Bio-Based Coating Materials Derived from Acetoacetylated Soybean Oil and Aromatic DICARBOXALdehydes

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Abstract: Bio-based coating materials were prepared from epoxidized soybean oil as a renewable source. Acetoacetylated soybean oil was synthesized by the ring-opened and transesterification reaction of epoxidized soybean oil, and its chemical structure was characterized by nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), and rheometric viscosity analyses. On the basis of acetoacetylated soybean oil, several bio-based coating materials were prepared using different aromatic dicarboxaldehydes (1,2-benzenedialdehyde, 1,3-benzenedialdehyde, 1,4-phthalaldehyde, 4,4′-biphenyldicarboxaldehyde) and characterized. The resulting films possess good performance, including the highest glass transition temperature of 54 °C, a Young’s modulus of 24.91 MPa, tensile strength of 5.65 MPa, and an elongation at break of 286%. Thus, this work demonstrates the Knoevenagel condensation reaction, which is based on soybean oil as a potential newer eco-friendly raw material.

Keywords: epoxidized soybean oil; acetoacetylated soybean oil; Knoevenagel condensation reaction; aromatic dicarboxaldehydes

1. Introduction

Currently, the development of renewable resources to replace petroleum-based raw materials in the areas of energy and materials is a prominent research field [1–3]. Vegetable oil, as a renewable resource, has attracted considerable attention owing to its low cost, availability, low ecotoxicity, and environmental sustainability [4,5]. Vegetable oils contain unsaturated C–C bonds; thus, epoxidation of vegetable oils is commonly employed to graft functional groups by ring-opened reactions [6–8].

Acetoacetate chemistry is an important class of versatile synthetic intermediates of thermoset resins [9,10]. The functional groups of acetoacetates allow an efficient crosslinking reaction with various compounds such as isocyanates [11], acrylates (Michael Reaction) [12], amines (enamine formation) [13], and aldehydes. Although there are many synthetic routes for the preparation of covalently bonded acetoacetates into resins, only a few examples have been reported that are applicable for bio-based coating materials. In 2002, the Trumbo group reported a novel bio-based coating material, which is based on an acetoacetylated castor oil and multifunctional amines; the acetoacetylated castor oil was obtained by a transesterification reaction between castor oil and t-butyl acetoacetate, and the properties of the coating were improved by increasing the temperature [14]. In 2012, the Webster group developed a bio-based coating material by amine-acetoacetate reactions between acetoacetylated
sucrose and multifunctional amines; the coatings exhibited a good balance of properties owing to the degree of enamine alkyl substitution or alkyl chain length [15]. Recently, our group reported a series of bio-based coating materials; the properties of these coatings were controlled by changing the content of acetoacetate groups by thiolene and transesterification reactions [16–19].

The Knoevenagel condensation reaction is as an important C–C bond forming reaction, which can be employed to synthesize many compounds such as herbicides [20], natural products [21], and functional polymers [22]. However, currently, few examples of bio-based coating materials have been reported, which utilized Knoevenagel condensation reactions. In 2019, our group reported the first bio-based coating materials, which were made via the Knoevenagel condensation reaction between acetoacetylated castor oil and aromatic dicarboxaldehydes; however, the coating had inferior mechanical properties [23].

In this paper, we show a novel bio-based coating material, which is based on the reaction between acetoacetylated soybean oil and aromatic dicarboxaldehydes. Acetoacetylated soybean oil was prepared by the ring-opened and transesterification reaction (Scheme 1) [24]. The primary novelties of this paper include the following: (1) Expanding a Knoevenagel condensation reaction base on acetoacetylated soybean oil, (2) obtaining good mechanical/chemical performance, 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 and have easy access to epoxy structures.

![Scheme 1. Synthesis of acetoacetylated soybean oil via the ring-opened and transesterification reactions [24].](image-url)
2. Materials and Methods

2.1. Materials

Epoxidized soybean oil (ESO), 1,2-benzenedialdehyde, 1,4-phthalaldehyde, 1,3-benzenedialdehyde, t-butyl acetoacetate, tetrafluoro boric acid, and 4,4′-biphenyldicarboxaldehyde were obtained from Sigma Aldrich (Shanghai, China). Ethyl acetate, benzaldehyde, toluene, methanol, tetrahydrofuran (THF), and ethyl acetate were obtained from Xiya Reagent (Chengdu, Sichuang, China). 1,8-Diazabicyclo (5,4,0) undec-7-ene (DBU), 4-dimethylaminopyridine (DMAP), triethylamine, and piperidine were obtained from Beijing Chemical Works (Beijing, China). All materials were used without any further purification.

2.2. Preparation of Soybean Oil-Based Polyols

The synthesis of soybean oil-based polyols was performed according to a previously patent reported study [24] (Scheme 1). A mixture of epoxidized soybean oil (60 g, 62.5 mmol), methanol (80 g, 2.5 mol), and tetrafluoro boric acid (0.1 wt % of epoxidized soybean oil) was heated in a 250 mL flask at 64 °C with magnetic stirring for 2 h. The mixture was quenched to room temperature, extracted by ethyl acetate, and washed with a saturated sodium chloride solution three times. The organic solvent was removed via rotary evaporation, and a colorless oil was obtained with a yield of 84%.

\[ \text{H NMR (CDCl}_3, 400 MHz): \delta (ppm) = 5.22 (s, 1H), 4.28–4.24 (m, 2H), 4.13–4.12 (m, 2H), 3.99–3.73 (m, 4H), 3.62–3.56 (m, 2H), 3.37 (s, 12H), 3.33–3.25(m, 4H), 2.29–2.26 (m, 6H), 2.06–1.96 (m, 6H), 1.85–1.79 (m, 2H), 1.58–1.43 (m, 8H), 1.28–1.22 (m, 6H), and 0.85–0.82 (t, 12H). \]

\[ \text{C NMR (CDCl}_3, 400 MHz): \delta (ppm) = 173.14, 84.30, 82.68, 72.48, 68.92, 65.03, 62.04, 58.10, 56.94, 56.59, 42.7, 34.06, 33.37, 29.88, 29.59, 25.90, 25.05, 24.75, 23.71, 14.03, 13.92. \]

GPC (theoretical formula weight = 1089); \( M_n = 1006, M_w = 1057, PDI = 1.05. \) Viscosity: 1.31 Pa s.

2.3. Preparation of Acetoacetylated Soybean Oil

The synthesis of acetoacetylated soybean oil was performed according to a previously patent reported study [24] (Scheme 1). A solution of soybean oil-based polyols (63 g, 57.9 mmol) and t-butyl acetoacetate (36.64 g, 0.232 mol) in a 250 mL reflux condenser flask was prepared, and then the reaction was heated with magnetic stirring to 110 °C under nitrogen atmosphere. At 100–110 °C, the liquid of n-butanol was removed, and a yellow oil was obtained with a yield of 85%.

\[ \text{H NMR (CDCl}_3, 400 MHz): \delta (ppm) = 5.21–5.16 (m, 1H), 4.96–4.92 (m, 4H), 4.23–4.20 (m, 2H), 4.09–4.07 (m, 2H), 3.41 (s, 4H), 3.32 (s, 12H), 2.27–2.23 (t, 6H), 2.19 (s, 12H), 2.27–2.23 (m, 6H), 1.55–1.49 (m, 6H), 1.58–1.43 (m, 8 H), 1.22–1.18 (m, 62 H), 0.81–0.78 (m,12H). \]

\[ \text{C NMR (CDCl}_3, 400 MHz): \delta (ppm) = 199.20, 172.09, 165.76, 80.23, 74.14, 67.78, 60.90, 57.28, 55.78, 49.07, 32.84, 30.76, 28.54, 27.97, 24.39, 23.66, 21.44, 12.94. \]

GPC (theoretical formula weight = 1426); \( M_n = 1169, M_w =1228, PDI = 1.05. \) Viscosity: 0.61 Pa s.

2.4. Polymerization of Bio-Based Coating Materials

The method used for the preparation of the coating materials is as follows (Scheme 2 and Table 1). A mixture of acetoacetylated soybean oil (1 g, 0.7 mmol) and crosslinker agent (1,2-benzenedialdehyde, 1,3-benzenedialdehyde, 1,4-phthalaldehyde, 4,4′-biphenyldicarboxaldehyde) (1.05 mmol) was dissolved in THF (3 mL) for 10 min (owing to the incompatibility of aromatic dicarboxaldehydes with acetoacetylated soybean oil, the coating of materials was performed in a solvent). Then, the catalyst (5 wt % of acetoacetylated soybean oil, DBU) was added to the mixture and mixed for another 10 min. Then, the mixture solution was poured into a poly(tetrafluoroethylene) (PTFE) mould (8 cm × 8 cm × 1.5 cm) and cured at ambient temperature (25 °C) to obtain a dry coating film (200–300 µm thick). The complete curing reaction was determined by FTIR.
was used to study the storage moduli and tan δ under controlled temperature. The samples were determined using a BK Drying Recorder (MICKLE Laboratory Engineering Co. Ltd., Gomshall, United Kingdom), and the results were analyzed using an ASTM D5895–2013. Thermogravimetric analysis (TGA) was performed using a TGA Q50 system (TA Instruments) (TA Instruments Q800, New Castle, DE, USA) at a heating rate of 10 °C min⁻¹. Rectangular films of 30 mm × 3 mm (length × width) were used for the test, for the final tensile strength and elongation at break of all the films were obtained from average values of at least three replicates of each sample. A dynamic mechanical analyzer (DMA) (TA Instruments Q800, New Castle, DE, USA) in tensile mode at a heating rate of 10 °C min⁻¹ was used to study the storage moduli and tan δ under controlled temperature. The samples were heated from −30 °C to 110 °C at a rate of 5 °C min⁻¹. Gel permeation chromatography (GPC) was obtained. The viscosities of different components and monomer mixtures were measured using a rheometer (Discovery HR-2 rheometer) (TA Instruments, New Castle, DE, USA) at room temperature (25 °C). The drying times for the coatings were determined using a BK Drying Recorder (MICKLE Laboratory Engineering Co. Ltd., Gomshall, United Kingdom), and the results were analyzed using an ASTM D5895–2013. Thermogravimetric analysis (TGA) was performed using a TGA Q50 system (TA Instruments) (TA Instruments Q800, New Castle, DE, USA) at a heating rate of 10 °C min⁻¹ under an N₂ atmosphere flow of 80 mL/min. Tensile property was determined using a dynamic mechanical analyzer (DMA) (TA Instruments Q800, New Castle, DE, USA) with a cross-head speed of 10 mm/min at 25 °C. Rectangular films of 30 mm × 3 mm (length × width) were used for the test, for the final tensile strength and elongation at break of all the films were obtained from average values of at least three replicates of each sample. A dynamic mechanical analyzer (DMA) (TA Instruments Q800, New Castle, DE, USA) in tensile mode at 1 Hz was used to study the storage moduli and tan δ under controlled temperature. The samples were heated from −30 °C to 110 °C at a rate of 5 °C min⁻¹. Gel permeation chromatography (GPC) was

| Sample Code | Acetoacetylated Soybean Oil | Crosslinker | Acetoacetate: Aldehyde Ratio |
|-------------|-----------------------------|-------------|-----------------------------|
| P1          | 1 g (0.7 mmol)              | 1,2-benzenedialdehyde (C1) (0.141 g, 1.05 mmol) | 1.0.75                      |
| P2          | 1 g (0.7 mmol)              | 1,3-benzenedialdehyde (C2) (0.141 g, 1.05 mmol) | 1.0.75                      |
| P3          | 1 g (0.7 mmol)              | 1,4-phthalaldehyde (C3) (0.141 g, 1.05 mmol) | 1.0.75                      |
| P4          | 1 g (0.7 mmol)              | 4,4′-biphenyldicarboxaldehyde (C4) (0.221 g, 1.05 mmol) | 1.0.75                      |

2.5. Characterization

1H and 13C NMR spectra were obtained using a Bruker AV-400 NMR (Bruker, Rheinstetten, Germany) with tetramethylsilane as an internal reference, and deuterated chloroform (CDCl₃) was used as a solvent. Infrared spectra (IR) were obtained using a Bruker-Vertex70 spectrometer (Bruker, Rheinstetten, Germany) in the attenuated total reflection (ATR) mode. An average of 32 scans of each sample in the range from 3500 cm⁻¹ to 500 cm⁻¹ was obtained. The viscosities of different components and monomer mixtures were measured using a rheometer (Discovery HR-2 rheometer) (TA Instruments, New Castle, DE, USA) at room temperature (25 °C). The drying times for the coatings were determined using a BK Drying Recorder (MICKLE Laboratory Engineering Co. Ltd., Gomshall, United Kingdom), and the results were analyzed using an ASTM D5895–2013. Thermogravimetric analysis (TGA) was performed using a TGA Q50 system (TA Instruments) (TA Instruments Q800, New Castle, DE, USA) at a heating rate of 10 °C min⁻¹ under an N₂ atmosphere flow of 80 mL/min. Tensile property was determined using a dynamic mechanical analyzer (DMA) (TA Instruments Q800, New Castle, DE, USA) with a cross-headspeed of 10 mm/min at 25 °C. Rectangular films of 30 mm × 3 mm (length × width) were used for the test, for the final tensile strength and elongation at break of all the films were obtained from average values of at least three replicates of each sample. A dynamic mechanical analyzer (DMA) (TA Instruments Q800, New Castle, DE, USA) in tensile mode at 1 Hz was used to study the storage moduli and tan δ under controlled temperature. The samples were heated from −30 °C to 110 °C at a rate of 5 °C min⁻¹. Gel permeation chromatography (GPC) was

Scheme 2. Synthetic route for coating materials.

Table 1. Sample codes and ratios of materials in the Knoevenagel addition reaction.
performed on a GPC apparatus (Waters 515; Waters, MA, USA) at 25 °C and a 5 µm Styragel HR5E column (Waters, MA, USA). Samples were diluted to 2 mg mL⁻¹ in tetrahydrofuran (THF) for GPC analysis. THF was used as an eluent at a flow rate of 1.0 mL min⁻¹. Molecular weights were determined using polystyrene standards (The system was calibrated by narrow polystyrene standards (Mw range: 200–300,000 g/mol)). The gel content was determined by fully immersing a known mass (W₁) of cured material in tetrahydrofuran for 24 h at ambient temperature, followed by filtering, drying, and reweighing of the solid remnants W₂. The gel content was calculated by the following equation: M (%) = W₂/W₁ × 100%. The tetrahydrofuran (THF) swelling of film was performed by immersing a known weight (W₀) of the film in a tetrahydrofuran bath, and the towel-dried sample weight (Wₜ) was obtained. The swelling of the film was calculated by the following equation: Q (%) = [(Wₜ − W₀)/W₀] × 100%.

3. Results and Discussion

3.1. Characterization of Acetoacetylated Soybean Oil

In this study, the oxirane group number of ESO used was 4 per molecule, which was confirmed by ¹H NMR spectroscopy (Figure S1a, Supporting Information). The chemical structure of the obtained acetoacetylated soybean oil was confirmed by nuclear magnetic resonance spectroscopy (NMR), GPC analyses, and Fourier transform infrared spectroscopy (FTIR). As shown in Figure 1a, the peaks (soybean oil-based polyols, red) at 2.9 ppm (b) and 3.1 ppm (a), which correspond to the oxirane group of epoxidized soybean oil (black), decreased after the ring-opened reaction (by approximately 84%, Figure S1b, Supporting Information), and a new peak (soybean oil-based polyols, red) at 3.6 ppm (c) appeared, which is assigned to the methyl of methanol grafted to epoxidized soybean oil (red). By comparing soybean oil-based polyols (red) to acetoacetylated soybean oil (blue), it was determined that the peaks (soybean oil-based polyols, red) at 3.9 ppm and 4.0 ppm shifted to 4.8–4.9 ppm (acetoacetylated soybean oil), and the peaks corresponding to the new acetoacetate groups appeared at 3.4 and 2.2 ppm (approximately 85%, in Figure S2b, Supporting Information). In addition, the ¹³C NMR spectra confirmed that acetoacetylated soybean oil was obtained. The peaks (soybean oil-based polyols, red) attributed to the epoxy bonds in soybean oil (black) at 55 ppm (g) and 56 ppm (h) decreased after the ring-opened reaction, and the new peaks of acetoacetylated soybean oil (blue) at 200 ppm (l) and 165 ppm (m) are shown in Figure 1b. Comparing the gel permeation chromatography (GPC) curves of ESO, soybean oil-based polyols (MA-ESO), and acetoacetylated soybean oil (MA-ESO-TBA) (Figure S3, Supporting Information), the average molecular weight was increased by ring-opened and transesterification reactions.

The FTIR spectra of ESO, soybean oil-based polyols (MA-ESO), acetoacetylated soybean oil (MA-ESO-TBA), and t-buty 1 acetoacetate are shown in Figure 2. The comparison of ESO (black) and MA-ESO (red) shows that the peak at 823 cm⁻¹ (corresponded to epoxy groups) disappeared and a new peak at 3600–3300 cm⁻¹ (OH group) appeared, which indicates that the ring-opened reaction of epoxidized soybean oil occurred to obtain hydroxyl groups. By comparing MA-ESO (red) and MA-ESO-TBA (blue), the peaks at 1731–1712 cm⁻¹ (the stretching vibration band of C=O of –COCH₂COCH₃) and 1350 cm⁻¹ (C–O stretch from the ester bond of –COCH₂COCH₃) were observed. These results indicated that acetoacetylated soybean oil was obtained by the ring-opened and transesterification reaction.
Figure 1. NMR spectra of acetoacetylated soybean oil: (a) 1H NMR spectra and (b) 13C NMR spectra.

The FTIR spectra of ESO, soybean oil-based polyols (MA-ESO), acetoacetylated soybean oil (MA-ESO-TBA), and t-butyl acetoacetate are shown in Figure 2. The comparison of ESO (black) and MA-ESO (red) shows that the peak at 823 cm\(^{-1}\) (corresponded to epoxy groups) disappeared and a new peak at 3600–3300 cm\(^{-1}\) (OH group) appeared, which indicates that the ring-opened reaction of epoxidized soybean oil occurred to obtain hydroxyl groups. By comparing MA-ESO (red) and MA-ESO-TBA (blue), the peaks at 1731–1712 cm\(^{-1}\) (the stretching vibration band of C=O of–COCH\(_2\)COCH\(_3\)) and 1350 cm\(^{-1}\) (C–O stretch from the ester bond of–COCH\(_2\)COCH\(_3\)) were observed. These results indicated that acetoacetylated soybean oil was obtained by the ring-opened and transesterification reaction.

Figure 2. FTIR characterization of acetoacetylated soybean oil.

The viscosities of ESO, soybean oil-based polyols (MA-ESO), and acetoacetylated soybean oil (MA-ESO-TBA) were also measured. As shown in Figure 3, the viscosity increased from 0.14 Pa s (epoxidized soybean oil, black) to 1.31 Pa s (soybean oil-based polyols, red) after the ring-opened reaction. The main reason for this is the increased intermolecular hydrogen bonding by the ring-opened reaction. Then, after the transesterification reaction (from soybean oil-based polyols to acetoacetylated soybean oil), the viscosity decreased from 1.31 Pa s to 0.61 Pa s, due to the disappeared hydrogen bonding interactions by the transesterification reaction [25]. However, compared to ESO and MA-ESO-TBA, the viscosity of MA-ESO-TBA was increased. The main reason for this may be that the molecular weight of MA-ESO-TBA was increased [26].
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In the initial study, we chose acetoacetylated soybean oil (MA-ESO-TBA) and 1,2-benzenedialdehyde as model starting materials to examine these coating materials, and the ratio of acetoacetate and aldehyde groups was 1:0.75, as previously reported [23]. As shown in Table 2, the film can be cured with piperidine as a catalyst (3 wt %) in 40 h (Table 2, Entry 1) and the curing time with DMAP (3 wt %) as a catalyst was 20 h (Table 2, Entry 2). When 1,8-diazabicyclo (5,4,0) undec-7-ene (DBU) (3 wt %) was used as a catalyst, the curing time could be reduced to 8 h with a good gel content of 83% (Table 2, Entry 3). Furthermore, we optimized the catalyst loading (DBU) and found that 5 wt % of DBU achieved the best curing time of 3.5 h, with a gel content of up to 88%.

Table 2. Optimization of the preparation reaction conditions.

| Entry | Catalyst          | CuringTime a (h) | Solvent-Swelling (%) | Gel Content (%) |
|-------|-------------------|------------------|----------------------|-----------------|
| 1     | Piperidine (3 wt %) | 40 h          | 315                  | 70              |
| 2     | DMAP (3 wt %)     | 20 h            | 302                  | 72              |
| 4     | DBU (3 wt %)      | 8 h             | 270                  | 83              |
| 5     | DBU (5 wt %)      | 3 h             | 220                  | 88              |
| 6     | DBU (8 wt %)      | 2.8 h           | 225                  | 85              |

a Dry through curing time.

In order to explain the Knoevenagel reaction mechanism of this cured film, we used ethyl acetate and benzaldehyde as model materials, 5 wt % of DBU as catalyst (similar reaction condition based on the best optimize reaction condition), and found that two types of compounds were obtained and determined by NMR (Model reaction section, Supporting Information). The result showed that the acetoacetyloxy group can react with the aldehyde group and obtained two structure types at molar ratios of 1:0.75. Similar Knoevenagel reaction mechanisms have been reported in the Raju group [27].

After the optimization of reaction conditions, four coating (P1, P2, P3, and P4) films were obtained by different crosslinkers (C1, C2, C3 and C4, respectively). The characterization data of four coating films are displayed in Table 3. Comparison of the four films shows that all films had good gel content (87–90%). The solvent-swelling (in THF) decreased from 220% to 130%; the main reason for this was that the crosslinking density from P1 to P4 is gradually increased.
### Table 3. Films made with different crosslinkers.

| Sample | Curing Time (h) | Solvent-Swelling (%) | Gel Content (%) |
|--------|----------------|----------------------|-----------------|
|        | Set to Touch   | Tack Free            | Dry Hard         | Dry Through     |
| P1     | 1.1            | 2.1                  | 2.6             | 3 h             | 220 | 88  |
| P2     | 1.2            | 3.2                  | 4.6             | 5.5 h           | 175 | 90  |
| P3     | 1.5            | 3.3                  | 5.0             | 6 h             | 156 | 92  |
| P4     | 1.6            | 4.1                  | 5.6             | 6.5 h           | 130 | 87  |

#### 3.2.1. FTIR Characterization of Films

These coating films were characterized by FTIR, and the spectra are shown in Figure 4. Acetoacetylated soybean oil spectrum was compared with those of the samples C1 and P1, C2 and P2, C3 and P3, and C4 and P4, which were produced by the Knoevenagel addition reaction. The peaks for P1, P2, P3, and P4 at 2745 cm\(^{-1}\) (a, –CHO stretching frequency) decreased after curing, and the gels of the coating materials (P1, P2, P3, and P4) had characteristic absorption peaks of benzene rings at 1600 cm\(^{-1}\) (b) and 1381 cm\(^{-1}\) (c). These results indicated that four coating films were successfully obtained. Similar reactions between aldehyde and acetoacetyloxy groups have been previously reported [23,27,28].

![Figure 4. FTIR spectra of the four films (P1, P2, P3, and P4), four crosslinkers (C1, C2, C3, and C4) and acetoacetylated soybean oil, and the peaks of a is CHO stretching frequency, b and c are the peaks of benzene rings.](image)

#### 3.2.2. Mechanical Properties

Figure 5 shows the storage modulus and loss factor (tan \( \delta \)) as a function of temperature for the four films with different crosslinkers (C1, C2, C3, and C4). It was observed that all films exhibited similar trends of the storage modulus (\( E' \)) values, as follows: Storage modulus decreased at a certain temperature and then stabilized (Figure 5a). The loss factors (tan \( \delta \)) of the four films are shown in Figure 5b. Specifically, only one peak is observed, which indicates that the four films exhibit homogeneous properties. The crosslinking density can be calculated by the equation \( V_c = E'/3RT \), which has been previously reported [29–31]. The crosslinking density, \( T_g \), and storage modulus of the four films (P1–P4) are shown in Table 4. Compared to the four films, P4 has the higher \( T_g \) and crosslinking density. The main reason for this may be that the crosslinker C4 has a lower steric hindrance structure.
The stress-strain behaviours of the four films are shown in Figure 6. By comparing P1, P2, and P3, it was determined that as the structural steric resistance of the crosslinkers (C1, C2, and C3, respectively) decreased, the crosslinking density and mechanical properties (elongation at break, Young’s modulus, and tensile strength) gradually increased (Table 4). Furthermore, P4 has the highest mechanical properties (elongation at break, Young’s modulus, and tensile strength), due to that P4 has the highest crosslinking density.

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3.2.3. Thermal Stability

Figure 7 shows TGA curves and their derivative curves for the four films, and the $T_{10}$, $T_{50}$, and $T_{\text{max}}$ data are summarized in Table 5. The thermal degradation profile of the four films shows two rapid thermal degradation steps at approximately 160–280 °C and 280–550 °C. The unstable ester groups were released at approximately 160–280 °C [32], and the chain scission of the corresponding
The glass transition temperature ($T_g$) values determined from the differential scanning calorimetry (DSC) thermograms are shown in Figure S4 (in Supporting Information) and Table 5. Three films (P1, P2, and P3) have similar $T_g$, and P4 has a higher $T_g$. These results are similar to the glass transition temperature ($T_g$) determined by DMA analysis.

![Figure 7. Curves (a) and DTGA curves (b) for the four films.](image)

Table 5. Thermal properties of the four films.

| Sample | TGA in Nitrogen (°C) | DSC $T_g$ (°C) |
|--------|----------------------|----------------|
|        | $T_{10}$ | $T_{50}$ | $T_{max}$ | $T_{10}$ | $T_{50}$ | $T_{max}$ |
| P1     | 234     | 363     | 449     | 16      |          |          |
| P2     | 268     | 372     | 473     | 14      |          |          |
| P3     | 257     | 368     | 485     | 17      |          |          |
| P4     | 256     | 381     | 531     | 34      |          |          |

$T_{10}$, $T_{50}$, and $T_{max}$ represent the temperatures that correspond to the mass loss of 10 wt %, 50 wt %, and the maximum mass loss, respectively.

4. Conclusions

A novel bio-based coating material was developed using the Knoevenagel condensation reaction between acetoacetylated soybean oil and aromatic dicarboxaldehydes. Acetoacetylated soybean oil was synthesized at ambient curing conditions, and its chemical structure was determined by NMR, FTIR, GPC, and viscosity characterization. Then, four bio-based coating materials were prepared by acetoacetylated soybean oil and aromatic dicarboxaldehydes. These coating materials were characterized by Fourier transform infrared spectroscopy. Thermal and mechanical properties were characterized by DSC, TGA, and DMA. These coating materials exhibit good mechanical/chemical performance. The characteristics of this novel system demonstrate the applicability of the Knoevenagel condensation reaction for soybean oil as a new eco-friendly raw material.

**Supplementary Materials:** The following are available online at [http://www.mdpi.com/2073-4360/11/11/1809/s1](http://www.mdpi.com/2073-4360/11/11/1809/s1), Figure S1 $^1$H NMR spectra of (a) epoxy soybean oil (ESO) and (b) soybean oil-based polyols (MA-ESO), Figure S2 $^1$H NMR spectra of (a) soybean oil-based polyols (MA-ESO) and (b) acetoacetylated soybean oil (MA-ESO-TBA), Figure S3 The GPC of acetoacetylated soybean oil, Figure S4 DSC curves indicate the glass transition temperature ($T_g$) of the four films. Figure S5 $^1$H NMR (400 M) spectrum of epoxy soybean oil (ESO), Figure S6 $^{13}$C NMR (400 M) spectrum of epoxy soybean oil (ESO), Figure S7 $^1$H NMR (400 M) spectrum of soybean oil-based polyols (MA-ESO), Figure S8 $^{13}$C NMR (400 M) spectrum of soybean oil-based polyols (MA-ESO), Figure S9 $^1$H NMR (400 M) spectrum of acetoacetylated soybean oil (MA-ESO-TBA), Figure S10 $^{13}$C NMR (400 M) spectrum of acetoacetylated soybean oil (MA-ESO-TBA).
acetoacetylated soybean oil (MA-ESO-TBA), Figure S11H NMR (400 M) spectrum of compound A, Figure S12
13C NMR (400 M) spectrum of compound A. Table S1. Properties of the acetoacetylated soybean oil.

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