



Feasibility of Castor Oil Derived Thermosetting Polymer as Low Dielectric Material

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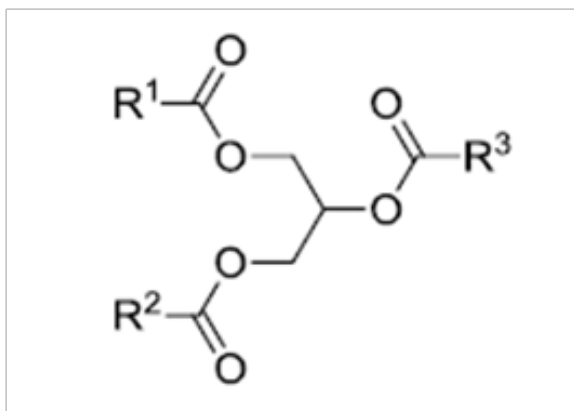
ABSTRACT

The present paper reports the synthesis of a thermosetting polymer derived from non-edible oil extracted from Castor seeds. Polymer synthesis was done using two different solvents namely methyl ethyl ketone (MEK) and acetone. It was interesting to observe that the two different solvents had contrasting effect on the mechanical properties of resulting polymer. Acetone derived polymer was less ductile and thick while MEK derived polymer was more ductile and thin. Also, the most interesting observation was the formation of random micropores during the drying of solvent cast films due to evaporation of solvents. In the case of acetone the pore size was larger as compared to the pores free film formed in MEK derived polymer. These studies suggested that a controlled evaporation of solvents during curing can be used to control the size of pores in the films which can be used as a membrane or filter. The bio-derived polymer was also reinforced with lignocellulosic sisal fibre derived from the leaves of *Agave sisalana*, to develop a lightweight polymer composite. Thin coating of the derived polymers can be used in application where low dielectric medium is desired.

KEYWORDS : Castor oil derived resinous polymer, synthesis and characterization, dielectric behaviour

1.0 Introduction

Triglycerides formed between glycerol and various fatty acids. (R^1 , R^2 , R^3 shown in the adjacent figure) are the main components of vegetable oils [1]. These fatty acids are mostly long straight-chain compounds having even number of carbon atoms.



The double bond in most of these unsaturated fatty acids possess a *cis* configuration. The degree of unsaturation at double bonds controls the chemical and physical properties of the vegetable oils. The functional groups associated with them render them useful for commercial applications. For instance, the fatty acid chains found in ricinoleic and vernolic acids consist of functional groups such as hydroxyl and epoxy groups respectively. By virtue of these important functional groups, various thermosetting resins, thermoplastics and biocomposites can be prepared from vegetable oils and their derivatives. Non-edible castor oil extracted from castor (botanical name) beans, is one among the family of vegetable oils that possesses a unique structure in which almost 90 % of the fatty acid chains bear an hydroxyl group (Fig. 1). These hydroxyl groups can be used to prepare

polymers, especially polyurethanes as has been reported extensively in the literature [1].

Fig.1: Chemical structure of castor oil

Based on this literature survey, castor oil was chosen as the raw mate-



rial for the synthesis of a resinous polymer and a matrix to form composites in the present work. The objective of the present work was to explore the dielectric properties of the bio-derived polymer for applications in which a low flexible dielectric medium is desired.

2.0 Materials and method

The selection of raw materials was based on the availability of non-edible vegetable oils and vegetable fibres that are found in abundance in India and other parts of the world. Castor oil was procured from Sigma Aldrich (however, large quantity of oil is available in Gujarat). Sisal fibres extracted from the leaves of plant *Agave Sisalana* were obtained from AMPRI, CSIR laboratory, Bhopal. The surface of these fibres were chemically treated with 3-aminopropyl tri-methoxysilane (APTMS) and then reinforced into the polymeric resin to form a polymer composite [3]. Samples were cast as thin sheets using solution casting method as shown in Fig. 2a..

Materials. Castor oil, isophorone diisocyanate (IPDI), dimethylol propionic acid (DMPA), 3-aminopropyl methoxysilane, Triethylamine (TEA), dibutyltin dilaurate (DBTDL) were purchased from Sigma Aldrich. Methyl ethyl ketone (MEK) and acetone were purchased from Ranchem, India. All materials were used as received without further purification.

MEK Method: In this method adopted from ref 1, castor oil (10.00 g), IPDI (6.23 g), DMPA (1.69 g) and 1 drop of DBTDL as catalyst were added to a three necked flask equipped with a nitrogen inlet, condenser, and thermometer. The mole ratio of the NCO groups of the IPDI, the OH groups of the castor oil, and the OH groups of the DMPA

was 2.0: 1.0 : 0.9. The reaction was carried out at 78°C for 1 h and then 50 mL of MEK was added to reduce the viscosity and prevent gelation. The reaction was kept for another 2 h at 78°C. After allowing the reaction mixture to cool down to room temperature, TEA (3 equiv. per DMPA) was added to the polyurethane solution and stirred for 30 min to neutralize all the carboxylic acid groups and to provide basic conditions for the sol-gel process. Finally, MEK was removed under vacuum using a rotary evaporator. The resulting solution was poured into a Borosil glass petri dish for drying at ambient temperature and then cured further at 50°C for 24 h to obtain thick transparent films as shown in Fig. 2b. (right)

Acetone method: In this method adopted from Ref 2, CO (30 g, 932 g/mol) and IPDI (16 g, 222.28 g/mol) were mixed in a flask in the presence of DBTDL as catalyst at 0.05 wt% of CO. The flask equipped with a nitrogen inlet was kept on a magnetic stirrer and reaction was carried out at 90°C for 2 hours in dry nitrogen atmosphere. The molar ratio of [CO]/[NCO groups] was 1/2.6. The resulting solution was kept aside to cool down. Before this solution could reach gel point, 4 g of this polymer was mixed with 20 ml of acetone in a beaker and the solution was charged using a magnetic stirrer. The mixture was heated at 40°C and stirred until a dilute solution was obtained. The solution was cast in a stainless steel mould at ambient temperature and then cured at 80°C for 24 hours. A thick transparent film was obtained. However, evaporation of residual acetone left pores in the film as shown in Fig. 2b. (left)

3.0 Results and discussion

Figure 2b shows the photograph of thick transparent film formed using two different solvents. A small sample of 1 cm x 1 cm was cut from these sheets and further used for dielectric characterization. The samples were electroded using conductive silver paste. Temperature and frequency dependent dielectric behavior of polymer (derived using two different routes) are shown in Fig 3 a,b and Fig 4 a,b respectively. It is evident from Fig. 3a,b that for acetone derived polymer dielectric constant at room temperature and at all frequencies was around 7 which steadily increased with increasing temperature. Dielectric loss also followed the same trend and it was below 0.2 at all temperatures and frequencies. However, when MEK was used as a solvent, the derived polymer showed a reduced dielectric constant around 5 but dielectric loss remained below 0.2. Dielectric behavior of polyurethanes derived from castor oil is explained using electronegativity [4]. It has been suggested that increasing the number of carbons in the back-bone lowers the dielectric constant [4]. This can be attributed to the increase in free volume, which decreases the number of polarizable groups per unit volume [5,6]. However, any inclusion of a backbone ether moiety drastically increases the dielectric constant, presumably due to the presence of more ether oxygen atoms in the backbone [7]. The dielectric loss $\tan(\delta)$ also follows the same trend. These explanations have been supported by the dielectric theory for polymers according to which dielectric constant increases due to increase in polarizability and low degree of free volume [8]. The difference in the dielectric constants of the same polymer derived using acetone and MEK can be attributed to the number of carbon atoms in the backbone and also to the crosslinking. It has been reported that the extent of cross-linking affects the stiffness of the resulting polymer. If the crosslinking is high a rigid polymer is obtained while low crosslinking leads to a flexible polymer [9]. The degree of cross-linking depends on the NCO/OH ratio. Branching occurs at the urethane linkage when NCO/OH ratio is low. Low degree of cross-linking allows the molecules freedom of movement resulting in the improvement in strength and creep resistance. When NCO/OH ratio is high, the probability of the formation of urea linkages is greater and, therefore, the branching takes place at the urea linkage points. A high degree of cross-linking restricts the mobility of the polymer molecules and, thus, the resulting polymer becomes a thermoset. In the present case, since NCO/OH ratio was kept same, the reason for different polymer properties can be attributed to the extent of mobility of polymer molecules in different solvents before the latter evaporated. In the case of acetone, molecular mobility was suppressed which led to a less flexible polymer compared to MEK derived polymer. In the case of MEK, less cross-linked polymers absorbed large amounts of solvent and, thus, swelled to form soft gels while in the case of acetone, highly cross-linked polymer was formed which could absorb less solvent molecules as a result of less molecular mobility. This effect was reflected in the dielectric properties of the two polymers derived

using two different solvents as discussed above.

4.0 Conclusions

Castor oil-based thermosetting polymer has been synthesized using two different routes. The choice of solvents greatly affects the quality of polymer synthesized. The incorporation of silane coated sisal fibres greatly improves the fibre-polymer interface. The improved fibre-matrix interface increased the crosslink densities of the composites and improved the mechanical strength of the composite. However, the curing time and temperature is a major constraint which needs to be reduced. The controlled curing can also be used to design a desired polymer film or membrane.



Fig. 2 Photograph of (a) sisal fibre reinforced castor oil derived polymer composite (b) polymer synthesis using Acetone (left) and MEK (right) as solvent

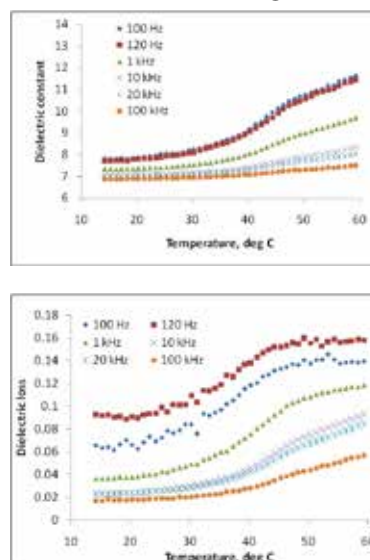


Fig 3 Temperature and frequency dependent (a) dielectric constant and (b) dielectric loss behavior of polymer derived from castor oil using Acetone as a solvent.

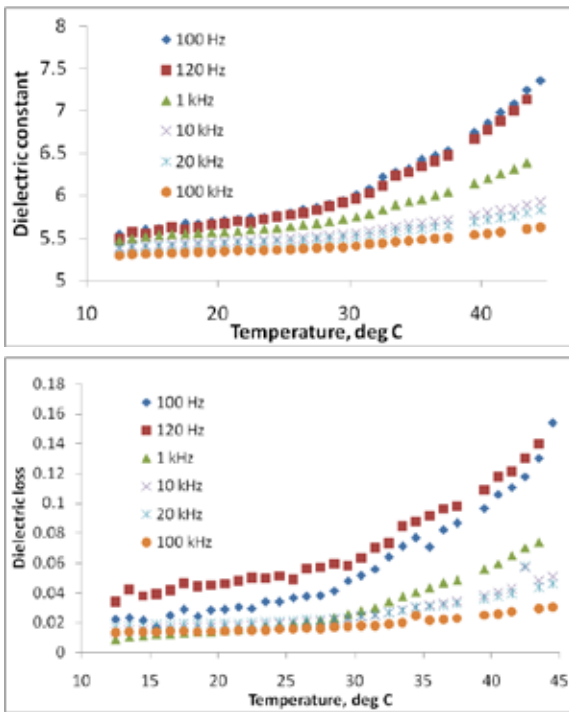


Fig 3 Temperature and frequency dependent (a) dielectric constant and (b) dielectric loss behavior of polymer derived from castor oil using methyl ethyl ketone as a solvent.

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