

# Preparation and Property Evaluations of PCL/PLA Composite Films

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**Abstract** Composite materials prepared from polylactic acid have been used more and more widely in many fields. However, PLA has high brittleness, which largely restricts its application. Blending PLA with polycaprolactone (PCL) helps improve the disadvantages of pure PLA. In this study, different molecular weights of PCL were used and blended with PLA in different proportions to form a composite film by melt blending. The mechanical properties, thermal properties, and water wettability of Composite films are evaluated to examine the influences of the relative molecular weight of PCL and PCL/PLA ratio. When the relative molecular weight of PCL is 50,000, Composite films have high stress, strain, hydrophilicity, thermal properties, and UV-resisting property, but their thermal properties are not affected. At a specific relative molecular weight of PCL and PCL/PLA ratio of 30/70, the films reach their maximum stress and exhibit high strain, good hydrophilicity, and UV transmittance lower

than 10%. Moreover, the PCL/PLA ratio has a marginal effect on the thermal properties of the films. This research has certain significance for promoting the application of PCL/PLA composite film in many fields.

**Keywords** Polycaprolactone · Polylactic acid · Molecular weight · Blending ratio

## Introduction

Biopolymers are now expected to replace petroleum-based plastics due to environmental and pollution problems [1]. Among biodegradable polymers, aliphatic polyesters are the most famous [2]. They include polylactic acid, polycaprolactone, poly(hydroxybutyric acid) and polyethylene oxide [3-7]. The main application areas of these materials are as follows: medical, agricultural and packaging. Among them, the application in the agricultural field is mainly used for plastic films. Thin plastic mulching films for agricultural applications are capable moisturization and heat preservation during the sowing period [8-11]. Commercially available agricultural plastic mulching films are commonly composed of polyethylene (PE), which does not satisfy the requirement for moisture retention[12]. Given that PE-based films cannot be degraded naturally, wasted films cause serious pollution to the environment, which in turn leads to the rise in the demand for degradable agricultural plastic mulching films [13-15].

Polylactic acid (PLA) features good bio-decomposition [XXX]; that is, PLA waste can be fully decomposed by organisms into carbon dioxide and water, which can be absorbed by plants in soils and do not cause environmental burden. PLA is a polymer from renewable resource and has been extensively used because of its renewability, biocompatibility and good thermomechanical properties. [16]. Therefore, PLA is a better candidate than PE for preparation of agricultural plastic mulching films [17]. However, PLA is brittle and lacks elasticity, which severely limits its application in the field of composite materials [18]. PCL is a promising synthetic biodegradable material, because of its very high flexibility and its hydrophobic nature [19]. Polylactic acid, PCL and blends thereof have been extensively studied for their wide range of applications [20, 21]

Blend modification involves the blending of two or more than two materials at specified ratios to retain the unique characteristics of each material. PLA can be subjected to blend modification. In addition, polycaprolactone (PCL) and PLA have comparable characteristics, such as good

biodegradability and biocompatibility. PCL has intrinsic properties and low toxicity and thus can be added to other materials to promote fluidity, impact resistance, and flexibility. Campos et al. [18] mixed PCL and PVA to produce biodegradable films and reported that films with PCL were better degraded than those with other polymers. Guerra et al. [22] used dip coating to prepare PCL/PLA composite tubes with qualified scaffolds. Li et al. [23] combined PCL and PLA at different ratios to produce bio-component composites for vascular grafts. Test results showed that vascular grafts with an appropriate amount of PCL possessed outstanding radical compression recovery; hence, PCL could be a suitable candidate for in situ formation of tissue-engineered vascular grafts. Karami et al. [24] electrospun PLA, PCL, and PLA/PCL (50/50) nanofibers; the combination of PLA and PCL exhibited the maximum drug release level and the optimal antibacterial effect against *Staphylococcus aureus*. Mittal et al. [25] proposed binary and ternary blends containing different amounts of PLA, thermoplastic starch, and PCL polymers; they found that the storage modulus decreased as a function of PCL content in the blends. Jain et al. [26] studied the influence of talc loading on the phase morphology of PLA/PCL/talc composites; the results showed that talc loading decreased the size of the PLA domain and the number of voids in the matrix.

PLA/PCL composites are commonly used in the medical field, but few have studied on the agricultural plastic mulch made by PLA. In this study, we blended PCL and PLA through melt blending and hot pressing to obtain films with improved properties relative to pure PLA. The influences of the relative molecular weight of PCL and the PCL/PLA blending ratio on the composite films are examined. In view of the fact that most of the current research on PLA is basically done around the structure, only a small number of researchers study the impact of the proportion of PCL/PLA on PLA. At the same time, considering the potential of PLA / PCL composite film in agricultural plastic film application. Therefore, this study contributes to the application of PCL/PLA composite films in diversified fields.

## **Materials and Methods**

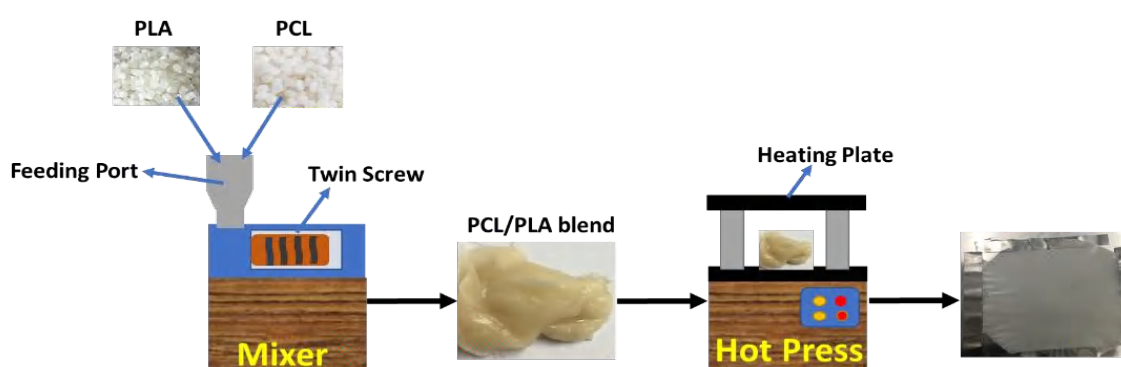
### **Materials**

PLA (2003D grade, Nature Works, US) has a melting flow index of 5–7g/10 min, a glass transition temperature of 60 °C, and a melting temperature of 157.3 °C. PCL6500 and PCL6800 (United States Solvay, US) have relative molecular weights ( $M_w$ ) of 50,000 and 80,000, respectively, and a

glass transition temperature of  $-60^{\circ}\text{C}$ .

### Preparation of samples

PCL and PLA masterbatches were first blended at a mixing ratio of 0/100, 30/70, 50/50, 70/30, and 100/0, and then poured into a twin-screw mixer at  $180^{\circ}\text{C}$  for 7 min at a rotary speed of 150 rpm. This melt-blending process is repeatedly conducted for 3 times, and finally the PCL / PLA blends were prepared. The obtained blends are then hot-pressed at  $180^{\circ}\text{C}$  for 1 min under a pressure of 25 Mpa to form the composite films with a thickness of  $180 \pm 50\ \mu\text{m}$ . The manufacture processing of the resultant PCL/PLA composite films is shown in Figure 1.



**Fig. 1** The manufacture processing of the PCL/PLA composite films.

### Tensile properties

The samples are firstly cut into the dumbbell-shape (dog bone shape). The tensile properties of the samples are measured at room temperature by using a computer servo control material testing machine (HT-2402; HungTa Instrument, Taiwan) according to test standard ASTM D882. The distance between the gauges is 20 mm, and the width is 4mm. The crosshead speed and load cell are set as 10mm/min and 5 kN, respectively. Five samples for each specification are used, and their results are averaged.

### Thermal properties

The differential scanning calorimetry (DSC) measurements are carried out using a differential scanning calorimeter (NETZSCH DSC200F3, Germany). Samples are heated from room temperature to  $200^{\circ}\text{C}$  at  $20^{\circ}\text{C}/\text{min}$  increments and held for 5 minutes to remove the thermal history. The samples are then cooled to  $30^{\circ}\text{C}$  at a cooling rate of  $10^{\circ}\text{C}/\text{min}$  and heated again to  $200^{\circ}\text{C}$  at  $10^{\circ}\text{C}/\text{min}$ . The

glass transition temperature ( $T_g$ ), and melting temperature ( $T_m$ ) are examined according to the scanning results.

### Morphology analysis

The tensile fracture surface of the PCL/PLA blend are processed through gold coating to avoid electrostatic charging and observed using a scanning electron microscope (SEM, TM3030, HITACHI, Japan).

### Water contact test

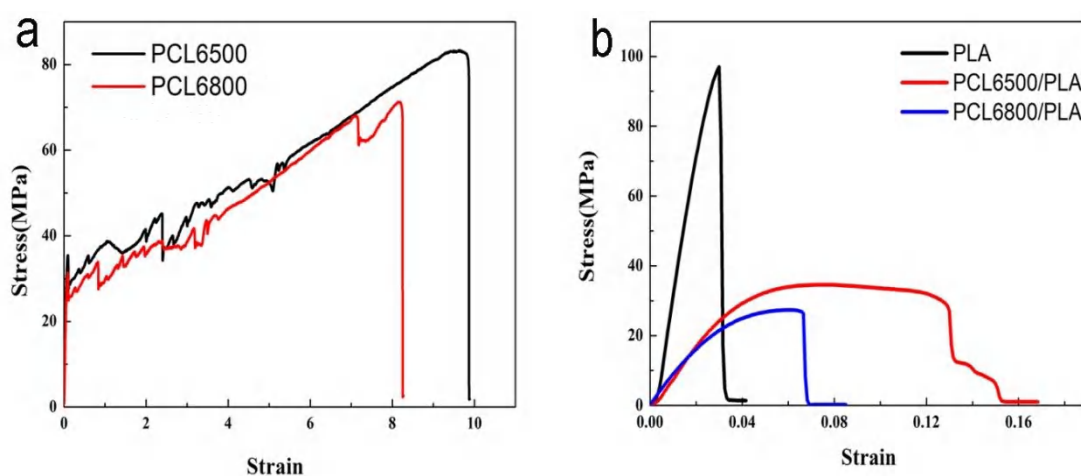
The water contact angle of the samples is measured at five random positions by using a contact angle measuring device (JC2000DM; Shanghai Zhongchen Digital Technology Apparatus, China), and the average of the results is obtained.

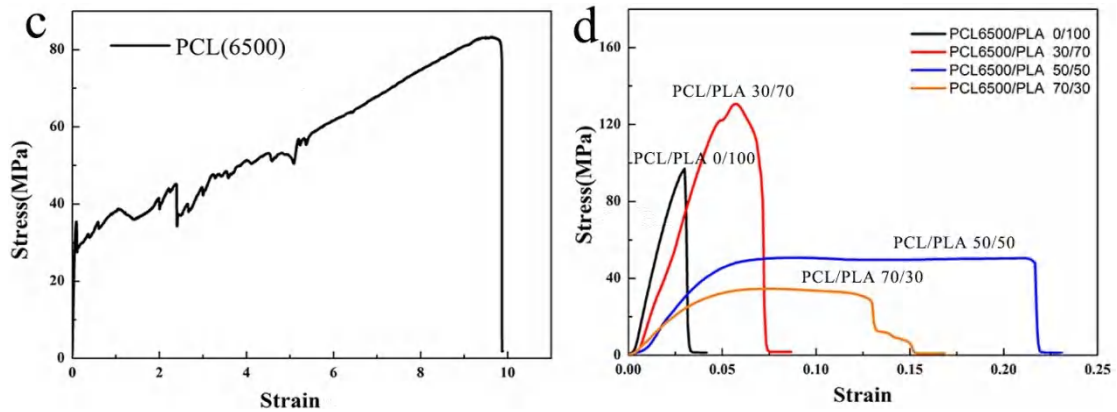
### UV resistance

UV resistance is characterized by UV transmittance and obtained using a UV intensity meter (UV-340A, Lutron Electronic Enterprise, Taiwan) with a medium-band UV light source (G15T8E; Sankyo Denki, Japan) according to GB-T 17032. The sample dimension is 5cm  $\times$  5cm. The difference in the UV absorptive capacity between the experimental and control groups is compared and calculated to obtain UV transmittance.

## Results and Discussion

### *Effect of PCL relative molecular weight and PCL/PLA ratio on mechanical properties*

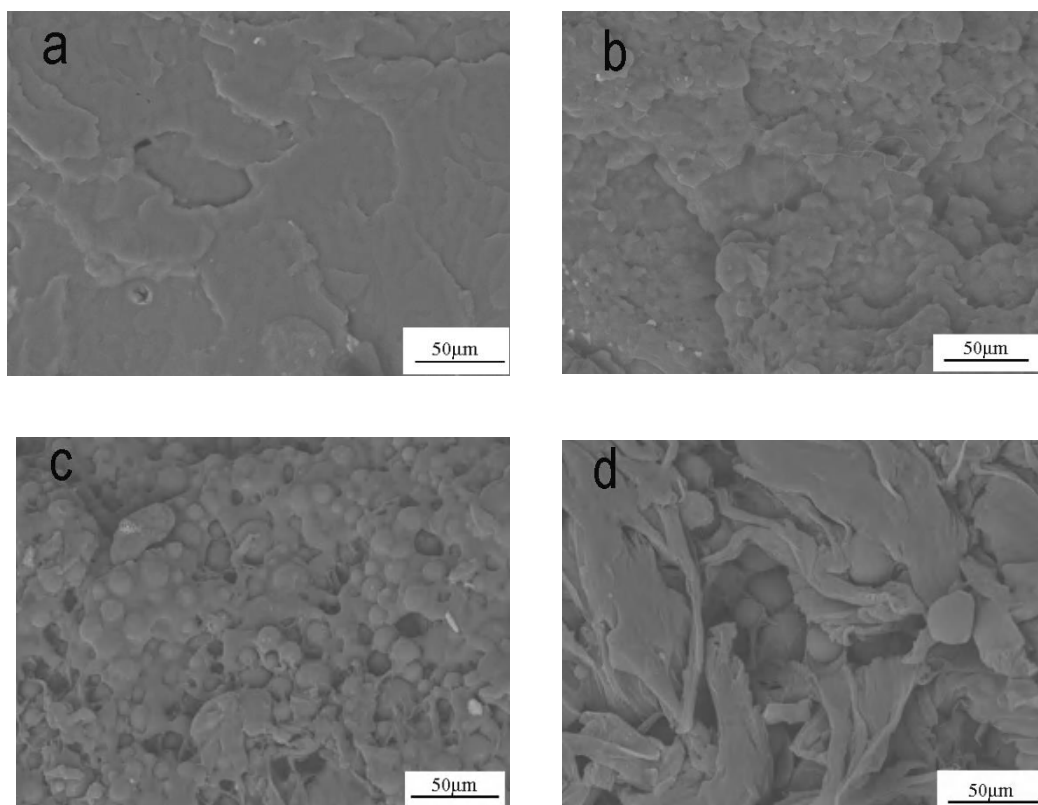


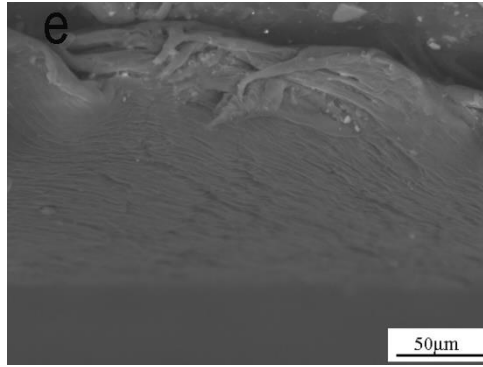


**Fig. 2** The stress-strain curves of: **a** PCL6500, PCL6800 films; **b** PLA, PCL6500/PLA, PCL6800/PLA films; **c** PCL6500 film; **d** PCL6500/PLA films as related to the PCL/PLA ratios.

Fig. 2 (a, b, c, d) show the stress–strain curves of PCL6500 (relative molecular weight: 50,000) and PCL6800 (relative molecular weight: 80,000) with a PCL/PLA ratio of 70/30 and those of PCL6500/PLA films with different PCL/PLA ratios (0/100, 30/70, 50/50, 70/30, and 100/0). The tensile strength and strain are 80.02 MPa and 10, respectively, for PCL6500 and 71.23 MPa and 8, respectively, for PCL6800. Toughness is the ability of a material to absorb energy during plastic deformation and fracture. The better the toughness, the less likely it is that brittle fracture will occur. The tough material is relatively soft, and its tensile elongation at break and tensile strength are relatively large. Hence, PCL6500 and PCL6800 have good toughness. Upon PLA addition, the mulching membranes show decreased tensile strength in Fig. 2b. The maximum tensile strength values of PCL6500/PLA and PCL6800/PLA films are 34.55 and 27.35 MPa, respectively, which meet the requirements for composite film. Moreover, the presence of PCL considerably improves the brittleness of PLA. The tensile strain values of PCL6500/PLA and PCL6800/PLA films are 0.07 and 0.13 higher than that of pure PLA films, respectively. Furthermore, the stress–strain curve of PCL6500/PLA films reaches the maximum value and then slowly decreases. The stress-strain curve of the PCL6800 / PLA film shows that the stress value drops sharply as the strain increases after the maximum stress value is reached. The results suggest that PCL6500/PLA films have increased toughness, and PCL6800/PLA films have increased brittleness. Using an appropriate relative molecular weight increases the number of tangled crystal chains, thereby horizontally and vertically strengthening the bonding between the molecular chains. In addition, using materials with higher relative molecular weight 80,000 causes excessive tangled molecular chains, rendering the mulching films with a stress concentration or higher crystallization that reflects higher brittleness [27-33].

PCL6500/PLA films have optimal performance and are selected for subsequent evaluation of mechanical properties. Fig. 2d shows the stress–strain curves of PCL6500/PLA films with different PCL/PLA ratios. The maximum tensile strength occurs when the PCL/PLA ratio is 30/70, indicating that the composite films with this ratio have the highest tensile strength and toughness. Increasing the amount of PCL adversely affects the tensile strength of the composite films. Pure PLA materials are highly brittle, whereas pure PCL materials are highly flexible. The use of PCL mitigates the high brittleness of PLA, and increasing the amount of PCL improves the tensile strain. The tensile strain reaches the peak at a PCL/PLA ratio of 50/50 and then decreases as a result of excessive PCL content [27, 31, 32]. The appropriate relative molecular weight helps to increase the number of molecular chain entanglements, which enhances the bonding among the molecular chains and improves the crystallization [XX]. With the excessive PCL content, entanglements of the molecular chain become less, resulting in the decrease of tensile stress [xx].

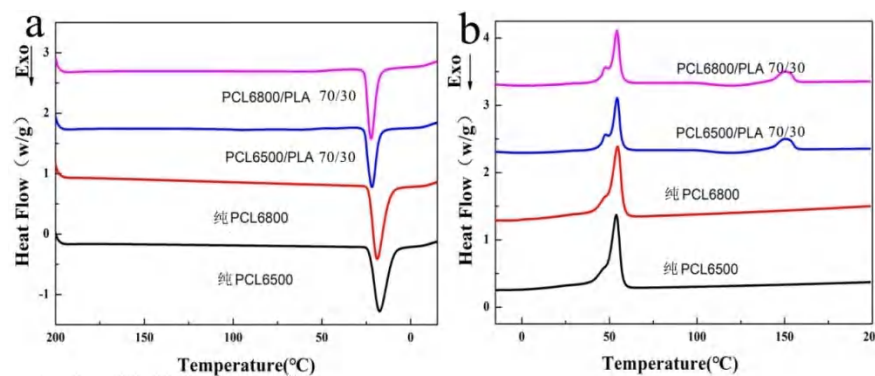




**Fig. 3** SEM images of the fractured PCL6500/PLA films made of PCL/PLA ratios of : **a** 0/100; **b** 30/70; **c** 50/50; **d** 70/30; and **e** 100/0

The SEM images of the fractured samples are shown in Fig. 3. The pure PLA films demonstrate a smooth fractured surface, reflecting low toughness and high brittleness in Fig. 3a. The fractured surface of the PCL6500/PLA film (30/70) is relatively even, which shows that PLA is primarily responsible for the fracture; meanwhile, PCL addition strengthens the toughness of the whole composites in Fig. 3b. A clear interface exists between PCL and PLA and shows a continuous sea-island structure. The PCL6500/PLA films (50/50) have balanced properties and a certain level of tensile strength and toughness in Fig. 3c. Moreover, the surface of the PCL6500/PLA films (70/30) has a filiform structure, which is primarily ascribed to PCL. As a result, the mulching films have good toughness but low tensile strength in Fig. 3d. Finally, the pure PCL films (100/0) have a fractured surface with a layered filamentous structure, leading to high toughness in Fig. 3e. The interface between PCL and PLA is obvious, and the fractured surfaces shown in the SEM images conform to the mechanical test results [31-35].

#### *Effects of PCL relative molecular weight and PCL/PLA ratio on thermal properties*



**Fig. 4** **a** The cooling; **b** the second heating curves of the mulching films

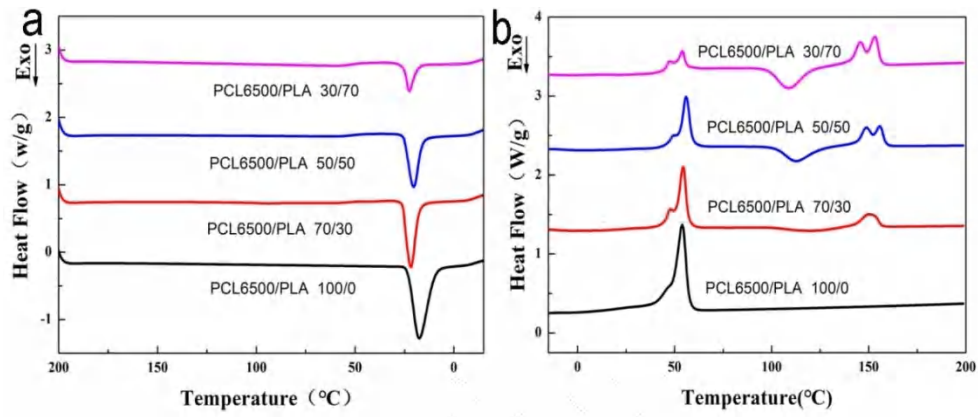
Fig. 4 (a, b) shows the cooling and second heating curves of the control group and the PCL/PLA films (70/30) made of two relative molecular weights of PCL. The DSC information is listed in Table 1, where  $T_c$  represents the crystallization temperature and  $T_m$  represents the melting point temperature. Fig. 4a shows that all of the four groups have significant cold crystallization peaks. Moreover, the exothermic peaks of the two pure PCL films have similar magnitudes and positions, consistent with the results of the two experimental groups. In comparison with the control group, the experimental groups have a right-shift exothermic peak, indicating that the PCL/PLA mixtures have an accelerating crystallization rate and level. The PLA phase is distributed in the PCL phase, and the molecular chains are re-aligned accordingly. The molecular chains do not significantly affect the cold crystallization.

**Table 1** DSC data of composite film

| Samples    | PLA   | PCL6500 | PCL6800 | PCL6500/PLA | PCL6800/PLA |
|------------|-------|---------|---------|-------------|-------------|
| $T_c$ (°C) | /     | 18.9    | 18.9    | 21.8        | 22.3        |
| $T_m$ (°C) | 157.3 | 53.9    | 54.7    | 57.0/150.3  | 56.6/150.8  |

$T_c$  (Crystallization temperature);  $T_m$  (melting temperature)

Fig. 4b displays the second heating curves. The experimental groups exhibit two remarkable endothermic peaks: a low-temperature peak with a large area and a spike shape and a high temperature peak with a small area and a flatter slope. The two endothermic peaks correspond to the melting points of **PCL** and PLA. Table 1 shows that the intensities of the low-temperature endothermic peaks of the experimental groups are slightly higher those that of the control groups. Hence, the presence of molecular chains of PLA restricts the mobility of the molecular chains of PCL. Meanwhile, the high-temperature endothermic peaks of the two experimental groups are found at **150.3 °C** and **150.8 °C**, which are lower than the melting point of pure PLA. This result may be due to the fact that the previous melting of PCL undermines the molecular chains of PLA. However, the difference in the relative molecular weights does not affect the second heating curves [31-33, 37-40].



**Fig. 5** **a** The cooling; **b** the second heating curves of the PCL6500/PLA films

The DSC curves of the PCL6500/PLA films and pure PLA film are individually displayed in Fig. 5 (a, b) and Table 2. Fig. 5a shows that the four groups of the PCL6500/PLA films have comparable exothermic peaks at similar positions during cooling. Table 2 shows that the cold crystallization temperature of the pure PCL films is 23.4 °C, and that of the three groups of the PCL6500/PLA films is approximately 25.7 °C. Hence, the crystallization rate of the mixtures increases. PLA typically does not have distinct exothermic peak during cooling, thereby implying that only PCL generates crystallization in the composite films. This observation also explains that increasing the amount of PCL enlarges the peak area.

**Table 2** DSC data of PCL6500/PLA films as related to different PCL/PLA ratios

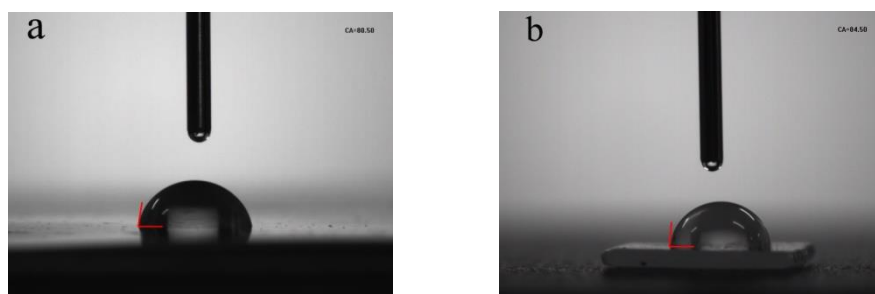
| Samples                 | PCL/PLA<br>0/100 | PCL/PLA<br>30/70 | PCL/PLA<br>50/50 | PCL/PLA<br>70/30 | PCL/PLA<br>100/0 |
|-------------------------|------------------|------------------|------------------|------------------|------------------|
| $T_c(^{\circ}\text{C})$ | /                | 25.7             | 25.7             | 25.8             | 23.4             |
| $T_m(^{\circ}\text{C})$ | 157.3            | 55.9/153.2       | 54.4/153.4       | 54.0/150.0       | 53.9             |

In the second heating curve in Fig. 5b, all of the three groups of the PCL6500/PLA films have two endothermic peaks; the low-temperature endothermic peak is due to the melting point of PCL, and the high-temperature endothermic peak correspondingly results from the melting point of PLA. Interestingly, for the 30/70 and 50/50 groups, an exothermic peak exists between two endothermic peaks and is referred to as the melt crystallization peak. This result indicates that PCL, the minority in the mixture, initiates movement during heating, as demonstrated by the melting of PCL. The static molecular chains of PLA restrict the movement of molecular chains of PCL, forcing them to re-align,

as demonstrated by the presence of melt crystallization. This phenomenon stops when more PCL is added.

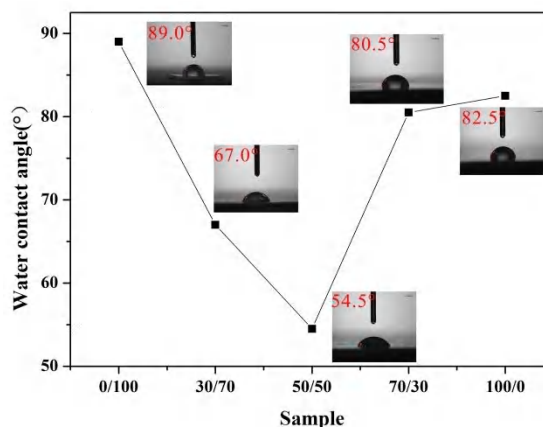
The second heating curve shows that increasing the amount of PCL enlarges the area of the low-temperature endothermic peak. In the PCL6500/PLA films, PCL and PLA exhibit their own crystallization region [30, 32, 38-40]. Based on the DSC results, the melting temperature of different PCL6500/PLA films is comparable. A 30/70 ratio is accompanied with a relatively high melting point of **PCL**, and 30/70 and 50/50 ratios allow **PCL** to crystallize again after melting. In summary, the thermal properties of the PCL6500/PLA films are not dependent on the PCL/PLA ratio.

#### *Effects of PCL relative molecular weight and PCL/PLA ratio on water contact angle*



**Fig. 6** Water contact angle of: **a** PCL6500/PLA; **b** PCL6800/PLA films

At a PCL/PLA ratio of 70/30, the water contact angles of the **composite films** containing two relative molecular weights are shown in Fig. 6 (a, b). The water contact angles are **80.5 °** for the PCL6500/PLA films and **84.5 °** for the PCL6800/PLA films, which are both lower than 90 °. **The PCL masterbatch in PCL6500 / PLA film has a relative molecular weight of 50,000 and high hydrophilicity.** Hence, the addition of PCL with low relative molecular weight to PLA triggers the **more molecules segments** of polar groups [40, 41]. **The reason is that, after PCL and PLA polymers are melt-blended, more polar groups such as carbonyl groups occur in the molecular segments, which accelerates the absorption of water molecules [42].**

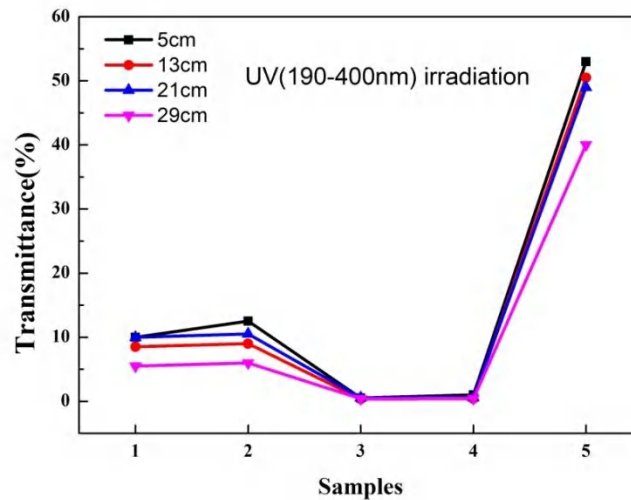


**Fig. 7** Water contact angles of PCL6500/PLA films made of PCL/PLA ratios of 0/100, 30/70, 50/50, 70/30, and 100/0.

As shown in Fig. 7, regardless of the PCL/PLA ratio, all of the PCL6500/PLA films have affinity to water. The pure PLA films have the maximum water contact angle and the lowest hydrophilicity. With increasing PCL content, the water contact angle of the PCL6500/PLA films decreases. When the content of PCL is increased to 50%, the hydrophilicity of PCL/PLA composite film is maximized. However, the hydrophilicity of the composite film decreases when the content of PCL continues to increase. It can be seen from the SEM image in Fig. 3 that the main reason for this phenomenon is that when the ratio of PCL/PLA is 50/50, a sea-island structure is formed, which contributes to the circulation of water molecules, and as the PCL content increases, the structure disappears and the passage of water molecules is blocked. Description an appropriate amount of PCL induces polar groups that can improve the hydrophilicity of PLA [40, 41].

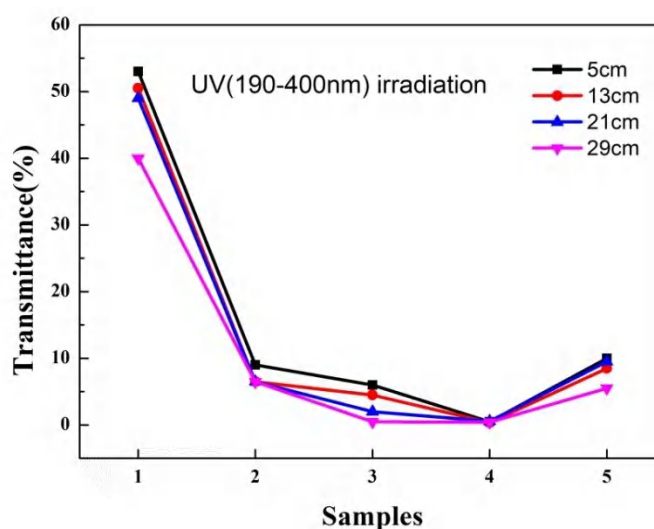
#### *Effects of PCL relative molecular weight and PCL/PLA ratio on UV resistance*

Long UV rays stimulate the growth of crops, increase the yield of the produce, and accelerate the synthesis of proteins, sugars, and acids. By contrast, short UV rays prevent the rapid growth of crops and provide crops with sterilization antibacterial efficacy that prevents diseases. Hence, the exposure of crops to an appropriate amount of UV rays has a positive influence on agricultural industry. However, the strength and time of UV exposure is not adjustable, and long-term exposure to high-strength UV is detrimental to crops. For example, the crops may wither or afflicted through gene mutation [43-46]. In response, the use of composite films is proposed to block UV. Based on the UV exposure observation, the UV transmittance of the composite films is computed in relation to the distance away from the UV source in Fig. 8. The results show that the farther the UV source is, the lower the UV transmittance of the composite films will be. The transmittance of the pure PLA films is higher than that of the PCL/PLA composite films (30/70). The PLA films can block less UV light rays than the PCL films. Regardless of the relative molecular weight of PCL, the PCL/PLA (30/70) composite films have 0% UV transmittance. The relative molecular weight of PCL does not affect the UV transmittance of the composite films.



**Fig. 8 UV transmittance (%) of PCL6500, PCL6800, PCL6500 / PLA, PCL6800 / PLA and PLA films.**

Fig. 9 shows the UV transmittance of the PCL6500/PLA films in relation to different distances from the UV source and different PCL/PLA ratios. A long distance from the source results in decreased UV transmittance. Pure PLA has the highest UV transmittance at each distance over the other films at different ratios. Moreover, the UV transmittance of the PCL6500/PLA composite films is inversely proportional to the distance from the UV source. Compared with the pure PLA films, the PCL6500/PLA composite films (30/70) show more noticeable decrease in UV transmittance, which is below 10%. Hence, the application of the PCL6500/PLA films (30/70) ensures a certain level of exposure to the sun. The UV transmittance of pure PCL is higher than that of the composite films, indicating that the combination of PCL and PLA provides excellent UV resistance. Hence, PCL6500/PLA films have high UV-resistance efficacy.



**Fig. 9** UV transmittance (%) of PCL6500 / PLA film at ratios of 0 / 100, 30 / 70, 50 / 50, 70 / 30 and 100 / 0.

## Conclusion

Based on the examination of the influence of PCL on composite films, PCL with a relative molecular weight of 50,000 contributes to mechanically strong composite films with high toughness and elongation at break and good affinity to water. The DSC analyses show that the relative molecular weight of PCL has a marginal influence on the thermal properties and UV-blocking efficacy of the composite films. Regardless of the relative molecular weight of PCL, all of the composite films have 0% UV transmittance. For PCL with relative molecular weight of 50,000, a 30/70 ratio provides the PCL6500/PLA films with the maximum strength and significantly improved toughness and hydrophilicity. The PCL/PLA ratio is not correlated with the thermal properties but affects UV-resistance efficacy. The UV transmittance of the PCL6500/PLA films is inversely proportional to the content of PCL. Specifically, a 30/70 ratio generates PCL6500/PLA films with UV transmittance lower than 10%. The proposed composite films exhibit the optimal strength, toughness, hydrophilicity, anti-frozen property, and UV-resistance efficacy and thus improve the drawbacks of PLA.

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