One-pot Treatment with Maleic Anhydride *vs*. the Interfacial Compatibility of Polycaprolactone-microcrystalline Cellulose Composites

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Polycaprolactone (PCL) is an eco-friendly and biodegradable synthetic polyester encouraged by various government authorities. These biodegradable bioplastics and lignocellulose composites have attracted people's attention. Usually, neat PCL has poor interfacial compatibility with potential reinforcing particles and poor mechanical properties, which limit its application. The drawbacks can be effectively solved with maleic anhydride (MA) and microcrystalline cellulose (MCC). In this study, PCL composites were prepared by the one-pot synthesis method. The roughness of the PCL-MA/MCC film was reduced 66.7%, the contact angle (CA) reached a maximum of 87.5°, and its tensile strength was effectively improved by 77.8%. The thermodynamic properties of PCL-MA were similar to PCL. In contrast to PCL, the thermodynamic properties of PCL-MA were minimally affected, and the main chain structure of PCL was not broken despite the formation of new chemical groups. Its interfacial compatibility and mechanical properties were effectively improved.

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INTRODUCTION

In recent years, there have been growing concerns about environmental pollution, and plastic waste is one of them (Mishra *et al.* 2018). The main drawbacks of biodegradable bioplastics based on lignocellulose include poor mechanical properties, poor fiber/matrix interface, and poor chemical resistance. Neat polycaprolactone (PCL) does not have the mechanical properties to be applied in high load-bearing applications (Li *et al.* 2019). Cellulose-based reinforcing particles have the potential to increase the elastic modulus and strength to breakage, assuming that good interfacial adhesion can be achieved. Therefore, it is of great interest to study the compatibility of lignocellulose with degradable bioplastics.

Compatibility refers to the ability of polymers to adapt to each other and form a macroscopically homogeneous material after blending. Interfacial compatibility of polymers refers to the bonding of two materials through chemical or physical interactions, including hydrogen bonding, coordination, bilayer, and weak interfacial layer interactions. It is possible to reduce the interfacial roughness and improve the interfacial adhesion by improving the compatibility.

Biodegradable materials can be an alternative to traditional plastics; PCL is a biodegradable synthetic polymer. It is used widely in tissue engineering, biomedical applications, lightweight applications, and toy manufacturing (Woodruff and Hutmacher 2010; Dhakal *et al*. 2018a; Khorramnezhad *et al*. 2021), *etc*. Although PCL has good degradability, the main drawback is its poor mechanical properties, which restrict its use in wide industrial applications. To overcome the problem, researchers have attempted blending it with reinforcing agents such as microcrystalline cellulose (MCC) (Ashori and Nourbakhsh 2010; Zulkifli *et al*. 2015; Chen *et al*. 2017; Murphy and Collins 2016), cellulosic fibers (Chen *et al*. 2017; Dhakal *et al*. 2018a,b), bioactive glass (Tamjid *et al*. 2011), *etc*. However, the problem has not yet been fully solved. The challenge is the lack of surface-chemical compatibility between the PCL matrix material and reinforcing particles. This problem can be effectively solved by chemical modification. Regarding the modification of PCL, the functionalization of PCL has been reported previously (Lee and Ohkita 2003; Arbelaiz *et al*. 2006; d'Ayala *et al*. 2009; Ortega-Toro *et al*. 2016; Alemán-Domínguez *et al*. 2018). However, these methods were usually complex. In this study, a one-pot synthesis method was used to enhance the mechanical properties and interfacial compatibility of PCL.

In addition, MCC has been studied as a reinforcing additive in polymer composites (Alshaghel *et al*. 2018). Microcrystalline cellulose is one of the important cellulosic products obtained from cellulose or biomass-derived pulp (Li *et al*. 2019). In this study, MCC served as reinforcing particle materials. Presently, cotton stalk is used in low-value products. With the growing concern for environmental protection and agricultural waste utilization, people have attempted high-value applications for the cotton stalk. Therefore, MCC was isolated from cotton stalk waste in this study.

This work aimed to improve the interfacial compatibility of PCL. The authors report a one-pot synthesis of polycaprolactone-maleic anhydride (PCL-MA) composites to enhance interfacial compatibility. The composite obtained from the one-pot synthesis was characterized and analyzed.

EXPERIMENTAL

Materials

The PCL was purchased from Perstorp AB (Malmö, Sweden). The maleic anhydride (MA) was obtained from Richjoint Co., Ltd. (Shanghai, China). Benzoyl peroxide (BPO) was obtained from Damao Chemical Reagent Factory (Tianjin, China). The cotton stalk was collected from Changji Hui Autonomous Prefecture (Xinjiang, China). All the other chemicals were from commercial sources.

Methods

PCL-MA preparation

The PCL and MA were first placed in dichloromethane in a 150-mL polymerization vessel. Then, the BPO was added to the reaction vessel and stirred at 60 rpm. BPO served as initiator. The reaction was carried out in dichloromethane solvent in an oil bath at 100 °C. The reactants were collected by filtration in ethanol, dried, and then extracted with ethanol for 24 h to purify the PCL-MA.

MCC preparation

The cotton stalk pulps were cooked and bleached in the laboratory. The kraft cooking process was completed in a laboratory digester under the following conditions: 23% active alkali, 25% sulfidity, a solid-to-liquid ratio of 1:15 (w/v), a temperature of 160 °C, and a duration of 3 h. Stabilized chlorine dioxide was used to bleach the cotton stalk pulp. Bleached pulps were hydrolyzed with 1 mol/L of HCI at 85 °C at a ratio of 1:10 and then were washed with distilled water until neutral.

PCL-MA/MCC film preparation

The PCL-MA/MCC film was used during the solvent casting technique. The PCL-MA/MCC solution (m PCL-MA: m MCC = 5:1) was cast on a clean tetrafluoroethylene mold and the solvent was evaporated at room temperature for 6 h under a fume hood.

Characterization

The Fourier transform infrared (FTIR) spectra of the samples were acquired using 32 scans on a Vector 33 spectrometer (Tensor 27; Bruker Corporation, Ettlingen, Germany) in the range of 400 to 4000 cm^{-1}. Potassium bromide was of spectral purity (Kermel, Tianjin, China), and the samples were mixed with KBr and pressed.

The surface hydrophilicity of the composite film was analyzed using contact angle (CA) measurements (OCA20; DataPhysics Instruments, Filderstadt, Germany).

A thermogravimetric analyzer (TGA Q500; TA Instruments, New Castle, DE, USA) was used to characterize the thermal stability. All samples were conducted under nitrogen flow, and the temperature was heated at a constant heating rate of 10 °C/min from 30 °C to 700 °C.

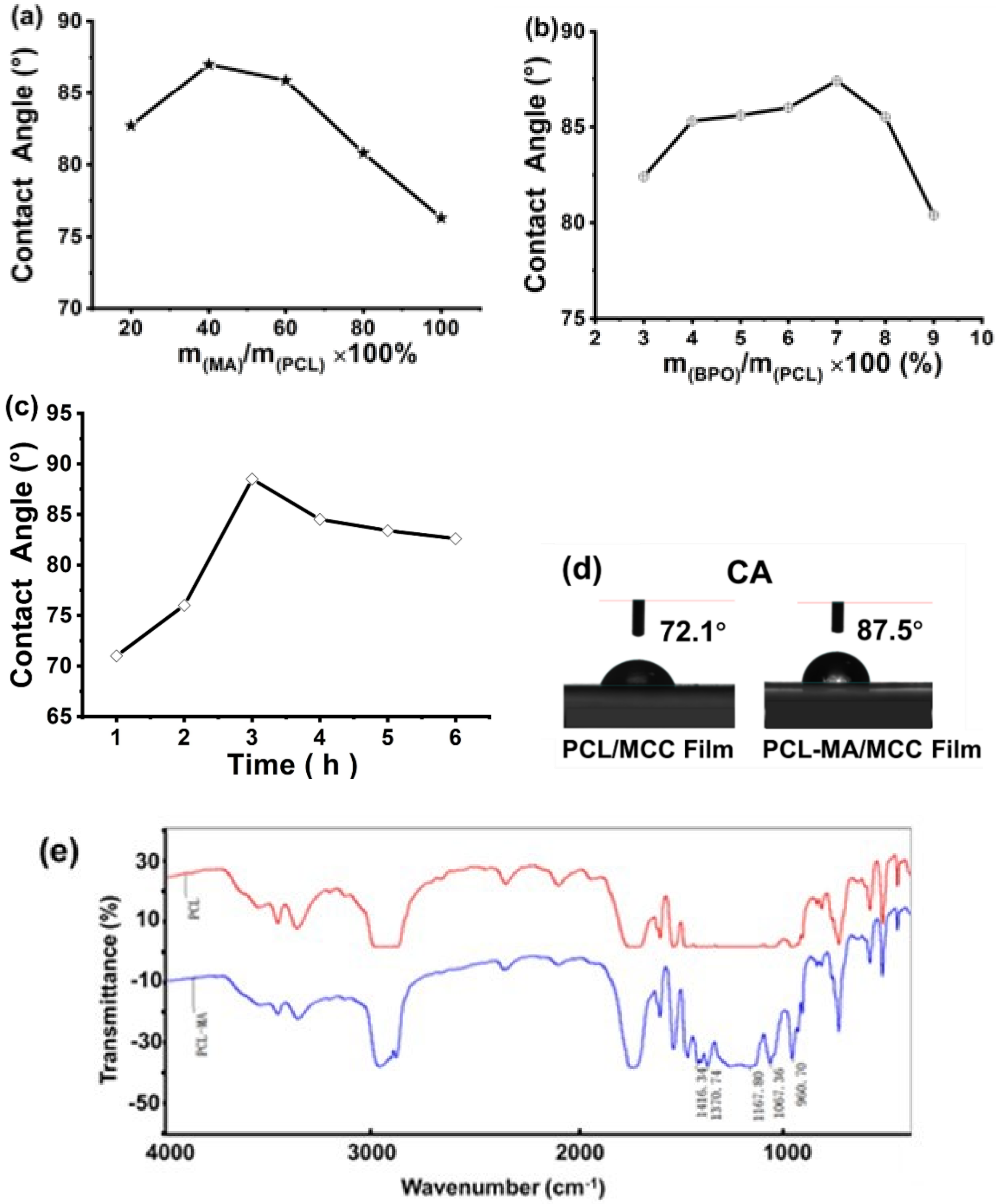
The mechanical properties of the film samples were determined at 5 mm/min using a universal testing machine (Series 5560; Instron Corporation, Norwood, MA, USA). A Surface morphology characterization was performed using a 3D Surface Profile Analyzer (Expert 3D; Breitmeier Messtechnik GmbH, Ettlingen, Germany).

RESULTS AND DISCUSSION

The chemical reaction of the reactants leads to a change in the chemical groups. The CA can reflect the chemical changes. The factors of reaction time, m(MA) and m(BPO), could affect the degree of modification and hydrophilic or hydrophobic character of PCL. Increasing the hydrophobicity of PCL means a higher value of the water CA. In this paper, the surface hydrophilicity of the composite film was analyzed were investigated by the CA. From Fig. 1(a), it was shown that the CA was at its maximum at 40% for m(MA)/m(PCL). As shown in Fig. 1(b), the optimum reaction time was 3 h. From Fig. 1(c), the CA was at its maximum at 7% for m(BPO)/m(PCL). The CA reached a maximum of 87.5° at a reaction time of 3 h. The hydrophobicity increased due to the increase of hydrophobic groups. Improving the compatibility of PCL is helpful to improve its hydrophobicity.

However, the hydrophobicity first increased and then decreased with the increase of MA and BPO content and reaction time. This was due to the increase of hydrophilic groups with an increase in MA addition, resulting in the increase of hydrophilicity. As shown in Fig. 1(d), the CA of the PCL-MA/MCC film was 87.5°, which was 21.4% greater than that of the PCL/MCC blank sample. It was attributed to the generation of new hydrophobic groups after modification, increasing the number of hydrophobic groups. The increase in hydrophobic groups made it possible to increase the CA of the PCL-MA/MCC film.

Differences between chemical groups in PCL-MA and PCL samples were tested using FTIR. The analysis helped to confirm the changes in chemical bonds and groups to clarify the main chemical reactions. Figure 1(e) shows the FTIR curves of PCL-MA/MCC. It can be observed that in the 1500 to 960 cm^{-1} regions was a newly formed absorption peak, indicating the generation of new groups. The peak at 1416.3 cm^{-1} was the characteristic peak due to the stretching vibration of -CH. The peak at 1370.7 cm^{-1} was the absorption peak due to the stretching vibration of both -CH$_3$ and -CH$_2$. The absorption peaks near 1167 to 1067 cm^{-1} are attributed to the vibrations of -HC=O and C-O (Tuama *et al*. 2020). The absorption peak near 960.7 cm^{-1} was due to the vibrations of -C-O-C- (Tuama *et al*. 2020).



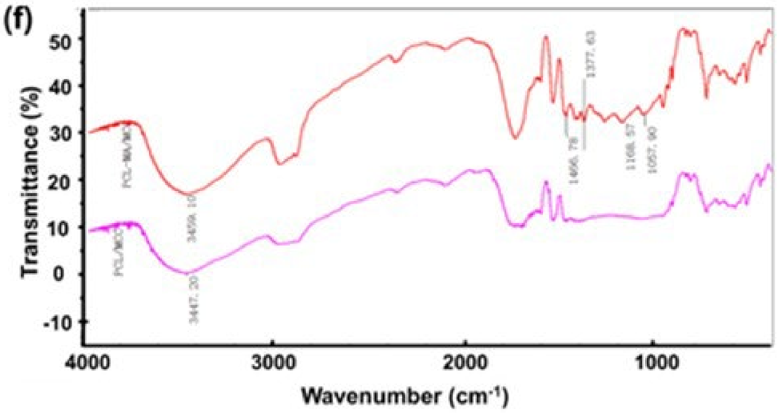


Fig. 1. (a to c) Influence of reaction condition; (d) contact angle (CA); (e and f) FTIR spectra

From previous studies, grafting reactions usually have been divided into three typical steps (Lee and Ohkita 2003; Wu 2003; Laurienzo *et al*. 2006; d'Ayala *et al*. 2009; Ma *et al*. 2014; Hemmati *et al*. 2015; Ortega-Toro *et al*. 2016). Based on the above new groups, it was assumed that the possible reaction process of MA with PCL during one-pot synthesis could also be divided into three steps. In the first step, BPO generated reactive radicals at high temperatures, which attacked the H-atom attached to the α-C atom of both PCL and activated PCL.

In the second step, the MA monomer opened its ring at a high temperature. The -C=C- and the anhydride group of the MA monomer were able to carry out ring-opening and polymerization reactions under the action of the initiator. In the third step, the activated PCL runs a grafting reaction with the ring-opened MA. Finally, PCL-MA composites were obtained. As shown in Fig. 1(e), the shifts of the PCL-MA sample from 1370.7 to 1377.6 cm^{-1} and 1167.8 to 1168.6 cm^{-1} were observed compared with the PCL-MA/MCC sample. Both were redshifted. The shifts of the FTIR absorption peaks indicate that the PCL-MA/MCC samples were more compatible than PCL/MCC samples.

Figure 2 reveals the thermal property of PCL-MA. As shown in Fig. 2(a), it could be divided into three stages. In the first stage, the mass decreased 10% at 364 °C. It was apparent that PCL-MA had good thermal stability under 364 °C. In the second stage, the mass dropped sharply to 7% in the range 364 to 437 °C, which was attributed to the breakage of chemical bonds such as C=O, C-O, and $-CH_2$.

The third stage was the gradual carbonization process of ash, and the final residue was 5% within the range 437 to 550 °C. As shown in Fig. 2(c), the melting temperature started at 44 °C and ended at 65 °C. The peaks of PCL and PCL-MA were at 59 °C. In general, the modification had little effect on its thermodynamic properties, which was probably because the main chain structure of PCL was not destroyed by the one-pot synthesis. Figure 2(a,b,c) shows that the thermodynamic property of PCL-MA was similar to PCL.

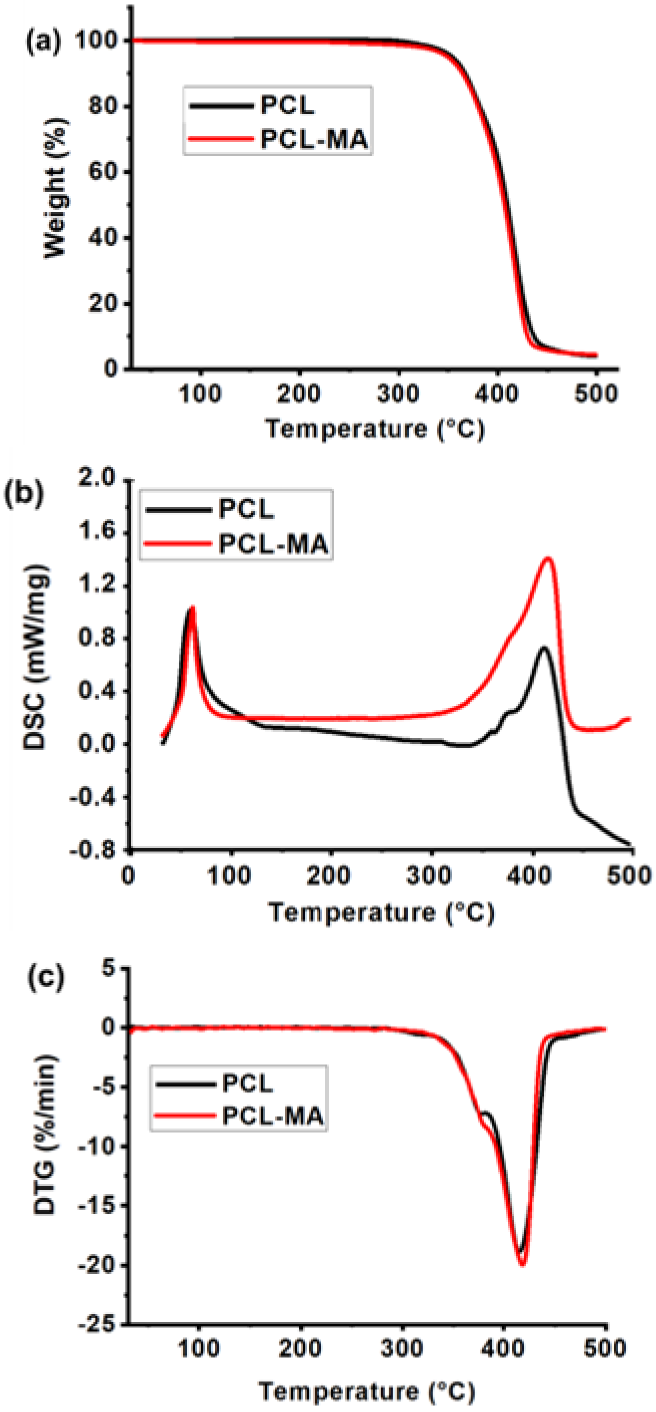
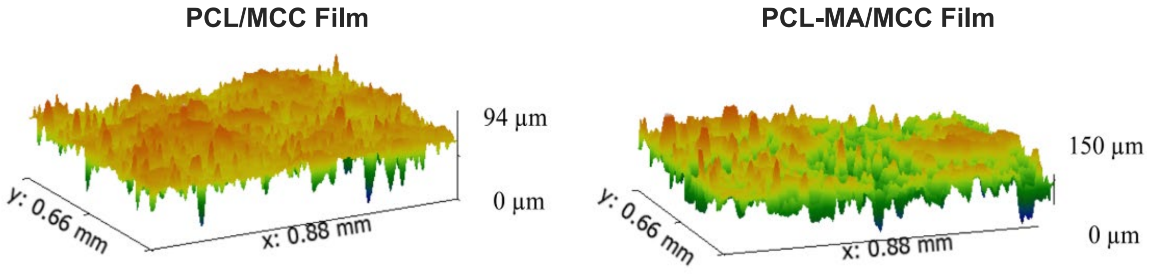


Fig. 2. The thermodynamic properties of PCL-MA and PCL

The surface roughness of the PCL/MCC and PCL-MA/MCC films was evaluated using a 3D Surface Profile Analyzer. Figure 3 shows the 3D morphological model of the samples. Table 1 presents the surface morphology parameters of samples. The roughness of PCL-MA/MCC was 5 µm, while that of PCL/MCC was 15 µm. The results show that the roughness decreased 66.7% after MA modification. The kurtosis can describe the degree of data center aggregation. As shown in Fig. 4, the peaks of height distribution were different between PCL-MA/MCC and PCL-MCC.



(a) (b)

Fig. 3. 3D surface morphology of PCL-MA/MCC and PCL/MCC film

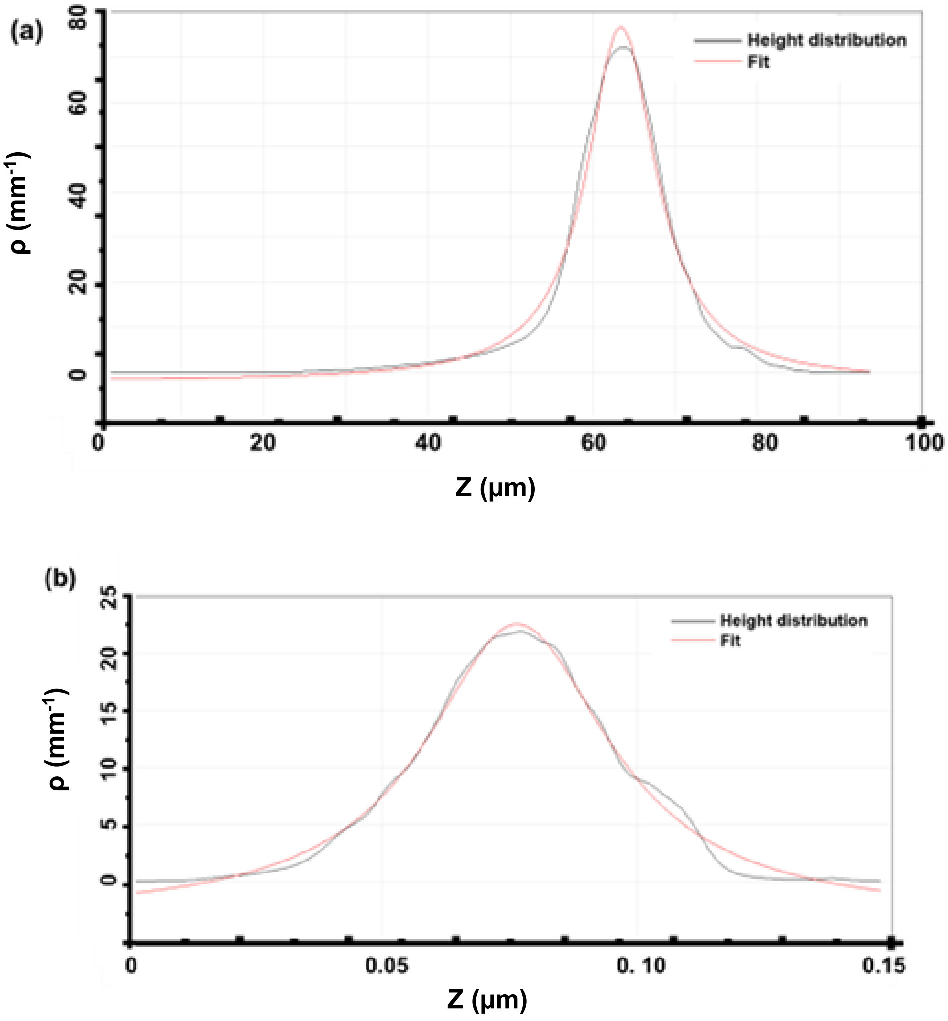


Fig. 4. Surface height line probability distribution maps of PCL-MA/MCC (a) and PCL/MCC (b)

The shape of the distribution peak of the surface height line of PCL-MA/MCC was relatively sharp. In comparison, Fig. 4(b) shows a flat distribution with a peak value of 0.2, and the distribution was relatively scattered. From the kurtosis parameter in Table 1, the height distribution was more concentrated compared PCL/MCC film. The PCL-MA/MCC film showed a smoother surface compared to PCL/MCC. The PCL-MA tightly encapsulated the microcrystalline cellulose, turning it into an internal filler, creating a uniformly smooth interface, and reducing roughness. This indicated that MA modification enhanced interfacial compatibility between PCL and MCC. The results showed that after blending PCL-MA and MCC, a more homogeneous material was formed. Consequently, the interfacial compatibility was enhanced.

Table 1. 3D Surface Morphology Parameters

	PCL-MA/MCC	PCL/MCC
Bottom	0 μm	0 μm
Kurtosis peak	94 μm	150 μm
Mean height	62 μm	76 μm
Roughness	5 μm	15 μm
Kurtosis	4.6	0.2

The mechanical properties of biodegradable materials are an important performance factor for biocomposites for lightweight applications and industrial practices (Zhao *et al*. 2017; Dhakal *et al*. 2018b). Figure 5 reflects the mechanical properties of the PCL-MA/MCC film and PCL/MCC film. The stress to breakage (tensile strength) of the PCL-MA/MCC film increased 77.8% compared with PCL/MCC film.

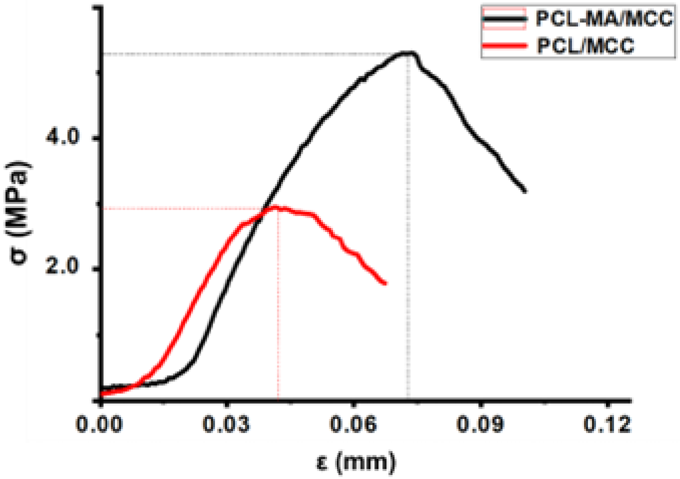


Fig. 5. Stress-strain curves for PCL-MA/MCC and PCL/MCC film

One possible reason for this is that the increased flexibility of PCL-MA sheets improved the compatibility with MCC and formed a relatively strong network. Another possible explanation is that it was attributed to heterogeneous nucleation. Heterogeneous nucleation is due to the presence of heterogeneous particles in the system, which preferentially form the crystal nucleus. Theoretically, the addition of MCC as a nucleating additive increases the nucleation density, and the size of the spherical crystals becomes smaller. As a result, the mechanical properties are improved. For the PCL-MA/MCC film, MA acts as a new nucleating agent, and thus PCL-MA undergoes heterophase nucleation.

Therefore, the mechanical properties of PCL-MA/MCC were improved compared to PCL/MCC.

CONCLUSIONS

1. The one-pot synthesis of maleic anhydride (MA) modified polycaprolactone (PCL) improved the compatibility of the composite film and reduced its hydrophilicity. For PCL-MA/MCC film, the contact angle (CA) reached a maximum of 87.5°. In contrast to PCL, the thermodynamic properties of PCL-MA were minimally affected, and the main chain structure of PCL was not broken despite the formation of new chemical groups.
2. The roughness of the PCL-MA/MCC film was reduced by 66.7% relative to PCL/MCC film. The PCL-MA encapsulated the MCC, forming a homogeneous smooth interface and reducing the roughness.
3. The PCL-MA could effectively improve its mechanical properties, and the tensile strength was increased 77.8%. Overall, the interfacial compatibility was enhanced.

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