

Preparation of Composite Films of Methacryloyl-modified Lignocresol and Polylactic Acid

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Methacryloyl chloride was grafted onto lignocresol to increase the acyl content of lignocresol and to enhance the interfacial compatibility of lignocresol and polylactic acid. The physical and mechanical properties of the modified lignocresol sample were studied. The methacryloyl-modified lignocresol was characterized by infrared spectroscopy (IR), ultraviolet-visible (UV) spectroscopy, and gel permeation chromatography (GPC). Unmodified and modified lignocresol samples were used to prepare composite films with polylactic acid, and its tensile strengths and elongations at breaks were analyzed after film formation. Thermal stabilities were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results indicated that methacryloyl group was successfully grafted onto lignocresol, and that the optimum dosage of methacryloyl chloride required was 0.5 mL per 0.5 g of lignocresol. When unmodified lignocresol was added to polylactic acid, the tensile strength gradually decreased as the amount of lignocresol increased. However, the composite films prepared from the methacryloyl-modified lignocresol exhibited a slower decline in tensile strength and displayed an increased elongation at break. The optimum mechanical properties were found using a 10% blend of modified lignocresol with polylactic acid.

Keywords: Lignocresol; Methacryloyl chloride; Polylactic acid (PLA); Blend composite films

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INTRODUCTION

Due to the rapid economic development seen in recent years, oil resources are being progressively consumed. In the long term, there will be a gradual shortage and depletion, with humans needing to develop effective biomass resources to replace oil resources. Lignocellulosic biomass has been delineated as one of the most promising alternatives. Lignin is one of the main components of the cell wall of lignocellulose, and it is the most abundant aromatic compound found in nature. At present, the main source of lignin is produced as a waste from papermaking and related industries, and the industrial utilization rate of lignin is less than 2% of the reserve. This is because of the complex structure of lignin. The separation and utilization of plant cell walls are primarily based on the use of carbohydrates, and the natural structure of lignin has often been severely damaged during the process of deriving cellulose fibers from wood (Evtuguin and Amado 2003; Lisperguer *et al.* 2009). In this study, a phase separation method was applied towards the separation of lignin, aiming to retain as much of the natural structure of lignin as possible (Funaoka 2013, 2015; Mikame and Funaoka 2006).

Poly(lactic acid) (PLA) is an aliphatic polyester and a popular biodegradable polymer due to its excellent mechanical properties, including plasticity and transparency. However, the limitations of PLA include high hardness, high brittleness, poor thermal performance, and low controllability of degradation rate, which limit its practical application (Liu and Zhang 2011). In recent years, a large number of studies have been conducted on the preparation of modified PLA materials by copolymerization, blending, plasticization, and composite preparation (Chen *et al.* 2014; Turalija *et al.* 2016; Yang *et al.* 2016). Of these, there have been some studies on the preparation of composite materials consisting of lignin/its derivatives and PLA (Gordobil *et al.* 2015; Wang *et al.* 2015; Murariu and Dubois 2016; Yang *et al.* 2016), but the interface between lignin and PLA molecules requires further improvement.

In a preliminary study, it was found that lignocresol could be used to prepare blended films with PLA in solutions due to its extremely high solubility in organic solvents, exhibiting a film-forming property. However, the mechanical properties of these films were not adequate. To improve the compatibility of PLA and lignin, a chemical modification was attempted by grafting methacryloyl groups onto lignocresol. This modification would help to reduce its hydroxyl group content and increase the acyl and ester contents of the lignocresol molecule while maintaining the relatively linear skeleton structure of lignocresol. It was expected that the mechanical properties of the modified lignocresol and PLA complex would improve, thus expanding the potential application of lignin into high value-added industries.

EXPERIMENTAL

Materials

Lignocresol was synthesized by a phase separation method using the extractives from 60-mesh poplar powder (Tree farm of Nanjing Forestry University, Nanjing, China) as a raw material (Funaoka and Abe 1989). The average molecular weight (M_w) was *ca.* 2700 g/mole. The ratio of *p*-cresol introduced was 0.8 mol/C₉, and the phenolic hydroxyl content was approximately 12%. The product dissolved well in methanol, ethanol, acetone, dioxane, and tetrahydrofuran solvents (Nanjing Chemical Reagent Co., Ltd., Nanjing, China).

Methacryloyl chloride (analytical grade) was purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). The PLA was purchased from Taicang Kaiherda Plastic Materials Co., Ltd. (Suzhou, China), and had a melt flow rate of 6 g/10 min and a density of 1.25 g/cm³.

Methacryloyl-modified lignocresol

Lignocresol (0.5 g), dioxane (10 mL), and triethylamine (Shanghai Macklin Biochemical Co., Ltd., Shanghai, China) (0.75 mL) were added to a three-necked flask. After the mixture had been stirred for 10 min at 14 °C, the required amounts (0.5 mL, 0.85 mL, or 1 mL) of a mixture of dioxane and methacryloyl chloride (20:17, v:v) were added dropwise, with the addition being completed in 10 min. After 50 min, enough hydroquinone (Gordobil *et al.* 2016) equivalent to 0.5% of the total reaction mass was added to terminate the reaction. The reaction mixture was then added dropwise to distilled water with cooling and stirring, centrifuged at a speed of 3500 rpm and a temperature of 5 °C, and the precipitate was collected as the reaction product. The product was vacuum-

dried and then ground to obtain the methacryloyl chloride-modified lignocresol product for film preparation.

Methacryloyl chloride-modified lignocresol and PLA blend film

Approximately 4 g of PLA was added to a three-necked flask, followed by 32 mL of CHCl_3 . The mixture was placed in a water bath at 90 °C to fully dissolve the sample. The required amounts of modified and unmodified lignocresol samples each were dissolved in 5 mL of CHCl_3 . The homogeneous solutions of the PLA and lignocresol samples were evenly mixed, and then slowly poured into a polytetrafluoroethylene grooved square mold (100 mm × 130 mm × 6 mm). After complete evaporation of the CHCl_3 solvent in a fume hood, a uniform lignocresol-PLA composite film was obtained. The amounts of unmodified and modified lignocresol samples added were 0%, 5%, 10%, 15%, and 20%.

Methods

Characterization of methacryloyl chloride-modified lignocresol

The molecular structure of the grafted methacryloyl chloride-modified lignocresol product was analyzed by Fourier transform infrared spectroscopy (FT-IR) and gel permeation chromatography (GPC). The specific measurement methods and instrument operating conditions followed were as described in previous literature (Ren *et al.* 2015).

The change in the phenolic hydroxyl group content was determined by ultraviolet-visible spectrophotometry. A sample of lignin (5 mg) was accurately weighed and dissolved in 10 mL of aqueous dioxane ($V_{\text{water}}:V_{\text{dioxane}} = 1:9$), and 2 mL of the resulting solution was transferred into two 50-mL volumetric flasks. One was diluted with 0.2 mol/L sodium hydroxide solution and the other was diluted with a buffer solution of pH = 6. After shaking evenly, the required amount of the solution was transferred to a cuvette, the buffer solution (pH = 6) was used as a blank for the spectrophotometer, and the absorbance values at 360 nm and 300 nm were measured and recorded as D_1 and D_2 , respectively. The concentration of hydroxyl groups was calculated as,

$$[\text{OH}] = 0.425\varepsilon_1 \pm 0.182\varepsilon_2; \varepsilon = D / (C \times L) \quad (1)$$

where C is the lignin solution concentration (g/L), D is the absorbance, and L is the cuvette thickness, $L = 1$ cm (Zakis 1994).

Physical and thermal properties of composite films

Following GB ISO 527-3 (1995), three dumbbell-shaped film specimens were cut from each sample film with a cutting tool, and the thickness of the central part of each film was measured at five points using a micrometer (Mitutoyo Measuring Instruments (Shanghai) Co., Ltd., Shanghai, China) to find the thinnest point. Subsequently, a universal tensile testing machine (CMT4303, MTS Industrial Systems (China) Co., Ltd., Shanghai, China) was used to measure the tensile strength at the thinnest point at a crosshead speed of 20 mm/min. The mechanical properties of all the film specimens prepared with modified and unmodified lignocresol (additions amounts: 0%, 5%, 10%, 15%, and 20%) were measured by the same method.

Thermogravimetry (TG) of the composite films was investigated using a TG/DTA 6200 device (SEIKO Instruments Inc., Tokyo, Japan). The TG was run at a heating rate of 10 °C/min under nitrogen using a heating temperature range of 0 °C to 600 °C (Qian *et al.* 2015). The films which have the best performance on mechanical properties (10% Lignocresol or modified lignocresol added) were further tested by TG.

Differential Scanning Calorimetry (DSC) experiments were performed in a Netzsch DSC 214 instrument under nitrogen atmosphere (40 mL min^{-1}). Sample weights of about 6 mg were sealed in aluminum pans and heated from $25 \text{ }^\circ\text{C}$ to $200 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$. Then the temperature was kept at $200 \text{ }^\circ\text{C}$ for 3 min, cooling the system down to room temperature at a rate of $20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$, and once again heating to 200°C at a heating rate of $5 \text{ }^\circ\text{C min}^{-1}$. The degree of crystallinity (X_c) was calculated using Eq. (2) (Gordobil *et al.* 2014),

$$X_c = (\Delta H_m / \Delta H_m^c) \times (100/w) \quad (2)$$

where ΔH_m is the melting enthalpy of the composite film, ΔH_m^c is the theoretical melting enthalpy of PLA (93.7 J/g), and w is the weight of PLA in composite film. The films that exhibited the best performance on mechanical properties (10% Lignocresol or modified lignocresol added) were further tested by DSC.

RESULTS AND DISCUSSION

Structural Properties of Methacryloyl Chloride-modified Lignocresol

IR analysis results

Infrared spectroscopy was employed to characterize the methacryloyl chloride-modified lignocresol products, and the results are shown in Fig. 1. When various amounts of methacryloyl chlorides were added (0.5 mL, 0.85 mL, and 1 mL) to 0.5 g of lignocresol, the intensity of the peak at 3400 cm^{-1} in the products was weakened to various degrees. However, the magnitude of the decline was not considerably different in the different products, and the hydroxyl peak did not completely disappear in any of them. The modified lignocresol showed characteristic peaks at wavenumbers 1325 cm^{-1} , 1220 cm^{-1} , and 1130 cm^{-1} from syringyl propane units, and peaks at 1270 cm^{-1} and 1040 cm^{-1} from guaiacyl units, which indicated that the skeletal structure of lignocresol was maintained after the graft modification reaction.

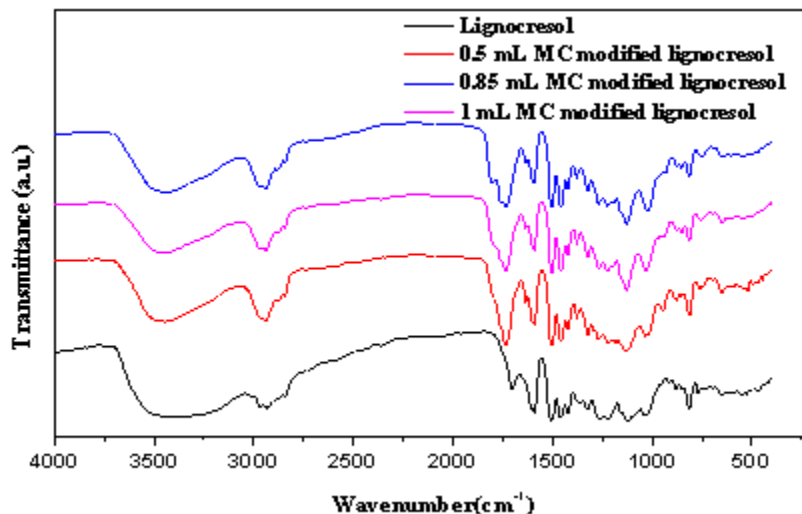


Fig. 1. FT-IR spectra of different dosages of methylacryloyl chloride (MC) modified lignocresol

A new peak characteristic of carbon-carbon double bonds appeared at 1640 cm^{-1} and indicated the successful introduction of methacryloyl chloride. In addition, the peak observed close to 1730 cm^{-1} could be assigned to the acyl group (either the carboxyl group or the ester bond), the intensity of which was much stronger than that observed before modification.

The effect of reducing the hydroxyl content of lignocresol after the first time of modification was not apparent (Fig. 1). To further enhance the modification effect, the synthetic process was repeated from one to four cycles. To reduce the total amount of chemicals used in the synthesis, doses of $0.5\text{ mL}/0.5\text{ g}$ of reagents were used for subsequent cycles of methacryloyl chloride grafting modification. The collected FTIR spectra of the methacryloyl chloride-modified lignocresol samples are shown in Fig. 2. As shown, the intensity of the peak at 3400 cm^{-1} caused by the hydroxyl groups was noticeably reduced after three or more modification cycles, which indicated that the purpose of the experimental design was achieved by increasing the number of modification cycles. In addition to the characteristic lignocresol peaks at 1325 cm^{-1} , 1220 cm^{-1} , 1130 cm^{-1} , 1270 cm^{-1} , and 1040 cm^{-1} , the intensities of the acyl and carbon-carbon double bond peaks at 1730 cm^{-1} and 1640 cm^{-1} from the introduced methacryloyl chloride were also increased markedly. Therefore, methacryloyl chloride could be successfully introduced through an increased number of modification cycles, and the hydroxyl content of the lignocresol was thus reduced.

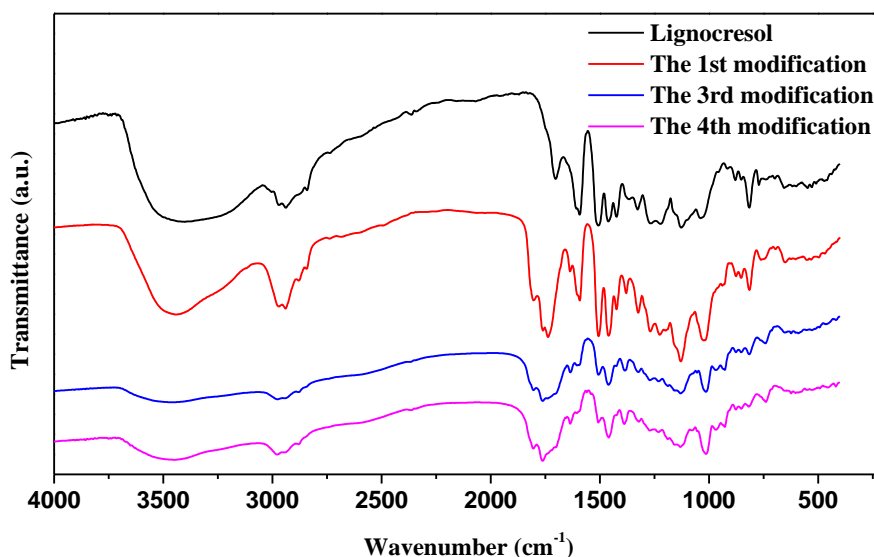


Fig. 2. FT-IR spectra of different times of modified lignocresol

Analysis of the hydroxyl contents of the modified products

The hydroxyl contents of lignocresol and its modified products were determined by UV-visible spectrophotometry, and the results are shown in Table 1. As shown in the table, the phenolic hydroxyl content decreased with the increased number of modification cycles, which suggested the successful introduction of methacryloyl chloride onto lignocresol. After four modification cycles, the hydroxyl group content decreased considerably, and the unreacted hydroxyl groups accounted for only *ca.* 10%. This was consistent with the IR spectral data discussed before, indicating that the grafting of methacryloyl chloride onto lignocresol proceeded as expected.

Table 1. Hydroxyl Content of Lignocresol and Modified Lignocresol

Sample	Concentration (g/L)	D_1	D_2	[OH] (%)
Lignocresol	0.0216	0.600	0.117	11.81 ± 0.99
The first modification	0.0212	0.303	0.111	6.07 ± 0.78
The third modification	0.0208	0.266	0.113	5.44 ± 0.99
The fourth modification	0.0200	0.085	0.056	1.81 ± 0.51

Molecular weight analysis of the modified products

The molecular weight distributions of lignocresol and its modified products are shown in Table 2. After the modification of lignocresol, using methacryloyl chloride, the molecular weight increased substantially, with the average molecular weight increasing from 2794 to 21937, and the polydispersity index (M_w/M_n) decreasing from 2.67 to 1.05. This indicated that the size of lignocresol was more homogeneous after methacryloyl chloride modification. Therefore, the prepared lignin had a lower polydispersity index than the original alkali lignin, while maintaining a certain degree of polydispersity. During the modification of lignocresol with methacryloyl chloride, the chloride ions caused some homopolymerization when attacking the hydroxyl groups of lignocresol due to the presence of vinyl groups, thus continuously increasing both the length of the chains and the molecular weight. However, due to the heterogeneity of the structure and molecular weight of natural lignin, the degree of difficulty when introducing *p*-cresol to the benzyl position of lignin during phenolization was variable. In this process, the degree of polymerization of methacryloyl chloride on lignocresol molecules with relatively high molecular weights was low due to the strong steric hindrance. In contrast, lignocresol with a lower molecular weight was grafted to produce homopolymers with higher degrees of polymerization. Therefore, the final reaction product showed better overall uniformity in the molecular weight distribution.

Table 2. Molecular Weight and the Dispersion Coefficient of Lignocresol and Modified Lignocresol

Sample	M_n	M_w	M_w/M_n
Lignocresol	1717	2794	2.67
Modified lignocresol	20833	21937	1.05

Analysis of the mechanical properties of lignocresol-PLA composite films

The effects of the addition of lignocresol and methacryloyl-modified lignocresol on the tensile strengths of PLA composite films are shown in Fig. 4. The addition of lignocresol and its modified product indicated a negative effect to various degrees on the tensile strength of the composite film, with the negative effect of the modified product being smaller. This might have been attributable to the tensile strength of the additive, which was not as high as that of PLA. In addition, the hydrogen bonding between the hydroxyl group of lignocresol and the PLA caused a certain degree of damage to the crystal structure of PLA. In contrast, the low hydroxyl content of the modified lignocresol would have lessened the damage to the crystal structure. Moreover, the modified product contained more hydrophobic groups that increased the compatibility with PLA resulting in a uniform distribution. The mean thicknesses of all films were in the range 2 to 3 mm.

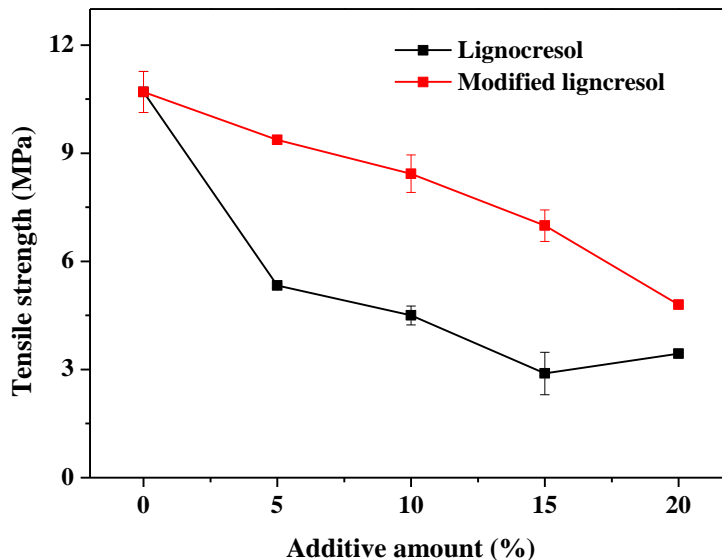


Fig. 3. The relationship between tensile strengths and lignocresol or modified lignocresol contents

The effects on the elongation at breaks of the PLA composite films with the addition of unmodified and modified lignocresols are shown in Fig. 5. As the amount of lignocresol content increased, the elongation at break of the composite film initially increased and then became constant. This was because of the increased compatibility between the modified product and PLA. In addition, the hydrogen bonding between some of the hydroxyl groups in lignocresol and the PLA allowed the PLA chain to grow. Moreover, the modified product had a stronger interfacial binding force than lignocresol, which weakened the tensile force in the process of breaking, and thus increased the elongation at break. The fact that lignocresol itself could undergo polymerization also affected the elongation at break and caused it to stabilize.

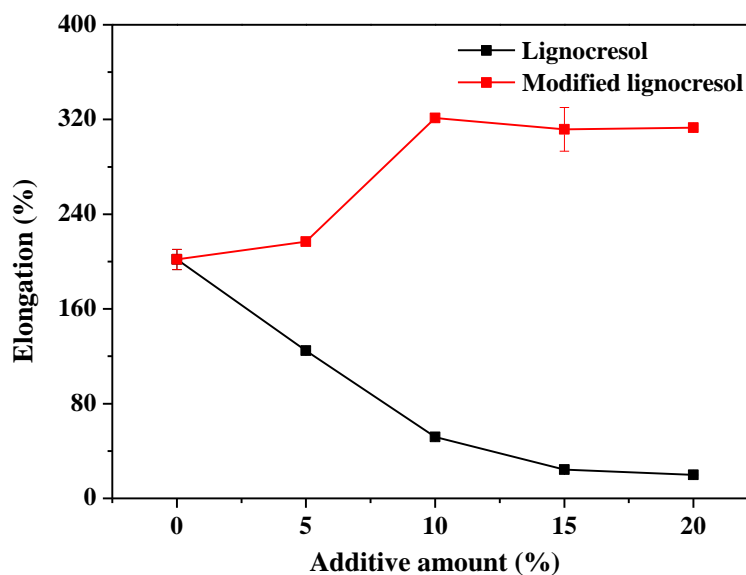


Fig. 4. The relationship between elongation at break and lignocresol or modified lignocresol contents

TG analysis of the composite films

The TG curves of PLA and PLA composite films are shown in Fig. 6. The derivative TG analysis (DTG) table of PLA and PLA composite films are shown in Fig. 7. The extrapolated onset temperature (T_{eo}), temperature of peak maximum (T_{max}), and residue percentage are shown in Table 3. It can be seen that when lignocresol and its modified products were added to PLA, it enhanced the thermal stability of the composite film. The values of T_{eo} increased from 298.2 °C to 330.7 °C and 335.8 °C after adding unmodified and modified lignocresols, respectively. The T_{max} also increased considerably.

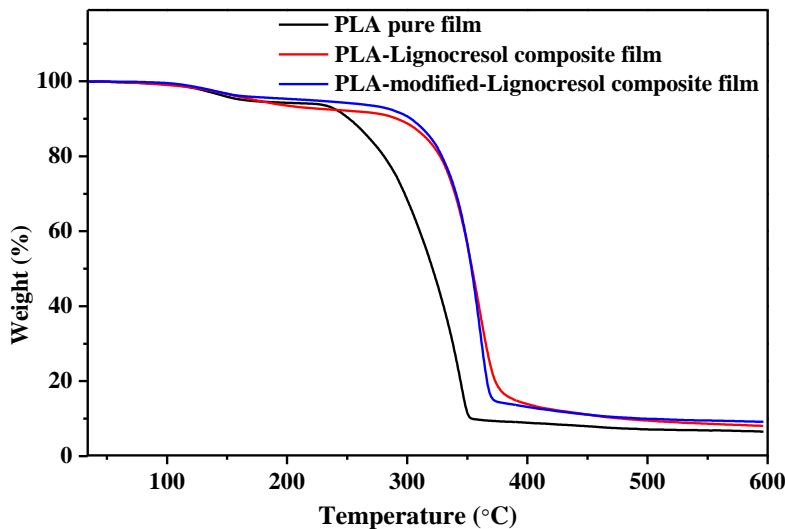


Fig. 5. The TG analysis curve of PLA and PLA composite films

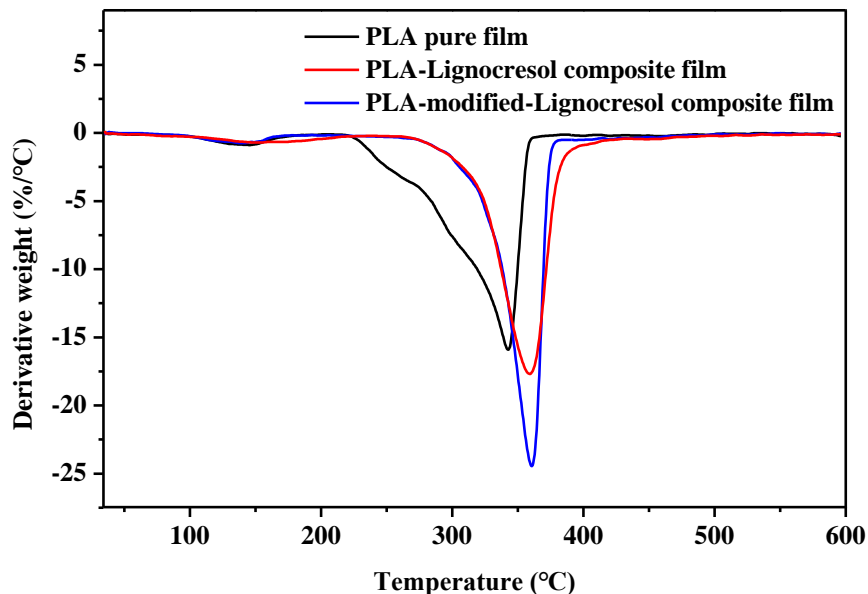


Fig. 6. The DTG curves of PLA and PLA composite films

It was assumed that the hydrogen bonding interaction between lignocresol and PLA occurred, which increased the thermal stability of the PLA-lignocresol composite films. When the lignocresol were further modified by methacryloyl chloride, part of the phenolic

hydroxyl groups in lignocresol were replaced by an acyl group. The acyl group can also form hydrogen bonding with PLA, and hence the modified lignocresol exhibited better compatibility with PLA due to the introduced acyl group. Therefore, the thermal stability of the PLA-modified-lignocresol composite was slight better than the PLA-lignocresol composite.

Table 3. DTG Analysis of PLA and PLA Composite Films

Samples	PLA Pure Film	PLA-LPs Composite Film	PLA-m-LPs Composite Film
T_{ei} (°C)	298.2	330.7	335.8
T_{max} (°C)	342.2	359.0	360.3
Residue (%)	6.51	8.08	9.15

DSC analysis of PLA films

DSC curves of PLA particles, PLA pure film, PLA-LPs composite film, and PLA-m-LPs composite film were shown in Fig. 7. The melting enthalpy and degree of crystallinity (X_c) are shown in Table 4. Compared to PLA particles and pure PLA film, it was thought that chloroform solvent undermined the crystal structure of the PLA to a certain extent during the casting film process, such that the crystallinities of two kinds of composite films both decreased. The addition of either lignocresol or modified lignocresol decreased the crystallinity of the composite, that should be caused by hydrogen bondings between hydroxyl groups on lignocresols and hydroxyl or carbonyl groups on PLA, which disrupted the the crystalline structure of PLA. As described above, the amount of phenolic hydroxyl groups decreased markedly after methacryloyl modification, such that methacryloyl-modified lignocresols formed less hydrogen bonds, and the extent of damage was relatively low, so the crystallinity of PLA-m-LPs composite showed slight higher than that of PLA-LPS composite.

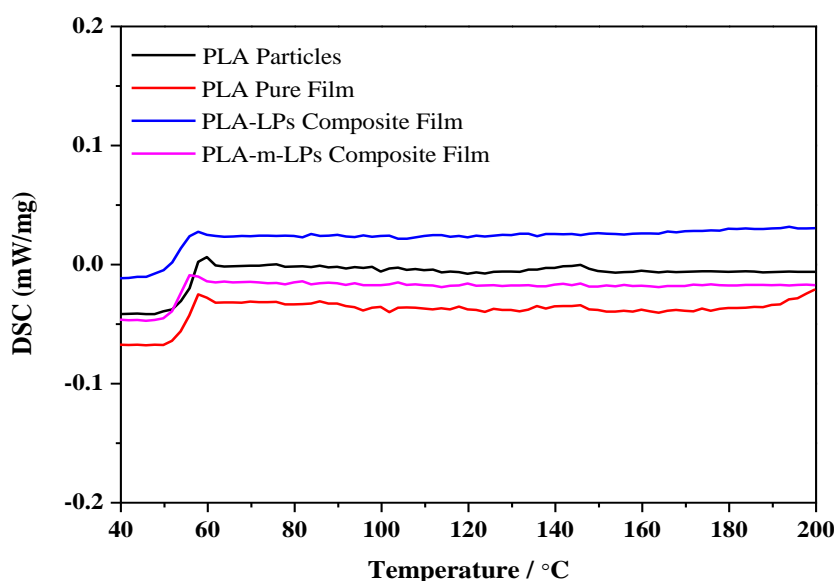


Fig. 7. DSC curves of PLA particles film and lignocresol added films

Table 4. Crystallinity of PLA Particles, Pure PLA Films and Composite Films

Sample	PLA Particles	PLA Pure Film	PLA-LPs Film	PLA-m-LPs Film
Crystallinity (%)	26.84	24.08	20.11	22.60
Enthalpy (J)	25.15	22.57	18.84	21.18
Weight (mg)	6.2	5.2	7.3	6.0

CONCLUSIONS

In this study, modification of lignocresol with methacryloyl chloride was investigated in terms of the optimum amounts of methacryloyl chloride addition and the effects of methacryloyl chloride modification on the properties of lignocresol/PLA blended composite films. The conclusions were as follows:

1. The hydroxyl content of lignocresol decreased considerably (from 11.8% to 1.8%) after four cycles of methacryloyl chloride modification. The peak intensities related to hydroxyl functional groups in the FT-IR spectra decreased substantially and those of acyl functional groups correspondingly increased.
2. During the formation of composite films of methacryloyl-modified lignocresol and PLA, increased amounts of modified product caused a gradual decrease in tensile strength. However, the magnitude of the decline was vividly smaller when unmodified lignocresol was used to prepare composite films.
3. The elongation at breakages of the composites formed using the modified product were much higher than that of PLA itself, with the value initially increasing and then stabilizing with increasing amounts of modified product. Based on the tensile strength and elongation at break values, the addition of 10% methacryloyl-modified lignocresol to PLA was optimal.
4. The addition of lignocresols and modified lignocresols to PLA enhanced the thermal stability of the composite films.

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