

## Research Article

# Fracture Toughness Improvement of Poly(lactic acid) Reinforced with Poly( $\epsilon$ -caprolactone) and Surface-Modified Silicon Carbide

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In this study, bio-based poly(lactic acid) (PLA)/polycaprolactone (PCL) blends and PLA/PCL/silicon carbide (SiC) composites were prepared using a solution blending method. The surface of the SiC whiskers was modified using a silane coupling agent. The effects of the PCL and SiC contents on the flexural properties, fracture toughness, morphology of PLA/PCL blends, and PLA/PCL/SiC composites were investigated using several techniques. Both the fracture toughness and flexural strength of PLA increased by the introduction of PCL and were further improved by the formation of SiC whiskers. Fracture surfaces were observed by scanning electron microscopy, which showed that the use of PCL as a reinforcing agent induces plastic deformation in the PLA/PCL blends. The SiC whiskers absorbed external energy because of their good interfacial adhesion with the PLA matrix and through SiC-PLA debonding in the PLA/PCL/SiC composites.

## 1. Introduction

Poly(lactic acid) (PLA) is a biodegradable, bioabsorbable, and renewable thermoplastic polyester that can be obtained by the ring-opening polymerization of lactide [1–4]. PLA is perhaps the most useful and promising biopolymer because of its abundance, outstanding mechanical performance, and high chemical resistance. PLA has been used in a variety of applications in the automotive, medical, and food industries [5–7]. Despite its high tensile modulus and strength, PLA has poor toughness due to its stiff backbone chain, which limits its use in many fields. Thus, blending with a ductile biodegradable polymer and addition of inorganic fillers has previously been reported as methods to improve the toughness of PLA [8–10].

Polycaprolactone (PCL) is a petroleum-derived, semi-crystalline, and linear aliphatic polyester that is biodegradable and biocompatible. PCL has high flexibility, with

a low glass transition temperature and melting point. The toughness of PLA is improved when blended with PCL, which acts as a plasticizer, and the resulting blend is likely to retain its biodegradability [11–14].

Several researchers have reported the preparation of biodegradable PLA/PCL blends with outstanding mechanical and physical properties. The morphological and thermal tests reported by Patrício and Bártolo indicated that PLA and PCL are immiscible polymers, and rheological tests showed that PLA/PCL blends prepared by a physical blending process have good thermal stability [15]. Tsuji et al. reported that the biodegradability of PLA/PCL blends prepared by melt blending could be manipulated by tuning the conditions of melt blending or the sizes and morphologies of the PLA- and PCL-rich domains [16]. Chen et al. demonstrated improved tensile extensibility of PLA/PCL blends [17]. Their results suggested that the combination of solution-coagulation and crosslinking

resulted in a good, stable dispersion of PCL in the PLA matrix, improving its tensile toughness. Harada et al. studied the reactive compatibilization of PLA/PCL blends with the addition of reactive processing agents [18]. The impact strength of the blends increased considerably at 20 wt.% PCL. Morphological characterization showed that the PLA/PCL blends form sea-island structures, in which PLA adopts a continuous phase and PCL a dispersed phase induced by the reactive processes. Urquijo et al. studied the effect of melt processing conditions on phase structure, morphology, and mechanical properties of PLA/PCL blends [19]. Injection-molded specimens were ductile and broke at elongation values close to 140%. The elongation at break of the hot-pressed specimens was lower, likely due to the large size of the PCL particles. However, PCL, being softer, decreased the tensile strength of the PLA/PCL blends in the high impact strength region (>30 wt.% PCL).

Generally, the addition of inorganic fillers to a polymer matrix can improve its mechanical properties, such as toughness, stiffness, and heat distortion temperature. Silicon carbide (SiC) is a ceramic material with good erosion and oxidation resistance, high strength, excellent thermal stability, and a high melting point. SiC is widely used in many industrial applications, such as the production of structural and functional materials [20, 21]. Dorigato et al. [22] studied the effect of various kinds of fumed silica nanoparticles on the mechanical performance of PLA. Their results showed that the fracture toughness of PLA was significantly increased with the addition of functionalized silica nanoparticles. Rashmi et al. [23] investigated the toughening of PLA with polyamide 11 and halloysite nanotubes. The impact strength of PLA was increased by the introduction of the polyamide 11 and further improved significantly with the addition of halloysite nanotubes.

In this study, bio-based PLA/PCL blends and PLA/PCL/SiC composites with low PCL and SiC contents were prepared by a solution blending method. The effects of the PCL and SiC contents on the mechanical properties, fracture toughness, and morphology of the prepared PLA/PCL blends and PLA/PCL/SiC composites were investigated by mechanical testing and scanning electron microscopy (SEM).

## 2. Experimental

**2.1. Materials.** PLA pellets (Lehua Plastic Material Firm, Dongguan, China) were obtained with a weight-average molecular weight of 200,000 g/mol. PCL with a glass transition temperature of  $-60^{\circ}\text{C}$  and melting point range of  $59\text{--}64^{\circ}\text{C}$  was obtained from Mingyuanxinzhong Co., Ltd. (Dongguan, China). SiC whiskers were supplied by Xuzhou Hongwu Nano Materials Inc., (China). The average diameter of the SiC whiskers was  $0.05\text{--}2.50\ \mu\text{m}$ , and the length-to-diameter ratio was  $\geq 20$ . The silane coupling agent KH570 was supplied by Xingfeilong Chem. Co., Jinan (China). Dichloromethane ( $\text{CH}_2\text{Cl}_2$ , YongDa Chemical Reagent Co., Tianjin, China) was used as the solvent.

**2.2. Surface Modification of the SiC Whiskers.** The silane coupling agent (1 g), ethanol (100 mL), and deionized water (10 g) were mixed in a 250 mL glass flask. The pH of the coupling agent solution was adjusted to 8-9 using a sodium hydroxide solution. The solution was sonicated at  $30^{\circ}\text{C}$  for 5 min. The SiC whiskers (1 g) were added to the solution, and the mixture was stirred at  $70^{\circ}\text{C}$  for 3 h. The surface-modified SiC whiskers were obtained after filtering, drying, and grinding the aforementioned mixture.

### 2.3. Sample Preparation

**2.3.1. Preparation of the PLA/PCL Blends.** PLA and PCL were blended at various ratios according to weight fraction, i.e., PLA/PCL = 100/0, 98.75/1.25, 97.5/2.5, 95/5, and 92.5/7.5. The desired amounts of PLA and PCL were mixed in  $\text{CH}_2\text{Cl}_2$  and stirred with a magnetic stirring bar at room temperature for 5 h. The  $\text{CH}_2\text{Cl}_2$  was removed from the solution by heating it to  $190^{\circ}\text{C}$  under reduced pressure. The mixture was then injected into a preheated mold, sprayed with a mold release agent, and compression molded at temperatures ranging from  $180^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  and at a pressure of 5 MPa.

**2.3.2. Preparation of the PLA/PCL/SiC Composites.** The weight content of PCL was set at 2.5 wt.%, and the SiC content was varied from 0.25 to 1 wt.%. The desired amounts of PLA, PCL, and SiC were mixed in  $\text{CH}_2\text{Cl}_2$  and stirred at room temperature for 5 h. The  $\text{CH}_2\text{Cl}_2$  in the mixture was removed by heating to  $190^{\circ}\text{C}$  and under reduced pressure. Then, the mixture was injected into a preheated mold, sprayed with a mold release agent, and compression molded at temperatures ranging from  $180^{\circ}\text{C}$  to  $200^{\circ}\text{C}$  at a pressure of 5 MPa.

**2.4. Characterization and Measurements.** The surface properties of SiC whiskers before and after surface modification were investigated using Fourier-transform infrared spectroscopy (FT-IR, Bio-Rad Co., Digilab FTS-165) (wavenumber range:  $400\text{--}4000\ \text{cm}^{-1}$ , resolution:  $4\ \text{cm}^{-1}$ , scans in triplicate, KBr pellet) and X-ray photoelectron spectroscopy (XPS, Thermo K-Alpha).

Flexural tests were performed according to ASTM D790-86 using a three-point bend configuration. The sample size was  $5\ \text{mm} \times 10\ \text{mm} \times 100\ \text{mm}$ . The preload, span-to-span ratio, and cross-head speed were 0.1 N, 16:1, and 2.1 mm/min, respectively. The range of maximum deflection was sample fracture. The flexural strength ( $\sigma_f$ ) and elastic modulus ( $E_b$ ) were determined using a three-point bending test and calculated as follows [24-26]:

$$\sigma_f = \frac{3PL}{2bd^2}, \quad (1)$$

$$E_b = \frac{L^3}{4bd^3} \frac{\Delta P}{\Delta m}, \quad (2)$$

where  $P$  is the applied load (in N),  $L$  is the span length (in mm),  $b$  is the width of the specimen (in mm), and  $d$  is the

thickness of the specimen (in mm).  $\Delta P$  is the change in force in the linear portion of the load-deflection curve (in N), and  $\Delta m$  is the corresponding change in deflection (in mm). The flexural strength and elastic modulus were obtained from the average of seven experimental values.

The critical stress intensity factor ( $K_{IC}$ ) of the samples was characterized via single-edge notched (SEN) testing in a three-point bending flexure. The three-point bending test was performed on a universal testing machine (Instron Model WDW3010) according to ASTM D-5045. The sample size used for these tests was 5 mm  $\times$  10 mm  $\times$  50 mm. The span-to-span ratio and cross-head speed were 4:1 and 1 mm/min, respectively. For the three-point flexural test, the  $K_{IC}$  was calculated as follows [27–29]:

$$K_{IC} = PBW^{1/2}Y, \quad (3)$$

where  $P$  is the rupture force (in kN),  $B$  is the specimen thickness (in cm),  $W$  is the specimen width (in cm), and  $Y$  is the geometrical factor. The fracture toughness was obtained from the average of seven experimental values.

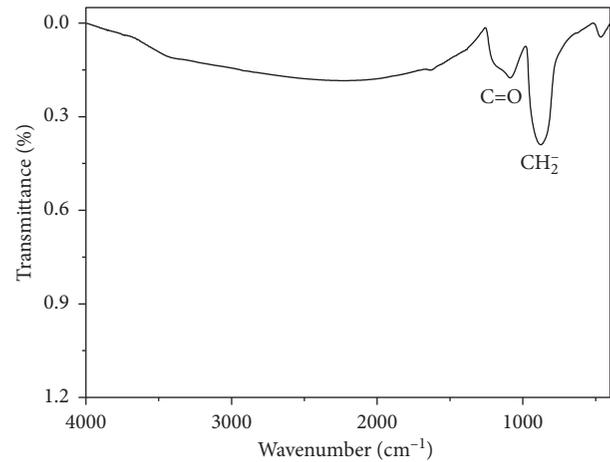
After the fracture tests, the morphologies of the blends were examined using field-emission scanning electron microscopy (FE-SEM, SU 8010/HITACHI).

### 3. Results and Discussion

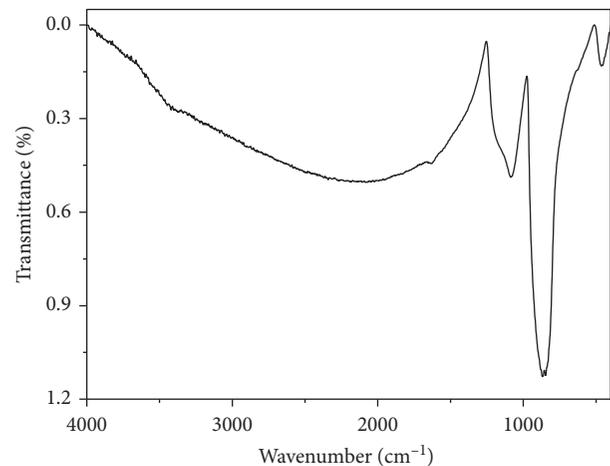
**3.1. Surface Modification of the SiC Whiskers.** Figure 1 shows the FT-IR spectra of the SiC whiskers before and after surface modification. The peaks attributed to the  $\text{CH}_2$ - and  $\text{C}=\text{O}$  groups were observed at 884 and 1095  $\text{cm}^{-1}$ , respectively. The areas of the  $\text{CH}_2$ - and  $\text{C}=\text{O}$  peaks before and after modification were calculated from the FT-IR spectra [30, 31], and the results are shown in Table 1. These peaks increased significantly upon the introduction of organic functional groups onto the surface of the SiC whiskers [32, 33].

Figure 2 shows the X-ray photoelectron spectra of the SiC whiskers before and after surface modification. The  $\text{O}_{1s}$  peak was observed at 533.8 eV, and it decreased significantly in intensity after surface modification due to the reaction of the silane coupling agent with the hydroxyl group on the SiC surfaces [34, 35]. These results demonstrated that the surface modification introduces organic functional groups to the surface of the SiC whiskers.

**3.2. Flexural Properties.** The mechanical performance of the PLA/PCL blends was evaluated based on flexural strength and elastic modulus measurements. Figure 3(a) shows the flexural strength of the PLA/PCL blends as a function of the PCL content. The flexural strength of the blends increased upon increasing the PCL content up to 2.5 wt.% PCL. The flexural strength of neat PLA was 80.8 MPa, whereas that of the blend containing 2.5 wt.% PCL was 36% higher (110 MPa) because of the good interfacial adhesion between the PCL and PLA matrix in the PLA/PCL blends [36, 37]. The flexural strength of the blends decreased above 2.5 wt.% PCL because of the dispersion state of PCL in the PLA matrix deteriorated at the high PCL content.



(a)



(b)

FIGURE 1: FT-IR spectra of SiC whiskers (a) before and (b) after surface modification.

TABLE 1: Areas of  $\text{CH}_2$ - and  $\text{C}=\text{O}$  peaks before and after modification from calculated TF-IR.

Peak	$\text{CH}_2$ -	$\text{C}=\text{O}$
Before modification	34.6	72.0
After modification	96.0	222.4

Figure 3(b) shows the elastic modulus of the PLA/PCL blends. The elastic modulus of the blends decreased gradually from 3.87 to 3.75 GPa for the 2.5 wt.% PCL blend (a 2.6% decrease) and to 3.23 GPa for the 10 wt.% PCL blend (a 16.5% decrease). These results could be attributed to the low glass transition temperature of PCL (61°C) [13, 38].

Figure 4(a) shows the flexural strength of PLA/PCL/SiC composites with 2.5 wt.% PCL as a function of SiC content. The flexural strength of the composites increased from 110 to 126.1 MPa with increasing SiC content. This could be attributed to the good interfacial adhesion between the SiC whiskers and PLA matrix [39, 40].

Figure 4(b) shows the elastic modulus of the PLA/PCL/SiC composites as a function of SiC content. The elastic

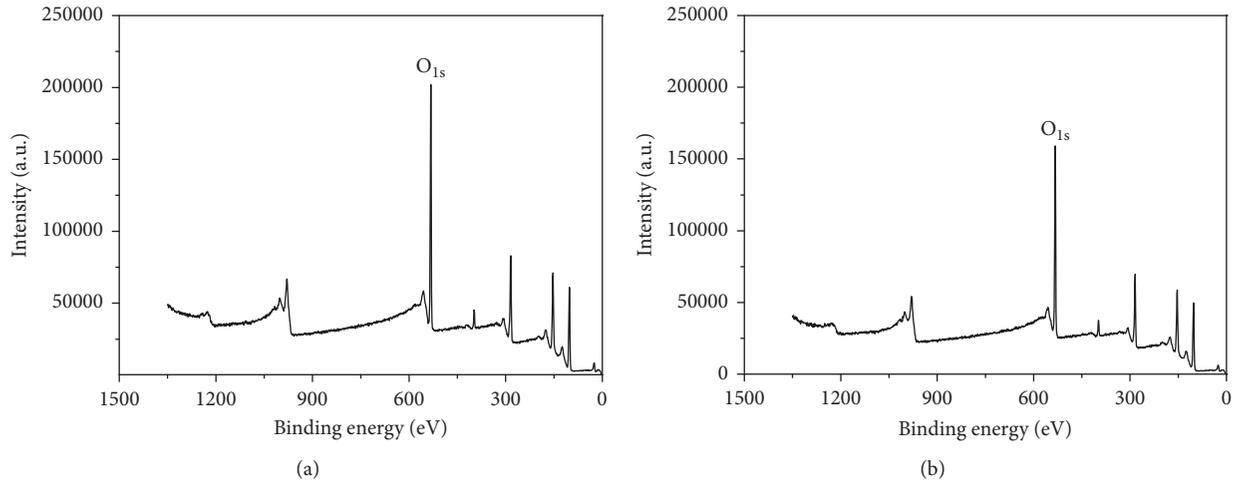


FIGURE 2: XPS spectra of SiC whiskers (a) before and (b) after surface modification.

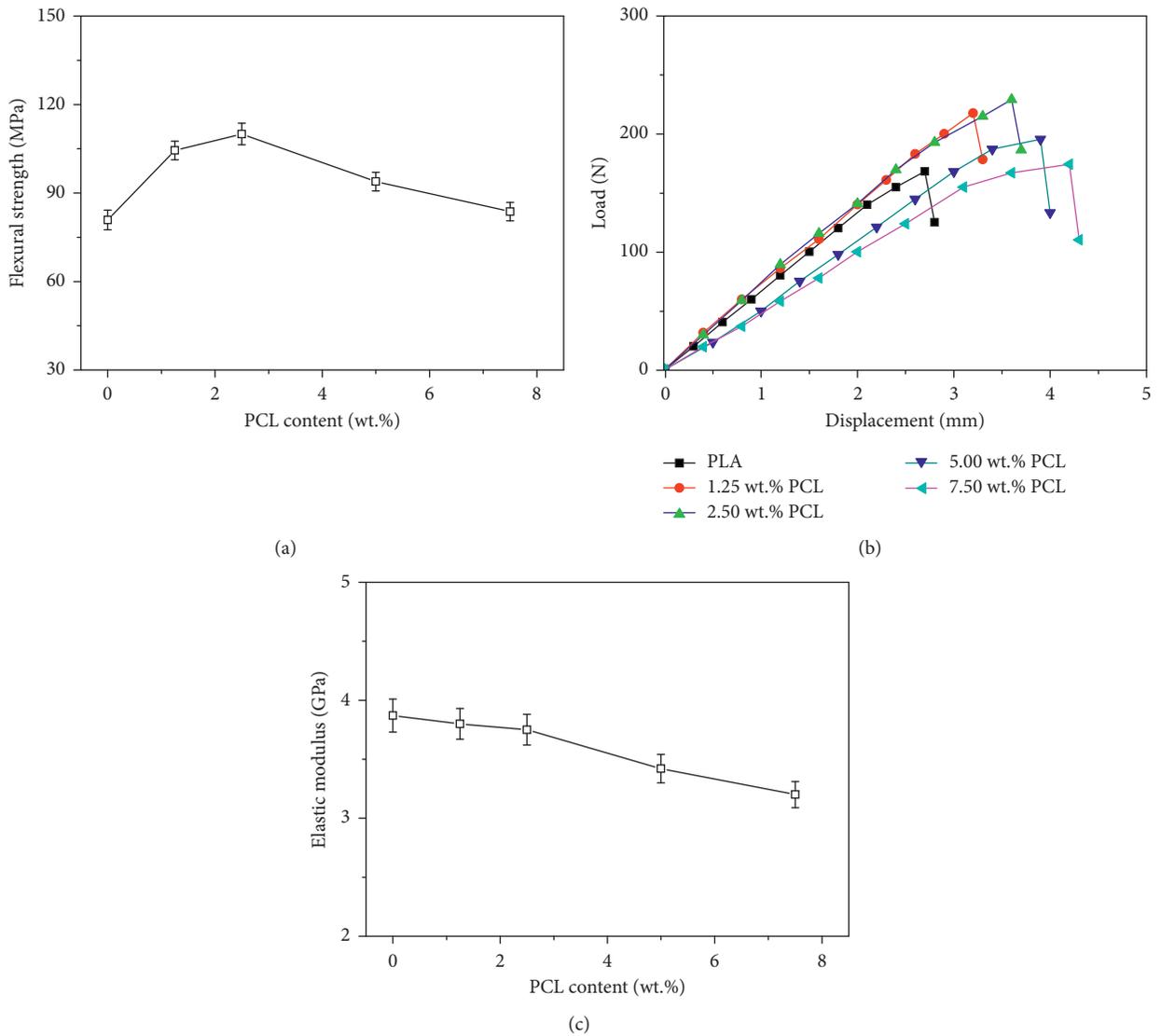


FIGURE 3: Flexural strength (a), load (b), and elastic modulus (c) of PLA/PCL blends.

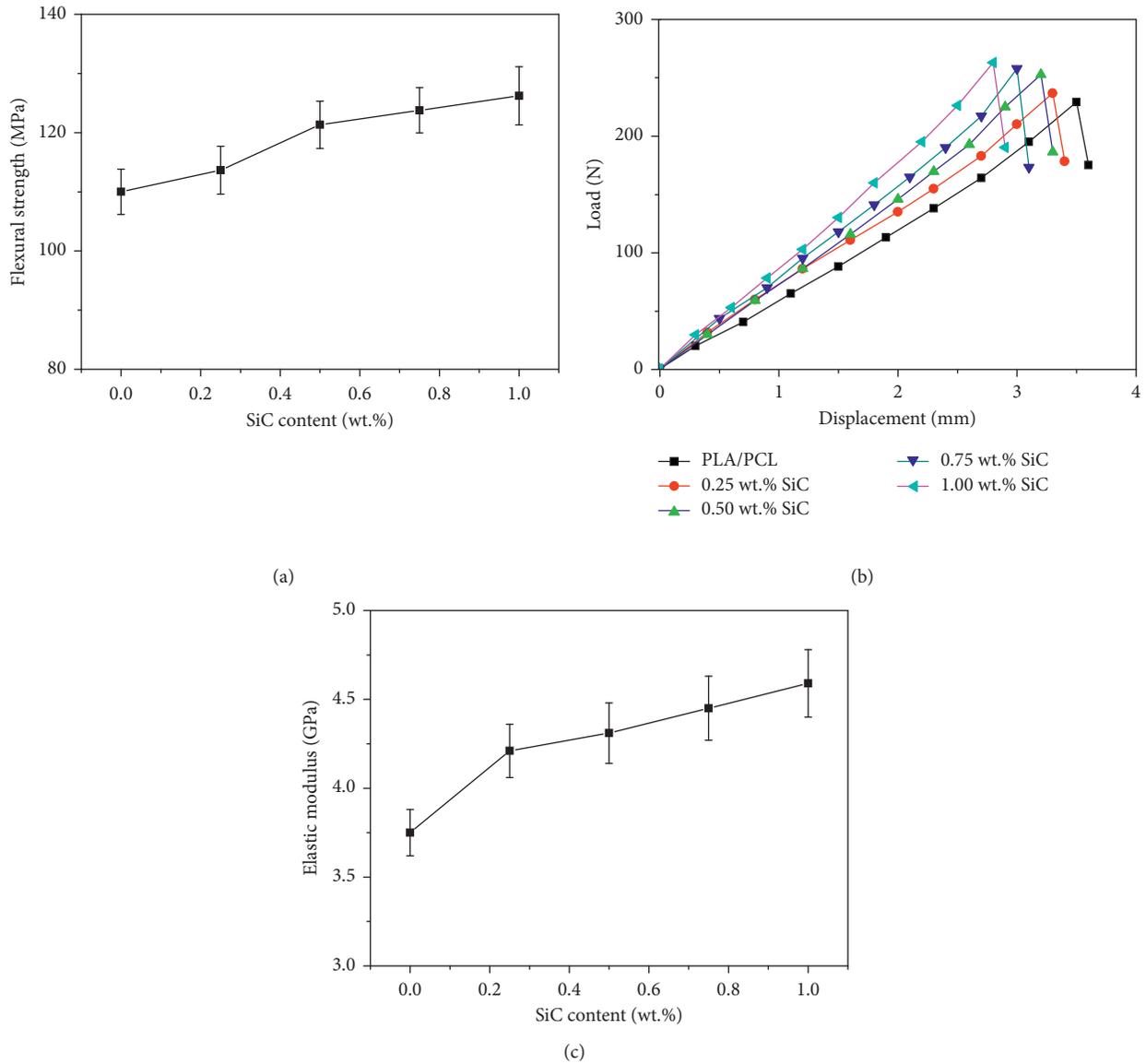


FIGURE 4: Flexural strength (a), load (b), and elastic modulus (c) of PLA/PCL/SiC composites.

modulus of the composites increased from 3.75 to 4.59 GPa with increasing SiC content. This was due to the restriction of the mobility of polymer chains in PLA under load by the dispersed rigid SiC whiskers [21, 41].

**3.3. Fracture Toughness.** The fracture toughness of the PLA/PCL blends was investigated by  $K_{IC}$  measurements. Figure 5 shows the  $K_{IC}$  values of the PLA/PCL blends as a function of PCL content. It was clear that  $K_{IC}$  was significantly improved upon the addition of PCL. Neat PLA was very brittle with a  $K_{IC}$  of  $1.22 \text{ MPa}\cdot\text{m}^{1/2}$ , whereas the blend containing 2.5 wt.% PCL had a  $K_{IC}$  of  $1.79 \text{ MPa}\cdot\text{m}^{1/2}$ , which was 47% higher than that of neat PLA. This increase in  $K_{IC}$  may be due to the elasticity and flexibility of PCL, which also shows good energy-absorbing capacity and stretches to accommodate the cracks produced by external forces [36, 42]. The  $K_{IC}$  value of the blends decreased slightly above 2.5 wt.% PCL as

the dispersion state of PCL in the PLA matrix deteriorated at high PCL content.

Figure 6 shows the  $K_{IC}$  values of the PLA/PCL/SiC composites as a function of SiC content. The  $K_{IC}$  value significantly improved with the addition of SiC.  $K_{IC}$  of PLA/PCL blend containing 2.5 wt.% PCL was  $1.79 \text{ MPa}\cdot\text{m}^{1/2}$ , whereas  $K_{IC}$  of the composite containing 2.5 wt.% PCL and 0.5 wt.% SiC was  $2.6 \text{ MPa}\cdot\text{m}^{1/2}$ , which was 45% higher than that of the blend without SiC. This trend was attributed to the good energy-absorbing capacity of the SiC whiskers dispersed in the PLA matrix and the SiC-PLA debonding. The debonding effectively transferred stress and increased the resistance to deformation and crack propagation, resulting in the increased fracture toughness of the PLA/PCL/SiC composites [43, 44]. The  $K_{IC}$  value of the composites decreased slightly above 0.5 wt.% SiC because of the slight agglomeration of SiC whiskers in the PLA matrix at a high SiC content.

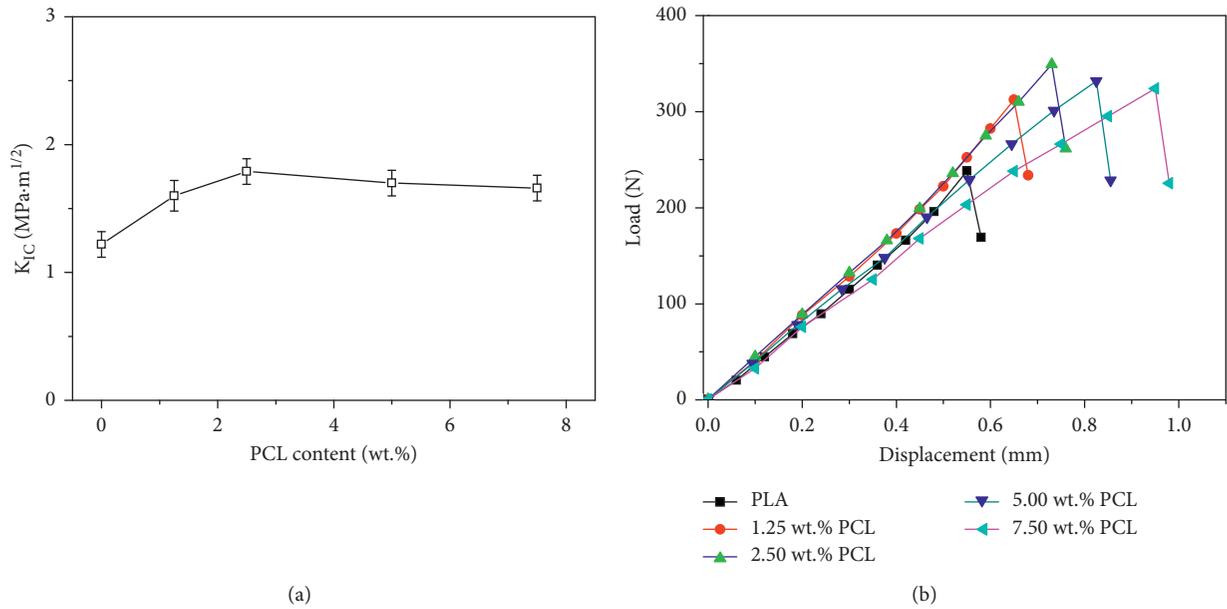


FIGURE 5: Fracture toughness of PLA/PCL blends as a function of PCL content.

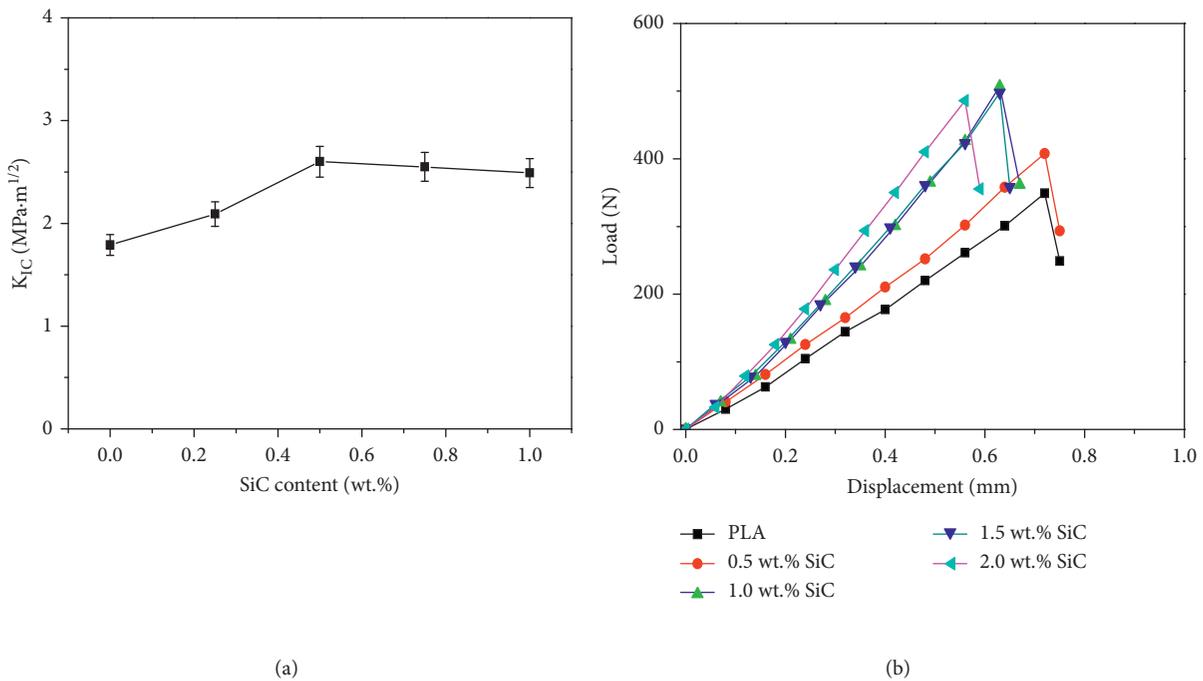


FIGURE 6: Fracture toughness of PLA/PCL/SiC composites as a function of SiC content.

**3.4. Morphology.** The toughness behavior of the PLA/PCL blends and PLA/PCL/SiC composites was further characterized by SEM observations. Figure 7 shows the SEM images of the PLA/PCL blends after the  $K_{IC}$  tests. Neat PLA exhibited a smooth and flat morphology (Figure 7(a)), indicating a brittle fracture surface [45]. Conversely, the SEM images of the blends show cracks and many ridges, indicating plastic deformation prior to fracturing. This accounts for the high fracture toughness of the blends, as shown in Figures 7(b)–7(e) [36, 46]. PCL is thermodynamically

incompatible with PLA [13, 15]. As shown in Figures 7(b)–7(e), PCL was relatively well dispersed in the PLA matrix at low PCL content.

Figure 8 shows the SEM images of the PLA/PCL/SiC composites after the  $K_{IC}$  tests. The SiC whiskers were bonded in a continuous PLA matrix and showed good interfacial adhesion. The introduction of SiC whiskers led to increased resistance to deformation and crack propagation through energy absorption by the SiC whiskers and SiC-PLA debonding in the PLA/PCL/SiC composites. This is in

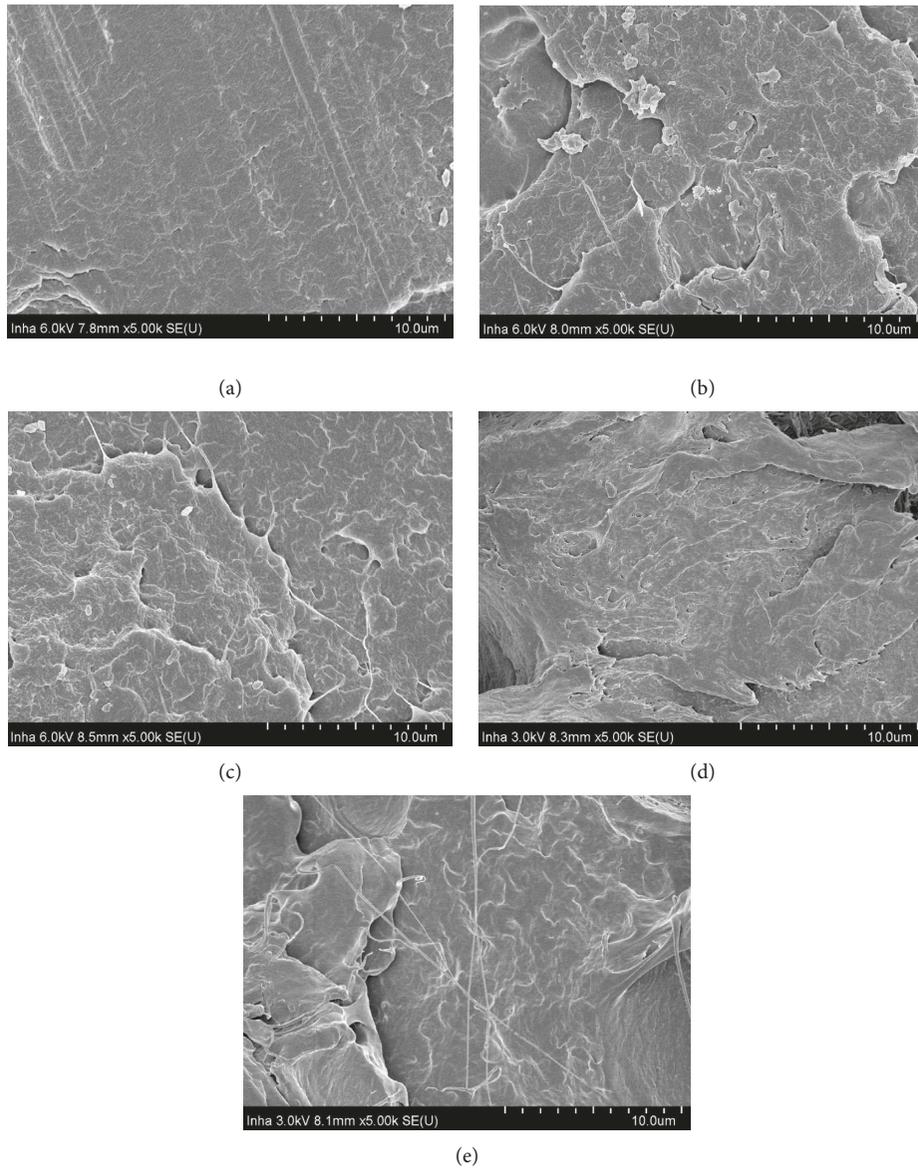


FIGURE 7: SEM micrographs of PLA/PCL blends after  $K_{IC}$  tests: (a) neat PLA; (b) 1.25 wt.% PCL; (c) 2.5 wt.% PCL; (d) 5 wt.% PCL; (e) 7.5 wt.% PCL (magnification of 5000).

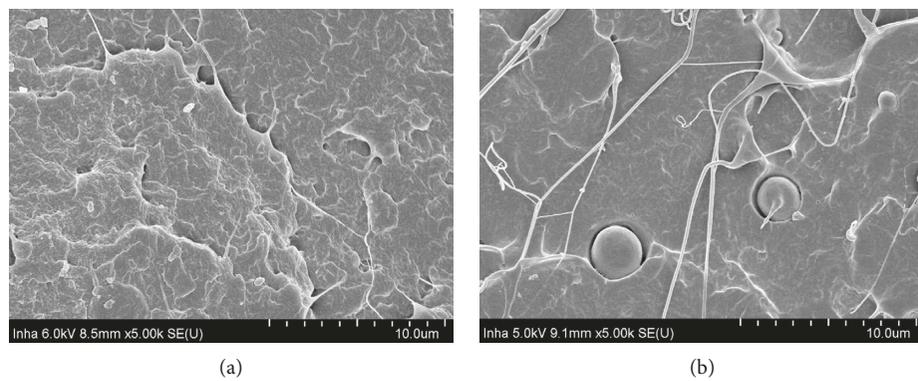


FIGURE 8: Continued.

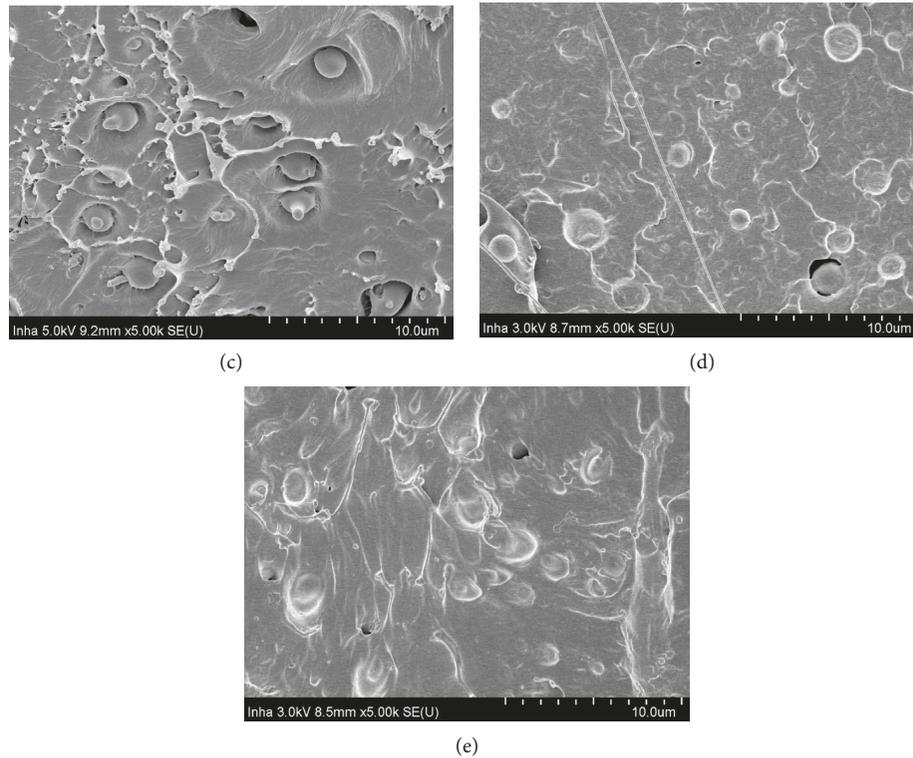


FIGURE 8: SEM micrographs of PLA/PCL/SiC composites after  $K_{IC}$  tests: (a) PLA/PCL (2.5 wt.% PCL); (b) 0.25 wt.% SiC; (c) 0.5 wt.% SiC; (d) 0.75 wt.% SiC; (e) 1.0 wt.% SiC (magnification of 5000).

agreement with the results showing that the SiC whiskers-reinforced PLA composites exhibited higher fracture toughness than that of the neat PLA or PLA/PCL blends [47, 48]. Generally, SiC whiskers were almost completely dispersed in the PLA matrix [13]. SiC was well dispersed in the PLA matrix at low SiC content (0.5 wt.%), and some SiC agglomeration was seen above 0.5 wt.% SiC.

#### 4. Conclusions

The mechanical properties, fracture toughness, and morphology of the prepared bio-based PLA/PCL blends and PLA/PCL/SiC composites were examined using multiple techniques. The surface of the SiC whiskers was modified using a silane coupling agent. The fracture toughness and flexural strength of the PLA were increased by the incorporation of PCL and further improved by the addition of SiC whiskers. The elastic modulus of PLA decreased after the introduction of PCL but increased after the addition of SiC whiskers. SEM images revealed that reinforcement of PLA with PCL induced plastic deformation. Simultaneously, the SiC whiskers absorbed external energy through good interfacial adhesion between the SiC whiskers and PLA matrix and debonding between the two materials in the PLA/PCL/SiC composites.

#### Data Availability

The data used to support the findings of this study are included within the article.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

#### Acknowledgments

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