

# Synthesis and characterization of bio-based polyurethane from benzoylated cashewnut husk tannins

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**Abstract.** Benzoylated tannin prepared by benzoylation of cashewnut husk tannin, was treated with hexamethylenediisocyanate in the presence of 1,4-butanediol as an extender to prepare thermosetting polyurethane. The sample was characterized using FT-IR and <sup>13</sup>C NMR spectra. Thermal, morphological, physico-chemical and electrical properties were also investigated. Polyurethane obtained was sensitive to moisture but had very good solvent resistance. Results show that  $T_g$  of the sample is 260 °C and thermal decomposition begins at 280 °C. The dielectric constant varies randomly with temperature. The conductivity of the sample was found to increase with increase in temperature but shows random variation at 90 and 150 °C.

**Keywords.** Cashewnut husk; benzoylated tannin; polyurethane.

## 1. Introduction

Polyurethane (PU) is an extremely versatile polymer which accounts for ~6% of global polymer consumption, and the polyurethane market is expected to reach \$53 billion by 2016 (Malhotra 2011). They find application in construction, automobiles and are used as coatings, sealants, adhesives and elastomers (Gary Howard 2002). Commercially, polyurethanes are prepared by the exothermic reaction of molecules containing two or more isocyanate groups with polyol molecules containing two or more hydroxyl groups. Increasing environmental awareness and increasing crude oil prices globally have urged researchers to search for new alternatives with good performance criteria and low-environmental impact for use as substitutes for petroleum based sources (Pillai 2010). Literature shows that polyurethane can be successfully prepared from bio-based materials. Plant oil such as soybean oil (Guo *et al* 2000; Eid Ismail *et al* 2011), castor oil (Hatice Mutlu *et al* 2010), linseed oil, sunflower oil, palm oil (Gerard Lligadas *et al* 2010), rapeseed oil (Clark 2001), ricinoleic oil (Petrovic 2008), betulinol (birch bark extract), D-glucose and hydroxy ethyl glucoside obtained by hydrolysis of starch (Mihail Ionescu 2005), lignin from cellulose industry (Narayan 2006), liquefied benzoylated wood (Yu Ping *et al* 2005) and soy flour (Raquez 2010) are renewable materials which were successfully employed in polyurethane preparation. Studies show that tannin extracted from different sources can be used for preparation of various polymer resins (Pizzi

1982). Jin-Jie (1998) synthesized rigid polyurethane by utilization of wattle tannin (WT) and *Acacia meamsii* bark (BK) as a partial replacement for synthetic polyols. *Anacardium occidentale*, cashew tree provides many raw materials to the polymer industry. Cashewnut husk contain about 35 to 47% tannin (Lokeswari *et al* 2010). Cashewnut shell liquid was used as source for polyol in polyurethane industry (Bhunja *et al* 1999). Literature survey reveals that tannins from cashewnut husk have not been used as polyol for PU preparation. In this paper, we have reported the chemical modification of tannin extracted from cashewnut husk by benzoylation and the preparation of polyurethane from benzoylated tannin with hexamethylene diisocyanate in the presence of extender, 1,4-butanediol. Benzoylation was carried out to reduce the number of –OH group of tannin which will reduce the cross-linking of the product. Increase in cross-linking will render polyurethane with brittle character (Ling Zhang 2008). Spectral, thermal, morphological, physico-chemical and electrical properties were evaluated for the synthesized polyurethane.

## 2. Experimental

### 2.1 Materials

The thin husk separated from the edible portion of cashew nut, obtained from the native plants of Kanyakumari district, Tamil Nadu, India, was used as a source for tannins. Analar grade benzoyl chloride, NaOH, hexamethylenediisocyanate (HDI), 1,4-butanediol and 1,4-diazobicyclo (2,2,2)octane, (Spectrochem) were used as obtained.

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## 2.2 Methods

Fourier transfer infrared (FT-IR) spectra was recorded using Berk-Elmer spectrophotometer by KBr pellet method.  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectrum was recorded using Bruker spectrophotometer at 5 KHz. Thermogravimetric analysis (TGA) study was carried out at flow rate of 30 (m)/min at  $10\text{ }^\circ\text{C}$  per min up to  $550\text{ }^\circ\text{C}$  with 2 mg of sample using-TGA50-Shimadzu analyser. Differential scanning calorimetry (DSC) was carried out at flow rate of 30 (m)/min at  $10\text{ }^\circ\text{C}$  per min with 1 mg of sample using Berk-Elmer calorimeter. Superscan S-550 instrument with a secondary electron detector and an acceleration voltage of 15 kW was used to record the scanning electron microscopy (SEM) images. Coefficient of thermal expansion studies was carried out using quartz-tube dilatometer according to ASTM D696 standards. Polyurethane samples of dimension  $2 \times 1 \times 1\text{ mm}$  were immersed in the respective solvents (50 mL) for a period of 25 days under room temperature and the loss in weight was determined using electronic balance. Water absorption and moisture resistance were calculated as per ASTM D570 standard. Flammability was determined by UL94V for small flame (IEC 60695-11-10). Dielectric constant was determined using impedance bridge at various temperatures from 75 to  $150\text{ }^\circ\text{C}$  in  $5\text{ }^\circ\text{C}$  increments at different frequencies from 100 to 1000 Hz. Conductivity measurements were carried out at different temperatures using megaohm meter.

## 2.3 Preparation of benzoylated tannin

Cashewnut husk was dried in shade, powdered and sieved through 0.5 mm mesh. 30 g of the powder was extracted by distillation with 200 mL of 70% aq. acetone at  $60\text{ }^\circ\text{C}$  (Hagerman and Butler 1978; Sharma *et al* 1998). The extract was then evaporated to dryness. Tannins were separated using thin layer chromatography and 0.1 g of tannin was benzoylated by treatment with 12 g of benzoylperoxide in the presence of 10% NaOH. The benzoylated product was filtered, dried and used as a source for polyol (Pizzi 1979).

## 2.4 Synthesis of polyurethane, PU b

1 part by weight of benzoylated tannin was dissolved in 6 parts by weight of solvent (methylene dichloride and acetone in 1 : 1 ratio by volume) in a three-neck flask. 6 parts by volume of HDI and 2 mL of 1% catalyst 1,4-diazobicyclo(2,2,2)octane were added drop-wise and the reaction was allowed to proceed for 5 min at  $60\text{ }^\circ\text{C}$  at a stirring rate of 2500 rpm. Then 0.05 parts by weight of 1,4-butanediol was added in drops and the reaction was allowed to proceed for 3 more minutes. The mixing ratio of polyol and HDI was varied and the above ratio was

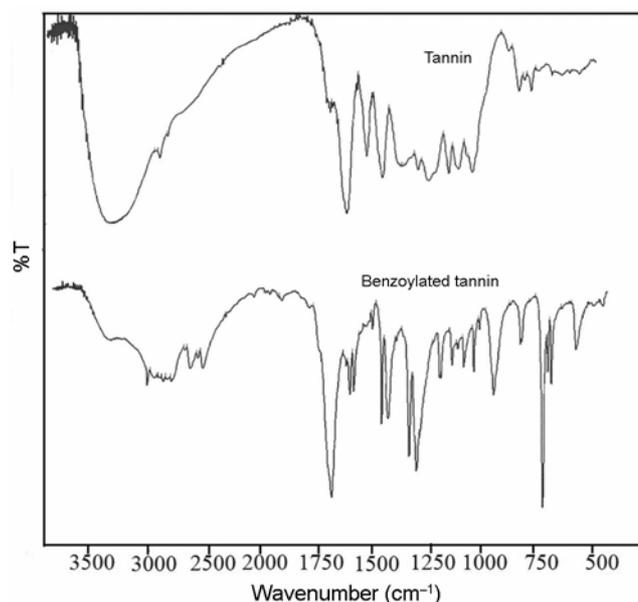
found to be exact for preparation of polyurethane. The polyurethane obtained was cured at room temperature for 3–10 h and molded (Pizzi 1979; Jin-jie 1998).

## 3. Results and discussion

The synthesized polyurethane, PU b sample, was characterized using FT-IR and  $^{13}\text{C}$  NMR spectra. Thermal, morphological, physico-chemical and electrical properties were also investigated.

**3.1a FT-IR spectral studies:** FT-IR spectrum (figure 1) of tannin shows characteristic absorption at  $3400\text{ cm}^{-1}$  which corresponds to O-H group (broad band due to H-bonding). Bands at 1610 and  $1518\text{ cm}^{-1}$  corresponds to asymmetric stretching of single and double bonds of aromatic compound,  $1296\text{ cm}^{-1}$  for C-H stretching (C-H-linkage),  $1284\text{ cm}^{-1}$  due to C-O-C asymmetric stretching,  $1448\text{ cm}^{-1}$  for aromatic ring stretching,  $1356\text{ cm}^{-1}$  correspond to C-H deformation (C-H-linkage). C-H bending (in-plane H-bond aromatic linkage) shows band at  $1236\text{ cm}^{-1}$  and bands at 1143 and  $1035\text{ cm}^{-1}$  correspond to ring stretching (aromatic linkage) and C-H bending (aromatic in-plane H-bonding) (Pizzi 1979; Jin-jie 1998).

FT-IR spectrum of benzoylated tannin (figure 1) shows characteristic broad absorption band at  $3390\text{ cm}^{-1}$  which corresponds to -OH group, but the band intensity for hydroxyl group has been greatly reduced in benzoylated tannin. Band at  $2924\text{ cm}^{-1}$  corresponds to -CH asymmetric and symmetric stretching vibration of substituted  $\text{CH}_2$  group. A very sharp and intense band appears at  $1685\text{ cm}^{-1}$  corresponds to carbonyl stretching vibration of



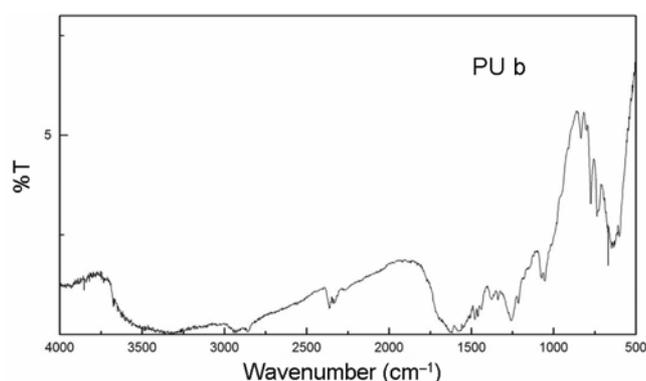
**Figure 1.** FT-IR spectra of tannin and benzoylated tannin.

conjugated ketones indicating benzoylation of tannins. Bands at 1610 and 1496  $\text{cm}^{-1}$  correspond to asymmetric stretching of single and double bonds of aromatic compound, 1292  $\text{cm}^{-1}$  due to C–O–C asymmetric stretching, 1448  $\text{cm}^{-1}$  to ring stretching (aromatic linkage), 1327  $\text{cm}^{-1}$  for C–H deformation and 1026  $\text{cm}^{-1}$  due to C–O–C symmetric stretching vibration. Sharp and intense band at 707  $\text{cm}^{-1}$  corresponds to stretching vibration of meta substituted aromatic ring (Pizzi 1979).

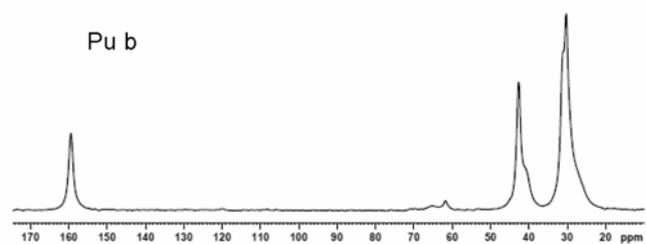
**3.1b FT-IR spectral studies of polyurethane:** FT-IR spectrum of PU b (figure 2) shows presence of amide I and II bands. The band at 1690  $\text{cm}^{-1}$  is due to carbonyl stretching vibration of (amide I band) of polyurethane. The combination of N–H deformation and C–N stretching vibrations (amide II band) occur at 1500 and 1200  $\text{cm}^{-1}$ , respectively. The –N–H stretching vibrations correspond to the broad band at 3300  $\text{cm}^{-1}$  and the band at 1330  $\text{cm}^{-1}$  corresponds to –CONH–asymmetric stretching vibrations. These bands are in good agreement with the values in the literature (Bhunja *et al* 1999; Hemul Patel *et al* 2010).

### 3.2 $^{13}\text{C}$ NMR studies of polyurethane

$^{13}\text{C}$  NMR spectra of polyurethane sample PU b is shown in figure 3. Spectra show a sharp peak at 159.4 ppm



**Figure 2.** FT-IR spectra of polyurethane, PU b synthesized from benzoylated tannin.



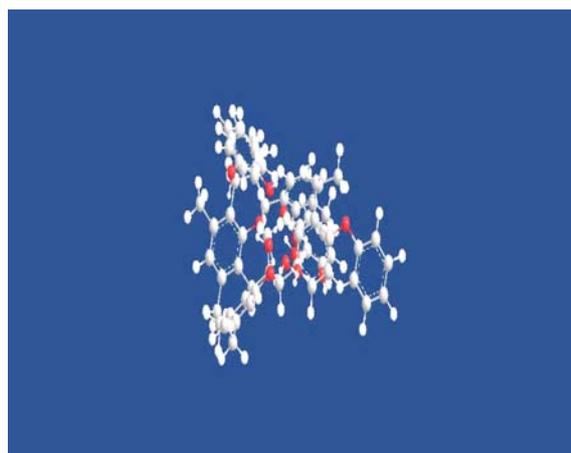
**Figure 3.**  $^{13}\text{C}$  NMR spectrum of PU b synthesized from benzoylated tannin.

corresponding to C5 and C7 atoms, the sharp peak at 40.7 ppm correspond to aliphatic C3 carbon atom and very sharp and intense band at 28–30 ppm due to C4 atom. PU b shows additional weak peak at 60 ppm corresponding to the existence of C4–C8 linkage (Mythili *et al* 2004; Vinod Kumar and Sethuraman 2004).

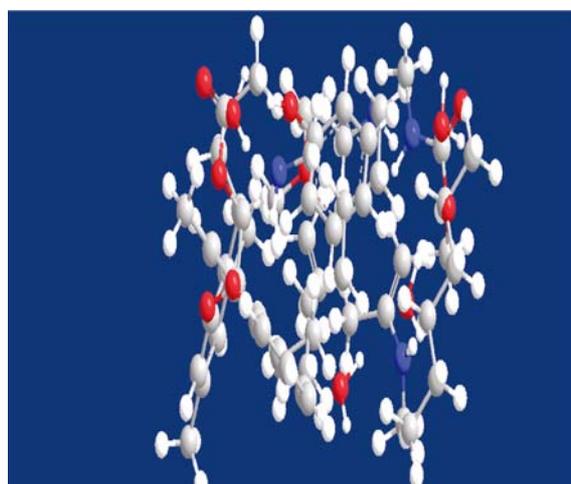
From the spectral data and literature (Pizzi 1979; Vinod Kumar and Sethuraman 2004) the structure of benzoylated tannin and the expected structure for the prepared polyurethane are shown in figures 4 and 5 and the entire scheme for polyurethane, PU b preparation is represented in scheme 1.

### 3.3 Thermal studies

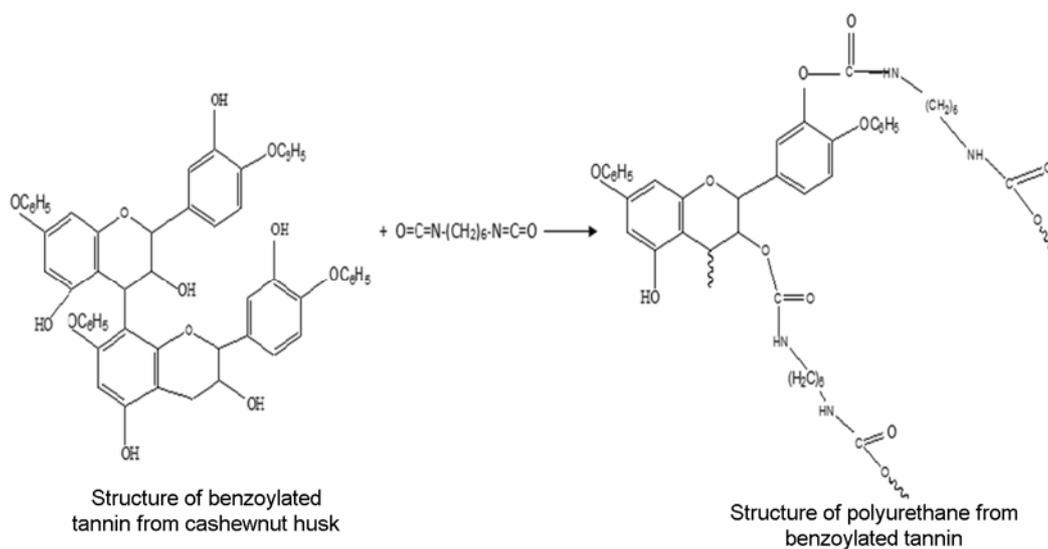
The thermal property is influenced by molecular weight, the cross links, degree of segments in hard and soft sequences, and elastically active branch points (Mythili *et al* 2004; Yu Ping *et al* 2005). TGA curve of PU b



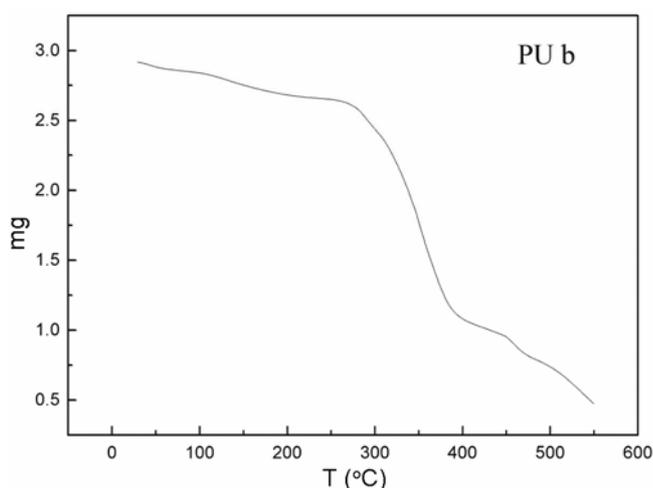
**Figure 4.** Structure of benzoylated tannin.



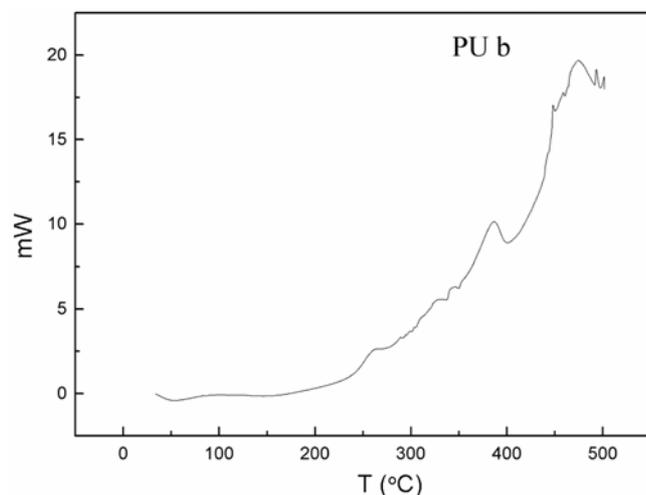
**Figure 5.** Structure of PU b from benzoylated tannin.



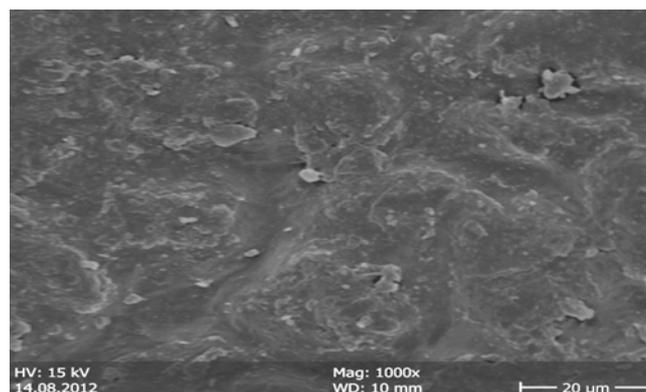
**Scheme 1.** Preparation of polyurethane, PU b from benzoylated tannin.



**Figure 6.** TGA of PU b.



**Figure 7.** DSC of PU b.



**Figure 8.** SEM image of PU b.

is shown in figure 6. TGA shows one weight loss zone at 280 °C. The decomposition starts at 280 °C and ends at about 380 °C and the percentage weight loss is about 11.9 (0.347 mg) which is attributed to the decomposition or decross-linking of polyurethane moiety or post-curing process.

DSC analysis (figure 7) shows the most prominent plateau at 260 °C, which contributes to glass transition temperature,  $T_g$ . The length of the hard segment blocks determine the softening point (Mythili *et al* 2004). The softening point of the polymer is around 290 °C, which is attributed to endothermic process. The exothermic peak at 380 °C is accounted for chemical reactions such as decomposition.

### 3.4 Morphological study

SEM image obtained for surface morphological study is represented in figure 8. Polyurethane contains hard and

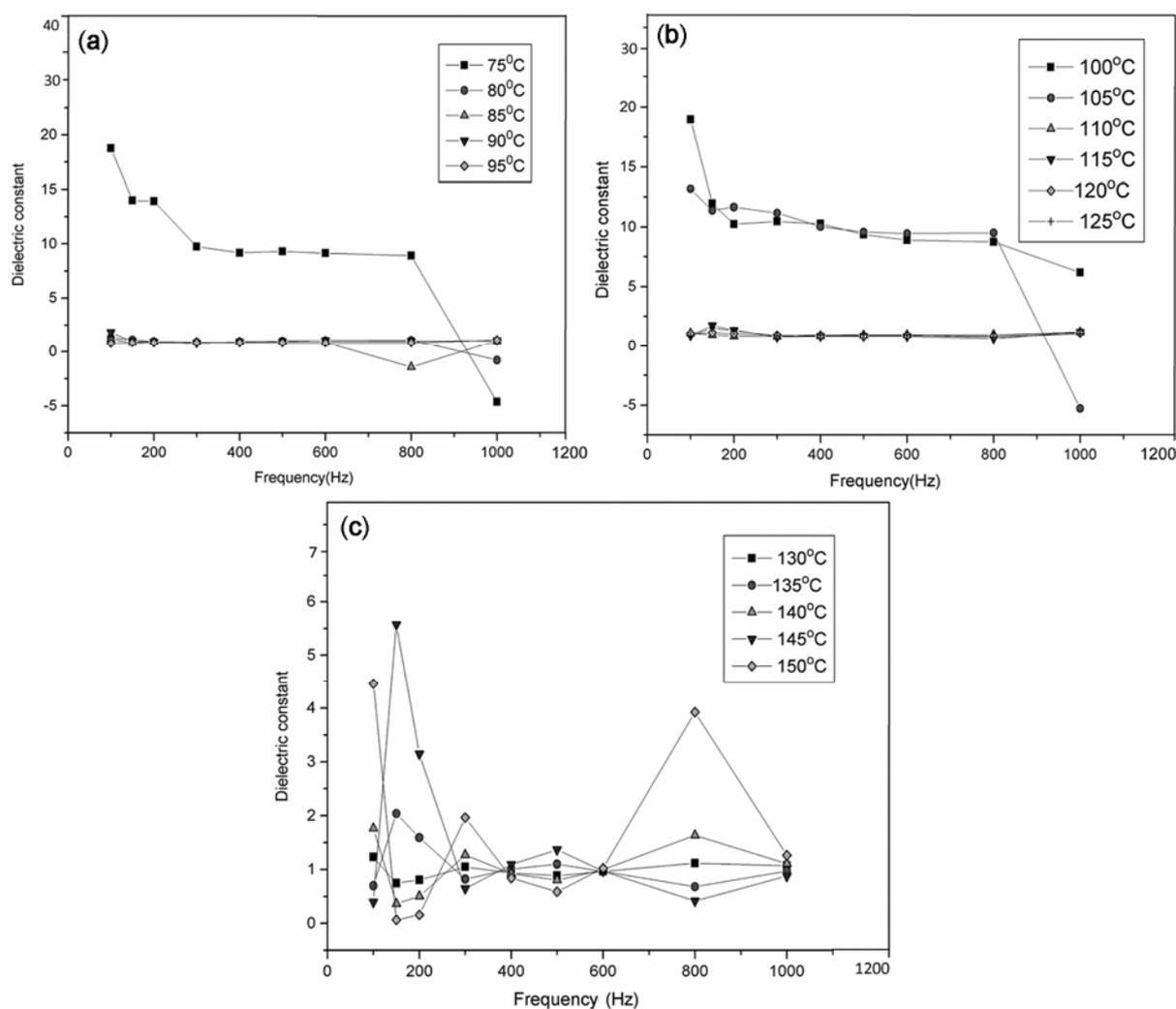
**Table 1.** Physicochemical properties of PU b.

Sample code	Water absorption	Moisture analysis	Flammability	Coefficient of thermal expansion (°C)
PU b	98.6%	2.2%	V <sub>0</sub>	6.9 × 10 <sup>-6</sup>

**Table 2.** Solubility of PU b in various solvents after 25 days of immersion.

Sample code	Solvents									
	Water	1N HCl	1N NaOH	THF	DMSO	Ethyl acetate	Benzene	Toluene	Ethanol	Diesel
PU b	-	-	+/-	+/-	-	-	-	-	-	-

Soluble (+), partially soluble (+/-) and insoluble (-).


**Figure 9.** (a–c) Variation of dielectric constant with frequency at different temperatures for PU b.

soft segments (Mythili *et al* 2004). The polyamide linkage constitutes the hard segment and the methylene linkage constitutes the soft segment. The hard and soft segments interact with each other and at one stage both the degree of polymerization and the interaction param-

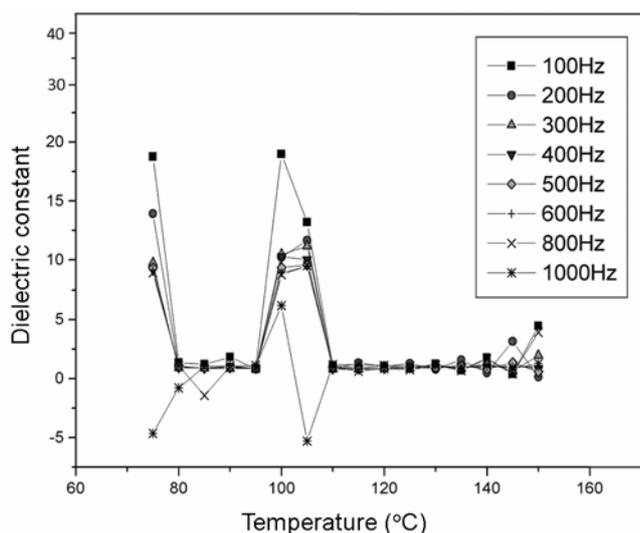
eter ( $\chi$ ) increases, the entire system crosses the thermodynamic boundary of a miscible system and phase separation occurs (Ling Zhang 2008). The association of domains also occur through hydrogen bonding. Figure 8 shows that phase segregation is not so prominent in PU b.

### 3.5 Physicochemical studies

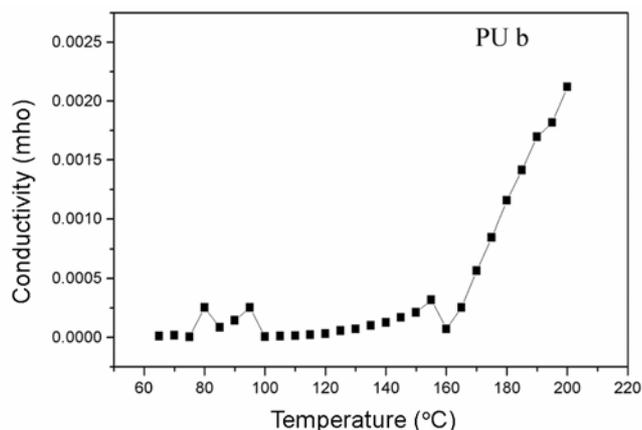
Water absorption, moisture analysis, flammability, coefficient of thermal expansion, and solubility studies (Vishnu Shah 1954; Tan and Chow 2011) were carried out in PU b and the results are shown in tables 1 and 2. Studies show that PU b was more sensitive to moisture

**Table 3.** Dielectric constant at two different temperature and frequency.

Temperature (°C)	Dielectric constant	
	PU b at 100 Hz	PU b at 1000 Hz
75	18.76106	-4.63898
150	4.45894	1.263484



**Figure 10.** Variation of dielectric constant with temperature as function of frequency.



**Figure 11.** Variation of electrical conductivity with temperature.

but insoluble in many solvents and have very good chemical resistance. Flammability studies shows that the after-flame time and after-glow times were  $>10$  s with no burning drops which categorize it under  $V_0$ . This shows that PU b has good flame resistance which is due to the high aromatic constituents of the polymer. The coefficient of thermal expansion values of PU b is  $6.9 \times 10^{-6}/^{\circ}\text{C}$ .

### 3.6 Electrical studies

**3.6a Dielectric constant:** The variation of dielectric constant of PU b as a function of temperature (figures 9a–c) ranging from 75 to 150 °C was studied at different frequencies from 100 to 1000 Hz. The values of dielectric constant at 75 and 150 °C at 100 and 1000 Hz are shown in table 3. The dielectric properties of a polymer are determined by the charge distribution and also by statistical thermal motion of its polar group. In case of polar polymers, the dielectric constant begins to drop at a certain frequency (Muhammad Akram *et al* 2005; Omed *et al* 2011). Figure 10 shows that at constant temperature, as frequency increases dielectric constant decreases for temperature 75, 80, 100 and 105 °C. For temperature region of 90 and 95 °C, there is no much variation in the dielectric constant with increase in frequency. At 85 °C, the dielectric constant shows a decrease at 800 Hz which then increases at 1000 Hz. Dielectric constant varies randomly with frequency as temperature rises above 105 °C. These factors can be attributed to variation in orientated polarization (Muhammad Akram *et al* 2005; Omed *et al* 2011).

The variation of dielectric constant as a function of frequency at different temperatures is shown in figure 12. It is observed that initially the dielectric constant decreases with increase in temperature and then increases suddenly at 100 °C after which, again there is a decrease. The random variation observed at around 70 and 100 °C is due to dielectric dispersion and is attributed to the ordinary motion of the molecules from one arrangement to another around the skeletal bond involving large scale conformational rearrangement (Vikram Yadav *et al* 2010).

**3.6b Electrical conductivity:** The conductivity measurement was carried out up to 200 °C. The conductivity of PU b was found to increase with increase in temperature but shows certain random variations at 80, 90, 150 and 165 °C as shown in figure 11. The initial decrease at 80 and 90 °C may be due to neutralization of charges. The increase in conductance is attributed to the change in geometry (Vinicius Pistor *et al* 2012), orientation of the molecules and the chain length (Chen 2003).

## 4. Conclusions

The polyurethane sample PU b, prepared from benzoylated tannin is a simple single-step process. The product

obtained had good thermal stability; the decomposition begins at 280 °C. PU b show good chemical resistance to acid, alkali and many organic solvents which make them categorized under  $V_0$  in flammability. The dielectric constant varied randomly with increase in frequency as a function of temperature. The electrical conductivity increased with increase in temperature but shows random variation at certain region around 90 and 150 °C. Results conclude that the product had good thermal, electrical properties and good chemical resistance. Additionally their flame resistance offer them an added advantage, suggesting that benzoylated tannins from cashewnut husk can be successfully employed as a substituent for petroleum based polyol in the preparation of polyurethane.

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