Studies on the Effect of Epoxidised Coconut Oil as a Plasticizer for Polyvinyl Chloride.

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Abstracts:

In ages of depleting fossil oil reserves and an increasing emission of green house gases it is obvious that the utilization of renewable raw materials is one necessary step towards a sustainable development. In particular, this can provide a raw material basis for daily life products and avoid further contribution to green house effects due to carbondioxide emission minimization. Plant oil renewable resources are green alternatives in polymer chemistry. Present study focused on the effectiveness of epoxidised coconut oil as a plasticizer for polyvinyl chloride (PVC). The study suggested that the epoxidised coconut oil was successfully incorporated into PVC sheets prepared along with (DOP) replaced by about 60%, showing overall good migration stability and low plasticizer exudation.

Index Terms – Plasticizer, Renewable, Plant Oil

INTRODUCTION

The ever-increasing demand for energy, the depletion of fossil fuels as well as the increase in global awareness regarding the environmental impact of fossil fuels has led to much research in search of renewable and sustainable sources of energy. Unlike conventional petroleum-derived lubricants, bio-based lubricants are clean lubricants having the chemical structure of a fatty acid. To date, many vegetable oils from edible and non-edible sources have been used to produce bio-based lubricants – however, those derived from non-edible sources are more attractive since they do not rely on edible feedstock which can be used for food production. Vegetable oils offer a number of advantages over conventional mineral oils since these oils are highly biodegradable and environmentally safe. Even though the thermo-oxidative stability of vegetable oils can be a problem, this issue can be overcome by chemical modification of the vegetable oils[1, 2, 3].

Vegetable oils were commonly used as poly (vinyl chloride) plasticizers, stabilizers, lubricants and starting materials to produce polyols, pre-polymers in surface coating formulations and to synthesize of polyurethane foams[4,5]. Use of Modified vegetable oil is a convenient way toward the goal of green chemistry, and is strongly recommended to use in polymer area and provide a good insight into the field of utilization of vegetable oil as polymeric material. In order to achieve further development in this field, improved method and modification, which give rise to better properties and constitute a minimal hazard, should be used instead of the petrochemical based material[6, 7, 8].

Plant oils have received considerable attention as renewable resources for the production of energy and chemicals in general and as a starting material for polymers with product properties in the range for commercial epoxy resins in particular[9, 10, 11]. Numerous studies have been carried out on the epoxidation of plant oils using organic per-acids such as per-formic acid, generated in situ using hydrogen peroxide. In the present study modified coconut oil is used as plasticizer for PVC[12, 13].

The physicochemical properties of the coconut oil were determined and the result revealed that the oil is pale yellow, with a specific gravity of 0.88, viscosity of 35.04 mm^2/s at 40°C, flash point of 220°C, cloud point of 24°C, pour point of 23°C, volatile matter of 99.72%, refractive index of 1.46, heat of combustion of 35.60 MJ/kg, acid value of 2.24 mg KOH/g, saponification value of 273.38 mg KOH/g, peroxide value of 3.02 meq/kg, iodine value of 9.11 mI^2/g and free fatty acid content of 5.64%[14].

MATERIALS AND METHODS

Coconut oil(CO)were purchased from local market, n-hexane, glacial acetic acid, concentrated sulphuric acid, hydrogen peroxide, brine solution, anhydrous sodium sulphate, calcium carbonate(CaCO3), di-octyl phthalate(DOP), poly vinyl chloride(PVC). All solvents and reagents were of analytical grade.

Epoxidation of Coconut Oil

The coconut oil was mixed with hexane and formic acid (1: 12 : 4 mol ratio) with respect to the carbon–carbon double bond of the plant oil) in a three necked round bottom flask (500 mL) equipped with a water bath, a magnetic stirrer, a condenser, and a dropping funnel. H_2O_2 (1 : 25 mol ratio with respect to the carbon–carbon double bond of the plant oil) was added drop wise while stirring at 400 rpm and 60°C for 0.5 h and the reaction mixture was stirred for another 12 h. After reaction, the water and hexane layer were separated. The hexane phase with the EO was washed with brine solution (5 wt % NaCl) until no peroxide was left in the mixture (peroxide test paper as an indicator). The hexane was removed by evaporation followed by drying in a vacuum oven till constant weight (up to 48 h). The EO was analyzed by FT-IR. The epoxide conversion for CO is around 58 mol %[15, 16, 17].

Preparation of PVC sheet

Samples were prepared using the formulations given in Table 1. Epoxidised coconut oil (ECO) was added as a substitute of DOP in increasing percent from 20, 40, 60, 80 and 100 of total plasticizer.

Plasticizer exudation test

Plasticizer exudation was evaluated by inserting a sample sheet (cut into 2.5 cm x 2.5 cm) between two pieces of tissue paper. The system was then placed in a drying oven at 40 o C for 48 h. After this period, the weight increment of paper was determined and the extent of plasticizer exudation was calculated.

Plasticizer migration stability test

Plasticizer migration from samples was carried out in three different solvents: petroleum ether, Methyl ethyl ketone (MEK), and water at25°C. Samples were weighed and kept in 20 ml of each solvent. After 72 h, the samples were taken out and dried at room temperature (30°C) for 24 h and the weights of the dried samples were determined. The percentage mass loss (equivalent to the plasticizer loss) of the samples was calculated.

Fourier Transform Infrared spectroscopy (FTIR)

The oil and modified oil samples were characterized by FTIR Spectrometer. By interpreting the IR spectrum, the chemical bonds in a molecule can be determined.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry was used in order to determine the glass transition temperature (Tg) of polymeric matrix. Tg is an important parameter in polymer characterization and is able to evaluate the plasticizing effects of substances added to polymeric systems.

Thermo gravimetric analysis (TGA)

TGA analysis measures the weight change of a material, either as a function of increasing temperature, or as a function of time, in an atmosphere of nitrogen, helium, air, other gas, or in vacuum. The thermal stability of the samples was studied by using Thermogravimetric Analyzer. The samples were heated from 35 to 800°C with a heating rate of 10°C /min under a nitrogen atmosphere with a nitrogen flow rate of 20 mL/min.

RESULTS AND DISCUSSION

Plasticizer exudation test

Plasticized PVC samples did not show any significant mass loss during the experimental period. Average exudation of DOP/ECO from PVC sheets was in the range of 0.14–0.16 %.

Plasticizer migration stability test

The migration stability of the DOP/ECO plasticizer system from PVC sheets was tested in three solvents (water, petroleum ether and MEK. PVC sheet with 0–100% DOP/ECO did not show water migration, indicating hydrophobic behavior of these sheets. When immersed in petroleum ether, these plasticized samples show a lower percentage of plasticizer loss; thus, improved extraction resistance and hence good migration stability property. This may be due to improved compatibility with PVC as compared to 100% DOP/PVC sheet due to improved polarity provided by epoxy groups in ECO. Migration stability; however, decreased slightly at higher ECO loadings. In case of MEK there was dissolution of samples for DOP/ECO.

FTIR Characteristics of ECO

The product ECO was characterized by FTIR to monitor the disappearance of double bonds and formation of epoxy groups. The characteristic peaks at 3,007.91 and 722.48 cm^{-1} are attributed to the stretching vibration of the double bonds: =C–H and cis-CH=CH, respectively. The presence of new peaks in the FTIR spectrum at 823.56 cm-1, attributed to the epoxy group, may confirm the success of the epoxidation reaction of CO. The other new peak at 3,468.64 cm^{-1} was attributed to the hydroxyl functional group, derived from the epoxy functional group via partial epoxy ring opening reaction. The epoxy ring opening could occur by acid catalysis in the presence of water associated with aqueous solution of H_2O_2 used.

The FT-IR spectrum of PVC resin with plasticizer (DOP/ECO) was also shown in the figure. The spectra shown 4 main regions: -CH stretching at 3000–2850 cm^{-1}, C=O stretching at 1750–1745 cm^{-1}, C-H bending at 1500–1400 cm^{-1} and -C-O stretching at 1100–1000 cm^{-1}.The figure shows the FTIR spectrum of 100% DOP/ECO (PCO1) and 60% DOP/ECO(PCO4).

Differential scanning calorimetry

DSC curves of pure and plasticized PVC films are shown in Figs. All samples exhibit a single Tg characterized as an endothermic deviation from the baseline. For pure PVC, Tg has been found to be 81°C, which is in the temperature range given in literature. Glass transition temperature of plasticized PVC systems with DOP/ECO in the increasing content of ECO is not very obvious from the DSC curve. It is about 60°C. However, at 100% ECO, the glass transition temperature tends to increase slightly equivalent to that of 100% DOP sheet. This may be due to their slight incompatibility at higher loadings in PVC sheet.

Thermogravimetric analysis

Thermogravimetric (TG) curves of 60% ECO/PVC showed similar behavior to that of 100% DOP plasticized PVC system with two mass loss peaks at 240°C and 440°C showing losses of 70% and 12% (for 60% ECO/PVC) The first plateau relates to the dehydro - chlorination of PVC, with formation and stoichiometric elimination of HCl, while the second is attributed to polymer cross-linking containing C=C bonds. From the TG curves, it can be seen that there is a shift to higher temperature as the percentage of ECO increases indicating that some interactions exist between the components leading to mutual stabilization. This may be due to lower kinetic chain length for dehydro chlorination of HCl in the PVC component.

CONCLUSION

The results of the present investigation shows that CO can be successfully utilized in epoxidation reaction using peroxy acid generated in situ. The completion of reaction was supported by FTIR spectral analysis. The application of ECO, as plasticizer, was studied in PVC. The information gathered from the present study suggested that the ECO was successfully incorporated into PVC sheets prepared along with DOP replaced by about 60%, showing overall good migration stability and low plasticizer exudation. The synthesized epoxidized oils could be an attractive intermediate or alternatives for the preparation of various derivatives of industrial importance having a potential application in plastic industry. Vegetable oil being relatively non-toxic, inexpensive commodity derived from natural triglycerides and epoxidation process is a relatively simple process.

Table 1- Formulation of PVC resin with plasticizer (DOP/ECO)

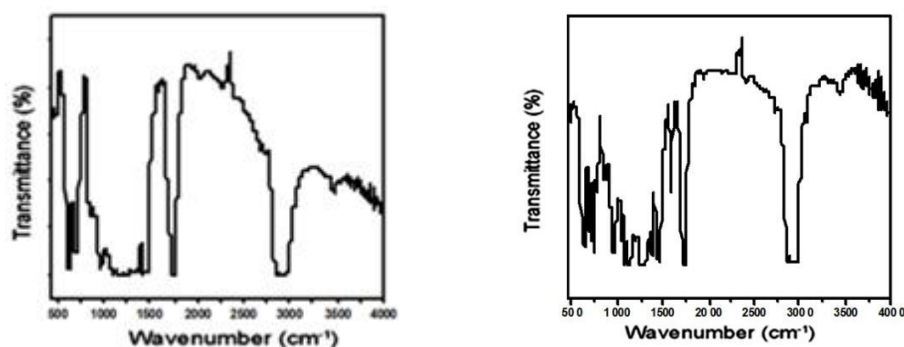| Sample Name	DOP/ECO Weight ratio	PVC (g)	DOP (g)	ERBO (g)	CaCO3 (g)
PCO1	100:00	10	5.0	0.0	0.1
PCO2	80:20	10	4.0	1.0	0.1
PCO3	60:40	10	3.0	2.0	0.1
PCO4	40:60	10	2.0	3.0	0.1
PCO5	20:40	10	1.0	4.0	0.1
PCO6	00:100	10	0.0	5.0	0.1

Figure 1 - FTIR spectrum of (a) 100% DOP/ECO (PCO1) and (b) 60% DOP/ECO(PCO4).

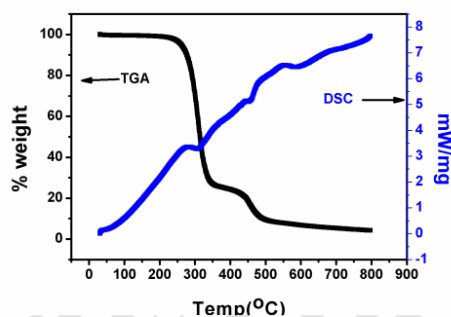
Figure 2 - TG curves of 60 % ECO/PVC

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