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Characterization and Polymerization of Epoxidized Methacrylated Castor Oil

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In this study, synthesis and polymerization of epoxidized methacrylated castor oil (EMETCO) is demonstrated. EMETCO is synthesized in two steps. Castor oil (CO) is methacrylated with methacryloyl chloride at the first step. Then the methacrylated castor oil (METCO) is epoxidized by Prilezhaev reaction. Structure of EMETCO is determined by ^{1}H NMR and IR techniques. EMETCO was copolymerized with acrylic acid (AA), styrene (ST), and methacrylic acid (MA). Thermal and mechanical properties of the synthesized polymers are evaluated. Among the polymers synthesized EMETCO-ST-MA polymer gives the highest storage modulus at 2.25 GPa. On the other hand, EMETCO-AA copolymer exhibited the lowest storage modulus at 350 MPa. Moreover, EMETCO-ST copolymer shows the lowest 5% weight loss temperature while EMETCO-MA exhibited the highest 5% weight loss temperature at 280 °C.

***Practical Applications*: Epoxidized Methacrylated Castor Oil is a bio-based epoxy acrylate monomer. The low viscosity and two different functional groups make this material suitable for many polymerization reactions and applications. This compound would be used as a replacement materials for many industrial monomers such as styrene, acrylated epoxidized soybean oil, or prepolymers in the future.**

1. Introduction

Epoxy acrylates are versatile compounds that contain an acrylate and an epoxide group. Due to the presence of different type of polymerizable groups, epoxy acrylates are often called as hybrid materials.[1–3] Acrylate groups can be polymerized via free radicalic reactions while epoxy groups can be polymerized via cationic reactions.[4–6]

Industrially, two types of compounds can be classified and produced as epoxy acrylate. First type is the condensation product of bisphenol A based epoxy resins and acrylic acid. At the end of the reaction, considerable amount of epoxy acrylates are obtained as main product. Besides main product, diacrylates, and unreacted epoxies can be found in the mixture as side products.[7–9] The resultant resin is actually not an epoxy acrylate resin and unfortunately, the side products cannot be removed from reaction medium. The second kind is glycidyl acrylates. The most used glycidyl acrylate is glycidyl methacrylate. This compound is not a resinous material and it is generally synthesized by the reaction between sodium or potassium salts of methacrylic acid and epichlorohydrin.[10–12]

Most of the industrially acceptable epoxy acrylates are petroleum based. Due to the environmental impact and sustainable development, bio-replacements of those epoxy resins are desirable. As a plant oil based materials, acrylated epoxidized soybean oil (AESO) may also be accepted as an industrial epoxy acrylate. Like bispehnol A based epoxy acrylates, AESO is also synthesized by the ring opening reaction of epoxidized soybean oil (ESO) with acrylic acid. During the condensation reaction, most of the epoxide groups consumed and minor amount of them still present at the end of the reaction. Many type of polymeric materials can be synthesized with AESO.[13–20] Besides AESO, epoxidized acrylated castor oil (EACO), which was found by our research group, would also be a promising material.[21]

As a continuation of the previous research, in this study, methacrylation and then epoxidation of castor oil was demonstrated. At the end of the modification reactions, epoxidized methacrylated castor oil monomer (EMETCO) was obtained. To the best of our knowledge, there would be no report about the epoxidation of methacrylated derivative of castor oil.

2. Experimental Section

Castor oil (CO) was obtained from Sankim (Istanbul, Turkey). methacrylic acid (MA), dichloromethane (DCM), 30% hydrogen peroxide, methacryloyl chloride (MC), acrylic acid (AA), methacrylic acid (MA), sodium sulfate, styrene (ST), tetrahydrofuran (THF) triethylamine (TEA), were purchased from Merck (Darmstadt, Germany). IR characterization of compounds and polymers was performed by Nicolet 380 FT-IR spectrometer with

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Smart Diamond ATR. The ^{1}H NMR spectra were recorded on a Varian 400-MHz NMR instrument operating at a frequency of 399.986 MHz for proton. Viscosity measurements were performed with Brookfield RVDV-II + P type viscometer at 20 °C. Thermal stabilities of the material were characterized by "Thermal Analyses" Q 50 model TGA instrument with a 10 °C min^{-1} heating rate under nitrogen atmosphere. The dynamic mechanical properties of the suitable polymers were measured with a dynamic mechanical analyzer DMA Q800 in the single-cantilever mode at a frequency of 1 Hz and a heating rate of 3 °C min^{-1} under nitrogen atmosphere. The samples for the DMA experiments were prepared with a microtome into rectangular shapes having the average dimensions of $12 \times 35 \times 3$ mm^3.

3. Experimental

3.1. Synthesis METCO

For a typical reaction, in a two necked 250 ml round bottom flask, 10 g of castor oil (0.0108 mol) was dissolved in 25 ml of dry THF then mixed with 3.54 g of TEA (0.035 mol). The solution is cooled in an ice bath to 5 °C and the solution of 3.65 g of methacryloyl chloride (0.035 mol) in 10 ml dry THF was added drop wise in 30 min. Mixture was stirred for 2 more hours. After finishing reaction, the solvent was removed in vacuo and the residue was dissolved in 50 ml DCM and washed with 50 ml saturated salt solution several times in 250 ml separatory funnel. After drying over dry sodium sulfate, 11 g of methacrylated castor oil (METCO) was obtained after removal of the solvent in vacuo. The yield was 90%.

3.2. Epoxidation of METCO

In a 250 ml flask, 10 g of methacrylated castor oil (METCO, 0.009 mol) was mixed with 4.0 g of formic acid (0.087 mol). While vigorously stirring of this mixture, 5.66 g of 30% H_2O_2 solution (0.05 mol) was added. The mixture was stirred approximately for 16 h at room temperature. After completion of the reaction, crude product was extracted with DCM. Then the DCM extract was placed in a separatory funnel, and washed with a series of solutions. First, the product was washed with approximately 50 ml of distilled water. The product was then washed with approximately 50 ml of a saturated sodium bicarbonate solution (aqueous). Both steps helped to neutralize the solution. Neutralization step was continued till water layer was neutral. Then, the organic layer was washed with 50 ml of a saturated sodium chloride solution. DCM layer was dried over anhydrous sodium sulfate. The sodium sulfate was filtered off, and the DCM was evaporated and 11.2 g of EMETCO was obtained (97% yield).

3.3. Polymerization of Monomers

For the polymerization reactions, monomer, or monomer mixture was mixed with 1% initiator (AIBN). Mixture was stirred at room temperature until all the initiator was dissolved. Then the solution was purged with nitrogen for 10 min. After that, test tube sealed, heated to 40 °C. After 2 h temperature was raised to 60 °C and material was waited for 16 h.

4. Results and Discussion

4.1. Synthesis and Polymerization of EMETCO

Synthesis of EMETCO, which is shown in **Figure 1**, was involved in two step. Methacrylation of castor oil with methacryloyl chloride was the first step and the epoxidation of the methacrylated castor oil was the second. Castor oil contains ricinoleic acid up to 90%. Ricinoleic acid is an unsaturated fatty acid and it contains a hydroxyl group at the twelfth carbon. Average value of hydroxyl groups per castor oil triglyceride is 2.7. Thus, when castor oil was reacted with methacryloyl chloride, the resultant METCO might contain up to 2.7 methacryloyl group per triglyceride. The amount of attached methacryloyl groups was easily calculated by ^{1}H NMR technique via finding the integration ratio of the hydrogens at the twelfth carbon to the hydrogens of α carbon of fatty acid residues. In the case of full conversion, it was found that this value approached to 0.45.

After methacrylation reaction, the resultant material was epoxidized with H_2O_2/HCOOH mixture. Suitable amount of METCO was first mixed with formic acid. Then the mixture was cooled to 5 °C. To this mixture, suitable amount of H_2O_2 solution was added dropwise. Addition was completed in 30 min. Temperature was adjusted to 5 °C during addition. The mixture was vigorously stirred for 16 h. Epoxidation percentage was monitored by the ^{1}H NMR technique. Integration ratio of epoxide hydrogens to methacrylate hydrogens was used for this examination. In every step of the synthesis, reactions were carried out under inert atmosphere. To the best of our knowledge, there is no report about the synthesis of epoxy derivative of METCO, by this work it was clarified that the reaction can proceed without any complication

Epoxide groups are strained tri-membered rings, at high temperatures and longer reaction times self-opening reactions

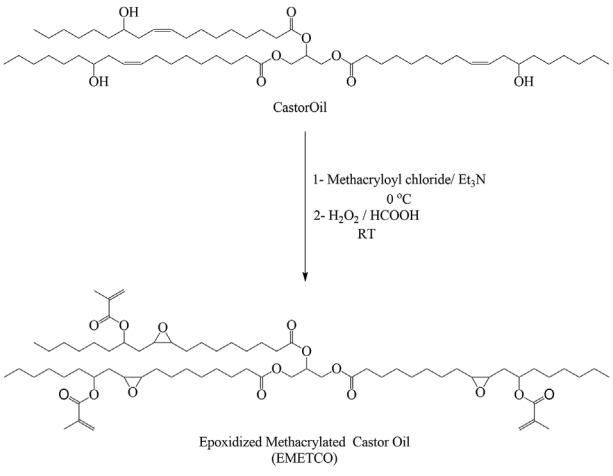


Figure 1. Synthesis of EMETCO.

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may take place. Thus the polymerization of EMETCO was performed with AIBN at 40 °C. After 15 min, gelation occurred. When benzoyl peroxide was used as an initiator, the polymerization reaction was accomplished at 90 °C. Unfortunately, crack formations of the resultant polymers was observed probably due to the self-opening reactions of epoxide groups at that temperature.

Copolymers of EMETCO with AA, MA, and ST were studied in this work. In the monomer mixture, the mol amount of AA or MA was approximately adjusted to the mol amount of epoxide groups in the EMETCO. Thus, 86% of EMETCO was, copolymerized with 14% AA. In the case of EMETCO-MA copolymer, the percentages was 84 for EMETCO and 16 for MA. It was expected that during radical polymerization, free carboxyl groups of AA, or MA reacted with epoxide rings. In order to observe the effect of carboxyl groups. EMETCO was polymerized with ST at 50–50 percentage. Then, 50% EMETCO was reacted with 10% MA-40% ST mixture. It was found that, EMETCO-ST-MA copolymer mixture showed the best thermal and mechanical properties than the other copolymers synthesized probably due to the reaction between epoxide groups of EMETCO and carboxyl groups of methacrylic acid monomers. When the polymers were extracted with diethyl ether by using soxhlet apparatus, less than. 0,5% of material could be extracted. FTIR of the extracts revealed that the extracts were only composed of saturated triglycerides. Homopolymers of ST, AA, or MA were not identified.

4.2. Characterization of EMETCO

FTIR spectra of CO, METCO, and EMETCO is shown in **Figure 2**. In the FTIR spectrum of CO, a peak appeared at 3400 cm^{-1} due to the presence of hydroxyl groups. The peak of ester carbonyl was observed at 1743 cm^{-1}. Other distinctive peaks of CO were depicted at 1655 and 3009 cm^{-1} and they showed the presence of carbon-carbon double bond. When methacrylate groups were introduced, the peak at 3400 cm^{-1} disappeared and a two peaks at 1743 and 1721 cm^{-1} could be observed. The peak at 1721 cm^{-1} belonged to methacrylate ester. Additionally, the new peaks at 1678 and 1637 cm^{-1} aroused and indicated the presence of the methacrylate double bond. When an epoxide group was inserted, a new and small peak could be observed at 830 cm^{-1} but in our case, it was not possible probably due to the interference of the peaks of other moieties. When the epoxidation occurred, disappearance of the small peaks at 1655 and 3009 cm^{-1} can also be observed. These peaks showed the presence of the double bonds of castor oil and after epoxidation, these peaks disappeared. However the double bond peaks of methacrylate group at 1678 and 1637 cm^{-1} did not vanish.

^{1}H NMR technique was also used to follow the reaction steps. The ^{1}H NMR spectra of CO, METCO, and EMETCO is shown in **Figure 3**. The double bond hydrogens of CO appeared at 5.2–5.3 ppm as two separate multiplet. Two hydrogens of glycerin moiety appeared at 4.0–4.2 and one hydrogen appeared at 5.15 ppm. The peaks of the hydrogens geminal to hydroxyl groups could be followed at 3.5 ppm. The hydrogens of α methylene to ester carbonyl was observed at 2.25 ppm. The peak of the hydrogens of β methylene to ester group was depicted at 1.6 ppm

When methacrylation occurred, the peaks of geminal hydrogens to hydroxyl groups disappeared and a new peak at 5,0 ppm was observed. Besides this, two new peaks appeared at 6 and 5.4 ppm due to the presence of double bond hydrogens of methacrylate moieties.

After epoxidation of those monomers two new peaks appeared at 2.5 and 2.7 ppm which belonged to hydrogens of the epoxide groups. According to the ^{1}H NMR finding, the integration ratio of epoxide hydrogens to methacrylate hydrogens was one which means almost 100% epoxidation took place.

Viscosity of the EMETCO monomer was measured by using Brookfield type viscometer at 20 °C. The viscosities of CO, METCO, and EMETCO was found as 1350, 600, and 2500 centipoise, respectively. On the other hand, viscosity of the AESO was found as 13100 centipoise which is compatible with the literature.[22]

4.3. Mechanical Properties of Materials Synthesized

DMA technique was used in order to evaluate the mechanical properties of the polymers synthesized. DMA data of the materials is shown as supplementary data. Homopolymer of EMETCO was so brittle and it was not possible to perform any mechanical measurement on the samples. Hence, the properties of EMETCO copolymers were evaluated. When 14% acrylic acid or 16% methacrylic acid was mixed with EMETCO, the mol number of carboxyl groups was equal to the mol number of epoxy groups of EMETCO monomer. Thus, it was expected further polymerization of carboxyl groups with oxirane rings during radical polymerization. Storage modulus of 14% acrylic acid copolymer of EMETCO was around 0,35 GPa. On the other hand, 16% methacrylic acid copolymer of EMETCO showed 0,7 GPa storage modulus. The storage modulus of EACO with% 10 AA copolymer is higher than the EMETCO-AA copolymer.[21] This observation would probably be the results of the reactivity ratios of EMETCO and acrylic acid. Due to the

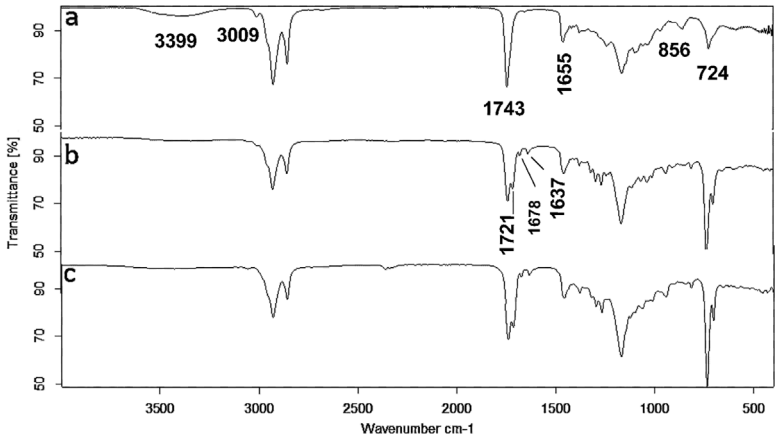


Figure 2. FTIR spectra of a) CO b) METCO c) EMETCO.

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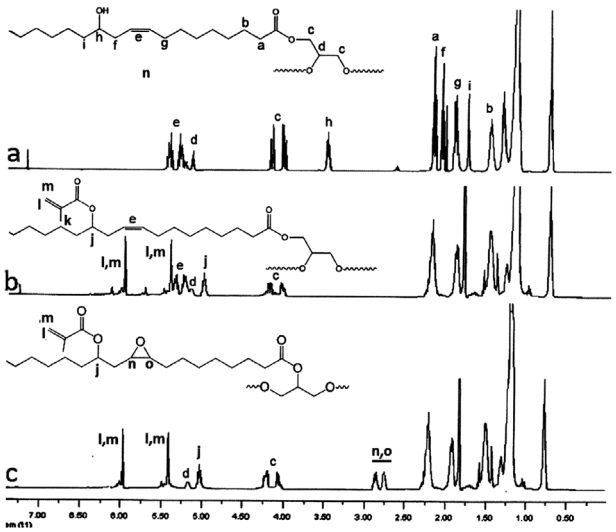


Figure 3. [1]H NMR Spectra of a) CO b) METCO c) EMETCO.

different reactivity ratios, polymerization of EMETCO, and acrylic acid generates incompatible regions which are responsible for low storage modulus. Storage modulus of EMETCO-MA was determined as 0.7 GPa. However, EMETCO-St (50–50%) copolymer showed 1.7 GPa at 25 °C. This result is better than AESO-ST (50–50%) copolymer. Storage modulus of AESO-ST copolymer is 0.9 GPa at 25 °C. Moreover, Storage modulus of EMETCO-ST-MA (50–40–10%) reached 2.25 GPa at 25 °C and it is obvious that this value is in the range of polystyrene storage modulus.[23–25]

In the literature, many works can be found on the acrylation, methacrylation and maleination of epoxidized soybean oil or other epoxidized oils. Due to the internal epoxy structure, these groups are not so reactive and after, acrylation, methacrylation, or maleination of these oils, some free epoxy residues can be determined. Thus, the resultant compounds would be accepted as epoxy acrylate resin. Among the acrylated epoxy plant oil triglyceride, AESO is the most used and industrially acceptable one. AESO-ST (50–50%) copolymer shows 0,9 GPa or 1.5 GPa storage modulus values depending on the curing conditions.[26–29] These values are below the values of EMETCO-St (50–50%) copolymer.

Tan δ values were also obtained from DMA experiment. Tan δ graphs of the copolymers synthesized are shown as supplementary data. EMETCO-AA copolymer showed a tan δ peak at 44 °C. EMETCO-MA, EMETCO-ST, and EMETCO-ST-MA copolymers showed tan δ values at 60, 65, and 80 °C respectively. EMETCO-ST-MA and EMETCO-ST copolymers exhibited tan δ values in the range of many industrial plastics.

4.4. Thermal Properties of Materials of Polymers Synthesized

TGA and DSC are the two valuable methods in order to determine thermal properties of any polymeric materials. Instead of DSC, DMA method was used in order to detect the Tg, of the polymers synthesized.

TGA gives information about thermal degradation pattern of the materials. TGA patterns of the materials are shown as Supporting Information. For the evaluation of the thermal stability, two data, which is obtained from TGA, can be used. First one is 5% weight loss temperature the other one is 50% weight loss temperature. EMETCO-AA copolymer exhibited 5% weight loss temperature as 260 °C. However EMETCO-MA copolymer showed at 282 °C. The lowest 5% weight loss temperature was observed at EMETC-ST copolymer at 221 °C.

The 50% weight loss temperatures of the copolymers almost appeared around 400 °C. This temperature was measured at 406 °C for EMETCO-AA copolymer and at 404 °C for EMETCO-MA copolymer.

5. Conclusion

In this study, by using cheap and renewable raw materials a new type of multi-functional plant oil-based monomer with low viscosity was synthesized. The new monomer contains approximately 2.7 mol of reactive epoxide and 2.7 mol of methacrylate groups per mol of triglyceride moiety. These epoxide and acrylate groups can be polymerized separately or together. By using these reactive groups, a vast variety of materials can be synthesized. The EMETCO-ST copolymer showed better mechanical and thermal properties than AESO-based polymers. Moreover, EMETCO-ST-MA polymer showed the storage modulus as high as the storage modulus of polystyrene while using only 40% of styrene. Additionally, It can be stated that the low viscosity of EMETCO, makes it a suitable candidate for many industrial applications.

Supporting Information

Supporting information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest

Keywords

biopolymers, castor oil, epoxidation, epoxy acrylates, renewable resources

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