixing technique. The crystallization behavior, morphology, and mechanical and dynamic mechanical properties of PCL/KF composites with various KF weight contents were investigated. The crystallization rate, tensile and storage moduli significantly improved as compared to the virgin polymer. The half times of PCL/KF composite (20 wt % fiber content) in isothermal crystallization at 40°C and 45°C reduced to 31.6% and 42.0% of the neat PCL, respectively. Moreover, the tensile and storage modulus of

the composite are improved by 146% and 223%, respectively, by the reinforcement with 30% KF. The morphology evaluated by SEM indicates good dispersion and adhesion between KF and PCL. Overall, these findings reveal that KF can be a potential reinforcement for the biodegradable polymer composites owing to its good ability to improve the mechanical properties as well as crystallization rate. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3512–3519, 2008

Key words: poly(ϵ -caprolactone); kenaf fiber; crystallization behavior; mechanical properties

INTRODUCTION

Polymer composites reinforced with plant-derived natural fiber, emerging as one kind of ecologically friendly materials, have attracted increasing attention from the standpoint of protection of the natural environments in recent years.^{1–3} Natural fibers have many advantages, for example low weight, renewability, biodegradability, low cost, low density, acceptable specific mechanical properties, ease of separation, and carbon dioxide sequestration,³ as compared to the traditional reinforcing fibers. Therefore, they have been looked upon as an eco-friendly and economical alternative to glass fibers. Natural fiber-reinforced composites are making inroads in many application areas including automobiles, housing, packaging, and electronic products.² The composites from natural fibers and conventional polyolefins have been studied extensively.⁴ Nevertheless, the vast use of the fossil-resource-based polymers has induced many environmental problems. Therefore, there is an increasing interest in developing eco-friendly green composites or biocomposites by reinforcing the biocompatible and biodegradable plastics with the plant-derived natural fibers.^{5–21}

Recently, aliphatic polyesters have attracted much research interest due to their biodegradability and biocompatibility.²² Poly(ϵ -caprolactone) (PCL) is one

of the typical aliphatic polyesters, and it is fully biodegradable, biocompatible, and nontoxic to living organisms.²³ Also, PCL has good resistance to water, oil, solvent, and chlorine. The unique properties of PCL render its potential in biomedical fields, and it has been used in the development of controlled drug delivery systems, as well as in surgical sutures and other resorbable fixation devices.^{14,24} On the other hand, kenaf has recently been gaining a lot of attention as biomass-based additive, and it is well known as a cellulosic source with ecological and economical advantages, exhibiting low density, nonabrasiveness during processing, high specific mechanical properties, and biodegradability.¹ Furthermore, it has been reported that kenaf has a significantly high ability to accumulate carbon dioxide, and its photosynthesis speed is at least three times higher than that of the usual plants, and it can absorb carbon dioxide 1.4 times its own weight.²⁵ Kenaf has been mainly used as textiles and paper for a long time, and recently composites of kenaf fiber (KF) and plastics have been studied owing to their promising properties.^{12,13,26,27}

Among the family of environmentally friendly biodegradable polymers, PCL has a good flexibility characterized by high fracture strain. However, PCL has a disadvantage in low thermal resistance and heat deflection temperature because its melting point is only about 60°C. Moreover, the modulus of PCL is very low, typically 200–400 MPa. These drawbacks have limited its commercial application to some extent. Therefore, it is considered that reinforcing

Correspondence to: Y. Inoue (inoue.y.af@m.titech.ac.jp).

PCL with kenaf fibers is possibly an efficient way to enhance its mechanical and thermal properties, as well as to decrease the cost of PCL-based materials.

This article presents the fabrication of the biodegradable composite from kenaf fiber and PCL by the melt mixing technique. Also, the effect of fiber weight contents on the crystallization behavior and mechanical and dynamical mechanical thermal properties of the composites will be investigated. Moreover, to study the influence of KF on the crystallization process of PCL, the isothermal crystallization kinetics of KF reinforced PCL composite with different KF contents is analyzed. In addition, the morphology of the composite is also evaluated by fractographic analysis with scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

PCL ($M_n = 179,000$, $M_w/M_n = 1.53$), supplied by the courtesy of Daicel Chemical, Japan, was used as received. Kenaf fiber (average length = 3 mm, average diameter = 25 μm , specific gravity = 1.48) was kindly supplied by the Nano Electronics Research Laboratories, NEC, Ibaraki, Japan.

Composite fabrication

Prior to processing, PCL and KF were dried under vacuum at 40°C for 48 h. The composites were fabricated by extruding the polymer and fibers after mixed in a single screw machine (Imoto Machinery, Kyoto, Japan) with a speed of 80 rpm at 100°C for 5 min. To obtain the desired film samples for various measurements and analysis, the composite was hot-pressed with a pressure of 10 MPa after melting at 100°C for 2 min, and then the hot-pressed sample was quenched to 25°C under room conditions. The samples are denoted as PCL/KF (x/y), where x and y represent the weight percentages of PCL and KF, respectively.

Measurements

Differential scanning calorimeter (DSC)

The crystallization behavior of the neat PCL and PCL/KF composites were analyzed by a Pyris Diamond DSC instrument (Perkin-Elmer Japan, Tokyo, Japan). The scales of temperature and heat flow at different heating rates were calibrated by using an indium standard. The samples were weighted and sealed in an aluminum pan. In the nonisothermal melt-crystallization, the melted samples were cooled to -50°C at a cooling rate of 10°C/min after melted at 100°C for 2 min. Subsequently, the crystallized

sample was heated to 100°C at 10°C/min to evaluate the melting behavior. In the isothermal melt-crystallization, the melted sample was cooled at a rate of 100°C/min to the desired crystallization temperature (T_c) after melted in the same conditions, and allowed to crystallize.

Polarizing optical microscopy (POM)

The spherulite morphology of the pure PCL and its composites was observed on an Olympus BX90 polarizing optical microscopy (Olympus, Tokyo, Japan) equipped with a digital camera. The sample was placed between a microscope glass slide and a cover slip, and the temperature was controlled by a Mettler FP82 HT hot stage. The sample was at first heated to 100°C and held for 2 min at this temperature, and then it was quenched to 45°C for the isothermal crystallization. The spherulite morphology was recorded by taking microphotographs after the crystallization finished.

Tensile test

Tensile properties were investigated with the aid of Shimadzu (Tokyo, Japan) EZ test machine at a cross-head speed of 5 mm/min. All the samples have a gauge length of 22.25 mm, a gauge width of 4.76 mm, and a thickness of about 0.65 mm. Each value of mechanical properties reported here was an average of seven specimens.

Dynamic mechanical thermal analysis (DMTA)

The storage modulus (E'), loss modulus (E''), and loss factor ($\tan \delta$) of the pure PCL and the composites were measured as a function of temperature (-70°C to 80°C) by a DMS210 (Seiko Instrument, Japan) equipped with SSC5300 controller at a frequency of 5 Hz and a constant heating rate of 2°C/min. The samples were thin rectangular strips with dimensions of about 30 × 10 × 0.65 mm³.

Scanning electron microscopy (SEM)

A JEOL scanning electron microscope (model JSM-5200) was used to evaluate the morphology of fractured surfaces of pure PCL and the composites. The samples were sputter-coated with gold particles up to a thickness of about 10 nm before the surface characterization.

RESULTS AND DISCUSSION

Nonisothermal crystallization

The nonisothermal melt-crystallization at 10°C/min and the subsequent melting at a heating rate of

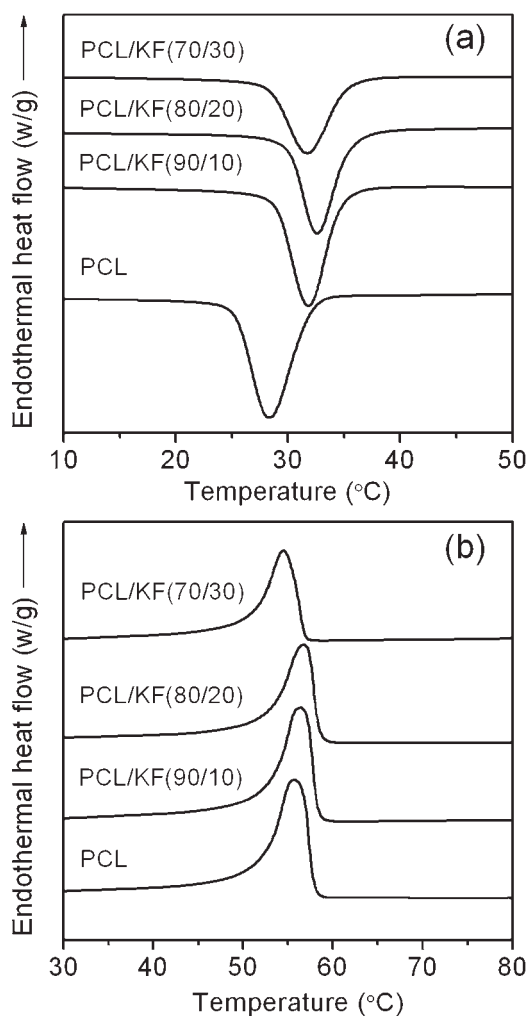


Figure 1 DSC curves of (a) nonisothermal melt-crystallization at a cooling rate of 10°C/min and (b) subsequent heating scanning at 10°C/min for PCL and its composites.

10°C/min of the neat PCL and PCL/KF composites are presented in Figure 1(a,b), respectively. The thermal properties, including the crystallization temperature (T_c), melting temperature (T_m), crystallization enthalpy (ΔH_c), melting enthalpy (ΔH_m), and the degree of crystallinity ($X_c\%$) obtained from the DSC analysis are summarized in Table I. The degree of crystallinity ($X_c\%$) was calculated from $\Delta H_m/\Delta H_m^0$, where ΔH_m^0 is the melting enthalpy expected for a polymer with 100% crystallinity, assuming that the heat of fusion ΔH_m^0 of PCL is 166 J/g.²⁸ As shown in Figure 1(a) and Table I, a marked increase of the crystallization peak temperature can be observed when small amount of fibers are incorporated in the PCL matrix. However, the crystallization peak shifts to lower temperature as the weight percent of KF is more than 20%, which signifies that the crystallization rate of PCL is enhanced firstly and then decreased with the increase of KF content.

Generally, the crystallization process of polymers includes two stages, that is, the nucleation and the

crystal growth. A primary nucleation process may be either homogenous or heterogeneous.²⁹ Homogeneous nucleation occurs sporadically in the melt by thermal fluctuation, whereas the heterogeneous one starts on the surface of microscopic insoluble particles dispersed randomly in the polymer melt, such as impurities or nucleating agents arbitrarily added. Whenever there is nucleating agent present in a polymer melt, it can affect the free energy balance for nucleation, usually so as to increase the nucleation rate and prevent homogeneous nucleation. For heterogeneous nucleation, due to a much reduced surface energy, the nucleation rate can increase by several orders of magnitude. Therefore, the effect of homogeneous nucleation can be totally smeared by heterogeneous nucleation.²⁹

As for polymeric composite system, the crystallization process becomes more complicated, and it is chiefly controlled by two factors.^{8,30} First, the additives, which have a nucleating effect on the crystallization, enhance the crystallization and so they have a positive influence on the degree of crystallinity. Second, the additives, which have a negative effect on the crystallization, hinder the migration and diffusion of polymeric molecular chains to the surface of the growing face of the polymer crystal in the composites, leading to a decrease in the crystallization rate. Due to the nucleation effect of KF, the crystallization rate of PCL was improved dramatically in the presence of small amount of KF. Nevertheless, the T_c value of the PCL/KF composites decreases with the increase of KF content when the weight percent of KF is larger than 20%, owing to the hindrance of polymer diffusion by KF. Furthermore, as shown in Table I, when the KF content is larger than 10 wt %, the degree of crystallinity of the composites reduces as KF content increases, which indicates that the KF fibers hinder the migration and diffusion of molecular chains to the surface of the nucleus in the composites. Similar results were also observed for the PLLA/talc (70/30) composite.⁹

Isothermal crystallization

The isothermal crystallization behavior of neat PCL and its composites with KF at 40°C and 45°C was also investigated by DSC, and the results are depicted in Figure 2(a,b), respectively. Clearly, the isothermal crystallization of composites is much faster than that of the pure PCL, confirming that the crystallization rate is effectively enhanced with the incorporation of KF. Moreover, crystallization kinetics was analyzed from the isothermal DSC results. The isothermal heat flow curve was integrated to determine the degree of crystallinity of the samples as a function of crystallization time. The relative crystallinity (X_t) at any given time was calcu-

TABLE I
Crystallization and Melting Behavior of Neat PCL and PCL/KF Composites

Sample	T_c (°C)	ΔH_c (J/g PCL)	T_m (°C)	ΔH_m (J/g PCL)	X_c (%)
PCL	28.3	-52.1	55.6	58.1	35.0
PCL/KF(90/10)	31.8	-55.8	56.4	59.9	36.1
PCL/KF(80/20)	32.6	-51.7	56.8	57.1	34.4
PCL/KF(70/30)	31.6	-50.1	54.5	55.9	33.7

lated from the integrated area of the DSC curve from $t = 0$ to $t = t$ divided by the integrated area of the whole heat flow curve.

The isothermal bulk crystallization kinetics was analyzed by the Avrami equation:³¹

$$X_t = 1 - \exp(-kt^n) \quad (1)$$

where n is an index related to the dimensional growth and the way of formation of primary nuclei, and k is the overall rate constant associated with both the nucleation and growth contributions. The linear form of eq. (1) is given as eq. (2):

$$\log[-\ln(1 - X_t)] = \log k + n \log t \quad (2)$$

The values of n and k are obtained by plotting $\log[-\ln(1 - X_t)]$ against $\log t$. Meanwhile, the crystallization half-time $t_{1/2}$, defined as the time when the crystallinity reaches 50%, can be determined from the kinetics parameters measured according to the following equation:

$$t_{1/2} = \left(\frac{\ln 2}{k}\right)^{1/n} \quad (3)$$

The crystallization parameters k , n , and $t_{1/2}$ of the materials crystallized at 40°C and 45°C are presented in Table II. Because of the heterogeneous nucleation effect of KF, $t_{1/2}$ reduces and Avrami rate constant k increases markedly with the addition of KF. On the other hand, due to the hindrance of polymer diffusion by KF, when the weight percent of KF is more than 20%, $t_{1/2}$ increases as the increase of KF content. With the incorporation of 20 wt % KF, the $t_{1/2}$ of the composite crystallized at 40°C and 45°C reduces to 31.6% and 42.0% of the neat PCL, respectively. Due to the more ordered crystal produced at higher T_c , ΔH_c of the pure PCL and its composites crystallized at 45°C is larger, compared with those crystallized at 40°C.

In addition, the spherulite morphology of pure PCL and PCL/KF (90/10) composite isothermally crystallized at 45°C was observed by POM, and the results are shown in Figure 3. Obviously, the nucleation density increases significantly and the spherulite size drops drastically with the addition of KF, con-

firmed that the KF can greatly accelerate the nucleation during the crystallization of PCL.

Tensile properties

The tensile properties of the neat PCL and its composites were evaluated, and their stress-strain curves are shown in Figure 4. Figure 5(a-c) presents the tensile strength, modulus, and fracture strain of pure PCL and its composites with various KF contents,

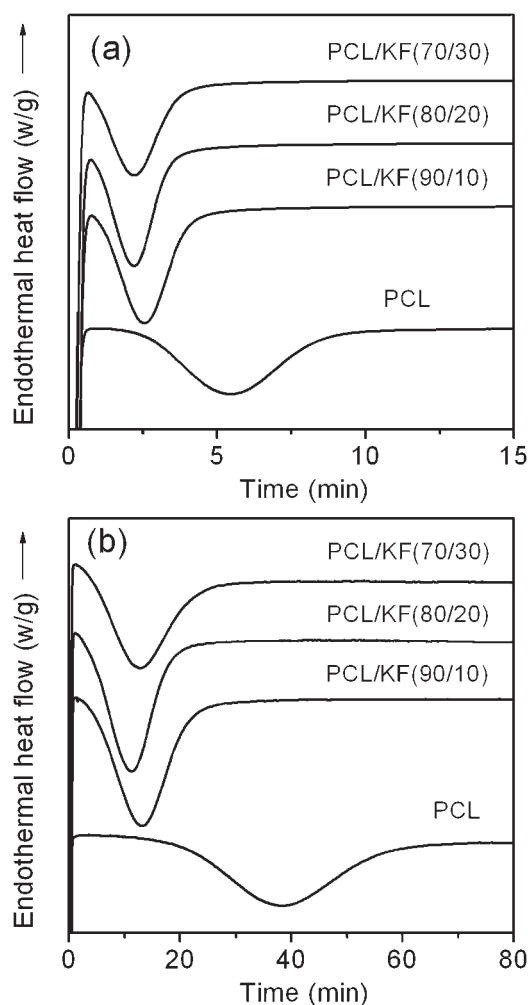


Figure 2 DSC curves of PCL and PCL/KF composites isothermally melt-crystallized at (a) 40°C and (b) 45°C.

TABLE II
Kinetic Parameters of Neat PCL and Its Composites Isothermally Melt-Crystallized at 40°C and 45°C

Sample	$T_c = 40^\circ\text{C}$				$T_c = 45^\circ\text{C}$			
	$t_{1/2}$ (min)	ΔH_c (J/g PCL)	n	$\log(k)$	$t_{1/2}$ (min)	ΔH_c (J/g PCL)	n	$\log(k)$
PCL	4.74	-49.9	2.88	-2.40	22.94	-52.7	2.81	-3.99
PCL/KF(90/10)	1.86	-49.2	2.58	-0.85	10.96	-50.9	2.74	-3.02
PCL/KF(80/20)	1.50	-48.4	2.49	-0.60	9.64	-50.1	2.56	-2.72
PCL/KF(70/30)	1.63	-47.9	2.38	-0.67	10.30	-49.5	2.40	-2.59

respectively. Mechanical properties of a short-fiber-reinforced composite depend on many factors, such as fiber content, fiber aspect ratio, fiber-matrix adhesion, and fiber orientation.¹ Besides, tensile strength is more dependent on the matrix and the compatibility between fiber and the matrix, while tensile modulus is more influenced by the fiber impregnation and fiber ratio.⁵ The pure PCL film has a yield strength of 13.8 MPa, a modulus of 244 MPa, and a fracture strain of 894.7%. As shown in Figure 5(a), the yield strength of the composites increases from 13.8 MPa (neat PCL) to 14.2 MPa with addition of 15 wt % KF. This can be explained by the fact that the filler is well wetted by the polymer matrix at low fiber content, which results in an efficient stress transfer from the PCL matrix to the fiber. Nevertheless, there is a decrease in the yield strength of PCL/KF composites afterward when the KF content is larger than 20 wt %. A possible explanation of this can be the agglomeration of KF fibers.

As depicted in Figure 5(b), the incorporation of KF improves the modulus of PCL significantly, signifying that the stress transfers from the PCL matrix to the stiffer fiber occurred. The tensile modulus of PCL/KF composite is improved by 146% at 30 wt % fiber content, 601 MPa, as compared with the neat PCL, 244 MPa. However, the fracture strain of the composites shows decrease with the increase of KF content, as shown in Figure 5(c). Generally, the addi-

tion of high fiber content increases the probability of fiber agglomeration, which creates regions of stress concentrations that require less energy to elongate the crack propagation.⁹ During tensile deformation, the stress can not transfer efficiently nearby these flaws, resulting in the failure of the specimen. On the other hand, in the composite all the elongation arises from the polymer since the KF is more rigid relative to the flexible PCL matrix. Hence, increasing the amount of filler decreases the amount of polymer available for elongation, and thus decreases the failure strain.

Dynamic mechanical thermal analysis

Figure 6(a,b) presents the dynamic storage modulus (E') and $\tan \delta$ of the pure PCL and PCL/KF composites, as a function of temperature, respectively. As seen in Figure 6(a), the storage modulus of PCL/KF composites is higher than that of the unfilled PCL matrix, indicating that the stress transfers from the matrix to the kenaf fiber. The E' value of the PCL/KF composite containing 30 wt % KF at 20°C increases by 223%, as compared to that of the neat PCL. Besides, the E' values decrease for both the pure PCL and the composites with increasing temperature, due to the softening of the polymer matrix.

As shown in Figure 6(b), the height of the $\tan \delta$ peak decreases with the presence of kenaf fiber. One

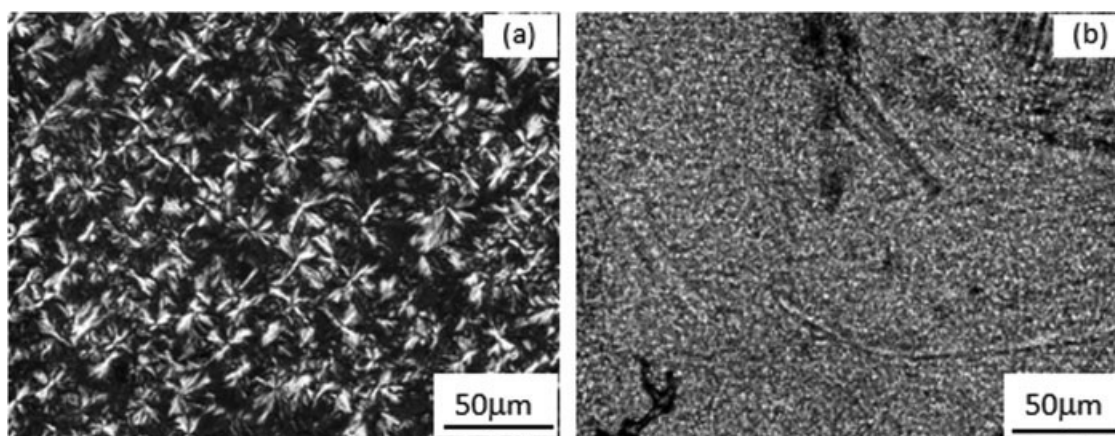


Figure 3 Optical micrographs of (a) neat PCL and (b) PCL/KF (90/10) composite isothermally melt-crystallized at 45°C.

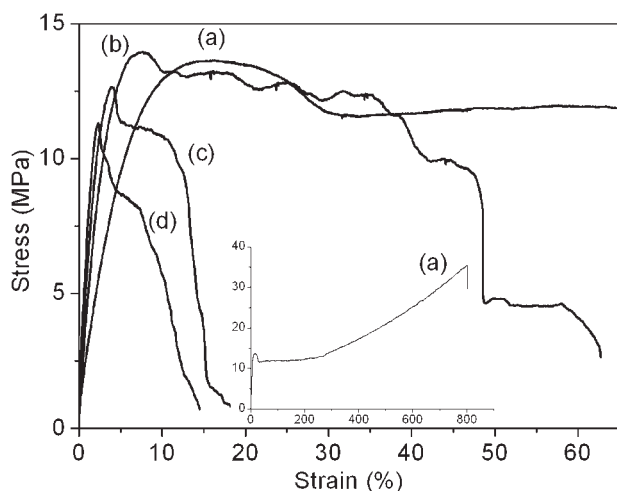


Figure 4 Tensile stress-strain curves of pure PCL and PCL/KF composites: (plot a) neat PCL, (plot b) PCL/KF (90/10), (plot c) PCL/KF (80/20), (plot d) PCL/KF (70/30).

possible explanation is that there is no restriction to the chain motion for the neat PCL, which results in a sharp and intense $\tan \delta$ peak. However, the presence of KF hinders the chain mobility, leading to the reduction of sharpness and height of the $\tan \delta$ peak.^{9,18} Furthermore, the damping in the transition region measures the imperfections in the elasticity and much of the energy used to deform a material during DMTA testing is dissipated directly as the heat.³² Therefore, with the presence of KF the molecular mobility of the materials decreases and the mechanical loss to overcome intermolecular chain friction is reduced. It has been also reported that the reduction in $\tan \delta$ also denotes an improvement in the hysteresis of the system and a reduction in the internal friction.³³

Morphology of composites

The morphology of the kenaf fiber was investigated by SEM, as shown in Figure 7(a,b). The figure reveals large-scale variations in the aspect ratio, diameter, and the morphology among KF samples. It is observed that the diameters of the fibers are ranging from 5 to 50 μm , and the surface of the fibers is rough with the adhesion of some smaller kenaf fibers and kenaf particles. These variations are probably on account of the different sources and the processing history of the fibers.

Furthermore, the morphology and fracture mechanism of the materials were evaluated by SEM. The SEM micrographs of the tensile fractured surfaces of the neat PCL and PCL/KF (70/30) composite are presented in Figure 7. As shown in Figure 7(c), the fracture surface of pure PCL is regular. Besides, the craze and fibril are observed in the surface, signifi-

ing that the fracture of PCL is in the "ductile" manner.³⁴ As depicted in Figure 7(d,e), the surface of KF is smooth in the composite, and the fibrils linking the fiber surface to the matrix can be observed. Fur-

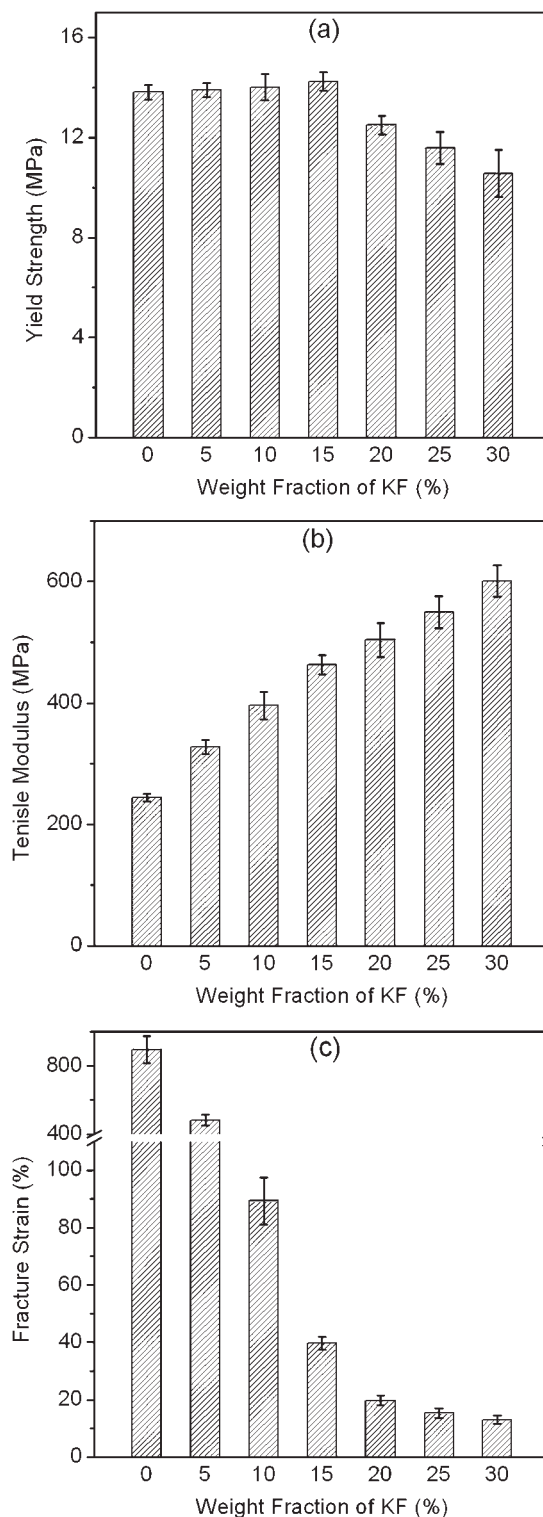


Figure 5 (a) Yield strength, (b) tensile modulus, and (c) fracture strain of neat PCL and PCL/KF composites with various KF contents.

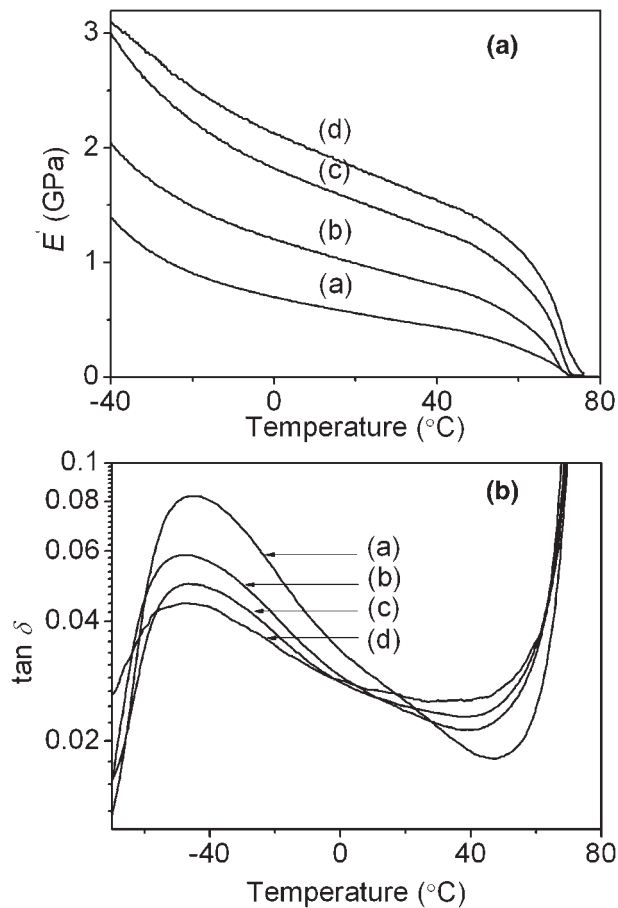


Figure 6 Temperature dependence of (a) storage modulus and (b) $\tan \delta$ of neat PCL and PCL/KF composites: (plot a) neat PCL, (plot b) PCL/KF (90/10), (plot c) PCL/KF (80/20), (plot d) PCL/KF (70/30).

thermore, it can be seen from Figure 7(f) that the fiber is obviously covered by a thin layer of PCL matrix. These all suggest that the fiber and polymer matrix are in good adhesion, which leads to better stress transfer between the matrix and the reinforcing fibers.

On the other hand, as seen in Figure 7(d), the fracture surface is irregular and the fiber pull-out is prevailed over fiber fracture. In addition, as shown Figure 7(f), the debonding of the PCL matrix and fiber is observed. These signify that the interface interaction between the fibers and polymer matrix can be further improved. The mechanical properties of composite greatly depend on the state of the filler dispersion and the strength of the interfacial interaction. According to Dong et al.,^{35,36} the interfacial interaction between bulk polymer and nucleating agent has a significant influence on the crystallization rate. Therefore, it is considered that the mechanical properties as well as the crystallization behavior can be further optimized through the use of compatibilizers or coupling agents to improve the interface interaction and the compatibility between the fiber and PCL matrix.

CONCLUSIONS

Bio-based filler reinforced polymer composite from PCL and kenaf fiber (KF) was fabricated, and its physical properties, especially crystallization behavior and mechanical properties were investigated. The incorporation of KF enhances the crystallization rate

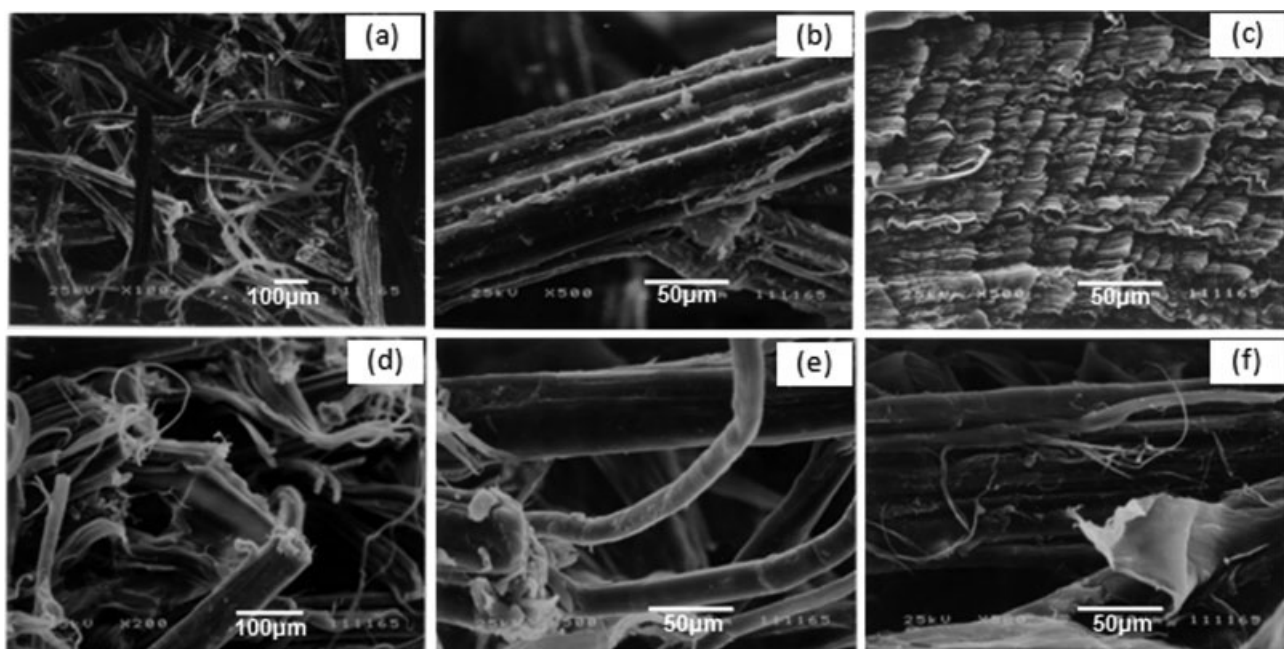


Figure 7 SEM micrographs of kenaf fiber: (a) $\times 100$ and (b) $\times 500$; freshly fractured surface of (c) pure PCL and the PCL/KF (70/30) composites: (d–f).

of PCL considerably. Moreover, the tensile modulus as well as the storage modulus is significantly improved by the reinforcement of KF. SEM analysis shows that KF and PCL matrix are in good adhesion, but it also reveals that the interfacial interaction between the fiber and polymer can be further improved. Hence, the use of natural fiber, as reinforcements in biodegradable polymer, is an efficient way to improve and optimize the properties of the biodegradable polymer. Moreover, it provides a sustainable alternative to conventional thermoplastic-based materials, and also gives an interesting alternative for production of low cost and ecologically friendly composites.

References

1. Saheb, D. N.; Jog, J. P. *Adv Polym Technol* 1999, 18, 351.
2. Bledzki, A. K.; Gassan, J. *Prog Polym Sci* 1999, 24, 221.
3. Mohanty, A. K.; Misra, M.; Drzal, L. T. *J Polym Environ* 2002, 10, 19.
4. Sanadi, A. R.; Caufield, D. F.; Jacobson, R. E.; Rowell, R. M. *Ind Eng Chem Res* 1995, 34, 1889.
5. Bhardwaj, R.; Monahy, A. K.; Drzal, L. T.; Pourboghra, F.; Misra, M. *Biomacromolecules* 2006, 7, 2044.
6. Pan, P.; Zhu, B.; Kai, W.; Serizawa, S.; Iji, M.; Inoue, Y. *J Appl Polym Sci* 2007, 105, 151.
7. Yang, A.; Wu, R. *J Appl Polym Sci* 2002, 84, 486.
8. Huda, M. S.; Drzal, L. T.; Misra, M.; Mohanty, A. K.; Williams, K.; Mielewski, D. F. *Ind Eng Chem Res* 2005, 44, 5593.
9. Huda, M. S.; Mohanty, A. K.; Drzal, L. T.; Schut, E.; Misra, M. *J Mater Sci* 2005, 40, 4221.
10. Keller, A. *Compos Sci Technol* 2003, 63, 1307.
11. Park, J. M.; Kim, D. S.; Kim, S. R. *Compos Sci Technol* 2003, 63, 403.
12. Serizawa, S.; Inoue, K.; Iji, M. *J Appl Polym Sci* 2006, 100, 618.
13. Nishino, T.; Hirao, K.; Kotera, M.; Nakamae, K.; Inagaki, H. *Compos Sci Technol* 2003, 63, 1281.
14. Jiang, G.; Evans, M. E.; Jones, I. A.; Rudd, C. D.; Scotchford, C. A.; Walker, G. S. *Biomaterials* 2005, 26, 2281.
15. Wong, S.; Shanks, R.; Hodzic, A. *Compos Sci Technol* 2004, 64, 1321.
16. Plackett, D.; Andersen, T. L.; Pedersen, W. B.; Nielsen, L. *Compos Sci Technol* 2003, 63, 1287.
17. Chen, B.; Sun, K.; Ren, T. *Eur Polym J* 2005, 41, 453.
18. Pothan, L. A.; Oommen, Z.; Thomas, S. *Compos Sci Technol* 2003, 63, 283.
19. Shanks, R. A.; Hodzic, A.; Ridderhof, D. *J Appl Polym Sci* 2006, 101, 3620.
20. Shin, Y. F.; Lee, W. C.; Jeng, R. J.; Huang, C. M. *J Appl Polym Sci* 2006, 99, 188.
21. Kori, Y.; Kitagawa, K.; Hamada, H. *J Appl Polym Sci* 2005, 98, 603.
22. Inoue, Y.; Yoshie, N. *Prog Polym Sci* 1992, 17, 571.
23. Sung, G. A.; Chang, G. C. *Macromol Rapid Commun* 2004, 25, 618.
24. Buffa, F.; Hu, H.; Resasco, D. E. *Macromolecules* 2005, 38, 8258.
25. Lam, T.; Hori, K.; Iiyama, K. *J Wood Sci* 2003, 49, 255.
26. Wambua, P.; Ivens, J.; Verpoest, I. *Compos Sci Technol* 2003, 63, 1259.
27. Rouison, D.; Sain, M.; Couturier, M. *Compos Sci Technol* 2004, 64, 629.
28. El-Hadi, A.; Schinable, R.; Staube, E.; Mueller, A.; Henning, S. *Polym Test* 2002, 21, 665.
29. Hoffman, J. D. *Polymer* 1983, 24, 3.
30. Albano, C.; Papa, J.; Ichazo, M.; Gonzalez, J.; Ustariz, C. *Compos Struct* 2003, 62, 291.
31. Avrami, M. *J Chem Phys* 1941, 9, 177.
32. Bleach, N. C.; Nazhat, S. N.; Tanner, K. E.; Kellomaki, M.; Tormala, P. *Biomaterials* 2002, 23, 1579.
33. Fay, J. J.; Murphy, C. J.; Thomas, D. A.; Sperling, L. H. *Polym Eng Sci* 1991, 31, 1731.
34. Lapique, F.; Meakin, P.; Feder, J.; Jossang, T. *J Appl Polym Sci* 2000, 77, 2370.
35. Dong, T.; He, Y.; Zhu, B.; Shin, K. M.; Inoue, Y. *Macromolecules* 2005, 38, 7736.
36. Dong, T.; Kai, W.; Pan, P.; Cao, A.; Inoue, Y. *Macromolecules* 2007, 40, 7244.