Effect of the Ratio of Acetylacetate Groups on the Properties of a Novel Plant-Based Dual-Cure Coating System

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Supporting Information

ABSTRACT: A novel plant-based dual-cure coating system based on a Michael addition reaction between bismaleimide (BDM) and modified acetoacetylated castor oil was developed. The BDM has a high reactivity toward acetylacetate groups, and the catalyst 1,4-diazabicyclo[2.2.2]octane (TEDA) was optimized by the rheological viscosity. The gel was characterized by Fourier transform infrared (FTIR) spectroscopy. Then, three films were prepared with the TEDA catalyst and analyzed with solid-state $^{13}$C NMR and FTIR spectroscopy. The thermal and mechanical properties of the three films were characterized by differential mechanical analysis, thermogravimetric analysis, and differential scanning calorimetry. We found that the cross-linking density, glass transition temperature ($T_g$), and Young’s modulus of the coating films increased with an increase in the ratio of acetylacetate groups from the modified acetoacetylated castor oil. This is the first study of the reaction of BDM with plant-based acetylacetate groups. Importantly, a quantitative ratio of acetylacetate groups can be obtained by a thiol–ene coupling reaction and a transesterification reaction, resulting in the formation of films having excellent performance.

INTRODUCTION

Currently, paint is present in many aspects of our lives, and it can be said that where materials are used, there is paint. With the increase in oil prices and the presence of global warming or the other environmental problems, the development of resins from renewable resources that can be replaced by petroleum-based coatings has become a priority.$^1-^5$ Vegetable oil is a promising renewable resource to prepare new coating systems because it has a unique chemical structure with ester groups and unsaturated sites, and this unique structure produces low-molecular-weight polymeric materials with versatile applications.$^6-^8$

It is an important method for preparing coating films by a Michael addition reaction, which has been used in ships, aircraft, and other fields.$^9$ To date, the use of petrochemicals as the raw coating materials with this method has been reported in many papers,$^{10,11}$ but a few articles report the use of raw coating materials from renewable resources. In 2002, the Trumbo group$^{12}$ found a novel Michael addition reaction between acetoacetylated castor oil and multifunctional alamine for a curable coating film. These films had different properties, but the maximum pencil hardness of the coating film was HB. In 2012, the Webster group$^{13}$ invented the Michael addition reaction based on acetoacetylated sucrose to produce a high-performance coating, but the acetoacetylated sucrose was obtained directly by a transesterification reaction. Recently, our group$^{14}$ reported a novel Michael addition reaction between multifunctional acrylate and acetoacetylated castor oil, but these coatings have poor mechanical properties.

Bismaleimide (BDM) resins are high-performance thermosetting polymers that have great promise in applications such as in elastomers, printed circuit boards, structural laminates, and aerospace.$^{15-17}$ The advantages of bismaleimide resins include mechanical stability, excellent processability, and thermal properties.$^8$ For commercial purposes, bismaleimide resins are usually used for curing with petroleum-based co-monomers.
such as polyesters, epoxies, and polyimides. However, to the best of our knowledge, it has not been reported that bismaleimides react with plant-based acetylacetate groups.

Because the thiol–ene coupling reaction has many advantages, such as simplicity, rapidity, and high yield, its use to modify the vegetable oils (or derivatives) is becoming a very promising research topic. In this work, we show a novel dual-cure coating film between bismaleimide (BDM) and acetoacetylated castor oil. The different ratios of the acetylacetate groups from the castor oil were determined by a thiol–ene coupling reaction and a transesterification reaction. The primary novelties for this paper include (1) expanding the BDM structure based on a Michael addition reaction into plant-based coating films, (2) obtaining a quantitative ratio of acetylacetate groups by a thiol–ene reaction and a transesterification reaction, and (3) demonstrating that this method has a very wide application value for renewable plant oils because vegetable oils contain many unsaturated C=C bonds.

Results and Discussion

Characterization of the Gel Time. In the initial study, we used the rheological properties to study the gel time of acetoacetylated castor oil and BDM in different catalysts [1,4-diazabicyclo[2.2.2]octane (TEDA), triethylamine (TEA), or piperidine]. At the gel point, the loss modulus value ($G''$) is equal to the storage modulus value ($G'$) and the viscosity ($\eta$) also increases dramatically. As shown in Figure 1, compared with the TEA and piperidine catalysts, the TEDA catalyst has the fastest gel time. Fourier transform infrared (FTIR) spectroscopy is used to confirm the gel in Figure 2. The characteristic peak at 3098 cm$^{-1}$ is assigned to the C–H stretching vibrations of BDM, and it is weakened significantly for the spectra from the gel. Moreover, the C=C=C– stretching in the gel at 1584 cm$^{-1}$ disappears, and the C–N–C asymmetry stretching vibration at 1389 cm$^{-1}$ is found in all spectra.

Characterization of Film. After studying the catalysts by rheological testing, we prepared a coating using the optimum cross-linking time. According to the abovementioned cross-linking system, we prepared film P1 and found that this film has a low pencil hardness. The possible reason is that the cross-linking density of the system is low. To improve the performance of the system, we increased the ratio of acetylacetate groups from the castor oil (for details, see the sections Preparation of Modified Castor Oil and Preparation of Modified Acetoacetylated Castor Oil), thus increasing the cross-linking density. As shown in Table 1, as the proportion of modified acetoacetylated castor oil increases, the pencil hardness of the system gradually increases, the curing time and acetone swelling decrease, and the gel rate and gloss are similar.

These films (P1–P3) were first characterized by Fourier transform infrared spectroscopy measurements. As shown in Figure 3a, the characteristic peaks of C–H stretching vibrations at 3098 cm$^{-1}$ and stretching vibrations of C=C at 1584 cm$^{-1}$...
The storage modulus and loss factor (tan δ) as a function of temperature of the three polymer films (P1–P3) are shown in Figure 4. As the temperature increased, the storage modulus exhibited \( E' \) a sharp drop, and it was followed by a modulus balance at higher temperatures. The loss factor (tan δ) curves for the three films are shown in Figure 4b. A peak maximum is observed in loss factor (tan δ) curves, which is taken as the glass transition temperature \( T_g \) for the three films. The cross-linking density (ve) was calculated by the following equation: \( ve = E'/3RT \), where \( R \) is the universal gas constant, \( E' \) is the storage modulus of the thermoset polymer in the rubbery plateau region at \( T_g + 50 \) °C, and \( T \) is the absolute temperature. The equation was reported by the Raju group,\(^{34,35} \) Soucek group,\(^{35} \) and Gu group.\(^{36} \) The storage modulus, \( T_g \), and cross-linking density of the three films (P1–P3) are shown in Table 2.

The stress–strain curves of the three films (P1–P3) are shown in Figure 5. From the three films, it can be seen that as the cross-linking density increases, the mechanical properties gradually increase, which increases the tensile strength from 3.46 to 7.68 MPa (Table 2). From Young’s modulus in Table 2 (P1 = 0.2057 ± 0.0070, P2 = 0.6331 ± 0.0215, and P3 = 1.0642 ± 0.0390), it is obvious that the mechanical properties of the films based on modified acetoacetylated castor oil improved.

Figure 6 shows the thermogravimetric analysis (TGA) curves (and their derivative curves) of the three films (P1–P3). All three films show a two-stage degradation process. In the range of 160–330 °C, first-stage degradation takes place, which is mainly due to the cleavage of unstable ester groups and sulfur–carbon bonds.\(^{37} \) In the range of 330–480 °C, second-stage degradation takes place, which is related to the corresponding polymer skeleton.\(^{38} \) The loss derivative temperatures at a loss of 10 and 50 wt % mass and maximum mass are summarized in Table 3. The main differences in the thermal degradation profiles of these three samples are in the first stage, which is related to the corresponding thermal stability of sulfur–carbon bonds.

### CONCLUSIONS

We demonstrated a novel plant-based dual-cure coating based on a Michael addition reaction between bismaleimide (BDM) and modified acetoacetylated castor oil. The catalyst (TEDA) was optimized by the rheological viscosity and characterized by Fourier transform infrared (FTIR) spectroscopy. Three films were prepared using the TEDA catalyst based on modified acetoacetylated castor oil obtained via a thiol–ene coupling reaction and a transesterification reaction. These films were characterized by solid-state \(^{13} \)C NMR spectroscopy and FTIR, and the mechanical and thermal properties were characterized by differential mechanical analysis (DMA), differential scanning calorimetry (DSC), and TGA. The results show that with the increased ratio of acetylacetate groups from diacetoacetylated castor oil improved.

### EXPERIMENTAL SECTION

**Materials.** Toluene, 2-mercaptoethanol, dimethyl sulfoxide (DMSO), and tetrahydrofuran were obtained from Xiya Reagent, China. Piperidine, 1,4-diazabicyclo[2.2.2]octane (TEDA), triethylamine (TEA), and t-butyl acetoacetate were obtained from Beijing Chemical Works. The 2-hydroxy-2-methylpropophene and \( \text{N,N'}-4,4' \)-diphenylmethane-bismaleimide-

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**Table 1. Properties of the Three Sample Films**

| sample codes | pencil hardness | cure time (min) | gel (%) | acetone swelling (%) | 60° gloss |
|--------------|----------------|----------------|--------|---------------------|-----------|
| P1           | H              | 140            | 91     | 91                  | 86        |
| P2           | 3H             | 80             | 93     | 78                  | 89        |
| P3           | 4H             | 45             | 93     | 35                  | 87        |

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**Figure 3.** (a) FTIR spectra of three films, BDM, and modified acetoacetylated castor oil. (b) Solid-state \(^{13} \)C NMR spectra of the three films.
mide (BDM) were obtained from Tianjin Jiuri Chemical Co., Ltd. (China). The castor oil (a1) was obtained from Sigma-Aldrich (China). All of the materials were used without any further purification.

**Preparation of Modified Castor Oil.** Castor oil a1 (1 equiv), 2-hydroxy-2-methylpropane (5 wt %), and 2-mercaptoethanol (1.65 or 3.3 equiv) in dichloromethane (DCM, 40 mL) were thoroughly mixed in a round-bottomed flask under nitrogen for 10 min. Then, the reactants were irradiated by UV-light irradiation (8 mW, 365 nm) for 5 h. The dichloromethane and excess 2-mercaptoethanol were removed, and a yellow oil of a2 (or a3) was obtained, as shown in Scheme 1 and Table 4 (for more details, see the Supporting Information).

**Table 2. Mechanical Properties of the Three Films Based on BDM with Modified Acetoacetylated Castor Oil**

| sample codes | tan δ | T g (at tan δ) (°C) | E' at T g + 50 °C (MPa) | cross-linking (re) (mol/m3) | Young's modulus (MPa) | stress at break (MPa) | elongation at break |
|--------------|-------|---------------------|-------------------------|-----------------------------|-----------------------|---------------------|-------------------|
| P1           | 1.26  | 26                  | 0.977                   | 112.19                      | 0.2057 ± 0.0070       | 3.46                | 40.15             |
| P2           | 0.42  | 62                  | 3.259                   | 339.58                      | 0.6331 ± 0.0215       | 6.03                | 34.43             |
| P3           | 0.35  | 79                  | 7.875                   | 785.13                      | 1.0642 ± 0.0390       | 7.68                | 29.97             |

**Table 3. Thermal Properties of the Three Films Based on BDM with Modified Acetoacetylated Castor Oil**

| sample codes | T10 | T50 | T max | DSC Tg (°C) |
|--------------|-----|-----|-------|--------------|
| P1           | 333 | 414 | 495   | 14           |
| P2           | 302 | 408 | 503   | 35           |
| P3           | 283 | 405 | 499   | 51           |

**Figure 4.** Dynamic mechanical thermal analysis of the three films (P1–P3): (a) storage modulus as a function of temperature and (b) loss factor (tan δ) as a function of temperature.

**Figure 5.** Stress–strain curves of the three films based on BDM with modified acetoacetylated castor oil.

**Figure 6.** (a) TGA curves and (b) their derivative curves for the three films (P1–P3) based on BDM with modified acetoacetylated castor oil.

**Figure S7.**
Scheme 1. Preparation of Modified Castor Oil by a Thiol–Ene Coupling Reaction

Table 4. Preparation of Modified Castor Oil

| sample codes | castor oil | t-butyl acetoacetate | yield (%) | GPC |  |
|--------------|------------|----------------------|-----------|-----|-----|
| a1           | a2         | 0.015 mol (1 equiv)  | 0.0248 mol (1.65 equiv) | 49  | 990 | 1079 | 1.09 |
|              | a3         | 0.015 mol (1 equiv)  | 0.0495 mol (3.3 equiv) | 93  | 1081| 1192 | 1.10 |

“Castor oil (a1) was obtained from Sigma-Aldrich (China).

Scheme 2. Preparation of Modified Acetoacetylated Castor Oil by a Transesterification Reaction

Table 5. Preparation of Modified Acetoacetylated Castor Oil

| sample codes | a2 or a3 | t-butyl acetoacetate | yield (%) | GPC |  |
|--------------|----------|----------------------|-----------|-----|-----|
| b1           | a2       | 0.015 mol (a2, 1 equiv) | 0.0675 mol (4.5 equiv) | 95  | 1359| 1492 | 1.10 |
|              | a3       | 0.015 mol (a3, 1 equiv) | 0.09 mol (6 equiv) | 91  | 1486| 1161 | 1.12 |

“Acetoacetylated castor oil (b1) was reported by our previous work.

Scheme 3. Rheometer Test of Cross-Linking Structures with Different Catalysts

Preparation of Modified Acetoacetylated Castor Oil. tert-Butyl acetoacetate (4.5 or 6 equiv) and toluene (30 mL) were added to the modified castor oil a2 (or a3) (0.015 mol, 1 equiv) in a 250 mL round-bottomed flask, and the solution was heated to 130 °C with stirring for 6 h and stopped when no more liquid evolved; then, the excess t-butyl acetoacetate was
removed, and finally, a yellow oil was obtained (b2 or b3), as shown in Scheme 2 and Table 5 (for more details, see the Supporting Information).

**Gel-Time Study Using a Rheometer.** As shown in Scheme 3 and Table 6, the rheological viscosity method was as follows. Acetoacetylated castor oil (0.5 g, 0.42 mmol) and \(N,N'-4,4'-\)diphenylmethane-bismaleimide (BDM) (0.226 g, 0.63 mmol) were added to 3 mL of DMSO in a sample bottle (3 × 5 cm²) and stirred for 2 min to dissolve completely. Then, the catalyst (TEDA, TEA, or piperidine) (0.036 mmol) was added, and after stirring for 1 min, a rheological test was performed immediately.

**Formulation of Coatings.** The methods to prepare the coating films are shown in Table 7 and Scheme 4, and the detailed experimental process is as follows. Modified acetoacetylated castor oil (b1, b2, or b3), TEDA, and BDM were dissolved in 2 mL of acetone (for a ratio of the functional groups to be 1:1), mixed for 15 min, and then poured into a mold (poly(tetrafluoroethylene), 8 cm × 8 cm × 1.5 cm). Finally, a dry film (100–200 μm in thickness) was obtained at ambient temperature (25 °C).

**Characterization of Coatings.** The FTIR spectra were obtained using a Bruker-Veretex70 spectrometer, and averages of 32 scans of each simple (P1–P3) ranging from 4000 to 500 cm⁻¹ were determined. Gel permeation chromatography (GPC) was performed on a GPC apparatus (Waters 515, Waters) at 25 °C. The \(^1\)H NMR and \(^{13}\)C NMR spectra were collected using a Bruker AV-400 NMR instrument, and the deuterated chloroform was used as the solvent. The solid-state \(^{13}\)C nuclear magnetic resonance spectroscopy was performed using a WB 600 MHz Bruker Avance III spectrometer, and the measurement was made with a 4 mm magic-angle spinning probe spinning at 12 kHz. Differential scanning calorimetry was performed on a TA calorimeter (Q800, TA) with a heating rate of 10 °C/min under a nitrogen atmosphere. The viscosity was determined using a TA Discovery HR-2 rheometer. Pencil hardness testing was performed by the ASTM D 3363 protocol. DMA tensile testing was performed using TA Instruments Q800 (New Castle, DE). Acetone swelling was calculated by the following equation: \[ M(\%) = \frac{W_1 - W_2}{W_2} \times 100\% \] with a film with a known weight \((W_1)\) in an acetone bath and the towel-dried sample weight \((W_2)\). The gel content was calculated by the following equation: \[ M(\%) = \frac{W_1}{W_2} \times 100\% \] with a film (2 cm × 2 cm pieces) with a known weight \((W_1)\), and the dried film was dipped in acetone for 48 h and dehydrated for 48 h at 60 °C to provide a weight of \(W_2\).

■ ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01234.

Synthesis, characterization (\(^1\)H NMR, \(^{13}\)C NMR, and GPC spectra and viscosity), calculation of the yield by \(^1\)H NMR, and viscosity of modified acetoacetylated castor oil; the DSC curves indicating \(T_g\) values of the three films (PDF)

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**Notes**
The authors declare no competing financial interest.

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**Table 6. Samples for the Rheometer Test with Different Catalysts**

| sample codes | acetoacetylated castor oil (mmol) | BDM (mmol) | catalyst (mol) | acetoacetate/\(-\text{C} = \text{C}\)− ratio |
|-------------|----------------------------------|------------|----------------|------------------|
| A           | 0.42 (b1)                        | 0.63       | 0.036 (TEDA)   | 1:1              |
| B           | 0.42 (b1)                        | 0.63       | 0.036 (TEA)    | 1:1              |
| C           | 0.42 (b1)                        | 0.63       | 0.036 (piperidine) | 1:1              |

**Table 7. Sample Names and the Ratio of Materials Used in the Michael Addition Reaction**

| sample codes | modified acetoacetylated castor oil (mmol) | BDM (mmol) | TEDA (mmol) | acetoacetate/\(-\text{C} = \text{C}\)− ratio |
|-------------|--------------------------------------------|------------|-------------|------------------|
| P1          | 1.05 (b1)                                  | 1.58       | 0.036       | 1:1              |
| P2          | 1.05 (b2)                                  | 2.36       | 0.036       | 1:1              |
| P3          | 1.05 (b3)                                  | 3.15       | 0.036       | 1:1              |

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**Scheme 4. Synthetic Route of the Three Films**

- **P1:** \(R = R_1\)
- **P2:** \(R = 1/2R_1 + 1/2R_2\)
- **P3:** \(R = R_2\)
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