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An Ambient Curable Coating Material Based on the Michael Addition Reaction of Acetoacetylated Castor Oil and Multifunctional Acrylate

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Abstract: In this work a novel ambient curable coating was synthesized based on the Michael addition reaction of acetoacetylated castor oil and a multifunctional acrylate. In the research, we used hexamethylene diacrylate as crosslinker to optimize the reaction conditions and found that a ratio of acetoacetylated castor oil to acrylate groups of 1:1.5 and a catalyst (DBU) loading of 2 wt % provided an appropriate curing time. The acetoacetylated castor oil was characterized by ¹H NMR and ¹³C NMR spectroscopy and the obtained coating characterized by FTIR to confirm the functionalization reaction. The tensile strength, cross linking density, and thermal properties of the resulting thermosets were investigated by dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Results demonstrated that the glass transition temperatures, tensile strength, and thermal degradation were significantly improved with higher cross-linking density. Moreover, we prepared films with different multifunctional acrylate cross-linkers and found that with the increase of cross-linking density, the swelling of the film rate decreased. Overall, thermosets made from Michael crosslinking technology provided a highly bio-based coating system.

Keywords: Michael addition reaction; acetoacetylated castor oil; ambient-cure

1. Introduction

Nowadays, replacing petroleum-based raw materials with renewable resources is a major contemporary challenge in terms of both economic and environmental aspects while the application of environment friendly and highly efficient processes has resulted in considerable attention in scientific research work [1–4]. Vegetable oils are considered to be one of the most important renewable resources due to their low price, easy availability, and renewable properties [5]. As a renewable resource, castor oil has often been the starting material for scientific researchers to prepare polymer materials [6]. At present, there are many reports on the use of castor oil or modified castor oil to prepare materials, such as polyurethane [7], UV cured resins [8], alkylated resins [9], and epoxy resins [10], etc.

In the Michael addition reaction, a nucleophile reacts with an activated olefin to produce a covalent bond between the Michael donor and acceptor [11]. Since the Michael reaction was discovered by Arthur Michael in the late 1800s, systematic studies on this reaction for the preparation of novel polymers and composites has received significant attention [12]. The Michael addition reaction has become one of the most useful C–C bond forming reactions, and it has been employed in the synthesis

of cross linked polymers such as hydrogels, thermoset resins, and coatings, where rapid cure and high conversions are necessary for performance [13–15].

At present, there are many reports on the use of this method to prepare coatings, and it has been employed in aircraft, ships, and other fields [16]. However, it has basically been reported that the raw materials used in coatings are petrochemical raw materials, and few articles have been concerned with using renewable resources as raw materials. In 2001, Trumbo et al. found that acetoacetylated castor oil and multifunctional amines can be cured to form films with different properties at 22–130 °C [17]. Webster et al. invented a novel Michael addition reaction coating between acetoacetylated sucrose and diamine, the coating is a highly tunable platform which can be used to develop a wide variety of coatings systems having different properties [18]. Recently, Webster et al. reported another Michael addition reaction coating in which the thermoset coatings made from sucrose soyate (AESS) Michael crosslinking technology provided a highly bio-based coating system with good hardness and chemical resistance [19]. However, the Michael addition reaction between acetoacetylated plant bases and acrylate groups has not yet been reported.

In this paper, we present a room-temperature, environmentally friendly coating material based on the Michael addition reaction of acetoacetylated castor oil and multifunctional acrylate. Structure–property relationships of the coatings system were studied based on the variation in the acetoacetylated castor oil to acrylate ratio, type of multifunctional acrylate cross linker used, and the use of a catalyst. The properties evaluated include the mechanical coating properties and thermal properties.

2. Materials and Methods

2.1. Materials

Trimethylolpropane triacrylate, pentaerythritol tetraacrylate, hexamethylene diacrylate, 4-dimethylaminopyridine (DMAP), castor oil, 1,8-diazabicyclo(5,4,0)undec-7-ene (DBU) and tert-butylacetoacetate were obtained from Sigma Aldrich (Shanghai, China). Piperidine, acetone, tetrahydrofuran (THF), and toluene were purchased from Beijing Chemical Works (Beijing, China). All the materials were used without further purification. The water used in this study was deionised and doubly distilled.

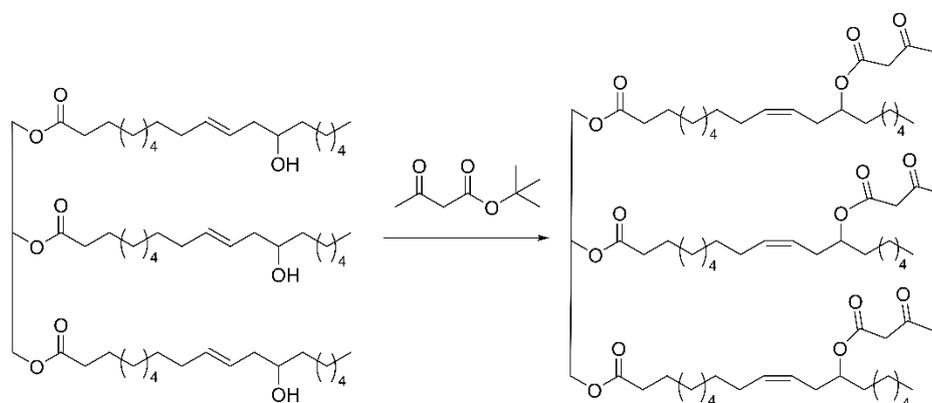
2.2. The Synthesis of Acetoacetylated Castor Oil

Scheme 1 shows the synthesis route, and the detailed synthesis steps are as follows: a 200-mL round-bottomed flask equipped with a magnetic stirrer bar and a condenser was charged with castor oil (25 g, 0.0269 mol), tert-butylacetoacetate (13.11 mL, 0.08 mol) and toluene (30 mL). The reaction mixture was heated to 130 °C and stirred for 2.5 h until there was no more liquid evolved, 36.25 mL of liquid was removed, including toluene (30 mL) and tert-butanol (6.25 mL), and unreacted tert-butylacetoacetate (or tert-butanol) under vacuum distillation at 130 °C. Finally, a yellow oil was obtained with a yield of 92%. ¹H NMR (CDCl₃, 400 MHz): δ(ppm) = 5.51–5.44 (m, 3H), 5.37–5.29 (m, 3H), 5.28–5.24 (m, 1H), 4.95–4.90 (m, 3H), 4.33–4.31 (m, 2H), 4.17–4.12 (m, 2H), 3.43–3.41 (m, 4H), 2.36–2.21 (m, 18H), 2.05–1.98 (m, 6H), 1.62–1.45 (m, 9H), and 0.91–0.86 (m, 9H). ¹³C NMR (CDCl₃, 100 MHz): δ(ppm) = 198.92, 171.54, 171.19, 165.49, 131.43, 122.95, 88.61, 73.68, 67.18, 60.78, 49.04, 48.97, 32.80, 32.64, 32.25, 30.72, 30.61, 30.50, 28.62, 28.35, 28.29, 28.12, 27.94, 27.87, 27.79, 27.75, 26.07, 24.09, 24.01, 23.60, 21.45, and 21.36; GPC (theoretical formula weight = 1189); *M_n* = 1155, *M_w* = 1290, PDI (Polymer dispersity index) = 1.12.

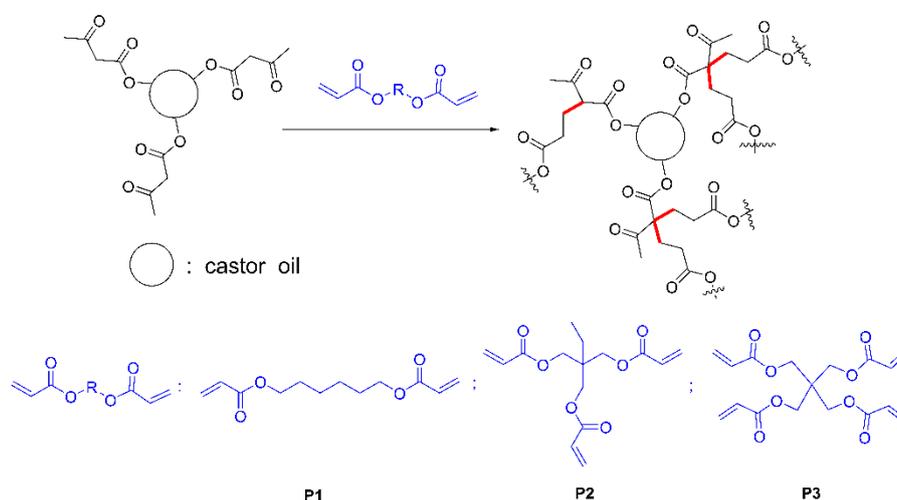
2.3. Preparation of Films

Scheme 2 and Table 1 show the method used to prepare the films while the detailed experimental process is as follows: Acetoacetylated castor oil (1 g) and olefin derivatives were dissolved in 5 mL of acetone (based on the functional groups to be 1:1.5), and then the catalysts were added to the mixture. After the mixture was stirred for 15 min, it was poured into a poly(tetrafluoroethylene) (PTFE)

mold (60 cm × 60 cm × 1.5 cm), and the films were cured at ambient temperature to give a dry film (850–950 microns thickness).



Scheme 1. The synthesis of acetoacetylated castor oil.



Scheme 2. Preparation of films using Michael addition reaction.

Table 1. Film codes and the ratio of materials of the Michael addition reaction.

Sample Code	Acetoacetylated Castor Oil	Cross-Linker	Acetoacetate:Acrylate Ratio
P1	1 g (0.84 mmol)	hexamethylene diacrylate (0.428 g, 1.89 mmol)	1:1.5
P2	1 g (0.84 mmol)	trimethylolpropane triacrylate (0.373 g, 1.26 mmol)	1:1.5
P3	1 g (0.84 mmol)	pentaerythritol tetraacrylate (0.333 g, 0.945 mmol)	1:1.5

2.4. Characterization

^1H and ^{13}C NMR spectra were obtained using a Bruker AV-400 NMR (Bruker, Rheinstetten, Germany) with tetramethylsilane as an internal reference. FTIR spectra were obtained using a Bruker–Veretex 70 spectrometer (Bruker, Rheinstetten, Germany) in attenuated total reflection mode, averages of 32 scans of each sample ranging from 2000 to 600 cm^{-1} were obtained. The viscosities of castor oil and acetoacetylated castor oil were determined using a TA Discovery HR-2 rheometer (TA Instruments, New Castle, DE, USA). The drying times of the coatings were determined using a BK Drying Recorder (TA Instruments, New Castle, DE, USA), and the results were analyzed using ASTM D5895-2013 [18]. The films were cast using a stainless-steel cubic film, each hemispherical ended steel needle was equipped with a brass weight to study the through-drying properties, the needle travel time was selected for 24 h, the drying times were evaluated as (set-to-touch, tack-free, dry-hard, dry-through times). Pencil hardness was measured according to the ASTM D3363 protocol [19].

Dynamic mechanical analysis (DMA) (or DMTA) (TA Instruments Q800, New Castle, DE, USA) in tensile mode at 1 Hz was used to study the storage module, loss module, and $\tan \delta$ under a controlled temperature. The samples were heated from -60 to 120 °C at a rate of 5 °C min^{-1} . Thermogravimetric analysis (TGA) was performed using a TGA-Q50 system obtained from TA Instruments. THF (or toluene) swelling was performed by immersion of a film of a known weight (W_1) in a THF (or toluene) bath, the towel-dried sample weight (W_2) and the oven-dried sample weight (W_1) were obtained, the THF (or toluene) swelling (M (%); amount of THF (or toluene) absorbed by the film) of the films was calculated according to the following equation: M (%) = $[(W_2 - W_1)/W_1] \times 100\%$. The gel content of the grafted samples (m_1) was determined by the extraction of samples in mixing boiling THF and toluene (1:1) for 24 h, then the extracted samples were dried in an oven at 50 °C till constant weight (m_2), gel content (%) = $[(m_1 - m_2)/m_1] \times 100\%$. A dynamical mechanical thermal analyzer (DMTA, TA Instruments Q800, New Castle, DE, USA) scan was performed in tensile mode in the temperature range from -60 to 120 °C, with a heating rate of 3 °C/min using a sample at a frequency of 1 Hz, the E' values in the rubbery region at $T > T_g$ were taken to calculate cross-link density: $\nu_e = E'/3RT$, where R is the universal gas constant and T is the temperature more than 50 °C greater than T_g .

3. Results

3.1. Characterization of Acetoacetylated Castor Oil

The NMR results of acetoacetylated castor oil and castor oil are as shown in Figure 1. In Figure 1a, the hydrogen on the carbon attached to the hydroxyl group shifted from 3.58 to 4.94 ppm, while the peaks of the new acetoacetate groups appeared at 3.42 and 2.34 ppm. In addition, the new peaks at 198 and 165 ppm of acetoacetylated castor oil can be seen in Figure 1b, and this signal indicates that the hydroxyl groups on the castor oil have been esterified. From Figure 2, we can see that the viscosity decreases from 0.53 to 0.28 Pa s after modification, which is mainly due to the disappearance of an intermolecular hydrogen bond [20].

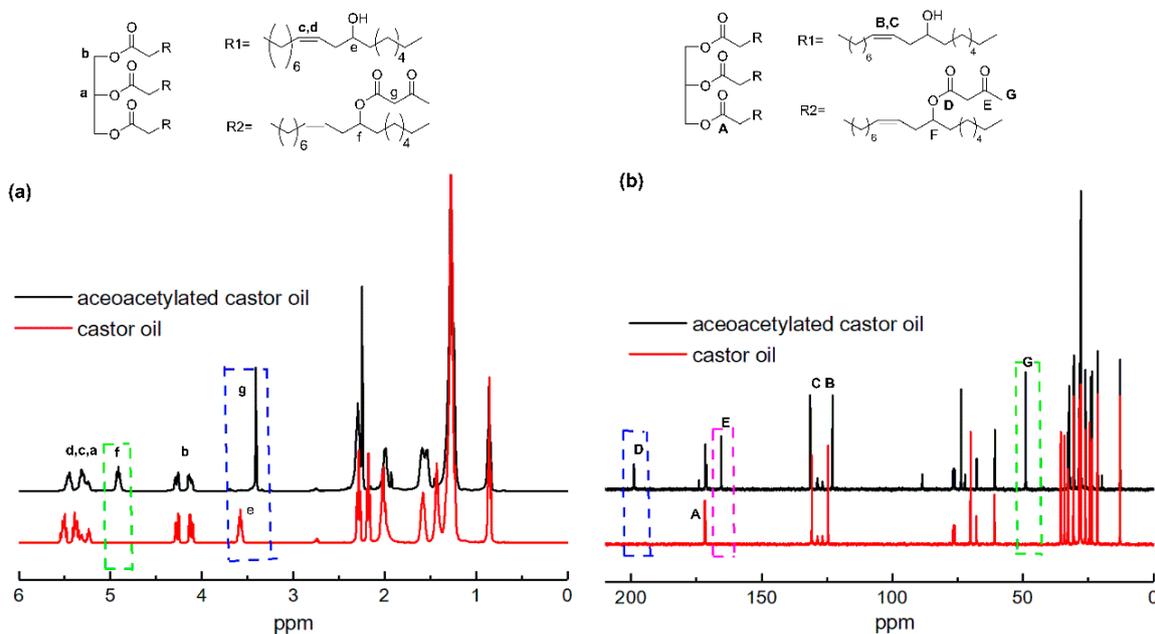


Figure 1. The NMR characterization of acetoacetylated castor oil and castor oil: (a) ¹H NMR spectra of acetoacetylated castor oil and castor oil; (b) ¹³C NMR spectra of acetoacetylated castor oil and castor oil.

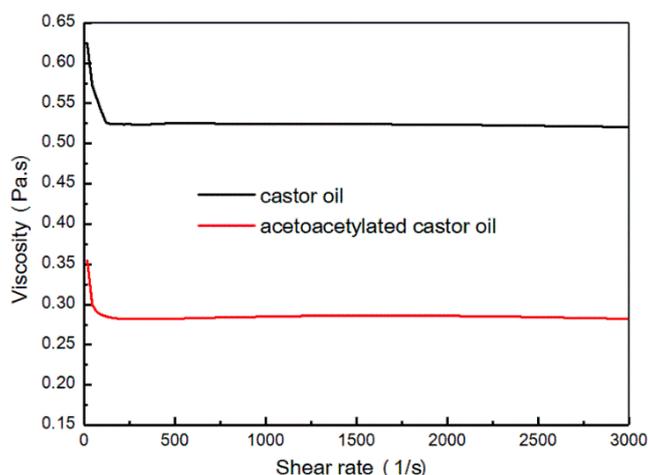


Figure 2. Rheological viscosity versus shear rate for castor oil and acetoacetylated castor oil.

3.2. Optimization of the Curing Reaction Conditions

In the initial study, we chose acetoacetylated castor oil and hexamethylene diacrylate as model starting materials to examine the ambient cured coatings. As shown in Table 2 the film cannot be cured with piperidine as a catalyst (Table 2, Entry 1), and the cure time with DMAP (1 wt %) as the catalyst was 15 h (Table 2, Entry 2), while on using DBU (1 wt %) as the catalyst the cure time can be reduced to 12 h with a good insoluble material content of 90% (Table 2, Entry 3). The catalyst loading was then investigated further and we found that 2 wt % of DBU achieved a lower curing time of 8 h with an insoluble material content rising up to 95%. Finally, the molar ratio of the reaction substrates was explored and the results show that 1:1.5 is the best ratio since acetoacetate can react with the acrylate group at molar ratios of 1:5 [21,22].

Table 2. Optimization of the curing reaction conditions.

Entry	Simple	Catalyst	Cure Time ^a (h)	Pencil Hardness	THF Swelling (%)	Gel Content (%)
1	1:1.5	Piperidine (1 wt %)	–	–	–	–
2	1:1.5	DMAP (1 wt %)	15	4B	265	82
3	1:1.5	DBU (1 wt %)	12	2B	218	90
4	1:1.5	DBU (2 wt %)	8	2B	201	95
5	1:1.5	DBU (3 wt %)	7.5	2B	215	92
6	1:1	DBU (2 wt %)	7	3B	220	91
7	1:2	DBU (2 wt %)	10	3B	245	86

^a: the dry through cure time.

The overlaid FTIR spectra of acetoacetylated castor oil, hexamethylene diacrylate, and the film (P1) are shown in Figure 3. It can be observed in the spectra that there is a decrease in the acrylate group concentration that results from a decrease in the intensity of the C=C band at 1632 cm^{-1} (C=C stretching for CH=CH₂), 1408 cm^{-1} (C=C scissoring for CH=CH₂), and 808 cm^{-1} (C=C out of plane deformation) [19]. These results indicated that the film was obtained by Michael addition reaction between the acetoacetylated castor oil and hexamethylene diacrylate.

After optimization of the reaction conditions and characterization, other multifunctional acrylates as cross-linkers were obtained, as shown in Figure 4 and Table 3. In Figure 4, the colors of the three films are slightly yellow and the characterized data of the three coatings are in Table 3. The pencil hardness values of the three coatings range between 2B and H. The dissolution rates of the films in THF are between 105% and 201%, the contents of insoluble material are 94%–97%.

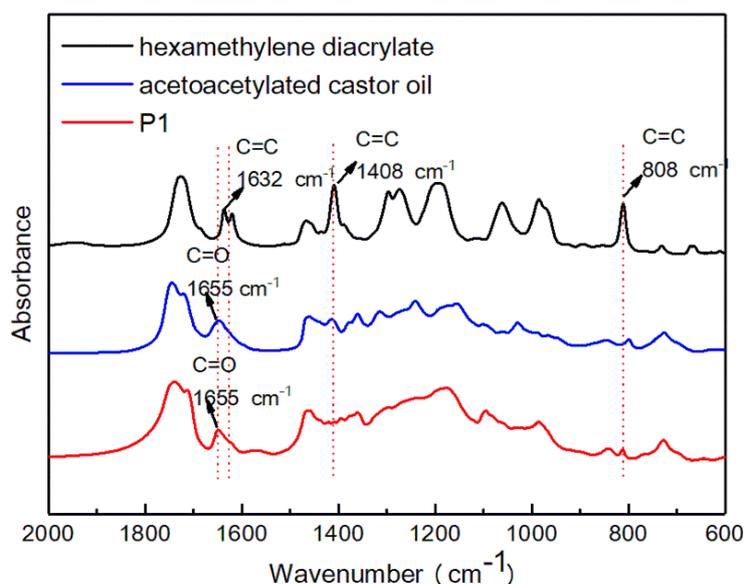


Figure 3. The FTIR characterization of acetoacetylated castor oil, hexamethylene diacrylate and the film (P1).



Figure 4. Pictures of the three films: the film prepared with hexamethylene diacrylate (a), trimethylolpropane diacrylate (b), and pentaerythritol tetraacrylate (c).

Table 3. The films of different cross-linking multifunctional acrylates.

Sample	Cure Time (h)				Pencil Hardness	THF Swelling (%)	Gel Content (%)
	Set to Touch	Tack Free	Dry Hard	Dry Through			
P1	1.5	4.2	6.5	8	2B	201	95
P2	1.2	3.3	5.1	6	B	162	94
P3	1.1	2.8	4	5	H	105	97

3.3. Characterization of the Films

3.3.1. DMA Analysis

Figure 5 shows the temperature dependence of storage modulus and loss factor ($\tan \delta$) of three film polymers. From Figure 5a, as the temperature increased to the glass transition, the storage modulus exhibited a sharp drop, which was followed by a modulus plateau at higher temperatures. The loss factor ($\tan \delta$) curves as a function of temperature for the three films are shown in Figure 5b. A peak maximum is observed in the $\tan \delta$ curves, which is taken as the glass transition temperature (T_g). The cross-linking density was calculated using the equation reported in [23,24]. The T_g , storage modulus, and cross-linking density of the three films are shown in Table 4.

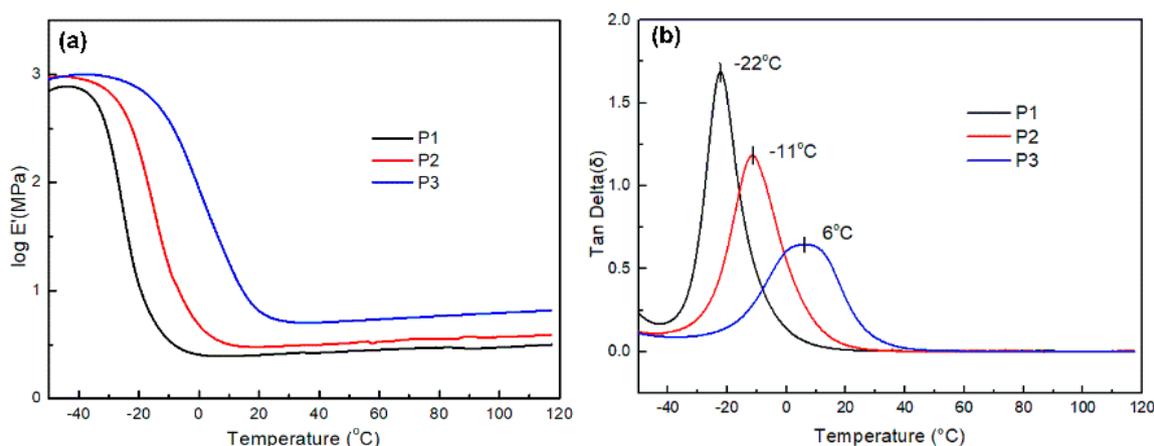


Figure 5. Dynamical mechanical thermal analyzer (DMTA) analysis of the three films: (a) storage modulus as a function of temperature of the three films; (b) loss factor ($\tan \delta$) as a function of temperature of the three films.

Table 4. Dynamical mechanical thermal analyzer (DMTA) data of the three films.

Sample	$\tan \delta$	T_g (at $\tan \delta$)	E' at $T_g + 50$ °C	T ($=T_g + 50$ °C) (K)	Crosslinking Density (ν_e) (at $T_g + 50$ °C)
P1	1.68	−22 °C	2.60 MPa	301	346 mol/m ³
P2	1.18	−11 °C	3.16 MPa	312	406 mol/m ³
P3	0.65	6 °C	6.55 MPa	329	798 mol/m ³

Figure 6 shows the tensile properties of the three films, and their Young's modulus are 0.0177 ± 0.0008 , 0.03192 ± 0.0005 , and 0.0451 ± 0.0006 MPa, respectively. Among the samples, it can be seen from Figure 6 that P3 has the strongest tensile properties, while P1 has the smallest tensile properties. The main reason is that P3 has a higher crosslinking density, so it has stronger tensile properties [25].

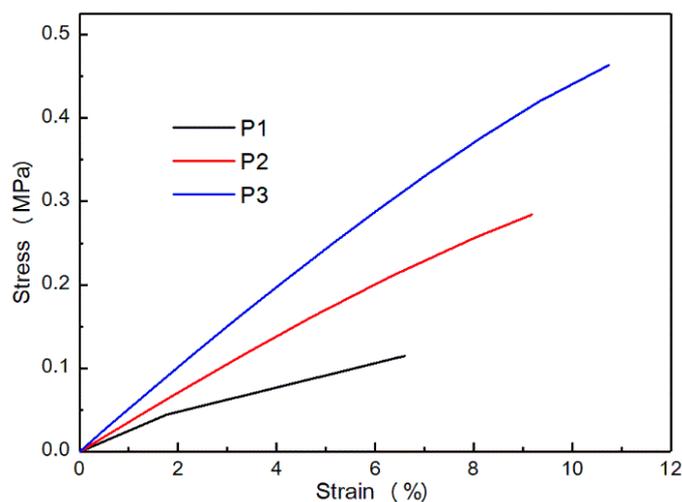


Figure 6. Stress-strain curves for the three films.

3.3.2. DSC Analysis

In Figure 7, it can be seen that the differential scanning calorimetry (DSC) thermograms of the three films and the glass-transition temperature (T_g) values of all the films were lower. However, with cross linking density increasing, the T_g values of the films increased from −31 to −10 °C. The results indicate that with increasing cross linking density, the properties of the film perform better [26].

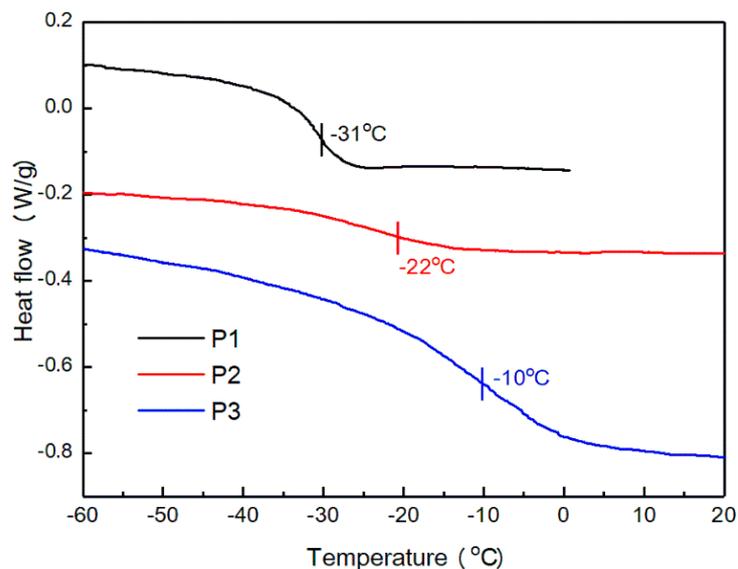


Figure 7. The DSC curves indicating glass transition of the three films.

3.3.3. TGA Analysis

The TGA curves and DTGA curves for the three films are presented in Figure 8. From the TGA analysis, the three films undergo more than one thermal degradation process. The degradation at the first stage occurs in the range of 280–350 °C and can be attributed to the dissociation of the modified ester bonds and carbon groups to form CO₂. In the second stage, when the temperature reaches 35 °C, a polymer skeleton occurs [27]. Compared to the three coatings, P3 has the higher degradation temperature; P1 has the lowest degradation temperature because the higher the cross linking density, the higher the thermal degradation temperature.

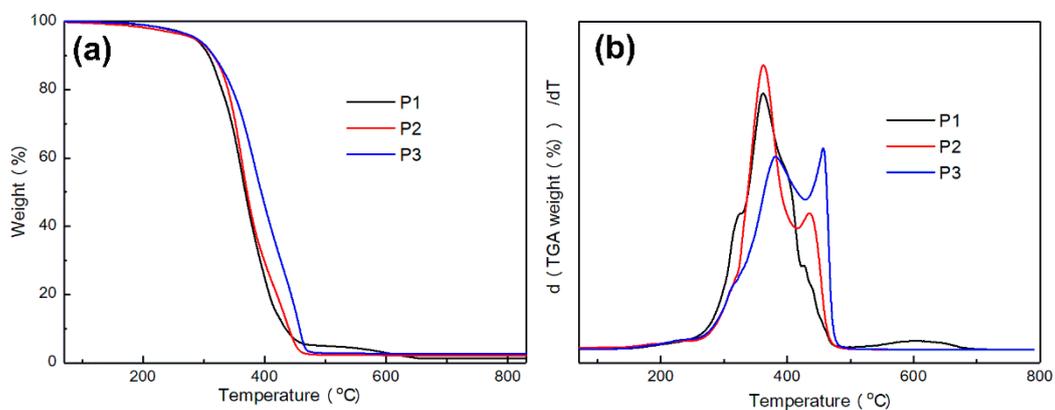


Figure 8. (a) The TGA curves of three films and (b) the DTGA curves of the three films.

3.3.4. Solvent-Swelling

Figure 9 shows the relationship between the dissolution rate and time of the three films in toluene and THF respectively. Comparing THF solvent to toluene solvent, it can be seen that the dissolution rates with THF are greater than with toluene and after soaking for 2 h the film dissolution rates then reach a maximum since the polarity of THF is greater than toluene. In addition, among the three groups of figures, the dissolution rate of P1 is the largest, and the dissolution rate of P3 is the smallest, indicating that with the cross-linking density increasing, the dissolution rate decreases [28]. The density of coatings was found to decrease with increasing insoluble material content, which was observed to be analogous to the increasing degree of swelling.

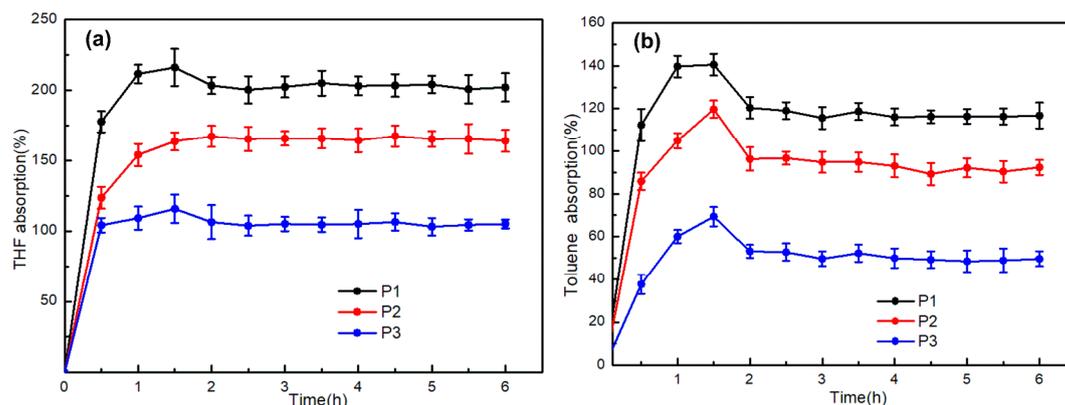


Figure 9. Solvent-swelling of three films: (a) THF absorption-time diagram; (b) toluene absorption-time diagram.

4. Conclusions

Acetoacetylated plant-based co-monomers were synthesized and employed in this study to serve as alternatives to some petroleum-based rigid monomers and to strengthen the thermosetting coatings derived from acetoacetylated castor oil and multifunctional acrylate crosslinker. The NMR signal results indicated that the hydroxyl groups on the castor oil had been esterified, the FTIR spectroscopy suggested that the film had been obtained by Michael addition reaction between the acetoacetylated castor oil and hexamethylene diacrylate. The thermal and mechanical coating properties with different crosslinking density were also evaluated by TGA, DSC, and DMA. The curing times of the cured coatings were studied by using different catalysts with different content of insoluble material, and it was found that 2 wt % of DBU achieved the lowest curing time when the insoluble material content rose up to 95%. In summary, this preliminary study showed that the Michael reaction of a multifunctional acylated cross linker can be used as a viable coating route that cures rapidly at ambient conditions.

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Conflicts of Interest: The authors declare no conflict of interest.

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