

The Effects of Epoxidized Acrylated Castor Oil (EACO) on Soft Poly (vinyl chloride) Films as a Main Plasticizer

Fei Song^{1,3}, Haoyu Xia², Puyou Jia^{1,3*}, Meng Zhang^{1,3}, Lihong Hu^{1,3}, Yonghong Zhou^{1,3*}

¹Chinese Academy of Forestry (CAF), Institute of Chemical Industry of Forest Products, National Engineering Lab for Biomass Chemical Utilization, Key Lab on Forest Chemical Engineering, State Forestry Administration and Key Lab of Biomass Energy and Materials, Jiangsu Province, 16 Suojin North Road, Nanjing 210042, P.R. China

²Nanjing Tech University, College of Chemical Engineering, 30 Pu Zhu Road, Nanjing 211800, P.R. China

³Nanjing Forestry University, Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Nanjing 211800, P.R. China

*Corresponding authors: email: yhzhou777@sina.com, jiapuyou@icifp.cn

In this work, an environmentally friendly type plasticizer was introduced. The synthesis consisted of two steps. In the first step, castor oil (CO) was acrylated and then the acrylated castor oil (ACO) was epoxidized with the presence of formic acid and hydrogen peroxide in the second step. The epoxidized acrylated castor oil (EACO) was characterized by FTIR and ¹H-NMR techniques. The EACO was used as a main plasticizer to obtain plasticized PVC materials and compared with DOP. The results showed that EACO improved polyvinyl-chloride (PVC) plasticization performance and reduced Tg from 81.06°C to 1.40°C. Plasticized PVC materials with EACO showed similar mechanical properties and better thermal stability than DOP. EACO had better volatility stabilities, migration and solvent extraction in PVC than DOP. EACO can be used to replace DOP to prepare soft films.

Keywords: Castor Oil, Poly(vinyl chloride), Epoxy Plasticizer, Thermal Property, Migration Resistance.

INTRODUCTION

Polyvinyl chloride (PVC) is one of the top five general-purpose plastics in the world, which has been widely used in building materials, medical equipment, household appliances and other fields^{1,2}. Flexible PVC materials usually contain a large amount of plasticizer because PVC is too stiff to be processed. Phthalates are the most widely used plasticizers around the world³. Many countries in the world have formulated relevant regulations to restrict the use of phthalates. Phthalates are easy to migrate from PVC materials, which decrease their service life. There are pieces of research reported that the phthalates have potential toxicity on human body⁴⁻⁶. Therefore, people urgently need to develop new types of non-toxic safe, environmentally friendly and migration-resistant plasticizers⁷. Vegetable oil has been used to synthesis plasticizers due to natural non-toxic, biodegradable, renewable and high molecular weights and others excellent performance^{8,9}. Many kinds of vegetable oil-based plasticizer has been developed such as soybean oil-based plasticizer¹⁰⁻¹², tung oil-based plasticizer¹³⁻¹⁵, palm oil-based plasticizer^{16,17}, cottonseed oil-based plasticizer^{18,19}, rice bran oil-based plasticizer^{20,21}, and so on.

Castor oil is one of the most produced oil. It is inherently functionalized and one of the most important inedible oils. Castor oil has rich double bond, hydroxyl and ester base active functional groups²², which is a kind of yellow oily viscous liquid with excellent physical and chemical performance, softness, difficult to precipitate, low volatility and migration capacity and can be directly used as plasticizers²³. Tsujimoto et al.²⁴ modified castor oil to obtain a polymer plasticizer and studied its plasticization of polylactic acid. The research revealed that only 5 wt% of the branched polymer was sufficient to plasticize polylactic acid. Mehta et al.²⁵ employed ricinoleic acid as raw materials, benzyl alcohol and octanoic acid esterification to produce a showing good compatibility and plasticization of PVC-based plasticizer. Recently,

our research group obtained a plasticizer with high flame retardancy through the incorporation of flame-retardant DOPO, diethyl phosphate and chlorinated phosphate into the epoxy castor oil structure²⁶⁻²⁹. Polyol ester plasticizers based on castor oil has also reported by Jia et al.³⁰ The results showed that polyol ester plasticizers based on castor oil significantly improved the thermal stability of the PVC sheet, and its plasticizing property was superior to DOP and ESO. Hydroxyl modification of castor oil has always been paid more attention for preparing fine chemicals. In recent years, Esen et al.³¹ firstly reported that epoxidized acrylated castor oil was used to prepare polymers. The similar work on the synthesis and polymerization of epoxidized methacrylated castor oil was also reported by Gürbüz et al.³². Sahin et al.³³ synthesized cross-linkable epoxidized maleinated castor oil by esterification between the hydroxyl and maleic anhydride and epoxidation. All these studies indicated that castor oil based polymers had good mechanical and thermal properties and showed better than some other plant oil based copolymers/networks such as soybean oil based polymers. Castor oil-based plasticizer has high and low-temperature resistance, and it can be used as main the plasticizer and secondary plasticizer.

In this study, we synthesized epoxidized acrylated castor oil (EACO, Fig. 1) and used as a main plasticizer to obtain plasticized PVC materials and compared with that of the industrialization plasticizer DOP. The molecular structure of the compound was identified with FTIR and ¹H NMR. Relevant test results displayed that EACO with abundant ester group and the epoxy group provides excellent compatibility, fastness to migration, heat stability and softening for PVC.

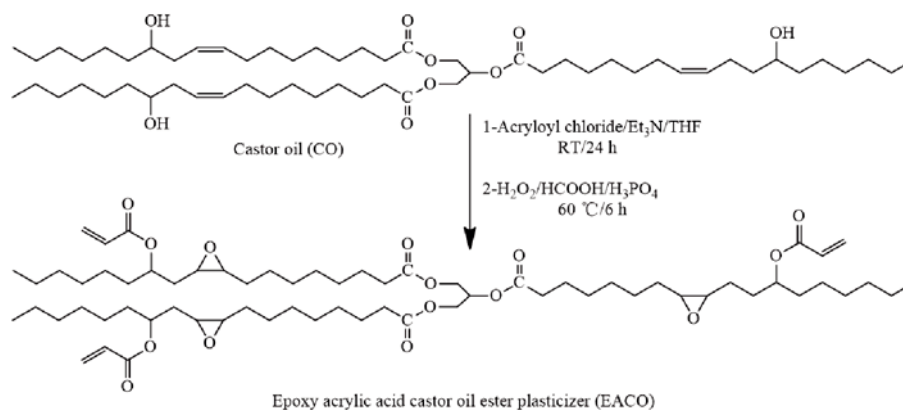


Figure 1. The design and synthetic scheme for EACO

EXPERIMENTAL

Material

Castor oil (CP), triethylamine (AR), phosphoric acid (AR), p-diphenol (AR) were purchased from Nanjing Chemical Reagent Co., Ltd, China. Tetrahydrofuran (AR), formic acid (AR) from Shanghai Titan Technology Co., Ltd. to buy. DOP (AR, Aladdin Inc.), Acryl chloride (AR, Energy Chemical, China), hydrogen peroxide solution (AR, 30% aqueous solution, Shanghai Zhanyun Chemical Co., Ltd, China.), anhydrous sodium sulfate (AR, Tianjin Ruijin Te Chemical Co., Ltd, China.) were used as received. Polyvinyl chloride (PVC) was procured from Hanwha (KM-31, South Korea) with K value 65.0 and degree of polymerization 1300 ± 100 .

Synthesis of acrylate castor oil (ACO)

A detailed description of the synthesis of ACO is as follows: To a solution of castor oil (9.33 g, 10 mmol), triethylamine (3.34 g, 33 mmol) and acrylic acid chloride polymerization inhibitor (500 ppm) in tetrahydrofuran (30 mL) was added dropwise acryloyl chloride (2.99 g, 33 mmol) below 10°C. Then, the reaction mixture was stirred at room temperature for 1 day. When the reaction was complete, precipitate was removed by suction filtration under reducing pressure and washed with tetrahydrofuran (5 mL \times 3 times). The solution in the suction flask was collected after washing three-time with 7 wt% sodium bicarbonate solution (100 mL). The organic layer was dried with anhydrous sodium sulfate and filtered. The filtrate was distilled under vacuum to give 10.89 g of ACO as the yellow viscous oil (98% yield).

Synthesis of epoxidized acrylated castor oil (EACO)

EACO was synthesized as follows: The above-obtained acrylate castor oil, formic acid, phosphoric acid was placed in a four-necked flask with electric stirring, a thermometer, a dropping funnel, a condenser and heated in a constant temperature water bath. The H₂O₂ was added dropwise uniformly at 40°C, and the reaction mixture was stirred at room temperature for 6 hours. The molar ratio of each substance is n (C=C): n (HCOOH): n (H₂O₂) = 1: 0.5: 1.4, H₃PO₄ is 0.5 wt% of acrylate castor oil. Then, the solvent was placed in a separatory funnel static stratification and removed the water layer. The organic layer was washed several times with 7 wt% sodium bicarbonate solution, brine saturated and deionized water. The organic layer was dried with

anhydrous sodium sulfate and filtered. The filtrate was distilled under vacuum to afford EACO as the pale yellow transparent viscous liquid. The acid value of castor epoxy acrylate was 0.96 mg KOH/g, and the epoxy value was 3.75%. Determination of acid, epoxy values was in accordance with the Chinese standards GB/T 1668-2008 and GB/T 1667-2008, respectively.

EACO/PVC blend film preparation

A certain amount of PVC was dissolved in 80 mL of THF at 30°C and mixed with 10%, 20%, 40%, 60% (w/w) of EACO, 60% (w/w) dioctyl phthalate (DOP) respectively. The mixture was thoroughly agitated by mechanical stirring for 3 h followed by sonication for 30 min. The samples were poured into petri dishes (d=19 cm) followed by slowly air drying at ambient temperature for 1 days then under reduced pressure for 1 days to remove traces of THF and to obtain thin films. Samples were labeled EACO-10, EACO-20, EACO-40, EACO-60, DOP-60.

Measurements and characterization

FT-IR Measurements. FTIR spectroscopy of the CO, ACO, and EACO was performed on a Nicolet IS 10 IR spectrometer (Nicolet Co., USA) in a range of 4000~500 cm⁻¹ and the resolution of 4 cm⁻¹.

¹H NMR Measurements. ¹H NMR spectra were confirmed by a Bruker ARX 300 nuclear magnetic resonance spectrometer with CDCl₃ as the solvent and tetramethylsilane as the internal standard.

Thermal Analysis. Thermogravimetric analyzer (TGA) measurements were performed NETZSCH TG 209F1 (Netzsch Instrument Crop., Germany) in a nitrogen atmosphere was used with a heating rate of 10°C/min and a temperature range of 35–600°C.

Differential scanning calorimetry. Differential scanning calorimetry (DSC) was served as detecting the glass transition temperature by a PerkinElmer DSC8000 apparatus, which was heat from -20.00°C to 120.00°C at 20.00°C/min in the nitrogen atmosphere. The DSC data for the second heating cycle was introduced.

Migration Test. Volatility test was according to ISO 176: 2005 (Determination of plasticizer loss of activated carbon determination.). In a suitable container by adding an appropriate amount of activated carbon, take the test piece all immersed in activated carbon, then close the lid and place in an oven at 70°C for 24 h, last removed activated carbon on the test piece surface to determine

the amount of quality loss. Repeat the experiment 3 times for each sample to calculate the average value.

Extraction test. Extraction test was characterized according to ASTM D1239-2014, which is “Standard Test Method for Resistance of Plastic Films to Extraction by Chemicals”. The PVC film cut into 25 ± 0.25 mm square test piece, in a laboratory environment of $23 \pm 2^\circ\text{C}$ and relative humidity $50 \pm 5\%$ for place at least 40 h, The weight of the sample is weighed, the recording quality is W_1 . Next, the PVC specimens were immersed in four solvents (n-hexane, distilled water, 10% (w/w) ethanol, petroleum ether) for 24 h. Finally, the sample plates were towel off and dried in an oven at 30°C for 24 h, then reweighed to marker W_2 . The mass loss rate is calculated as Eq. (1).

$$\text{Weight loss, \%} = [(W_1 - W_2)/W_1] \times 100 \quad (1)$$

Tensile properties Test. Tensile properties test was measured by a CMT4000 universal testing machine (according to ISO 527-2: 1993) with stretching rate of 20 mm/min at 50% humidity and $23 \pm 1^\circ\text{C}$. Each named sample need test at least three times.

RESULTS AND DISCUSSION

Synthesis and characterization

FTIR and $^1\text{H NMR}$. In this study, a highly functionalized vegetable oil-based plasticizer monomer was obtained by esterification of the castor oil hydroxyl group and selective partial oxidation of its double bond. The chemical structure of the raw materials and the products during the reaction were identified by FTIR and $^1\text{H NMR}$. Fig. 2 presents the FTIR spectra of CO, ACO, and EACO. In the FTIR spectra of CO, there are characteristic peaks at 3410 cm^{-1} due to the O-H stretching vibration, peaks at around 3010 cm^{-1} , 1650 cm^{-1} , 853 cm^{-1} and 725 cm^{-1} ascribed to carbon-carbon double bonds of castor oil, the peaks at 1742 cm^{-1} represented C=O. In the FTIR spectra of ACO, the peaks for O-H disappeared, the new peaks for C=O appeared at 1723 cm^{-1} due to the formation of new acrylate esters. Two new peaks appeared at 1637 cm^{-1} and 1619 cm^{-1} also demonstrated that the presence of acrylate double bond³⁴. As seen from the EACO, the peaks for carbon-carbon double bonds

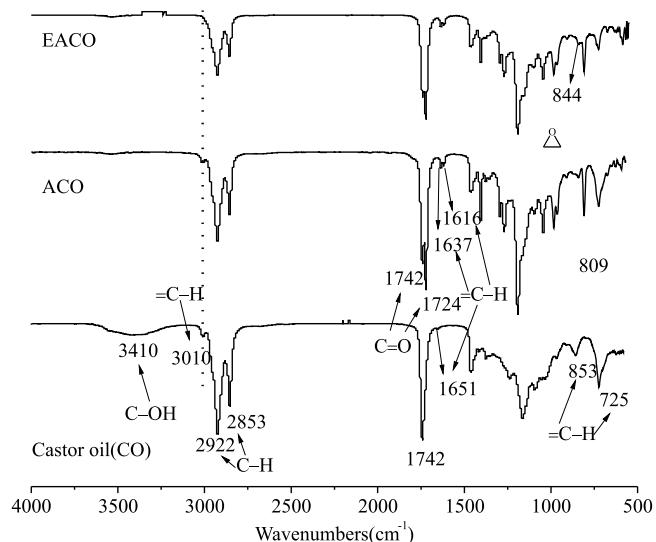


Figure 2. FTIR spectra of CO, ACO and EACO

of castor oil at 3010 cm^{-1} disappeared and the peaks for the epoxy group at around 844 cm^{-1} appeared³¹. Fig. 3 presents the $^1\text{H NMR}$ spectra of CO, ACO, and EACO. In the spectrum of CO, the signals at 3.6 ppm (proton 1) and 4.1–4.2 (proton 2) ppm were assigned to glycerin moiety protons. The signals of methine protons of double bond hydrogens were observed at 5.4–5.5 ppm (proton 10 and 11). The signals at 3.6 ppm (proton 13) attributed to hydrogen in the tertiary carbon (-C-CH-) which is bound to hydroxyl. In the spectrum of ACO, the new signals at 5.8–6.4 ppm (proton 20, 21, and 22) belonging to the hydrogens of acrylate moieties³⁵. The shift of all the signals of proton 13 from 3.6 ppm to 4.9 ppm proves that there is no CO in ACO product. In the spectrum of EACO, the signals of methine protons of double bond hydrogens disappeared. There are new signals ascribing to epoxy protons at 2.9 ppm and 3.0 ppm. Also, signals of proton 20, 21, and 22 have no change. All the results showed that EACO was obtained³².

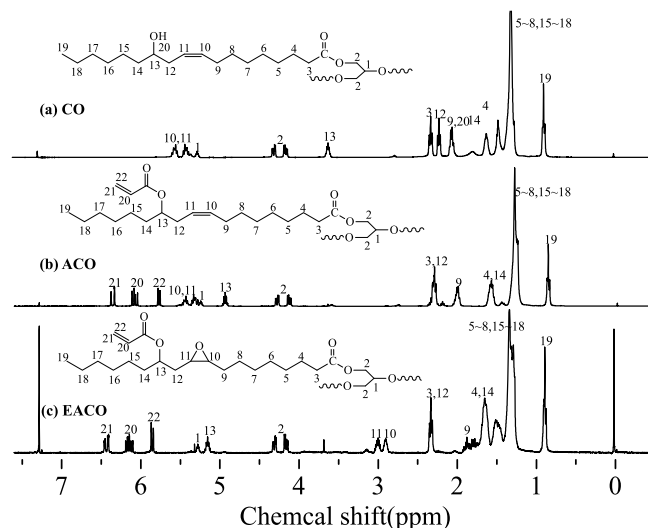
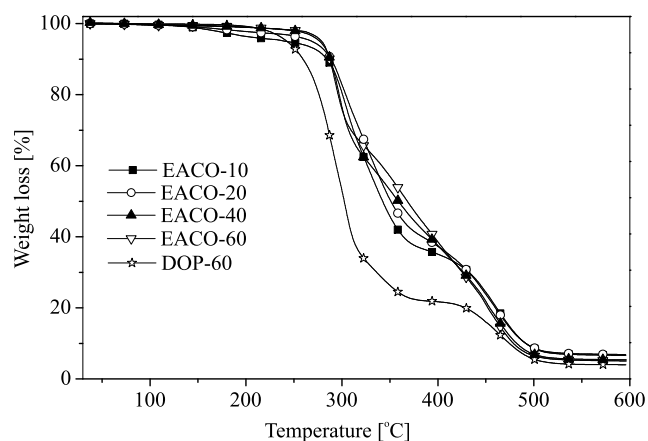
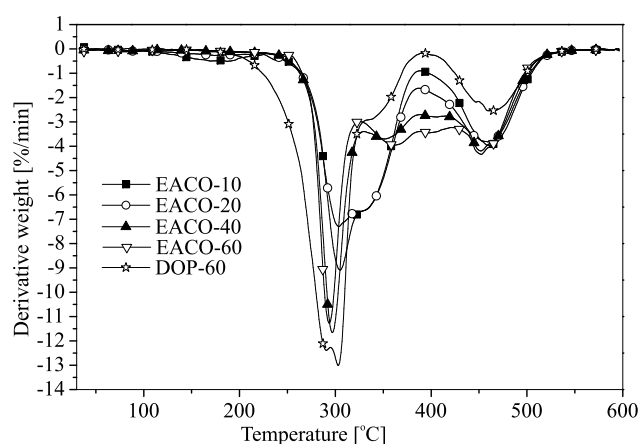


Figure 3. $^1\text{H NMR}$ spectra of CO, ACO and EACO

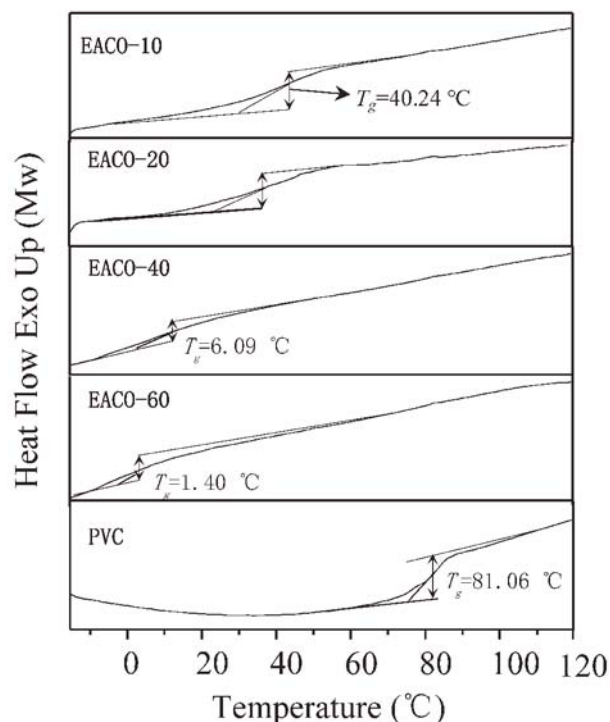
Thermogravimetric analysis. The TGA and DTG curves of PVC plasticized with different plasticizer under N_2 are illustrated in Fig. 4 and Fig. 5, and the data are summarized in Table 1. As shown in Fig. 4, all of the PVC blends were thermal stability in nitrogen atmosphere below 200°C and exhibited a two-stage thermal degradation process occurs in the subsequent heating. The first stage (about $210\sim 320^\circ\text{C}$) is the fastest degradation corresponding to PVC macromolecular chain chlorine elimination and fracture, the formation of conjugated olefins, HCl, some chlorinated hydrocarbons^{36, 37}. The second stage at about $440\sim 480^\circ\text{C}$ is more complex due to cross linking containing C=C bond. The process of thermal degradation of polyenes involves the molecular chain C-C bond breaking to form small molecules, meanwhile, aromatization produces aromatic compounds, aromatic compounds further thermal degradation³⁸. As shown in Table 1, the degradation temperature for 5% weight loss (T_5) and 50% weight loss (T_{50}) rises with the increase of EACO. Most importantly, the T_5 and T_{50} temperatures of EACO-60 increased by 36.05°C and 65.6°C compared with DOP, respectively. EACO improved the thermal stability of PVC films than DOP.

Table 1. TGA Data of different PVC blend film

Sample	EACO-10	EACO-20	EACO-40	EACO-60	DOP-60
$T_5/^\circ\text{C}$	241.28	268.64	275.77	278.84	242.79
$T_{50}/^\circ\text{C}$	342.55	351.08	357.71	367.90	302.33

**Figure 4.** TG curves under a nitrogen atmosphere**Figure 5.** DTG curves under a nitrogen atmosphere

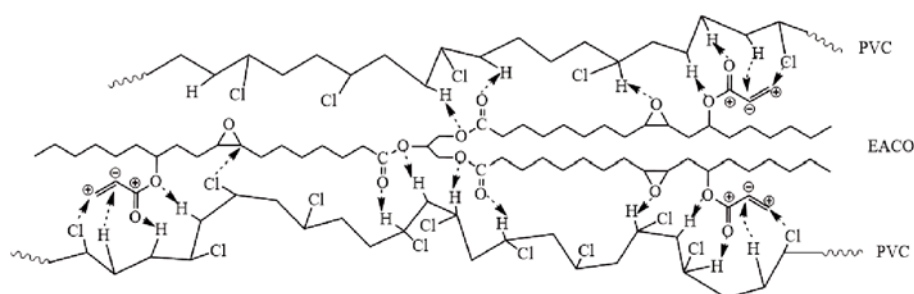
Glass Transition Temperature. Glass transition temperature (T_g) is the inherent nature of amorphous polymer materials. The T_g s of EACO-10, EACO-20, EACO-40, EACO-60, and pure PVC were determined by DSC, and the results are summarized in Fig. 6. PVC is a polar polymer chain, the interaction between the molecular chains strong, arranging relatively closely, hindering by the twisting of the molecular chain. T_g of PVC was 81.06°C . The T_g s of EACO-10, EACO-20, EACO-40 and EACO-60 were 40.24°C , 37.99°C , 6.09°C , and 1.40°C , respectively, was significantly lower than PVC. Plasticizer molecules can be wedged between PVC molecular chains, reduces PVC-PVC cross-linking to weaken the interaction between the PVC polymer chains so that the blended sample T_g decrease³⁹. This means that EACO has good compatibility, which makes it well and evenly

**Figure 6.** Nonisothermal DSC curves and T_g s of the the sample EACO/PVC

disperse in the PVC molecular matrix, then reduced the T_g of the sample following the EACO increase. Fig. 7 exhibits a potential interaction between EACO and PVC molecules in the plasticized system.

Migration analysis. Migration is the phenomenon that polymer plasticizer molecules flow from high concentrations of plasticized vinyl to low concentrations of media. Specific performance is liquid extraction, penetration into solids and volatilization in the air. Related research results show that the plasticizer migration is affected by the compatibility with polymer, plasticizer polarity and structure, temperature/humidity and contact media conditions¹³.

The volatile mass of samples EACO-10, EACO-20, EACO-40, EACO-60 and DOP-60 was 1.86%, 1.55%, 1.57%, 1.17% and 17.14%, respectively. These data illuminate that the volatility resistance of vegetable oil-based plasticizers EACO is better than DOP in PVC products. This is due to the large molecular weight of EACO and abundant ester and epoxy groups in the molecular structure that form hydrogen bonds with the PVC

**Figure 7.** Possible interplay between EACO and PVC molecules in the plasticized system

molecular chains^{40,41}, as seen in Fig. 7. Impressively, the films plasticized with EACO still shows excellent volatility stability with the EACO increasing volatility resistance. These findings indicate that the EACO plasticizer was compatible with PVC and was not easily extracted.

Fig. 8 shows the extractability of the PVC blends in 4 solvents. It can be seen from the figure that as the EACO content of the plasticizer increases, the resistance to extraction of the sample reveals a downward trend. EACO emerges exhibits excellent extracting resistance at lower levels ($\leq 40\%$). The results can be attributed to the plasticizer is surrounded by PVC molecules when it is lower level, reducing the contact with the reagent. DOP exhibited poor drawout resistance among the four solvents. The EACO-60 exhibited excellent resistance to draw-out in both distilled water and 10% ethanol and exhibited less draw-out resistance to n-hexane and petroleum ether difference. EACO can bound to PVC molecules by hydrogen bonding to attain stability due to EACO has a large number of polar groups (ester and epoxy groups) and a large molecular weight, as seen in Fig. 7. So, the higher molecular weight and greater numbers of polar groups can improve the migration stability and volatility of the plasticizer.

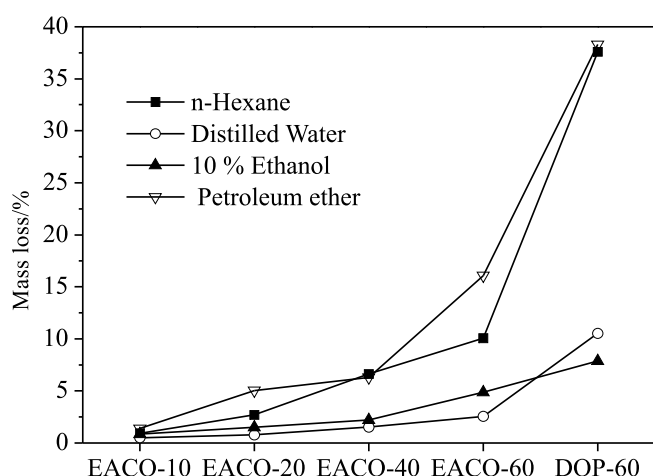


Figure 8. Extractability of the PVC blends at $23 \pm 2^\circ\text{C}$ for 96 h

Tensile properties analysis. Table 2 reveals the mechanical properties of different samples of PVC blends. As can be seen from Table 2, the elongation at break of the sample increases greatly with the addition of EACO. The elongation at break of EACO-60 is similar to that of DOP-60, which can reach 97.11% of DOP. This demonstrates that EACO has similar plasticizing effect compared to DOP, which improves the flexibility and athletic ability of PVC molecular chains. Therefore, the obtained EACO can be used to replace phthalate plasticizers.

Table 2. Tensile properties of PVC blends

Sample	Elastic modulus [Mpa]	Elongation at break [%]	Tensile streng [Mpa]
EACO-10	44.56 \pm 19.90	160.51 \pm 28.90	1.82 \pm 0.18
EACO-20	28.58 \pm 5.50	197.08 \pm 28.71	1.73 \pm 0.23
EACO-40	6.09 \pm 1.15	322.11 \pm 2.17	1.90 \pm 0.12
EACO-60	0.87 \pm 0.04	514.80 \pm 32.10	2.08 \pm 0.16
DOP-60	0.40 \pm 0.09	530.11 \pm 65.17	1.56 \pm 0.44

CONCLUSIONS

In this study, a kind of environmentally friendly plasticizer epoxidized acrylated castor oil (EACO) was prepared from castor oil. The molecular structure of EACO was identified with FTIR and ^1H NMR. Performance of PVC blends plasticized with EACO were explored as primary plasticizer and compared with DOP. Thermogravimetric analysis shows that the thermal stability of EACO is better than DOP and increases the carbon residue of PVC blends. Migration tests indicate that migration resistance is: EACO>DOP. The tensile test shows that the plasticizing effect of EACO on PVC is similar to that of DOP, and its elongation at break is 97.11% of DOP. In summary, castor oil-derived EACO has good potential as a plasticizer for PVC and can be used to replace DOP for preparing soft films.

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