

Synthesis and characterization of castor oil-based polyurethane for potential application as host in polymer electrolytes

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Abstract. Polyurethane (PU) based on polyol, derived from castor oil has been synthesized and characterized for potential use as a base material for electrolytes. Transesterification process of castor oil formed a polyol with hydroxyl value of 190 mg KOH g⁻¹ and molecular weight of 2786 g mol⁻¹. The polyols together with 4,4'-diphenylmethane diisocyanate were used to synthesize the desired bio-based PU. The molecular structure of PU was investigated by Fourier transform infrared (FTIR) spectroscopy. The disappearance of NCO peak in the FTIR spectrum at 2270–2250 cm⁻¹ showed that diisocyanate has completely reacted to form PU. Morphological characteristic of the PU film was analysed using scanning electron microscopy, whereas thermal characteristics of the materials were characterized using dynamic mechanical analysis and thermal gravimetric analysis. The cross-sectional micrograph showed that the prepared film was highly amorphous and homogeneous. Thermal studies revealed that the film had low glass transition temperature, -15.8°C, and was thermally stable up to 259°C. These observations indicated the synthesized PU possessed favourable properties to act as a base material in polymer electrolytes.

Keywords. Castor oil; transesterification; polyol; 4,4'-diphenylmethane diisocyanate; polyurethane.

1. Introduction

Polyurethanes (PUs) are versatile materials and widely used in both industry and everyday life. They can be used for many applications, such as tubings, footwear, industrial machinery, coatings and paints, elastic fibres, rigid insulations, soft flexible foam, medical devices, and many others.^{1–3} PUs are included in both thermoplastic and thermosetting polymers. Research and development in the field of PUs is increasing year to year showing the rapid growth in PU industry. The polymers are mainly produced by the isocyanation of diisocyanate (NCO) with polydiol (OH) of various molecular weights.⁴ Large selections of polyols and isocyanates are available, which permit the design of polymers for many applications. PUs serve the mankind in its various roles such as flexible, rigid, semi-rigid, elastomers, surface coatings, and adhesives. A review on the background and history of urethane foams and elaborations on their potential future utility has been written by Khemani.⁵

The properties of PU depend on certain factors such as the content of the reactive groups, the degree of cross-linking and the entanglement of the reacting monomers.

In order to meet specific requirement, their structures can be tailored by selecting appropriate polyols and polyisocyanates. In industry, only a few diisocyanates or polyisocyanates are commonly used, while a variety of polyols are available. Therefore, the choice of polyol typically determines the properties of the created PUs.⁶ In addition to petroleum-based polyols, vegetable oils such as soybean oil, canola oil, palm oil, sunflower oil, corn oil, linseed oil and nahar seed oil^{7–9} have been extensively studied as bases for various polyols used for the manufacture of PUs for different applications.

The preparation of polymers from vegetable oils is currently receiving increasing attention because of the economic and environmental concerns.^{10–13} Raw materials based on vegetable oils have a number of excellent properties for producing valuable polymers such as PU, alkyd, polyester, amide and epoxy resins. Vegetable oils are triglycerides of fatty acids. In order to use these compounds as starting materials for PU synthesis, it is necessary to functionalize them to form polyols. Castor oil (*Ricinus communis*) from the family of *Euphorbiaceae* is a promising starting raw material for PU due to low toxicity and availability as a renewable agricultural resources. The major constituent in the castor oil is ricinoleic acid (12-hydroxy-*cis*-9-octadecenoic acid), which is a hydroxyl containing fatty acid. The most common

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chain lengths in these fatty acids are 18 and 20 carbon atoms which can be either saturated or unsaturated, where unsaturation of the double bonds are located at the 9, 12, and 15 carbon. By using enzymes or chemicals to modify the unsaturated fatty acid and introducing hydroxyl functional groups, castor oils could be converted into polyol. There are many literatures on modified castor oil PU for application in bridge decking, adhesives and thermal insulation.^{14–16} However, modification of PU for use as host in polymer electrolytes has not yet been reported in the literature. PU has unique multiphase structure formed from soft segment and hard segment in the polymer chains. Soft segment could contribute as polymeric solvent to solvate the cation and hard segment could function in maintaining the electrochemical stability. Therefore, it would be used as PU polymer electrolytes in the fabrication of electrochemical devices.¹⁷

The aim of this work is to synthesize PU from renewable resource, castor oil with desired properties for application as host material in polymer electrolytes as an alternative to petrochemical-based PU. Nevertheless, there is no report related to the potential of castor oil-polyol-based PU as host in polymer electrolytes. The synthesis is carried out at room temperature without additives, cross linkers and chain extenders. The work comprises of the transesterification of castor oil followed by polymerization of PU. The materials were characterized including optical, morphological and thermal properties. Although there are many methods and sources to synthesize PU, the transesterification of polyol from castor oil could give highly amorphous PU with low molecular weight and low glass transition temperature, T_g , value. Unlike crystalline phase, the polymeric chain in the amorphous phase is more flexible, which results in enhancement of segmental motion to enable easy ion migration.

2. Experimental

2.1 Materials

Castor oil, glycerol (99.9%), ethanol (99%), methanol, potassium hydrogen phthalate, phthalate anhydride, potassium hydroxide, phenolphthalein and tetrahydrofuran (THF) were supplied by R&M Marketing, Essex, UK, while 4,4'-diphenylmethane diisocyanate (MDI) and lithium iodide (LiI) were obtained from Merck and Aldrich, respectively. All the reagents were of analytical grade and used without further purification.

2.2 Preparation of castor oil-based PU films

The PU films were obtained by two steps of procedures. In the first step, the castor oil was modified to obtain polyol of desired acid value and in the subsequent step it

was reacted with MDI to obtain flexible films. Transesterification of castor oil was performed under nitrogen atmosphere. The set-up consisted of four-necked glass reactor of 1000 ml capacity with 250 mm height and 150 mm in diameter equipped with a mechanical stirrer. Heating was carried out by means of 1000 ml heating mantle. Nitrogen was supplied at a constant flow rate to avoid any oxidation reaction within the reactor. One of the necks of the reactor was equipped with a reflux condenser. The reactor was filled with castor oil and 15 wt% of glycerol was added to it. The percentage of the mixture was fixed according to the Patton formula¹⁸ to obtain the hydroxyl value of below 200 mg KOH g⁻¹. The mixture was slowly heated until it reached 210°C. The temperature was maintained at this value under constant stirring at 200 rpm. The small amount of reaction mixture was taken out and mixed with methanol in the ratio of 1 : 4 to check the solubility of the mixtures. A clear and homogeneous solution was obtained, indicating the formation of monoglycerides. The mixture was allowed to cool to 120°C before it was latter continuously stirred at ~200–220°C after the addition of an appropriate amount of phthalate anhydride. The progress of condensation reaction and its stability were confirmed by checking its acid value according to the procedure recommended in ASTM D1639-90E. For this purpose, samples were taken out at regular intervals and checked for an acid value using the titration method and phenolphthalein was used as indicator. The time required to complete the reaction was about 10 h. The resulted polyol was stored in dark bottles away from direct sun light. The produced polyol was mixed thoroughly with MDI using a digital magnetic stirrer at room temperature condition in the weight percentage (wt%) ratios of 20 : 80 (NCO : OH) and 40 : 60 (NCO : OH). MDI was slowly added to polyol and THF was used as the solvent. The complete reaction of PU was confirmed by the disappearance of NCO peak at 2270 cm⁻¹ in Fourier transform infrared (FTIR) spectra. The resulting solution was poured into a Teflon mould and left for slow evaporation of solvent. To ensure complete curing, the films produced were kept in a desiccator before they were characterized. For polymer electrolytes preparation, composition of NCO : OH that formed PU was dissolved in 10 ml THF before the addition of lithium iodide in different wt% (10–40 wt%) and stirred for 4 h. The homogeneous solutions were then casted in Teflon Petri dishes and left at room temperature for slow drying until free-standing films were obtained.

2.3 Analytical measurements

The interaction of chemical structures of polyol and PU prepared using castor oil was characterized using Perkin-Elmer Frontier FTIR/MIR spectrophotometer through attenuated total reflectance (ATR) scanning from

550 to 4000 cm^{-1} with a resolution of 2 cm^{-1} . The molecular weight, M_w , of polyol and PU-based castor oil was determined by the gel-permeation chromatography (GPC) technique using the Waters equipment with refractive index detector, Water 717 plus Autosampler and Water 600 Controller. THF was used as the eluent with flow rate of 1 ml min^{-1} at 16 bar. Dynamic mechanical analysis (DMA) was performed in order to determine the glass transition temperature, T_g , of the synthesized PU. The analysis was performed using Perkin Elmer DMA 8000 dynamic mechanical analyser with a film-tension mode of 1 Hz. Rectangular PU film specimens of $20 \times 10 \times 0.60$ mm (length \times thickness \times width) were used for the analysis. The samples were cooled and held isothermally at -60°C before the temperature was increased to 180°C at a rate of 2°C min^{-1} . T_g values of the samples were obtained from the peaks of the $\tan \delta$ curves. The thermogravimetric analysis (TGA) was carried out in order to study thermal stability of the PU films. The TGA was done using the Setaram LABSYS Evo simultaneous thermal analyser. The experiment was carried out under nitrogen atmosphere from 30 to 600°C at $10^\circ\text{C min}^{-1}$ heating rate. The morphology of the cross-section of polymer films was observed using ZEISS EVO MA 10 scanning electron microscope at $\times 2000$ magnification with 10 kV electron beam. Sample was fractured and coated with gold using sputter coating machine for 90 s before the analysis. Conductivity measurements of the polymer electrolytes were done using impedance spectroscopy, Solartron SI 1260 impedance/Gain-Phase Analyser. The measurements were performed over frequency

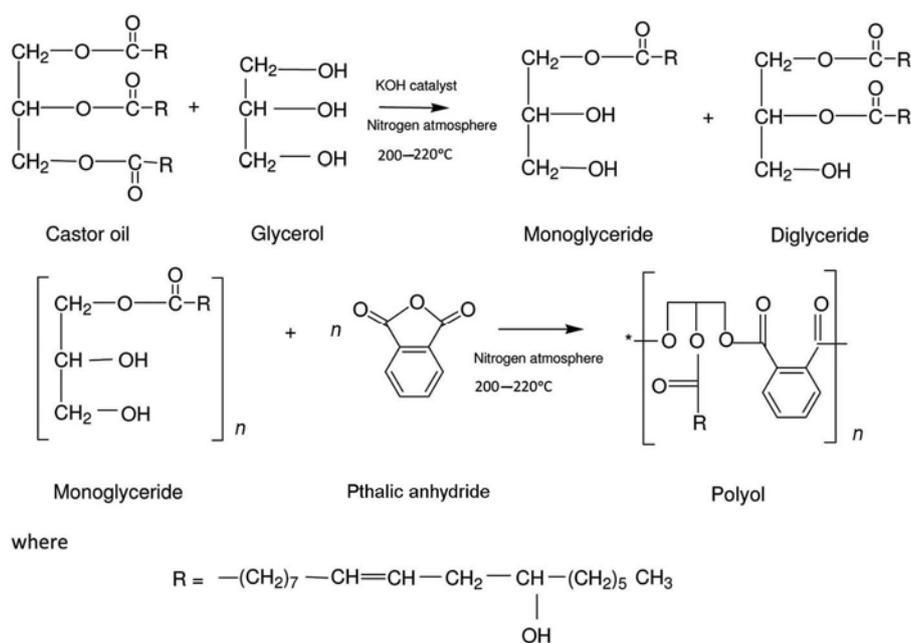
range of 10 Hz–5 MHz with amplitude of 100 mV at room temperature. The samples were sandwiched by two polished stainless-steel blocking electrodes. The values of bulk resistance, R_b , of the electrolytes were determined from the Nyquist plots obtained. Conductivity, σ values were calculated using equation

$$\sigma = \frac{t}{R_b A},$$

where t is the thickness of the electrolyte and A the electrolyte–electrode contact area.

3. Results and discussion

Scheme 1 shows the transesterification of castor oil-based polyol. Esterification began after phthalate anhydride was added to the mixture of oil and glycerol and after some-time, water was collected and the mixture turned into a clear brownish solution. From the titration that was done at a certain interval of time during the heating and stirring processes, the calculated acid value of the reaction was found to decrease gradually throughout the reaction. This proves that the reaction has progressed and polyester polyol was formed. The polyol obtained has an acid value of 3 mg KOH g^{-1} . The hydroxyl value of the polyol was obtained using 848 Titrimo Plus equipment and its value is 190 mg KOH g^{-1} . According to Petrovic, polyols with OH numbers of about 200 mg KOH g^{-1} and less give semi-rigid PUs of moderate or low crosslinking density when crosslinked with diisocyanate.¹⁹ Figure 1 shows FTIR



Scheme 1. Schematic representation of the preparation of castor oil-based polyol.

spectra of castor oil and synthesized castor oil-based polyol. The characteristic band of ester group C=O stretching appears at 1730 cm^{-1} and that of O–H functional group at 3550 cm^{-1} . These bands confirm the esterification reaction of polyol.

As mentioned earlier, PU films were produced by the reaction of MDI with castor oil-based polyol. Two different PU formulations were used (table 1). Formulation 1 contains NCO and OH in the weight ratio of 20 : 80, while Formulation 2 contains NCO : OH ratio of 40 : 60. Figure 2 presents the FTIR spectra of the synthesized castor oil-based PU in the region $550\text{--}4000\text{ cm}^{-1}$. For Formulation 2, the presence of peak at 2270 cm^{-1} indicates that the isocyanate has not completely reacted. The absence of peak at 2270 cm^{-1} is an indicative of the absence of NCO groups in the structure of Formulation 1 (NCO : OH (20 : 80)). On the other hand, new peaks at 1512 and 3369 cm^{-1} corresponding to --NH vibration (--NH--C=O--) and absorbance band around 1740 cm^{-1} characteristic of the C=O group are present in the FTIR spectra.²⁰ According to Narine *et al*,²¹ the band around 1740 cm^{-1} indicates that the hydrogen bonded C=O group vibration region is overlapped with the free C=O group vibration region. The absence of the isocyanate peak and appearance of amine and carbonyl peaks indicate a complete conversion of monomers to urethane.^{22–24} Therefore, for further investigation, only Formulation 1 was used. It is referred as PU in the following paragraphs. The photograph of castor oil-based PU film is shown in figure 3.

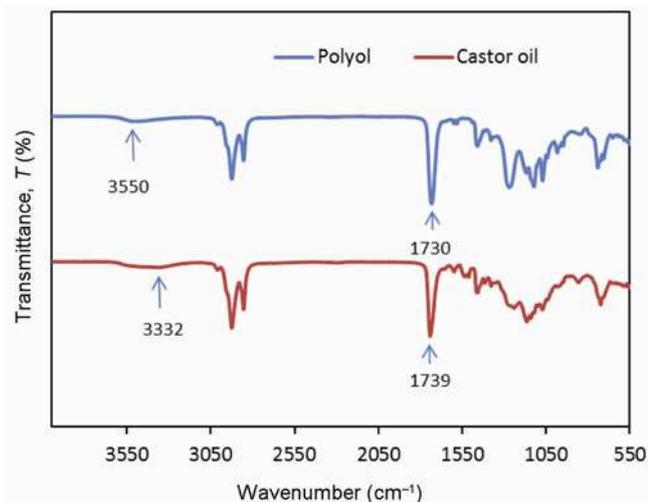


Figure 1. FTIR spectra of castor oil and polyol.

Table 1. Weight ratio of NCO : OH in different formulations.

Formulation	NCO : OH	Physical observation
1	20 : 80	Soft and flexible
2	40 : 60	Rigid and brittle

In this work, molecular weight of samples was determined by using gel-permeation chromatography. From the chromatogram that was not shown here, the molecular weight of castor oil is 1023 g mol^{-1} , close to the value reported by other researcher which is 963 g mol^{-1} .¹⁴ The synthesized castor oil-based polyol gives a molecular weight of 2786 g mol^{-1} . This value is suitable to form flexible PU.^{25,26} The molecular weight of synthesized PU in this work is $11,942\text{ g mol}^{-1}$. Table 2 summarizes the molecular weight of samples.

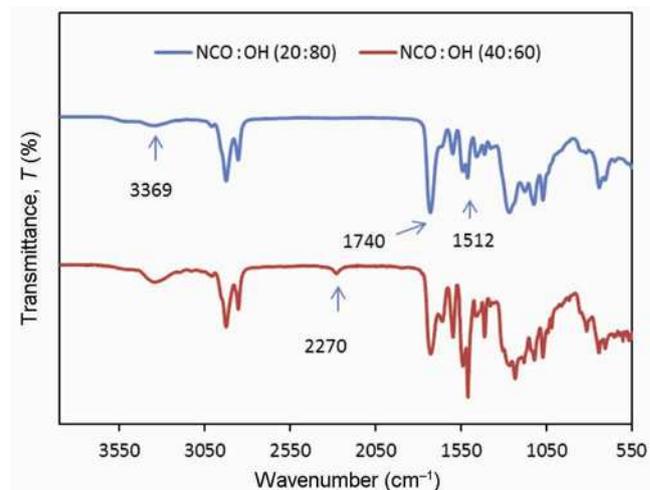


Figure 2. FTIR spectra of castor oil-based polyurethane.

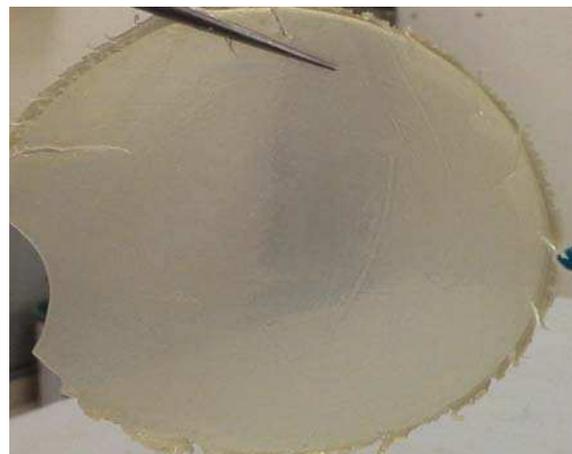


Figure 3. Photograph of castor oil-based polyurethane film.

Table 2. Values of molecular weight of castor oil, polyol and polyurethane.

Sample	Molecular weight, M_w (g mol^{-1})
Castor oil	1023
Polyol	2786
Polyurethane	11,942

Table 3. Decomposition temperatures, T_d and percentage weight losses of polyurethane film.

Weight loss (%)			Total weight loss (%)	Residue after 600°C (%)
T_{d1} 258–330°C	T_{d2} 313–430°C	T_{d3} 410–560°C		
4.7	47.7	34.8	87.2	12.8

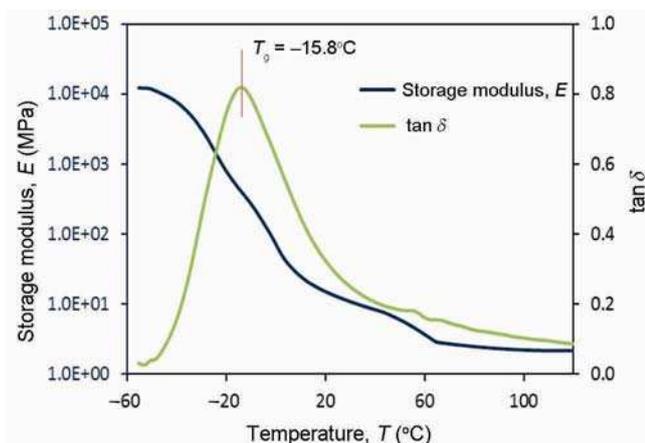
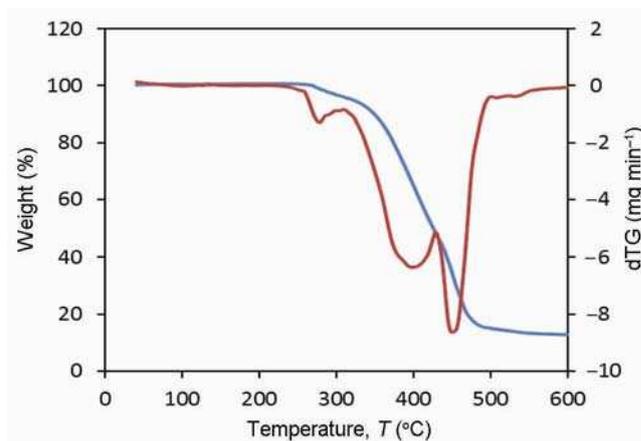
**Figure 4.** Tangent delta and storage modulus as a function of temperature for polyurethane.

Figure 4 depicts the plot of storage modulus, E and $\tan \delta$ vs. temperature of PU film. E is slightly decreased from -60 to -40°C , then decreases rapidly after -40°C until a rubbery plateau is observed in higher temperature. This change corresponds to glass–rubber transition and $\tan \delta$ reaches its maximum peak simultaneously. The plot shows one $\tan \delta$ peak, indicating homogeneous nature of the film. The value of glass transition temperature, T_g , is given by the peak maximum (α relaxation) of $\tan \delta$ vs. temperature curve. The T_g value obtained for the PU film is -15.8°C . T_g values of PUs are depending on the properties of the synthesized polyols, therefore the values could vary from -50 to 80°C . Júnior *et al* reported the value of thermoplastic PU based on castor oil is -30°C whereas Liu and co-workers²⁷ obtained a T_g value of 22.3°C for castor oil-based PU. On the other hand, Yeganeh and Shamekhi²⁸ obtained values of T_g between 47 and 61°C for the PUs synthesized from different compositions of castor oil and glycolysed poly(ethylene terphthalate) (PET).

Illustrated in figure 5 are thermogravimetric and derivatives of thermogravimetric curves for PU. Three decomposition stages are observed. Table 3 lists the decomposition temperatures, T_d , and the percentage weight loss after decompositions. The first degradation stage, T_{d1} , is observed at 259°C which achieves a maximum temperature, T_{max} , at 271°C . The T_{d1} is corresponding to the degradation of urethane linkages. From the first degradation stage, it can be concluded that the film is

**Figure 5.** Thermogravimetric and derivative thermogravimetric curves of polyurethane.

thermally stable from room temperature until the temperature started to decompose. The second step of thermal degradation, T_{d2} , is observed from 313°C up to 400°C . The third step of thermal degradation, T_{d3} , begins at 429 to 550°C . T_{d2} corresponds to the liberation of free isocyanate and T_{d3} is attributed to the decomposition of soft segment of the PU.^{29,30} The TGA result suggests that the PU is stable from ambient temperature up to 259°C .

The morphology of cross-sectional area of the castor oil-based PU film is shown in figure 6. As seen in the figure, the film is smooth and no phase separation is observed. The smooth morphology of the film shows that the film is highly amorphous. This characteristic is favourable for a host of polymer electrolytes as ion conduction occurs in amorphous region.

In order to determine whether the synthesized PU can be used as host in polymer electrolytes, a doping salt, LiI has been added to the biopolymer. The plot of conductivity of PU polymer electrolytes with the addition of salt is illustrated in figure 7. The conductivity of pristine PU is $1.18 \times 10^{-11} \text{ S cm}^{-1}$ increased to $4.92 \times 10^{-8} \text{ S cm}^{-1}$ with the addition of only 10 wt% LiI. The conductivity increased by three orders of magnitudes compared to pristine PU and reached maximum value up to $1.42 \times 10^{-6} \text{ S cm}^{-1}$ upon the addition of 30 wt% of LiI. Further addition of salt resulted in a decrease in conductivity. The increase in conductivity was contributed by the number of conducting species in the electrolyte caused by dissociation of LiI ions. This occurred due to

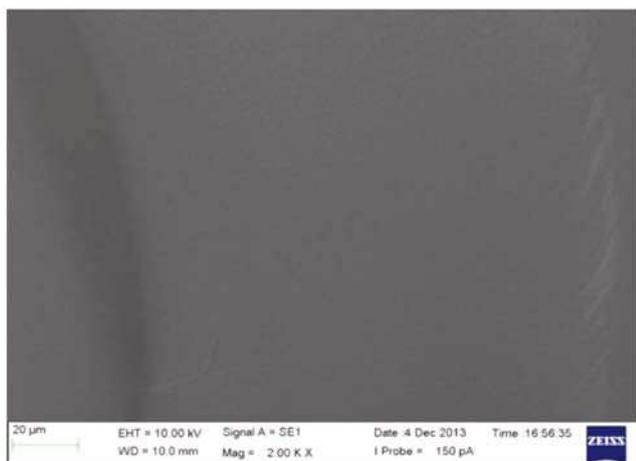


Figure 6. SEM image of cross-section of castor oil-based polyurethane film.

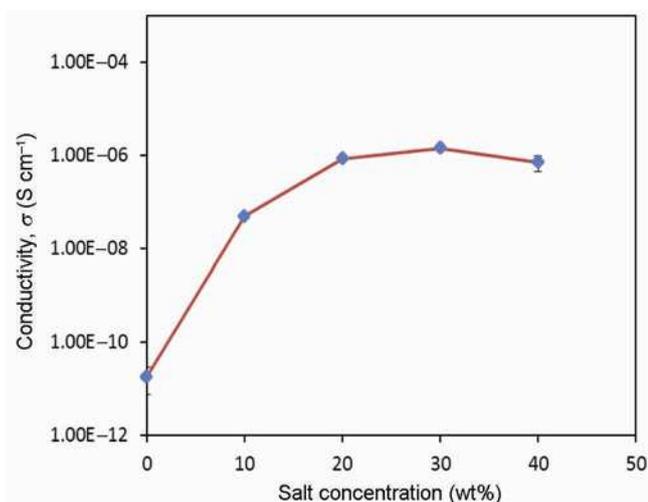


Figure 7. Conductivity of castor oil-based polyurethane with the addition of different wt% of lithium iodide.

the presence of coordinating atoms in the polymer host. The conducting species or free mobile ions present in the polymer may increase the amorphous structure, thus eases the ion migration. The decrease in conductivity after optimum value is probably due to ion association or ion aggregation.^{31,32}

4. Conclusions

A castor oil-based polyol was successfully synthesized via transesterification. The polyol has an acid value of 3 mg KOH g⁻¹ and OH number of 190 mg KOH g⁻¹. Using this polyol, PU was successfully synthesized as confirmed by FTIR results. The film prepared using the synthesized PU demonstrated highly amorphous, low T_g value of -15.8°C and was free standing as well as good thermal stability, up to 259°C. The PU shows a

conductivity value upon the addition of salt up to 1.42×10^{-6} S cm⁻¹ with the addition of 30 wt% of LiI. These results indicated that the castor oil-based PU possessed favourable properties for the application as host in polymer electrolytes.

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