Diester Based on Castor Oil Fatty Acid as Plasticizer for Poly(vinyl chloride)

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ABSTRACT: Castor oil is a renewable resource that has potential uses as an environmental friendly material for a range of applications. In recent years, much efforts have been driven to develop alternate plasticizer for medical and commodity plastics due to growing concerns about dioctyl phthalate (DOP) for flexible poly(vinyl chloride) (PVC). In this study, a bio-based plasticizer was synthesized by a two-step esterification reaction of castor oil fatty acid (COFA) with benzyl alcohol and octanoic acid in the presence of catalyst (dibutyl tin dilaurate). The structure of the octanoic ester (OE) was confirmed by proton nuclear magnetic resonance, Fourier transform infrared spectroscopy, acid value, and hydroxyl value. OE was used as a coplasticizer in PVC for partial replacement of DOP. The addition of OE exhibited good incorporation and plasticizing performance in the PVC sheets. Incorporation of OE resulted in good plasticizing, tensile strength, percentage elongation, exudation, thermal stability, and chemical resistance because of the presence of long carbon chains of COFA. Differential scanning calorimetry (DSC), thermogravimetric analysis, and color measurements were also performed to evaluate the effect of OE. With the increase in OE, DSC and hardness results showed marginal deviation from those obtained for DOP-plasticized sheets. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40354.

INTRODUCTION

Poly(vinyl chloride) (PVC) is widely used for various commercial applications for decades.[1] However, it has found limited use in many applications because of its inherent limitations such as inadequate flexibility, difficulties in melt processing, and low thermal stability. To overcome these difficulties, plasticizers are added to PVC.[2] Plasticizers are the low-molecular-weight compounds that when added to a substance converts it from rigid to relatively more flexible and softer compounds.[3] This is also one of the most efficient ways to modify the thermal and mechanical properties of the polymer.[4] The plasticizers typically with low molecular weights space themselves between the polymeric chains thereby increasing the interchain space. This results in the reduced cohesive interactions between the polymer chains accompanied by reduced crystallinity of plasticized polymer. As a result of which, the mobility of the polymer chains increases making the polymer more flexible and soft.[5]

In the recent years, about 90% of the plasticizers produced worldwide were esters of phthalic acid. To make PVC processable for a number of applications, 30–40% of plasticizer mass is added.[6] The esters of phthalic acid, particularly bis(2-ethylhexyl phthalate),[7] commonly known as dioctyl phthalate (DOP), and dibutyl phthalate (DBP),[8] are the most widely used plasticizers

for PVC. Plasticized PVC has numerous applications, such as in medical, pharmaceutical, packaging, and consumer sectors.[9]

There are two types of plasticizers. The one that are incorporated as a comonomer are known as internal plasticizers, and the other ones that are not chemically bonded to the polymer matrix are known as external plasticizers.[10] DOP and most other PVC plasticizers are categorized as external plasticizers, and they do not form chemical bonds with the polymers they are dispersed in, but rather they form weaker physical interactions in the amorphous regions of the polymer. Therefore, external plasticizers leach out of PVC and enter the surrounding environment.[11]

Since 1940s, the toxicity of phthalates is being studied and reported to have adverse effects on the fertility in humans when exposed to phthalates.[12] DOP, the commonly used plasticizer, is also detected in soils, wastewater, air, and sewage media. The European Union and some states in the United States such as California have already placed permanent restrictions on the use of DOP, and DBP in plastic toys to keep children's toys free from phthalate contaminants.[13] Manufacturers and consumers are increasingly worried about this issue, considering the perspectives for expanding plasticized PVC applications. Extensive research is going on to find alternative plasticizers that are able

to replace conventional plasticizers for medical and other commodity plastic products.[14] These additives should be nontoxic and biodegradable, and in addition, when applied in a polymer matrix, these additives should improve the appearance and mechanical properties of the film.[11] In recent years, vegetable oil modification (e.g., production of epoxidized oil and synthesis of biodiesel oil) has attracted the interest of manufacturers and researchers as these products are obtained from natural renewable sources and can be used as raw materials in chemical industries.[12,15]

Epoxidized vegetable oils are largely studied for this purpose. Epoxidized soya oil (ESBO) with annual worldwide production of 20,000 tons is most commonly used as a coplasticizer with DOP. Other epoxidized vegetable oils, such as oils based on rice oil and sunflower oil, are also used in the industry as stabilizers and plasticizers.[16–18] The epoxy moieties in such structures are known to trap the hydrochloric acid liberated during processing of PVC products. Higher the number of epoxy group in the epoxidized oil, the compatibility of the plasticizer and PVC improves due to increasing polarity. As a result of which, the mechanical, chemical, and thermal properties are improved.[19] The migration of such plasticizers is also reported to be lower than DOP because of its high molecular weight and the hydrophobic character.[20] Bouchareb and Benaniba[5] reported epoxidized sunflower oil (ESO) as a better coplasticizer than ESBO at 40% replacement of DOP with improved thermal and mechanical properties.

In addition to epoxidized oils, various ester-based products are also used as coplasticizers. These include esters of citric acid, succinic acid, isosorbide, maleic anhydride, fumaric acid, and fatty acids. The high concentration of ester groups present in such products increases the miscibility of the two components because of higher polarity. As of 2007, DOP has been replaced by a commercial phthalate-free plasticizer, 1,2-cyclohexane dicarboxylic acid diisononyl ester (sold under the trade name Hexamoll® DINCH, BASF).[20] The main problem with all these systems is the inferior physical and mechanical properties under the service condition used and high cost.[21]

The main objective of this work was to study castor oil fatty acid (COFA)-based diester as PVC-compatible plasticizer for development of environment and health-friendly bio-based plasticizer. The plasticizer was prepared via a two-step reaction of COFA with benzyl alcohol (BA) and octanoic acid (OA). This was used as plasticizer for PVC along with different concentrations of DOP and was evaluated for physical, mechanical, chemical, and thermal properties.

MATERIALS

The PVC used in this study with K-value 60 was a stabilized, commercially available emulsion-grade material provided by Phiroze Sethna, Thane, India. DOP was procured from a local supplier and had specific gravity = 0.9861. COFA was kindly provided by Jayant Agro, Mumbai, India. This was evaluated for hydroxyl and iodine numbers before proceeding for the reaction. Analytical grade BA, methanol, OA, and dibutyltin dilau-

rate (DBTDL) were purchased from S.D. Fine Chemicals (Mumbai, India) and were used as received.

METHODS

Synthesis of Octanoic Ester

The two-step esterification reaction of COFA was carried out with BA and OA using DBTDL as a catalyst. In the first step, castor oil was reacted with BA in a molar ratio of 1 : 1 in the presence of 0.3% (w/w) DBTDL catalyst. The reaction flask fitted with Dean-Stark apparatus, temperature controller, and nitrogen gas inlet was heated to 170–180°C. Xylene was used as an azeotropic solvent to remove water formed during the reaction. Samples were withdrawn at regular interval of 1 h until acid value dropped below 5 mg of KOH/g of sample. After the reaction was complete, the reaction mixture was cooled down below 100°C. In the second step, the mixture was reacted with OA in the presence of DBTDL catalyst at 170–180°C. Samples were withdrawn at regular interval of 1 h until the acid value dropped below 20 mg of KOH/g of sample. It was further washed with methanol and lukewarm water to remove any unreacted OA and was checked for change in acid value till it dropped below 5 mg of KOH/g of sample. The organic layer was then dried in an oven at 60–65°C to remove the traces of methanol. The purified product was then evaluated for its physical and chemical characteristics. Figure 1 represents a schematic presentation of the synthesis of diester plasticizer from COFA.

Preparation of PVC Sheets

Requisite quantity of PVC in powder form, plasticizers [DOP and octanoic ester (OE)], and heat stabilizer (Table I) were weighed and mixed. Various combinations of samples were prepared with varying DOP and OE ratios, wherein mixed plasticizer-to-PVC ratio 52 : 100 was kept constant. The viscosity and viscosity buildup of these mixture was also measured.

Six compositions of the well-mixed ingredients were processed on a two-roll mill at a temperature between 160 and 170°C. The blending was continued for 15 min to obtain a homogeneous compound.
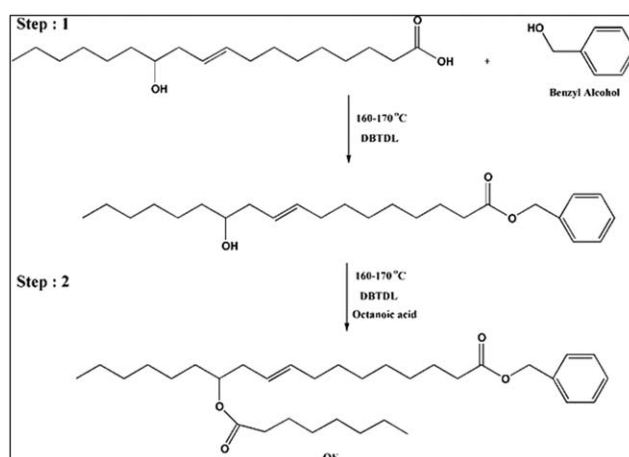

Figure 1. Schematic representation showing preparation of octanoic ester from castor oil fatty acid via esterification reaction with benzyl alcohol and octanoic acid.

Table I. Formulation of PVC Plasticization (grams per 100 grams of PVC)

Sample	DOP	OA
POD 1	52	00
POD 2	46.8	5.2
POD 3	41.6	10.4
POD 4	36.4	15.6
POD 5	31.2	20.8
POD 6	26	26

Sheet Preparation

PVC sheets for miscellaneous analyses were prepared by pressing the plasticized polymer compound in a metallic frame with General Chemicals SHP30 laboratory press equipped with heated plates. The pressing temperature and pressure for each composition was 160°C and 1500 psi, respectively. The samples were then evaluated for various performance properties.

Characterization and Testing

The prepared OE was measured for specific gravity, acid value, and hydroxyl value. The viscosities of the various plastisol mixtures were determined in accordance with standard ASTM D-445 method using Brookfield viscometer.

Acid Value. Acid value is a measure of free carboxyl acid functionality present in a compound. The acid number is the number of milligrams of potassium hydroxide required neutralization of free acid present in 1 g of a substance. The acid number was determined in accordance with ASTM D-1980 (mg KOH/g).

Hydroxyl Value. Hydroxyl number (or hydroxyl value) is an indication of degree of acetylation and is a measure of the number of hydroxyl groups present in a compound. The hydroxyl number is the number of milligrams of potassium hydroxide corresponding to hydroxyl groups in 1 g of polymer. The hydroxyl number was determined in accordance with ASTM D-1957 (mg KOH/g).

Specific Gravity. The specific gravity of the OE product was determined in accordance with ASTM D-891 (g/cm^3).

Fourier Transform Infrared Spectroscopy (FTIR). The analyses were carried out using a Spectrum-One Fourier transform infrared (FTIR) spectrometer spectrometer (Perkin–Elmer, Waltham, MA). The spectra were acquired in the range of 4000 to 600 cm^{-1} at a resolution of 4 cm^{-1}.

Nuclear Magnetic Resonance Spectroscopy. Nuclear magnetic resonance spectroscopy (NMR) spectra were recorded on Mercury Plus NMR spectrometer (400 MHz; Varian) using CDCl$_3$ as solvent. The chemical shifts in the discussion are reported in parts per million.

Mechanical Testing. The mechanical properties of the plastics were evaluated by determining the percentage elongation and ultimate tensile strength in tensile mode with a Lloyd Instrument LR10K equipped with pneumatic grips and provided with a 100 N load cell. The initial grip separation was 50 mm, whereas the cross-head speed was 50 mm/min. The sheets were cut into dumbbell shape with the help of pneumatic cutter containing a dumbbell-shaped die, which was prepared according to the ASTM D-638. The thickness of the specimen was 2 mm, as measured with a digital caliper. The samples were conditioned at room temperature for at least 40 h before testing. The elongation of testing specimen was calculated from grip separation by the software automatically. The tensile strength was expressed as the maximum force at break divided by the initial cross-sectional area of the film strip and the elongation at break as a percentage of original length.

Hardness Test. The Shore A and D hardness test was carried out according to ASTM D-2240 using a commercially available Durometer Type A and Type D hardness tester (Shore Instrument and Manufacturing Company, Jamaica, NY). This method is based on an indenter penetration test and requires a sample thickness. Three measurements were made on each sample type.

Chemical Resistance Test. To appraise critical conditions of the plasticizer application, chemical resistance of the plasticizer from samples were carried out. The liquids selected as penetrants were xylene and mineral turpentine oil (MTO). Chemical resistance of the plasticized PVC samples was determined in accordance with ASTM D-1239.

Chemical resistance experiments were performed in closed flasks with 50 mL of each penetrant at room temperature. Periodically, the samples were removed and dried for measurement of weight loss.

Exudation Test. Exudation of the plasticizer was evaluated by placing a sample of film between two pieces of tissue paper. The combined system (sample + paper) was then placed in a room temperature for 48 h. After this period, the increment in weight of the paper was determined by simultaneously weighing the sample, and the extent of plasticizer exudation was calculated.

Color Measurements. Color measurements of all PVC samples were compared using Color Quest XE colorimeter, available from HunterLab; 20-mm transmission cell; HunterLab Universal software, version 4.10 or equivalent; Black and White color reference available from HunterLab. This spectrophotometer is useful for both opaque and translucent materials.

Differential Scanning Calorimetry. Differential scanning calorimetry (DSC) analysis was performed under nitrogen atmosphere with DSC Q-100 equipment (TA Instrument) calibrated with *n*-octane and indium. All the samples were heated from −50°C to 100°C at a heating rate of 10°C/min.

Thermogravimetric Analysis. Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere on DSC Q-100 instrument for the temperature range of 100–650°C at heating rate of 10°C/min.

RESULTS AND DISCUSSIONS

Our study investigates the suitability of OE as a bio-based coplasticizer for PVC. The physiochemical properties of the OE product were evaluated by acid value, hydroxyl value, specific gravity measurements, FTIR, and ^{1}H-NMR technique. The acid and hydroxyl values of the purified OE product were observed

to be 0.64 and 33.26 mg KOH/g, respectively, which confirmed successful completion of reaction. The color of the product on the gardener scale was observed to be 11 → 12. The Brookfield viscosity of the BE product was observed to be 53 cPs at 25°C. The relative density and the refractive index were measured to be 0.978–0.988 and 1.342–1.398, respectively, at 25°C. The boiling temperature of the OE product was observed to be well above 325°C.

The structure of the OE was confirmed by FTIR spectroscopy and ^{1}H-NMR as shown in Figures 2 and 3, respectively. An obvious absorption peak at 1723 cm^{-1} belonged to carbonyl of the ester group. The presence of peak observed at 3018 cm^{-1} was due to the insertion of aromatic moiety in the long-chain fatty backbone. The aliphatic C—C bonding could be confirmed by the presence of sharp bands at 2929 and 2854 cm^{-1}. The presence of long-chain aliphatic double bonds in the COFA structure could be confirmed by the presence of transmission band at 1454 cm^{-1}. The detailed elaboration of the absorption bands is as given in Figure 2. The ^{1}H-NMR spectrum evaluated for OE sample is as shown in Figure 3. The presence of aromatic protons in the structure can be confirmed by the signals observed at 7.1 and 7.4 ppm. The aliphatic double bond present in the fatty acid backbone could be observed by the peaks at 5.5 ppm. The protons attached to carbon from benzyl ester bond can be confirmed by the signal observed at 5.3 ppm. All other aliphatic protons from long chains can be related to various peaks observed between 1.2 and 2.3 ppm.

The plasticizer demand for PVC sample was calculated as per ASTM D-1755 standard method of evaluation of plasticizer absorption value. The absorption values for OE and DOP were measured to be 51.72 and 53.13 per 100 g of sample, respectively. The lower absorption value for OE can be attributed to its lower viscosity, which helped its penetration through the polymer chains with improved wettability. Furthermore, to investigate the compatibility of these two components, six different mixtures with variable proportions of the two [from 0 : 100 to 50 : 50 (w/w) of OE : DOP] were prepared in test tubes. The samples were then mixed by vigorous shaking to form homogeneous mixtures and kept for 24 h. All the mixtures
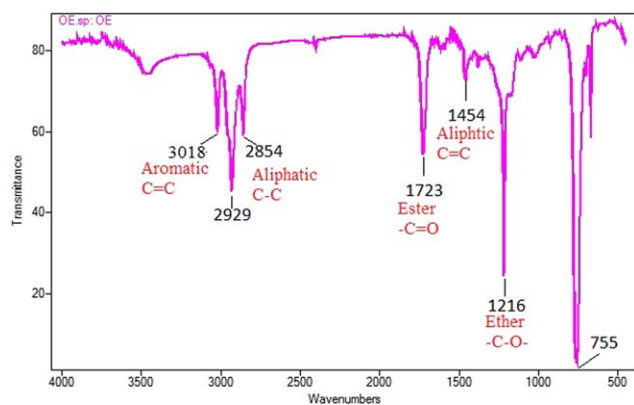

Figure 2. FTIR spectrum for octanoic ester product analyzed with chloroform as solvent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
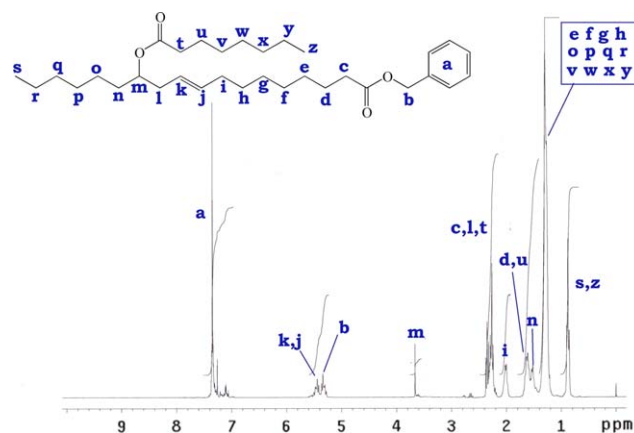

Figure 3. ^{1}H-NMR spectra of octanoic ester evaluated in CDCl$_3$ solvent. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

showed complete miscibility with each other after 24 h, forming homogeneous solutions that could be attributed to their similar chemical nature. The compounding of all these PVC plastisols was done with 52 phr of plasticizer content. The primary plasticizer, DOP, was replaced with OE product at variable proportions. The mixed formulations resulted in homogeneous mixture without any visible separation. The ester moieties present in both DOP and OE are polar in nature, which results in good compatibility with PVC. The replacement of DOP with OE does not result in significant change in polarity of the plasticizer mixture. Therefore, all the plastisol mixtures were homogenously mixed.

Viscosity of the plastisol prepared is an important parameter and governs the ease in processing. Therefore, it is really important to examine the viscosities of the plastisol solutions prior to application and to study the effect of OE on change in viscosity on aging. All the viscosity measurements were carried out after 1 h of the plastisol preparation. It was observed that the viscosity of the combinations decreased significantly as the OE proportion in the formulation was increased, as shown in Table II. This was primarily due to the effective thinning offered by OE component. From the literature available, it is known that on storage, DOP results in the increase in viscosity of the prepared PVC plastisol mixture.[22] To investigate the effect of OE product on the viscosity buildup, viscosities of all the combinations were measured after 7 days. As indicated in Table II, the viscosity

Table II. Viscosity Measurements of the Plastisol Mixtures (at 25°C)

Sample	Viscosity (cp)	% Increase in Viscosity (after 7 days in cp)
POD 1	9759	52.53
POD 2	8246	49.40
POD 3	7948	45.97
POD 4	6974	41.46
POD 5	5508	41.32
POD 6	5126	39.67

showed a gradual decrease with increase in the concentration of OE. In general, the viscosity decreased for POD 6 with respect to POD 1. This result indicated that by increasing the concentration of OE in the system, plasticization of PVC can be increased. The decrease in viscosity of all DOP–OE systems could be due to the long hydrocarbon chains of the COFA, which by their plasticizing action prevent sufficient interaction between the polymer chains of PVC and thereby make the sliding of these chains more facile. This plasticizing effect increased with the increase in the concentration of OE in the PVC matrix. These results indicated that there is no chemical reaction occurring between the two plasticizers, as the viscosity of the system is lower than that of the PVC–DOP system.

PVC Sheets

All the compression-molded plasticized PVC films with average thickness of 2 mm ± 0.5 mm with different compositions of plasticizers were white in color, homogeneous, smooth, and opaque. The higher concentration of OE above 50% resulted in the migration of plasticizer after 24 h of processing. This suggested that higher concentration of OE was not able to hold the polymer chains together and created cavities due to long-chain structure.

The presence of unsaturation in the OE product was expected to result in the yellowing of PVC sheets. The study conducted showed similar outcomes as expressed in Table III. As the proportion of the OE was increased, the yellowness of the PVC sheets gradually increased. In addition, the whiteness of PVC sheets plasticized with OE and DOP combinations was observed to be lowered than those with only DOP. This phenomenon can also be due to the generation of hydrochloric acid during processing at high temperature. This effect is not observed in cases where epoxidized oils are used as coplasticizers with DOP. Epoxy groups react with hydrochloric acid thereby giving excellent color retention.[4]

Mechanical Properties

The mechanical properties of the plasticized PVC sheets were determined using tensile strength measurement, elongation, and hardness. The continuously increasing stress of a polymer sample above the point at which the material begins to flow finally leads to rupture of the sample. The plasticizers help in improving the flexibility and elongation of plastic materials by weakening the interchain interactions. The tensile strength and elongation at break of the plasticized PVC samples with OE and DOP as plasticizer system are shown in Figures 4 and 5, respec-
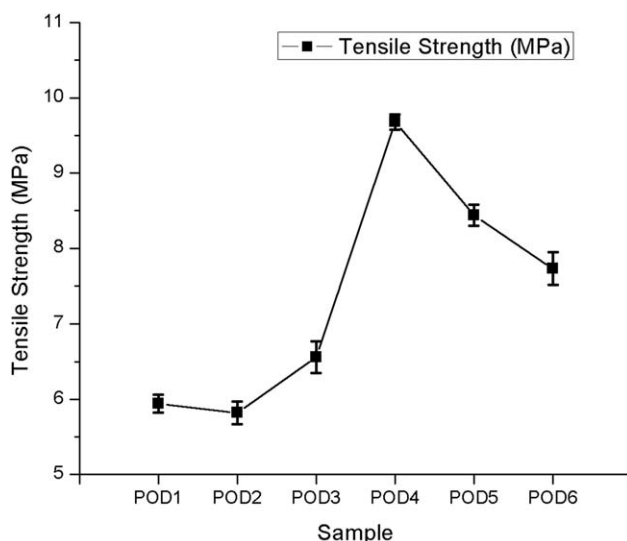

Figure 4. Tensile strength (MPa) of the various PVC sheet samples.

tively. POD 4 showed the highest tensile strength and elongation at break among the series. The tensile strength and elongation appeared to be increasing from POD 1 to POD 4 and then it reduced at POD 5 and POD 6, suggesting that the change in tensile strength is not linear. The increase in tensile strength could be due to decrease in viscosity of the blend with increasing OE content, which increased the overall plasticizing efficiency of the blend. In case of POD 5 and POD 6, the tensile strength was observed to be reduced; however, it was still higher than that of POD 1, POD 2, and POD 3. The results indicated that the proportion of plasticizers in POD 4 could be the optimum to replace DOP within the given set of parameters. Similar study conducted by Benaniba and Valeire revealed that ESO when used as coplasticizer with DOP showed marginal decrease with increasing ESO proportion. However, because of the different grades of PVCs used in these two studies, it is not fair to compare the properties quantitatively. The trend observed suggested a continuous decrease in tensile strength after about 30% replacement of DOP by ESO.[4] Bouchareb and Benaniba[5] in their study concluded that ESO performs better than ESBO when used as 40% replacement for PVC. Epoxidized *Mesua ferrea* seed oil can be used as DOP substitute but with lower tensile strength. The tensile strength in such case can be improved with incorporation of about 25% nanoclay as a filler.[23] In contrast to epoxidized plasticizers, ester plasticizers give improved

Table III. Yellowness Index and Hardness Test of Plasticized PVC Samples

Sample	Yellowness	Whiteness	Haze	Shore A	Shore D
POD 1	−17.93	−9.136	30.94	90	45
POD 2	16.232	−30.068	19.681	90	46
POD 3	25.393	−57.637	18.312	93	47
POD 4	37.505	−89.644	19.784	94	48
POD 5	49.603	−117.728	23.875	94	48
POD 6	54.192	−134.621	21.05	95	50
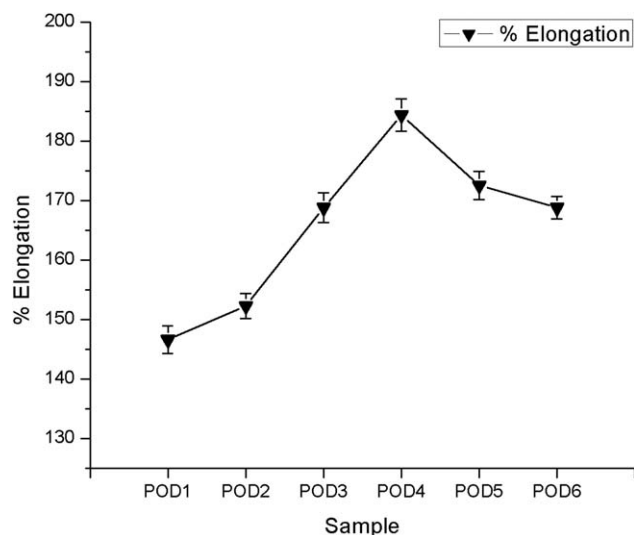
Figure 5. Percentage elongation of various PVC sheet samples.

Figure 6. Chemical resistance of PPVC films in xylene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tensile strength probably due to higher polarity, which helps the polymer chain hold themselves more tightly. Ester product prepared from glycerol, acetic acid, and benzoic acid is proven to give higher tensile strength and hardness than DOP.[24] In our study, OE when studied as coplasticizer for DOP resulted in the improvement of tensile strength when used up to 30% in contradiction to most of the epoxidized plasticizers reported.

The increase in tensile strength is generally accompanied by the decrease in percentage elongation. OE as a coplasticizer resulted in completely opposite trend. As the OE content was increased from 10 to 30%, the percentage elongation also increased with increasing tensile strength. Beyond 30% replacement, the elongation was also observed to decrease. Here, the increase in percentage elongation could be attributed to polar group of the plasticizer, which could combine with the chlorine atom in the PVC chain. This reduces physical crosslinking points between the chlorine atoms in the PVC molecular chains, shielding the polymer chains from interacting with each other and increasing the chain segmental motion in PVC. Hence, with the increase in the content of OE (plasticizer), this effect was obvious. The trend observed also suggested that due to combined effect of both the plasticizers, there was uniform increase in both tensile strength and percentage elongation together rather than decrease in one parameter with increase in another. The same trend was observed when both the properties reduced in case of POD 5 and POD 6. In contrast, epoxidized oils perform differently by providing reactive crosslinking sites and thereby reducing the segmental motions of the polymer chains.

Generally, the increased tensile strength comes with higher hardness properties due to rigid and compact backbone. However, in this study, for all the PVC sheets, there was no significant difference observed in hardness properties. The results of the Shore A and Shore D hardness measured in triplicates are as furnished in Table III. The lower number indicates a softer material. In this study, hardness test did not show any noticeable difference with the increase in OE content in the polymer matrix. The average value of Shore A and Shore D hardness was found to be 93 and 48, respectively.
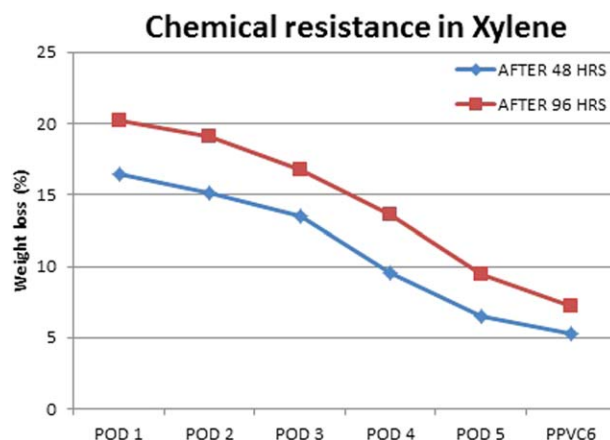
Chemical Resistance

The most important property to be tested was the leaching of a plasticizer from the product. For this purpose, the exudation test was performed to measure the mass loss from the plasticized PVC during the experimental period of 48 h at room temperature. The study revealed that none of the PVC sheets showed significant mass loss during the test. This can be attributed to the excellent compatibility of the two plasticizer components. Furthermore, the migration of plasticizer in solvents was also evaluated and is expressed in terms of the percentage weight loss after immersion in solvents. An increase in weight indicates that the chemical has penetrated the samples, whereas decrease in weight indicates that some additives are volatilized. The mass variation data of all the samples versus the time of contact with solvents, that is, xylene and MTO, are given in Figures 6 and 7, respectively.

As expected, the rate of leaching increased with the duration of testing from 48 to 96 h. The initial rates appeared to be higher and then decreased as the OE content increased. However, to evaluate the effects of structure on the rates of leaching, it is necessary to consider a series of closely related compounds.[25]
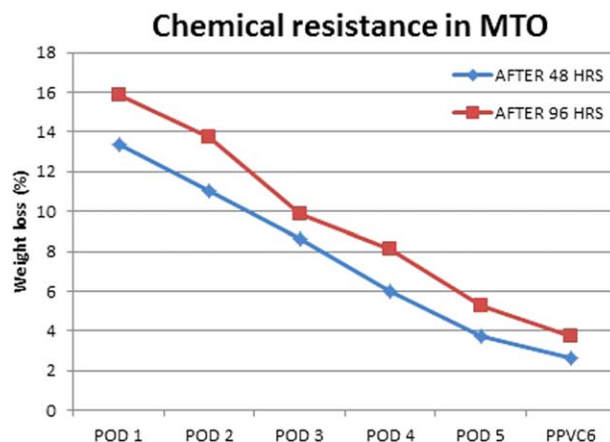

Figure 7. Chemical resistance of PPVC films in MTO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
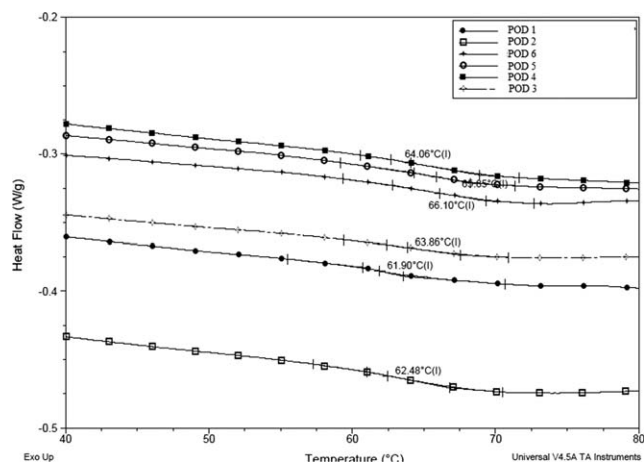
Figure 8. DSC thermogram of plasticized PVC samples plotted as heat flow against temperature.

The distribution of polarity in the chemical structures of the polymer and plasticizer molecules is of great importance in determining their compatibility, as well as the degree of flexibility imparted to the polymer. For a plasticizer to be compatible with relatively polar polymers such as PVC and to provide the desired flexibility, it requires both polar and nonpolar parts. The plasticizer molecules must have a polar part to effectively get compatible with PVC. The nonpolar part of the plasticizer serves to attenuate the attractive forces between PVC chains, thus increasing the free volume and imparting flexibility to the polymer. For plasticizer leaching to occur, there must first be the movement of the plasticizer molecules to the interface of the plastic and the medium and then there must be desorption of the plasticizer into the medium. Thus, the polarities of the medium and plasticizer molecules are of great importance in determining the rates of leaching.

It can be observed that samples from POD 1 to POD 3 showed considerable rate of leaching, but the others showed a considerable resistance to leaching, with weight loss not exceeding 6%

within the duration of test. When the polymer matrix comes in contact with the solution, the solution attacks the polymer matrix and penetrates through it and the plasticizer–PVC bond is weakened to an extent wherein the plasticizer tries to leach out and the extraction solution further enters the matrix and slowly fills the vacant locations in the matrix. As a result of this, PVC can shrink and become hard and stiff exhibiting cracks on the surface and subsequently resulting in decreasing rate of plasticizer migration.

Thermal Properties

The glass transition temperatures of the plasticized PVC samples were determined by DSC and plotted as heat flow versus temperature (Figure 8). A single glass transition temperature for each of the studied blends provided proof of excellent miscibility and compatibility between OE plasticizer, DOP, and PVC. All six samples exhibited a single T_g characterized as an endothermic deviation on the baseline and were lower than that of the virgin PVC polymer ($T_g = 97°C$). In general, shifting of T_g to lower temperatures is regarded as the plasticization of the polymeric material and is dependent on the efficiency of plasticization of another material called plasticizers.[26,27] The analyzed plasticized PVC films showed T_g values ranging between 61.9 and 66.10°C, respectively. The presence of OE plasticizer in PVC–DOP polymeric matrix increased its T_g value gradually when compared with PVC–DOP samples (POD 1). Although difference in T_g was not to a large extent, these results contribute that significant plasticizing effect is promoted by OE addition in the PVC material.

Similarly, TGA studies are used to study the thermal stability and thermal behavior of the material. The thermal behavior of PVC with varying proportions of DOP and OE in plasticized samples is shown in Figure 9. In the first stage of PVC degradation, it is proven that the PVC results in the formation of HCl and is followed by the formation of polyene sequence with conjugated double bonds (Figure 10).[4,5] At low temperature, molecular dehydrochlorination plays a fundamental role, whereas at
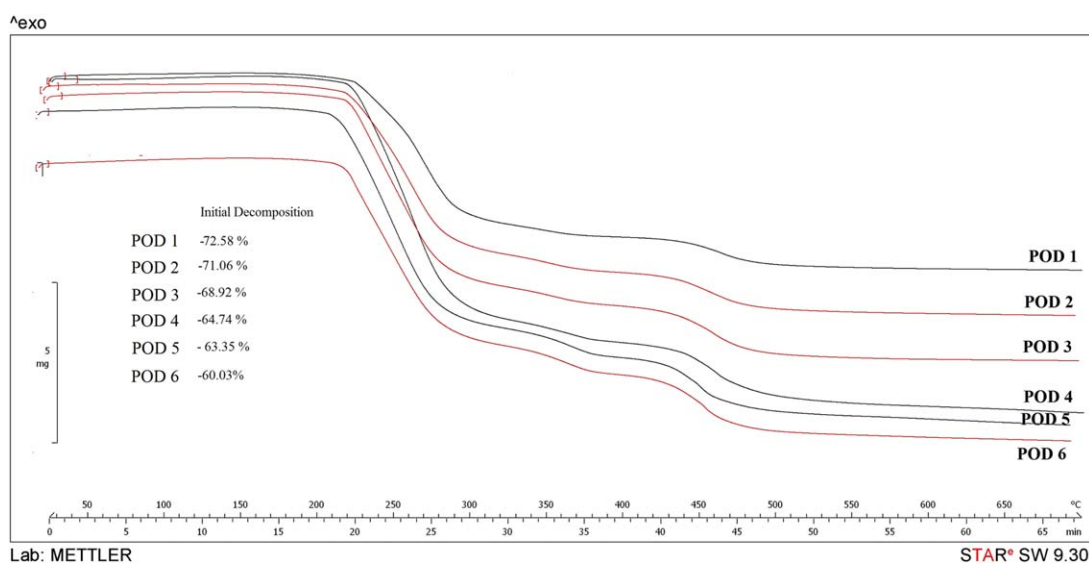

Figure 9. TGA thermogram of plasticized PVC samples plotted as weight loss against temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
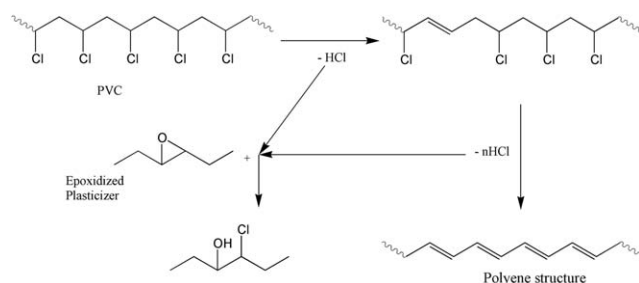
Figure 10. Schematic representation showing degradation reactions of PVC and reaction of HCl with epoxidized plasticizer.

higher temperature, the radical mechanism becomes relevant. HCl formed further catalyzes the degradation process releasing more HCl and the formation of polyenes occurs. During the first decomposition stage of various systems, 58.63–73.62% sample was decomposed. It was observed that the decomposition rate decreased with the increase in OE content in the system. At about 230°C, POD 1 resulted in maximum decomposition of 73.62%, whereas 58.63% decomposition occurred in POD 6 sample. Last decomposition stage was observed at 400–450°C, resulting in the degradation of complete polymeric backbone. The study conducted revealed that the initial decomposition could be lowered with increasing OE proportion in the plastisol formulation.

CONCLUSION

In this study, OE was synthesized and used as a coplasticizer in PVC along with DOP, and its physiochemical properties were studied. OE can be used as partial replacement of DOP at up to 30 wt %, displaying enhanced mechanical properties and chemical resistance in xylene and MTO. OE obtained in this study shows good incorporation and plasticizing performance into PVC formulation resulting in lower viscosity and viscosity buildup, which leads to reduction in processing-related difficulties without use of external shear. The glass transition temperature of plasticized PVC samples showed marginal increase as the OE content was increased. Improved tensile strength, percentage elongation, chemical resistance, and thermal degradation of plasticized PVC samples were observed with the increase in OE content. Shore hardness was observed to be increased with the increase in OE concentration but not significantly. Furthermore, plasticizer migration was not observed in proportion to the concentration of the plasticizer replaced. Therefore, this modified plasticizer is suitable to be used as a coplasticizer (up to 30 wt %) in PVC along with DOP in plasticized PVC applications.

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