

# Studies on Epoxidised Castor Oil as Co-Plasticizer with Epoxidised Soyabean Oil for PVC Processing

Gouni Thirupathiah<sup>1</sup>, Sukanya Satapathy<sup>1</sup> and Aruna Palanisamy<sup>1,\*</sup>

<sup>1</sup>Polymers & Functional Materials Division, Indian Institute of Chemical Technology, Uppal Road, Tarnaka, Hyderabad, 500007, Telangana State, India.

\*Corresponding Author: Aruna Palanisamy. Email: aruna@iict.res.in; arunap73@rediffmail.com.

**Abstract:** An acidic cation exchange resin has been used to prepare epoxidised castor oil (ECO) which was used as a co-plasticizer with epoxidised soyabean oil (ESBO) for processing polyvinyl chloride (PVC). The structure of ECO was confirmed and its physico chemical properties were evaluated. PVC/ (ESBO&ECO) blends were prepared by melt mixing and compression molded into sheets. The specimens were evaluated for tensile properties, impact strength and hardness. While the tensile strength did not vary much, the elongation reduced with the replacement of ESBO with ECO. Dynamic mechanical studies revealed that the glass transition temperature increased with incorporation of ECO, however, the storage modulus was not altered much. Replacing 20% of ESBO with ECO resulted in blends with desired thermal and mechanical properties without affecting the processability of PVC.

**Keywords:** PVC; plasticizer; epoxidised castor oil; tensile strength

## 1 Introduction

Processing of PVC requires additives that lead to balance between processing properties, functional characteristics, durability, cost and environmental impact. Sustainable additives such as isosorbide esters, soya derivatives or hydrogenated phthalate of low molecular weight polymers and reactive plasticizers have been used for processing PVC. Among them, ESBO and isosorbide diesters, obtained from vegetable oils are renewable resources, having excellent plasticizing properties for PVC and represent a non-toxic alternative to the phthalates [1-3]. However, in India, soybean oil is not produced much and being edible it goes largely for domestic consumption. Among the various non edible oils, castor oil is abundantly available and India contributes to about 55-60% to the world production.

The two main routes to functionalize vegetable oils include the transformation at the ester linkages or double bonds. Among the two approaches, epoxidation is the most commonly used route for functionalizing triglycerides. According to reported literature, castor oil was subjected to epoxidation by using a mole ratio of 1:0.5:1.5 (double bond: Acetic acid: hydrogen peroxide) using Amberlite IR 120 as catalyst (10%) at a temperature of 50°C [4] Jin et al. synthesized ECO from castor oil (91.8 g, 0.14 mol), glacial acetic acid (21.0 g, 0.35 mol), Amberlite (23 g), toluene (40 g), and 30% H<sub>2</sub>O<sub>2</sub> (56.7 g, 0.5 mol) (oxirane value 2.8%) [5]. Chakrapani et al. employed methyltri-n-octylammonium diperoxotungstophosphate (MTTP) as catalyst using both 30 and 50% hydrogen peroxide to synthesize ECO with an oxirane value of 3.6-3.5% [6]. Epoxidation of castor oil was carried out with in situ formed peracetic and performic acids as the oxidizing agents using cationic ion-exchange resins as catalyst by Goud et al. [7]. In this work, comparison of the kinetics of the epoxidation of castor oil with performic and peracetic acid generated in situ in presence of cation exchange resin (Amberlite IR-120) as catalyst at 30, 50, 70, 85°C was carried out. Reports on the formation of castor oil epoxide as biolubricant using Amberlite IR 120 as catalyst (15%) mass suggested an oxirane value of 4.86 (against 5.05) with 96% conversion [8].

Among the castor oil derivatives, ricinoleates and epoxidised ricinoleate are reported as plasticizers for PVC [9]. Synthesis and potential application of flame retardant plasticizer from vegetable oil for PVC based on castor oil have also been reported [10-14]. Phosphorus containing castor oil based derivative was synthesized and characterized which was used as an internal flame retardant plasticizer after alkynylation and covalently linked to azide functionalized PVC matrix via click chemistry. The method not only prepared soft PVC materials without migration but also provided a general method for efficient use of vegetable oil based plasticizer [12]. Castor oil based polyol esters (COPE-1, ECOPE-1, COPE-2 and ECOPE-2) were used as primary plasticizer to process PVC. The results showed that castor oil based polyol esters could significantly improve thermal stability of PVC blends [15]. Castor oil derivative containing synergistic flame retardant groups of nitrogen and phosphorus was used to modify PVC through click reaction resulting in flexible PVC materials with zero migration and enhanced flame retardant property [16].

Acetylated castor oil is used worldwide as a secondary plasticizer for PVC, it finds extensive use in PVC electrical cable industries where it is used with primary plasticizers like Dioctyl Phthalate (DOP) or Tricresyl phosphate (TCP) in concentrations ranging from 10-20% [17,18]. Epoxidised acetylated castor oil imparts flexibility and improves thermal stability to vinyl and may be used as a sole plasticizer in compositions where in the plasticizer content does not exceed 45% [19]. In addition to this acyloxy or aryloxy ester prepared from hydroxy stearic acid were evaluated as plasticizer for PVC copolymer. Many of them were found to be primary plasticizer having outstanding low temperature performance when employed or used at a 35% level [20]. Acetyl ester of ricinyl ester of pentaerythritol could be incorporated as sole plasticizer up to 100 per hour level without showing any sign of incompatibility [21]. Acetylated ricinoleates of lower alcohols are also useful for wetting and dispersing fillers and pigments. Methyl ester is generally compatible and is an all purpose plasticizer. It is considered superior to all other castor oil derivatives because it gives very low brittle point temperature and flexural modulus. Other important properties favoured by methyl acetyl ricinoleate are stabilization of organosols and plastisols and ease of processing by virtue of its antistick character. Epoxidised acetylated di ricinoleate of dihydric organic compound produced by epoxidation of acetylated ethylene glycol diricinoleate and phthalyl ester of alkyl ricinoleates have also been tried for compounding PVC [22,23].

Literature reports suggest that there are no studies on the utilization of ECO with high oxirane value as plasticizer/co-plasticiser for processing PVC. Hence in the present work, ECO (high oxirane value) has been tried as a co-plasticiser with ESBO. The method provides a versatile way to prepare bio-plasticizer from vegetable oils, and it is expected to partially replace petroleum-based plasticizer in PVC materials manufacture. Resin catalysed epoxidation reactions have been reported to exhibit better conversions and yield. Since Amberlite is imported and not available easily, we have tried Seralite SRC-120 as a substitute for Amberlite to epoxidise castor oil with good conversion and yield.

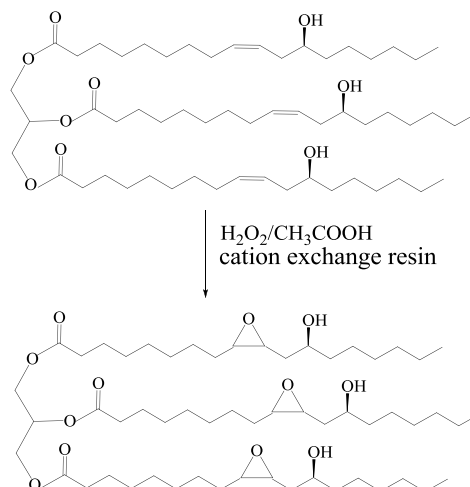
## 2 Materials

Castor oil (BSS grade) was procured from Ramcharan oil mills, Hyderabad. Hydrogen peroxide (LR, 30% v/v), and acetic acid (glacial, extrapure) were purchased from Rankem and Seralite SRC 120 (strongly acidic cation exchange resin) was purchased from SRL chemicals. PVC (suspension grade-K67) was procured from local distributors of Chemplast Sanmar Ltd. in Hyderabad, India with apparent density of 0.535-0.585 gcm<sup>-3</sup> and VCM content of < 1 ppm. ESBO (oxirane value 6.3, sp. gr. 0.97-0.99) was kindly supplied by Makwell Plasticizers, Mumbai. Organo tin stabilizer (STS-MTM) was kindly provided by S V Plastochem Pvt. Ltd., Nashik.

## 3 Synthesis of Epoxidised Castor Oil

In 5 litre jacketed reactor, 500 g of castor oil (BSS grade) was first added followed by the addition of 325 g of resin. The reaction mixture was stirred and was cooled to 10°C. When the reaction mixture temperature reached 10-15°C, 48 ml of acetic acid was added and the stirring continued. Following this, 350 ml of H<sub>2</sub>O<sub>2</sub> was then added drop wise over a period of 45 min to 1h and homogeneous mixing was

ensured. After completion of  $H_2O_2$  addition, the temperature was raised to  $45^\circ C$  and once attained, it was increased to  $55^\circ C$ . At the end of 5 h, the reaction mixture was cooled; ethyl acetate was added and stirred for 10 minutes, and allowed to separate. The aqueous layer with the resin was removed and the organic layer transferred to the separating funnel. 10% saturated bicarbonate solution was added to the organic layer and washed well followed by washing with saturated sodium chloride solution. The organic layer was then dried over, anhydrous sodium sulphate and solvent removed on rotavapor. Residual/traces of solvent were removed under vacuum maintaining a temperature of  $60^\circ C$ .



Scheme: Epoxidation of castor oil

#### 4 Preparation of PVC/ECO Blends and Sheets

100 g of PVC was mixed with 40 g of plasticizer (ESBO and ESBO + ECO mixtures) and tin stabiliser using a disperser mill by mechanical stirring for 1 h. The PVC blends were labeled as ECO0%, ECO10%, ECO20%, ECO30%, ECO50% (refer table). These blends were compounded into a homogeneous mixture at  $150^\circ C$  for 10 min in a sigma mixer (SC Dey and Co.) and sheets (2 mm thickness) were made using a Compression molding hydraulic press (SC Dey and Co.) at  $170^\circ C$  for 8 min. The specimens for mechanical tests were prepared from these sheets in a pneumatic cutter using required ASTM D die.

**Table 1:** Codes and composition of the PVC/plasticizer blends

S.no.	Code	Composition (g)*	
		ESBO	ECO
1	ECO0%	40	0
2	ECO10%,	4	36
3	ECO20%,	8	32
4	ECO30%,	12	28
5	ECO50%	20	20

\* Weight of the PVC taken for each formulation = 100 g;

Weight of tin stabilizer = 4 g (4% by weight of PVC).

## 5 Characterization

Acid value (A.V.), Iodine value (I.V.) and % oxirane oxygen content were determined according to ASTM D 1957-86, AOAC Official Method of Analysis, 1984, and ASTM D 1652-97 methods respectively. Moisture content was determined using Karl Fischer Titrator, Mettler toledo. The infrared spectrum of ECO was obtained with a Perkin Elmer Spectrum-100 FT-IR spectrometer at room temperature by averaging 8 scans. The spectral resolution was  $4\text{ cm}^{-1}$  and the frequency range covered 4000 to  $400\text{ cm}^{-1}$ .  $^1\text{H}$  NMR spectroscopic analyses was carried out in an AVANCE-300 spectrometer (Bruker, switzerland) in  $\text{CDCl}_3$  solution at  $25^\circ\text{C}$ . Dynamic mechanical analyses of plasticized PVC films were done to determine the thermo-mechanical properties with increase in ECO content by using a dynamic mechanical analyzer (DMA-Q800) in the temperature range  $-80$  to  $120^\circ\text{C}$  at a heating rate of  $3^\circ\text{C}/\text{minute}$  and with a film tension mode at 1 Hz. The glass transition temperature of PVC films were obtained from the peak of the  $\tan \delta$  curves. The tensile properties of PVC films were measured using universal testing machine (AGS-10k NG; Shimadzu Corp, Japan), with a crosshead speed of  $10\text{ mm}/\text{min}^{-1}$  according to ASTM D 638 with type IV specimens. Tensile strength, elongation at break, Young's modulus of each specimen was the mean of an average value of three replicates. Notched Izod impact strength of the plasticized PVC specimens was evaluated using an Impactometer (Tinius Olsen, USA) as per ASTM D256 with a notch depth of 2.54 mm and notch angle of  $45^\circ$  using a 7 J hammer. Volatility measurements of PVC samples were carried out as follows. Weighted PVC samples ( $25\text{ mm} \times 25\text{ mm} \times 1\text{ mm}$ ) were heated in an oven that was previously set at  $70^\circ\text{C}$  for 24 h and cooled to room temperature in a desiccator for 1 h. The weight changes were measured before and after heating. The volatility rate was calculated as the ratio of the evaporated and the initial plasticizer [12,15]. Solvent extraction tests were based on ASTM D1239-98. The test condition was restricted at a temperature of  $23 \pm 2^\circ\text{C}$  and  $50 \pm 5\%$  relative humidity. The PVC specimens were immersed in five different solvents (distilled water, soybean oil, 10% (v/v) ethanol, 30% (w/v) acetic acid and petroleum ether). Samples were weighed and kept in 200 mL of each solvent. After 24 h, the solvent extracted PVC specimens were rinsed and then wiped up. Afterwards, all of the PVC specimens were dried under the test conditions in oven at  $30^\circ\text{C}$  for 24 h and reweighed. The extraction loss was calculated according to the Eq. (1):

$$\text{weight loss}(\%) = \left[ \frac{W_1 - W_2}{W_1} \right] * 100 \quad (1)$$

where  $w_1$  = initial weight of test specimen, and  $w_2$  = final weight of test PVC specimen. Exudation tests of the plasticizers were carried out by placing a sample of PVC films between two pieces of vegetable parchment. The system (PVC film and vegetable parchment) was then placed in a drying oven at  $40^\circ\text{C}$  for 72 h. Afterward, the weight increment of the vegetable parchment and the extent of the ECO plasticizers exudation were calculated according to Eq. (1).

## 6 Results and Discussion

### 6.1 Epoxidation of Castor Oil

Despite its lower I.V. as compared to other vegetable oils, castor oil has been selected because it is non edible and available in India in large quantity. The parameters like the mole ratio of  $\text{H}_2\text{O}_2$ : double bond: Acetic acid, loading of the catalyst (with respect to the weight of oil), time of the reaction, temperature etc. have been optimized to get the maximum conversion and yield. Based on this, the optimized conditions have been arrived at (as given in the procedure).

**Table 2:** The physico chemical properties of epoxidised castor oil

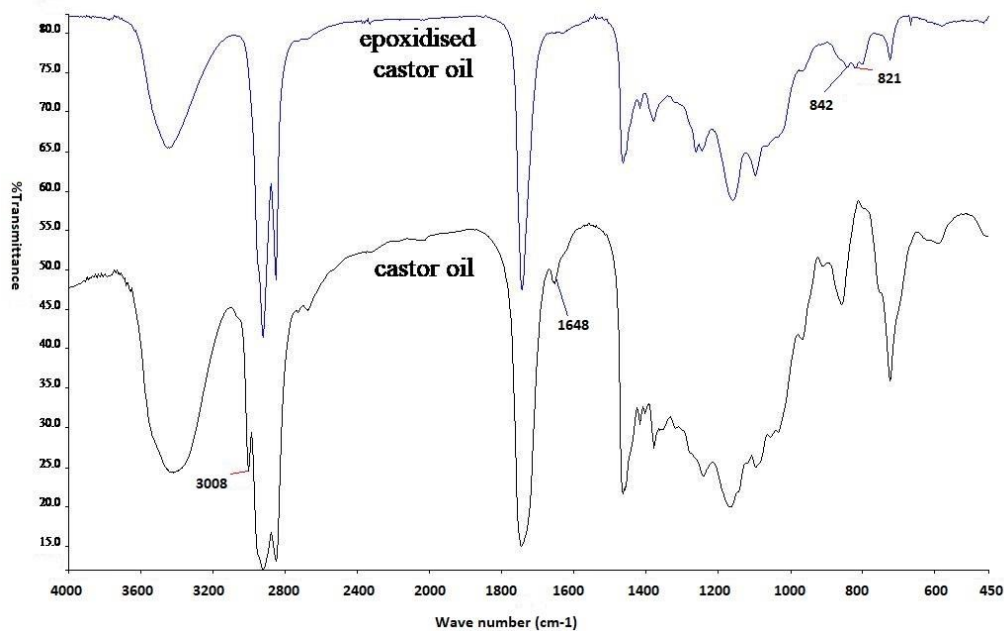
Property	Units	value
Colour and appearance	-	Pale yellow viscous liquid
Acid value	mgKOH/g	< 1.0
Oxirane value	%	4.6-4.7 (min.4.6)
Moisture content	% w/w	0.15 max
Iodine value	g/100 g	< 8
pH	-	6.5 - 7.0

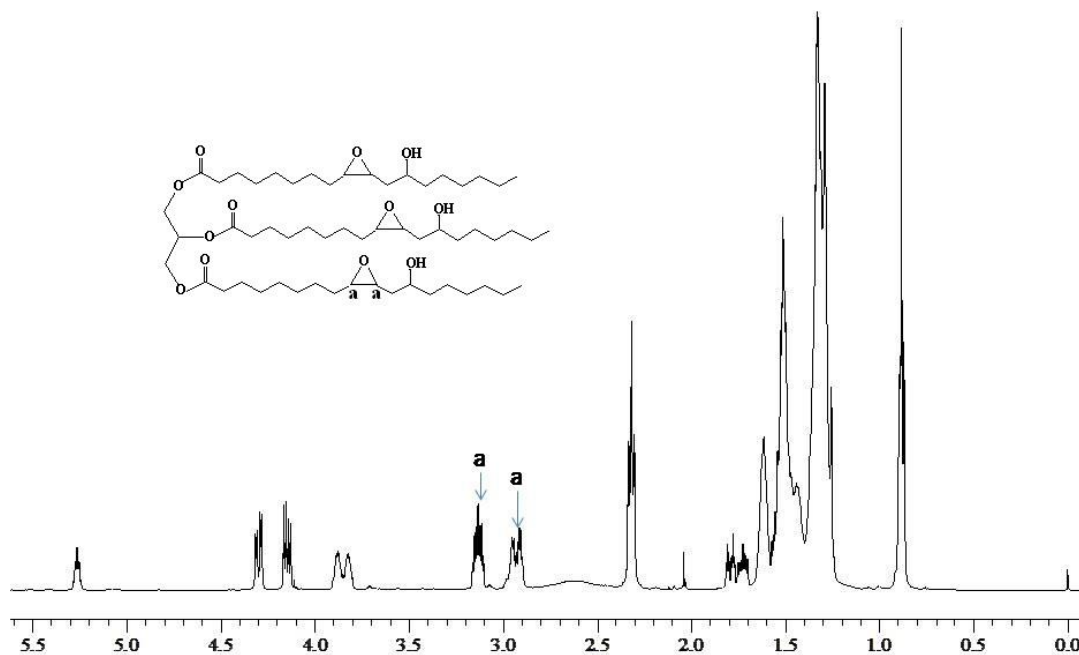
The epoxidised oil was subjected to FT-IR and NMR studies to confirm the structure.

### 6.2 Spectral Properties

In the FTIR spectrum of castor oil (Fig. 1) the double bond stretching is observed around  $1648\text{ cm}^{-1}$  while the peak does not appear in the epoxidised oil. In addition, the  $=\text{CH}$  stretching vibration around  $3000\text{ cm}^{-1}$  in the castor oil spectrum is found to be absent in the epoxy. However, the peaks corresponding to the epoxy group or the oxirane group is found around  $821$  and  $842\text{ cm}^{-1}$  which confirms the conversion of the double bonds. This proves that the double bonds of castor oil have been converted to epoxy groups.

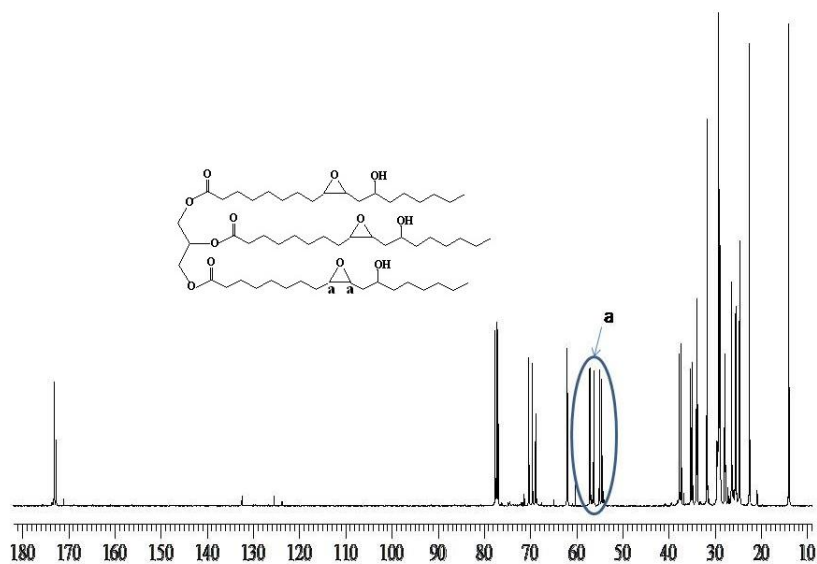
In order to confirm the chemical structure of ECO, the  $^1\text{H}$  NMR was investigated, which is shown in Fig. 2. The methyl protons were found at  $\delta = 0.89$  ppm (peak 1), the methylene protons  $[-(\text{CH}_2)_n-]$  were at  $\delta = 1.15$  ppm and  $\delta = 1.3$  ppm. A multiplet at  $\delta 2.3$ - $2.4$  was ascribable to the methylene protons at C-11 and C-8, respectively. The proton signals in the  $\delta = 3.3$  ppm correspond to protons on the epoxy groups, which indicated that the  $-\text{CH}=\text{CH}-$  of castor oil (which appears as a multiplet at  $\delta 5.6$ - $5.4$ ) reacted with hydrogen peroxide solution to give epoxidised castor oil. The peak at  $\delta = 3.85$  ppm was assigned to  $[-\text{CH}_2-]$  connected with  $[-\text{C}=\text{O}]$ . The presence of a hydroxy function as the chemical shift of hydroxy proton appeared as a broad singlet at  $\delta 3.65$ . The protons of the glycerol part of triglyceride resonated around  $4.0$ - $4.5$  and  $5$ - $5.5$  [24].

**Figure 1:** FT-IR spectrum of castor oil and ECO



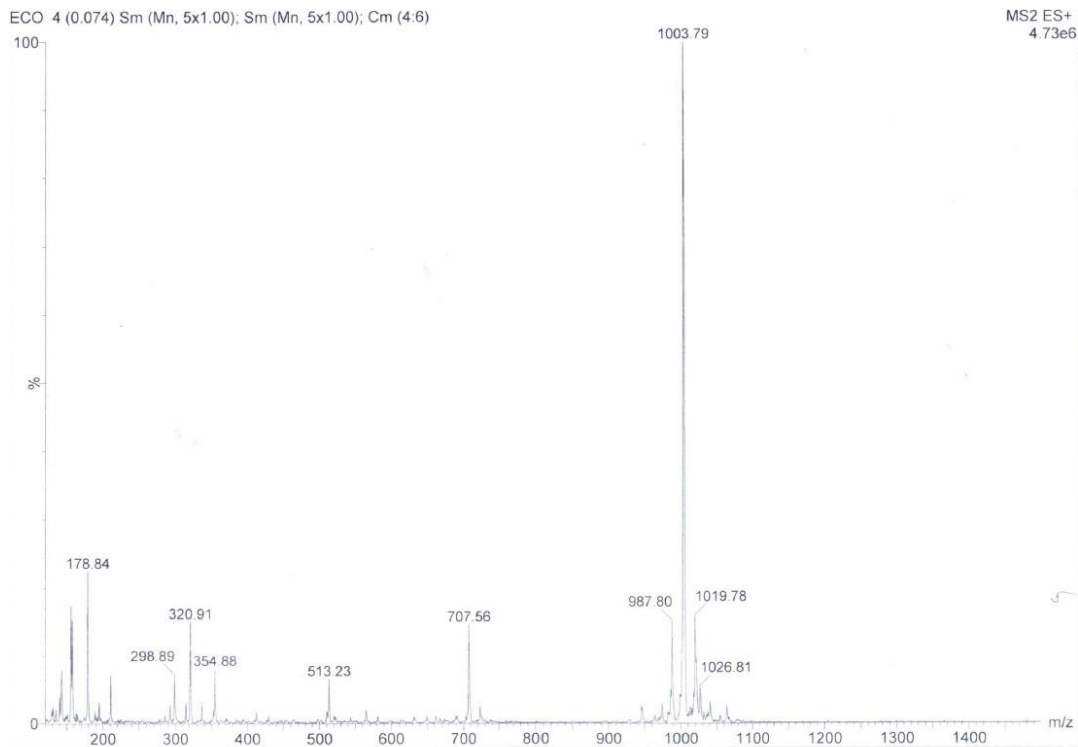
**Figure 2:** Proton NMR spectrum of epoxidised castor oil

In the  $^{13}\text{C}$  NMR spectrum of ECO shown in Fig. 3, one can clearly see the peaks corresponding to the carbon atom of the epoxy group around 55 ppm against the peaks around 125 and 135 ppm corresponding to the olefinic carbons of castor oil [24].



**Figure 3:**  $^{13}\text{C}$  NMR of epoxidised castor oil

The calculated mass of ECO is found to be around  $\sim 970$ - $980$  while the ESI-MS spectrum shows the peak around 1003 which is the  $M+23$  (sodium ion) peak. The experimental value is around 980 (i.e.,  $1003-23$ ) and it matches with the theoretical value thus confirming the molecular weight of ECO.



**Figure 4:** ESI-Mass spectrum of ECO

### 6.3 Plasticised PVC

The films did not show any signs of degradation, or colour change upon incorporation of ECO. With increase in loading of ECO above 50%, PVC could not be processed easily and the sheets showed severe bleeding of ECO.

### 6.4 Mechanical Properties of PVC Blends

The elongation at break, tensile strength and Young's modulus of PVC blends are presented in Tab. 3. Continued increasing of the ECO concentration did not show any marked changes in the values of tensile strength as well as percent elongation. However, adding 10% ECO, the tensile strength slightly decreased compared to the neat sample which may be due to a measurement error. Hence, it can be concluded that the ECO showed good plasticization efficiency in combination with ESBO. The young's modulus increased remarkably with addition of ECO (10-50%) compared to that of film with ECO0%, indicating that increase in content of ECO can impart high level of rigidity in the plasticized PVC. The impact strength of the PVC blends showed markedly different tendency from tensile strength and elongation at break with the increase in ECO content. The impact strength of PVC / ECO blends was increased with increase in ECO loading up to 20% and thereafter it decreased in comparison with PVC / ECO0%. The remarkable increase of impact strength may be due to excellent compatibility between the PVC/ESBO + ECO blends. Tab. 3 also indicates that the blends containing ECO show slightly improved hardness than without it which means that ECO has good wettability in the PVC system. The mechanical studies suggest that the mixture of ECO and ESBO can indeed impart well balanced properties in the PVC which can be applicable for certain finished products.

**Table 3:** Mechanical properties of processed PVC sheets

Sample	Tensile strength (MPa)	Elongation at break (%)	Young's Modulus (MPa)	Notched Izod Impact Strength (J/m) (No Break)	Hardness Shore D
ECO0%	25.07 ± 0.55	348.37 ± 53.39	41.05 ± 8.03	271.67 ± 6.50	43
ECO10%	23.03 ± 0.44	298.12 ± 22.25	56.33 ± 7.96	338.57 ± 6.47	46
ECO20%	25.13 ± 1.95	305.37 ± 30.15	67.18 ± 2.97	366.5 ± 4.09	47
ECO30%	25.65 ± 1.16	326.32 ± 12.70	89.32 ± 4.27	119.5 ± 0.50	47
ECO50%	25.76 ± 2.20	275.27 ± 59.46	191.78 ± 15.93	190.0 ± 1.13	49

**Table 4:** Solvent extraction tests

Sample	Exuda- tion loss (%)	Volatility resistance (%)	Solvent resistance				
			Distilled water	10% ethanol (w/v)	Acetic acid (30%w/v)	Soyabean oil	Pet. ether
ECO 0%	2.674	0.181	0.12	-0.02	0.08	0	0.37
ECO 10%	3.184	0.1761	0.046	-0.18	-0.18	0.189	-1.26
ECO 20%	3.094	0.1428	0.029	0.15	0.029	0.09	-1.04
ECO 30%	3.614	0.1128	0.03	0.14	0.02	0.0	-1.01
ECO 50%	2.720	0.1274	-0.05	-0.13	0.01	0.19	-0.80

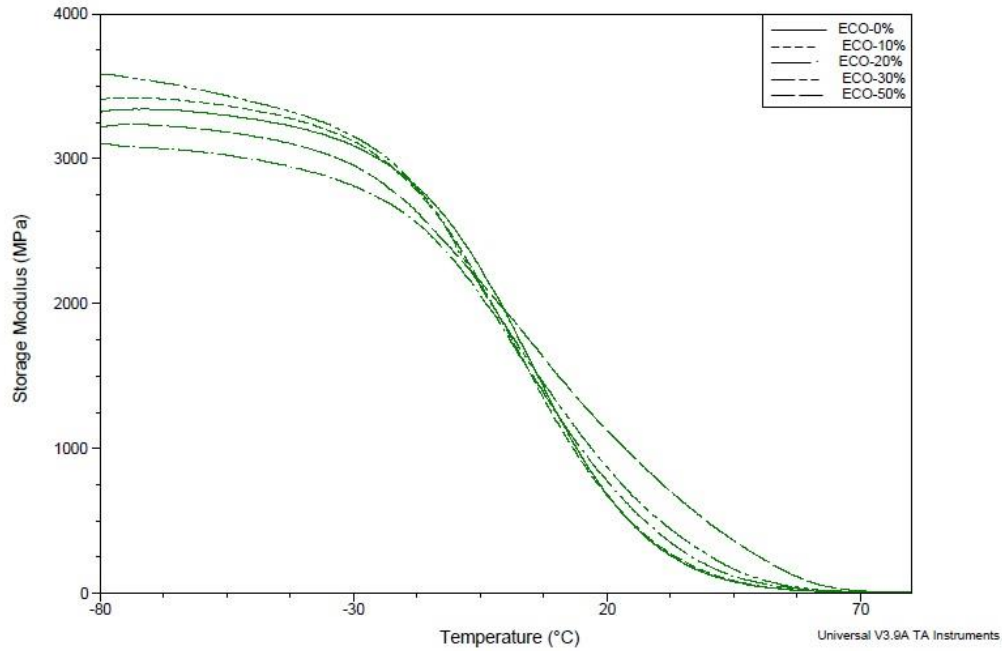
In the exudation test (Tab. 4), the plasticized PVC samples, during the experimental period (40°C/72 h), showed the exudation loss of ESBO, ECO 10%, ECO 20%, ECO 30% and ECO 50% as 2.674, 3.184, 3.094, 3.614 and 2.720%, indicating that the combined vegetable oil based plasticizers (ESBO + ECO) were fully compatible with PVC. With increasing proportion of ECO in ECO + ESBO mixture, there is no significant change in the exudation loss.

The volatility stability of the plasticizers ESBO + ECO in the PVC system was investigated, and the results are tabulated in Tab. 4. The volatile mass of PVC/ESBO+ECO blends with increase in ECO content from 0 to 50% in the PVC was 0.181, 0.1761, 0.1428, 0.1128 and 0.1274 respectively. This trend suggests that the volatility resistance of the PVC films is good in presence of mixed biobased plasticizers. There is a slight but not a remarkable decrease in the volatility resistance with increasing amount of ECO. The migration stability of the PVC blends in 5 different solvents was investigated by the leaching tests. PVC blends samples showed different levels of migration resistance when they were immersed in different solvents. The blends showed good solvent resistance in all solvents. However, in petroleum ether, there was a weight gain for all the compositions, especially for those with higher ESBO loading probably indicating that the dissolution of Pet. ether into the PVC matrix is leading to weight gain. This may be due to the presence of OH groups in the castor oil back bone which might aid PVC to take up pet ether.

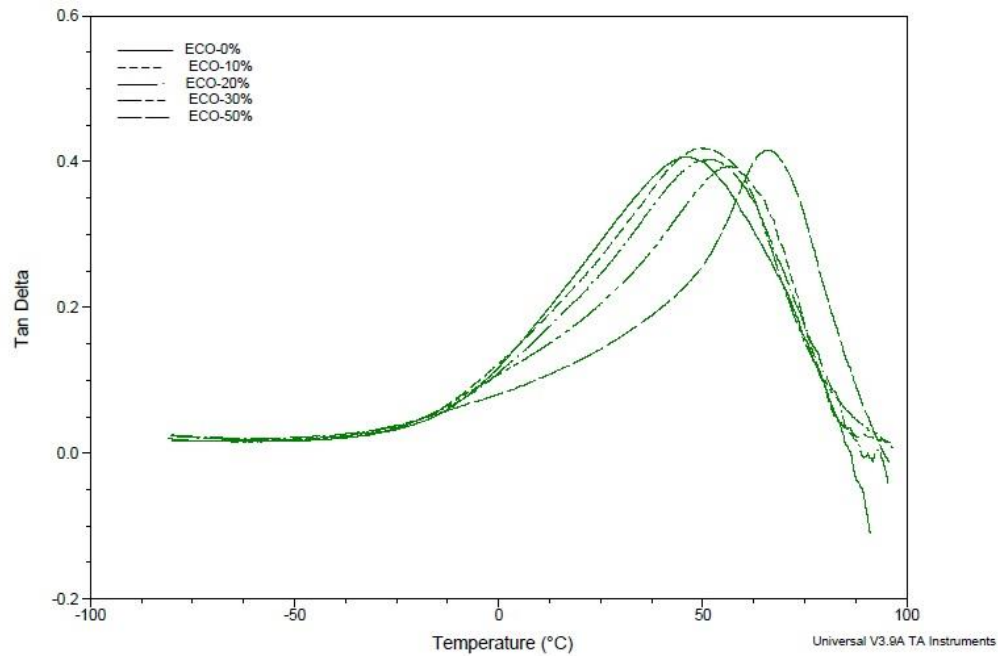
**Table 5:** Glass transition temperatures and storage modulus values of various compositions

Sample	Storage modulus (MPa) @-80°C	Glass transition temperature (Tanδ)	Tan delta (peak max)
ECO 0%	3347	45.4	0.4050
ECO 10%,	3417	49.7	0.4144
ECO 20%,	3067	52.2	0.4018
ECO 30%,	3534	56.1	0.3932
ECO 50%	3230	65.9	0.4160





**Figure 5:** Storage modulus vs. temperature curves of the plasticized PVC



**Figure 6:** Storage modulus vs. temperature curves of the plasticized PVC

Plasticizers are generally low molecular weight organic additives which are used to soften rigid polymers. Fig. 5 shows the results of DMA experiments run on PVC samples with differing amounts of ECO along with ESBO. As shown in the tan delta curve (Fig. 6), the addition of plasticizer lowers the glass transition ( $T_g$ ) temperature of virgin PVC which is around  $84.2^\circ\text{C}$  indicating the compatibility of PVC and plasticizer [15]. But the values were still higher than that of the samples plasticized with 40%

ESBO (45.4°C). Replacing ESBO with ECO led to increase in the T<sub>g</sub> values. ECO-50% showed higher and sharper tan peak compared to ECO0%, with narrow range of relaxation times. All binary blends (ECO10%, ECO20% and ECO 30%) have tanδ peak max values in between these two. This shows that blends are homogeneous (miscible) and addition of ECO improves the homogeneity. A reduction of sharpness and height of the tan peak is due to the restriction of the chain mobility in the polymer [25]. Therefore, increasing the ECO content of the blend increases the chain mobility in the PVC matrix and led to sharper peaks and height increment of tanδ during dynamic mechanical deformation.

Below the T<sub>g</sub>, all the compositions show almost the same modulus. However, the extent of the decrease in the modulus was found to vary with ECO loading. It is known that the extent of decrease in stiffness and changes in the softness of the plasticized PVC depend on both the level of plasticization and the nature of the plasticizer [26]. With the introduction of ECO into the polymer system, the drop in the storage modulus decreased with temperature and the curves were less steep with higher loading of ECO. This implies that the addition of ECO is not softening the polymer.

## 7 Conclusion

A biobased plasticizer was synthesized by epoxidation of castor oil using an acidic cation exchange resin. The structure of the epoxidised oil was confirmed by proton NMR, <sup>13</sup>C NMR and ESI-mass spectroscopy. The oxirane value was found to be around 4.6-4.7. The ECO was blended with PVC using a melt mixer to act as a plasticizer during processing. The efficiency was evaluated by comparing it with well know plasticizer-namely ESBO. There was no significant change in the tensile strength or elongation, however, the modulus increased remarkably. The impact strength was found to increase upto 20% and then on gradually decreased. The exudation loss was more and volatility less compared with the control whereas all compositions with ECO showed a weight gain in Petroleum ether. Based on the dynamic mechanical tests, it was concluded that the addition of plasticizer raised the glass transition (T<sub>g</sub>) temperature and ECO50% showed a narrow tan peak compared to ECO0%. Hence, the reported plasticizer can be used for developing rigid PVC pipes and profile applications like doors and windows. These results indicate that ECO could be used as a secondary plasticiser for PVC with ESBO at lower levels without any adverse effect on the processing of PVC and its mechanical properties.

**Acknowledgement:** Sukanya Satapathy wishes to acknowledge Department of Science and Technology, Government of India, Women Scientists Scheme [Grant No. SR/WOS-A/CS-36/2016(G)] and corresponding author Aruna Palanisamy wishes to acknowledge Ministry of environment, forests and climate change (Grant No. F.No.1-2/2013-CT) for the funding (manuscript communication number: ICT/Pubs/2019/065).

## References

1. Markarian, J. (2007). PVC additives-what lies ahead? *Plastics, Additives and Compounding*, 9(6), 22-25.
2. Mehta, B., Kathalewar, M., Mantri, J. (2014): Bio- based Co- plasticizer for PVC in addition with epoxidised soyabean oil to replace phthalates. *Research and Reviews: Journal of Engineering and Technology*, 3(4), 20-30.
3. Brostow, W., Lu, X., Osmanson, A. T. (2018). Nontoxic bio-plasticizers for PVC as replacements for conventional toxic plasticizers. *Polymer Testing*, 69(A1-A2), 63-70.
4. Sinadinovic-Fiser, S., Jankovic, M., Borota, O. (2012). Epoxidation of castor oil with peracetic acid formed in situ in the presence of an ion exchange resin. *Chemical Engineering and Processing*, 62, 106-113.
5. Jin, F., Park, S. (2007). Thermal and rheological properties of vegetable oil-based epoxy resins cure with thermally latent initiator. *Journal of Industrial and Engineering Chemistry*, 13(5), 808-814.
6. Chakrapani, S., Crivello, J. V. (1998). Synthesis and photoinitiated cationic polymerization of epoxidized castor oil and its derivative. *Journal of Macromolecular Science Part A-Pure and Applied Chemistry*, A35(4), 691-710.

7. Goud, V. V., Patwardhan A. V., Pradhan N. C. (2006). Strongly acidic cation exchange resin of sulphonated polystyrene type used as catalyst for epoxidation of castor oil with peracetic acid and performic acid. *Solid State Science and Technology*, 14(1), 62-68.
8. Borugadda, V. B., Goud, V. V. (2015). In situ epoxidation of castor oil using heterogenous acidic ion exchange resin catalyst (IR 120) for biolubricant application. *Tribology Online*, 10(5), 354-359.
9. Wypych, A. (2012). *Database of plasticizers*, 2nd edition. Chemtec Publishing, Toronto.
10. Feng, G., Jia, P., Zhang, L., Hu, L., Zhang, M. et al. (2015). Synthesis of a novel phosphorus-containing plasticizer based on castor oil and its application for flame retardancy of polyvinyl chloride. *Korean Journal of Chemical Engineering*, 32(6), 1201-1206.
11. Jia, P., Hu, L., Zhang, M., Feng, G., Zhou, Y. (2017). Phosphorus containing castor oil based derivatives: potential non-migratory flame retardant plasticizer. *European Polymer Journal*, 87, 209-220.
12. Jia, P., Zhang, M., Hu, L., Feng, G., Bo, C. et al. (2015a). Synthesis and application of phosphaphenanthrene groups-containing soyabean-oil-based plasticizer. *Industrial Crops Production*, 76, 590-603.
13. Jia, P., Zhang, M., Hu, L., Liu, C., Feng, G. et al. (2015b). Development of vegetable oil based plasticizer for preparing flame retardant poly (vinyl chloride) materials. *RSC Advances*, 5, 76392-76400.
14. Jia, P., Zhang, M., Hu, L., Feng, G., Bo, C. et al. (2015c). Synthesis and application of environmental castor oil based polyol ester plasticizers for poly(vinyl chloride). *ACS Sustainable Chemistry and Engineering*, 3(9), 2187-2193.
15. Jia, P., Zhang, M., Hu, L., Bo, C., Zhou, Y. (2015d). Synthesis, application, and flame-retardant mechanism of a novel phosphorus-containing plasticizer based on castor oil for polyvinyl chloride. *Journal of Thermal Analysis and Calorimetry*, 120(3), 1731-1740.
16. Jia, P., Ma, Y., Zhang, M., Hu, L., Li, Q. et al. (2019). Flexible PVC materials grafted with castor oil derivative containing synergistic flame retardant groups of nitrogen and phosphorus. *Scientific Reports*, 9, 1-8.
17. Bhatnagar, R. K., Jain, A. K. (1972). Castor oil based plasticisers for PVC resins. *Industrial Chemistry Journal, Annual Report*, 136-137.
18. Potnis, S. P., Khanolkar, A. G. (1969). Plasticisers I important secondary plasticisers for PVC. *Popular Plastics*, 14(4), 25-30.
19. Bhatnagar, R. K., Jain, A. K. (1970). Plasticisers for PVC resins. Indian Patent 116841.
20. Knight, H. B., Lee, P. W., Palm, W. E., Koos, R. E., Swern, D. (1959). Esters of hydroxystearic acids as primary low-temperature plasticizers for a vinyl chloride-Vinyl acetate copolymer. *Journal of the American Oil Chemists' Society*, 36(9), 382-388.
21. Bhatnagar, R. K., Singh, S. (1969). Plasticisers for polyvinyl chloride resins. Indian Patent 105491.
22. Bhatnagar, R. K., Jain, A. K. (1970). Epoxidised acetylated casor oil. Indian Patent 105490.
23. Bhatnagar, R. K. (1974). Plasticisers for PVC resins. Indian Patent 132043.
24. Gurunathan, T., Mohanty, S., Nayak, S. K. (2015). Isocyanate terminated castor oil-based polyurethane prepolymer: Synthesis and characterization. *Progress in Organic Coatings*, 80, 39-48.
25. Madera-Santana, T. J., Misra, M., Drzal, L. T., Robledo, D., Freile-Pelegrin, Y. (2009). Preparation and characterization of biodegradable agar/poly(butylene adipate-co-terephthalate) composites. *Polymer Engineering and Science*, 49(6), 1117-1126.
26. Hernandez, R., Pena, J. J., Irusta, L., Santamaria, A. (2000). The effect of a miscible and an immiscible polymeric modifier on the mechanical and rheological properties of PVC. *European Polymer Journal*, 36(5), 1011-1025.