



Full Length Research Article

SYNTHESIS AND CHARACTERIZATION OF CARDANOL/PHENOL RESIN BASED POLYURETHANES

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ABSTRACT

The production of polyurethanes from cardanol, a renewable organic resource obtained as a by product of the cashew industry. Cardanol based novolac type phenolic resins were synthesized by condensing cardanol phenol mixture with furfuraldehyde in different molar ratios in the presence of hydrochloric acid as catalyst. The novolac resins were treated with polyethylene glycol – 400 to produce polyols. The polyols were condensed with toluene -1,6 - diisocyanate in presence of dibutyl tin laurate to produce polyurethanes and characterized by thermal, mechanical, SEM and X-ray diffraction studies. These studies revealed the high performance character of the polyurethanes.

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INTRODUCTION

Polyurethanes are most versatile group of industrial important polymers in today's world. There have been a number of works based on polymers from Cashew Nut Shell Liquid derivatives. CNSL, an agricultural by product of the cashew nut processing industry and a renewable resource, is a source of a long chain, meta substituted phenol which promises to be an excellent monomers for polymer production. CNSL occurs as a reddish brown, viscous fluid in the soft honey comb structure of the shell of cashew nuts. Many researchers have investigated its extraction, chemistry and composition (Bhunia *et al.*, 1999). CNSL contains four major components: cardanol, cardol, anacardic acid and 2- methyl cardol (Ikeda *et al.*, 2000). Cardanol, which can be obtained by thermal treats of CNSL, is a phenol derivative mainly composed of the meta substitute of a C15 unsaturated hydrocarbon chain with one to three double bonds (Kim *et al.*, 2007). Alkyl groups are known to improve the solubility alignment properties, dielectric properties and gas permeability properties of polymers. Numerous studies have been carried out using the reactivity of the hydroxyl group in cardanol. The synthesis, mechanical and thermal properties of polyurethanes based on cardanol

furfuraldehyde resin has been reported earlier (Mythili *et al.*, 2005). Furfuraldehyde, the heteroaryl aldehyde is obtained as an agricultural waste product which has an extensive application in the formation of resins (John Crabtree *et al.*, 1982). Polyurethanes provide a versatile range of properties and find extensive applications especially in the biomedical field which include synthesis of catheters of wide range (Scheuer Leeser *et al.*, 1972), pacemaker lead insulation (Hasthorne, 2001), polyurethanes vascular grafts (Zdrahala, 1966) and artificial heart valves (Sathiyalekshmi *et al.*, 2000). In the present study cardanol / phenol-furfural resins were used for the production of polyurethanes. The thermal, mechanical properties, SEM and X-ray crystallinity have been evaluated.

MATERIALS AND METHODS

Cashew Nut Shell Liquid (CNSL) was obtained from M/S Kumaraswamy Chemicals, Cuddalore, Tamil Nadu State, India. Cardanol was separated from CNSL by vacuum distillation at 3 - 5 mm Hg. The fraction distilled at 230° - 240°C was collected. Phenol, furfuraldehyde, dibutyl tin laurates, toluene -1,6 -diisocyanate and silicone oil were received from Sigma - Aldrich Chemicals (USA). The chemical were used as received.

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INSTRUMENTS

The polyurethanes were subjected to differential thermal analysis (DTA) / thermo gravimetric analysis (TGA) studies at a rate of 10°C/min. in air using Universal V4.3A TA instruments. Tensile strength was determined using H-5KS Hounsfield Test equipment S series. The values represented are an average mean of about 6-10 samples. Tensile specimen of dimensions 130 x 10 x 1 mm was used. The surface morphology of the polyurethanes were carried out by Jeol 6390LV model scanning electron microscope (SEM) with accelerating voltage of 0.5kV to 30kV, resolution of 4nm(30kV) and magnification of 300,000. The X-ray diffraction analysis has been done using Bruker S D8 diffractometer with angular range 10° to 80° in 2θ and a filtered Cu Kα radiation source (λ=1.5406) was used.

Synthesis of Polyurethanes

Cardanol was separated from CNSL by direct double vacuum distillation (5-10mm Hg) in the temperature range 180°-240°C. Three novolac resins were synthesized using Cardanol, furan-2-aldehyde, phenol and hydrochloric acid as catalyst as per the formulation given in Table 1.

Table 1. Formulation for Cardanol based novolacs C1, C2 and C3

Resin	Mole ratio of Cardanol	Mole ratio of phenol	Mole ratio of furfuraldehyde	Mole ratio of Catalyst
C1	5.4	0.6	1	1
C2	4.8	1.2	1	1
C3	4.2	1.8	1	1

Cardanol/phenol furfuraldehyde resins were synthesized using cardanol and phenol weighed into a three necked flask, fitted with a Leibig's condenser, ground joint thermometer and a dropping funnel. 1 mole of furfuraldehyde and hydrochloric acid were added. The mixture was heated in a nitrogen atmosphere using a rotamandle at 150 ±5°C for three hours. 1.0 mole of resin and 3.0 moles of PEG-400 were mixed in a three necked flask fitted with a Leibig's condenser, ground joint thermometer and a dropping funnel. The mixture was heated in a nitrogen atmosphere using a rotamandle at 150 ± 5°C for three hours. The water vapour formed was removed applying vacuum at 20 mm Hg. Polyol terminated novolac resin and TDI were mixed in the weight ratio of 2:1. DBTDL catalyst and toluene solvent were added. The reactants were heated in a three necked flask fitted with a condenser, a ground joint thermometer and a dropping funnel in nitrogen atmosphere at 120° C for 30 minutes. The product was degassed fully in vacuum and then cooled to 60° C and casted in clean silicon coated glass plates. The polymer was cured in vacuum oven at 80° C for 48 hours and analyzed. Polyurethanes prepared from polyol terminated novolac resin were coded as C1U, C2U and C3U respectively.

RESULTS AND DISCUSSION

Thermal properties of Polyurethanes

DTA and TGA of polyurethanes are presented in Table 2. The thermal stability of obtained polyurethanes, C1U, C2U and C3U were studied with TGA at a heating rate of 10°C/min in a nitrogen atmosphere. It can be seen that the decomposition of the polyurethanes in a nitrogen atmosphere do not takes place below 295°C. The thermal decomposition of the polyurethanes, C1U, C2U and C3U involves at least two overlapping steps; a small drop below 300°C is followed by the main loss weight above 450°C. The first stage degradation confirms the polyurethane linkage (Hepburn, 1982). The first weight loss is related to the decomposition of urethane bonds, which takes place through the dissociation to isocyanate and alcohol (Levchik *et al.* 2004). The weight loss in the first step increases as the percentage of phenol increases, in accordance to the existence of a higher amount of weaker urethane bonds

Mechanical properties

The mechanical properties of polyurethanes are largely influenced by the presence of aromatic groups, long alkyl side chain, extent of cross linking and the effect of secondary bonding forces (hydrogen bonding). The higher hardness is observed in C1U in comparison to its counterpart C2U and C3U though the cross link density is more or less similar. The same trend is also reflected in the case of tensile strength. This may be attributed to the higher degree of hydrogen bonding interactions physical cross links in the former.

Morphological studies

C1U and C2U is a flake like structure. The morphology of the flakes is almost uniform and shapeless. In C3U, the spherical shape gets distorted. The grains are coming close together and form the grains larger than C2U. This may be due to the agglomeration of spherical grains and hence the grains are not spherical and the distribution is not symmetrical.

X-ray Diffraction study

X-ray diffraction (XRD) by films is the most widely employed method for determining the three dimensional structure of solids (Dent Glasser, 1977). For C1U, C2U and C3U, the diffractogram shows a broad band from 8° to 55° in 2θ, 8° to 57° in 2θ and 10.9° to 53° in 2θ respectively. The broadness of the peak reveals the non crystalline nature of the sample. The grain size is low at its calculated value, using the Scherer's formula is about 13nm, 13nm and 14nm. Peaks are diffuse and halo that indicates the amorphous nature of the C1U, C2U and C3U. On increasing the phenol content peak height gradually decreases. This indicates the improved polymer nature of the samples without crystalline grains.

Table 2. Thermal properties of Polyurethanes

Polyurethane	TGA data			DTA data			
	Temperature (°C) at the end of each stage of degradation (weight Loss, %)			Exo ₁	Endo ₂	Exo ₃	Exo ₄
	T _{start}	1 _{st}	2 _{nd}				
C1U	240.32	480.4	-	210.34	325.72	390.62	446.74
C2U	95.41	225.94	310.4	151.20	210.41	-	446.68
C3U	265.38	472.75	-	249.67	280.99	354.44	451.75

Conclusion

Using cardanol, one of the components of CNSL various resins were prepared along with furfuraldehyde and considerable quantity of phenol. The prepared polyurethanes from these resins and toluene-1,6-diisocyanate have higher thermal stability. From X-ray diffraction studies, it was confirmed that, the addition of phenol decreases the crystallinity.

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