

# Preparation and Properties of Novel Green Poly(ether-ester urethane)s Insulating Coatings Based on Polyols Derived from Glycolyzed PET, Castor Oil, and Adipic Acid and Blocked Isocyanate

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**ABSTRACT:** To utilize renewable resource raw materials as well as trying to recycle polymeric materials, three new polyols (PEE1-3) were prepared from transesterification reaction of postconsumer poly(ethylene terephthalate) (PET), different molecular weights of poly(ethylene glycol) (PEG), and glycerine. The intermediate hydroxyl-terminated compounds were chain extended via esterification reaction with adipic acid (AA), and the products were reacted with castor oil (CO). These polyols were cured by blocked isocyanate (BIC) made from trimethylol propane, toluene diisocyanate, and *N*-methyl aniline. All of starting materials and final films were characterized by conventional methods. Curing condition was optimized via gel content mea-

surements. Crosslink density of samples was determined via equilibrium swelling method, using Flory–Rehner equations. Effects of structural parameters on physical, electrical, mechanical, and dynamic mechanical (DMTA) properties of the polyurethane coatings were investigated. Comparison of results with commercially available product shows that the prepared green coatings have environmental benefits as well as high performance for metal insulator coatings too. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1853–1859, 2007

**Key words:** renewable resources; recycling; polyurethanes; coatings; electrical insulators

## INTRODUCTION

Polyurethane varnishes for enameled wire are widely used in the electrical industry, in particular, for obtaining solderable enameled wires. The excellent dielectric properties of the polyurethanes film combined with their excellent physical properties provide a superior insulating system. Chemical structure of polyurethanes is a determining factor that affects the properties of final polymers. Especially, the nature of polyol used for the preparation of polyurethanes can considerably influence physical properties.<sup>1,2</sup>

Polyester polyol made from glycolization of poly(ethylene terephthalate) (PET) wastes with different alcohols is one of the most important classes of low cost polyol suitable for production of different kinds of polyurethane products. PET is extensively used for making different articles. Nowadays, more attention is paid in the management of waste plastics, and PET waste has become one of the most valuable recyclable materials today.<sup>3</sup> PET waste can be depo-

lymerized by glycolysis by glycols in the presence of catalysts to obtain oligomeric polyols. The polyols can be used for the preparation of value-added products such as polyurethanes.<sup>4–12</sup>

Vegetable seeds oils have been actively utilized to develop various valuable resins.<sup>13–20</sup> Such resins have found extensive applications as varnishes and surface-coating materials as long with their other applications. Among vegetable oils, castor oil represents a promising raw material based on its low-cost, low toxicity, and its availability as a renewable agricultural resource. Its uniqueness stems from both unsaturation and nonconjugated hydroxyl functionality.

Major constitution of castor oil is used commercially in large amounts, ricinoleic acid (12-hydroxy-*cis*-9-octadecenoic acid), is a hydroxyl fatty acid.<sup>21</sup> The ricinolate can also enhance the performance of the other polyols when blended for specific properties. A high level of compatibility with these compounds can improve electrical insulation, environmental stability, chemical resistance, and physical properties.

There are several reports concerning the use of castor oil (CO) and its derivatives for the preparation of polyurethane compounds such as IPNs,<sup>22–32</sup> cast elastomers,<sup>32–39</sup> and polyurethane-insulating coatings.<sup>40–42</sup>

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In this work, novel kind of (PEE1-3) were developed by glycolization and transesterification of the mixture of PET, different molecular weight of PEG, and CO and postesterification with AA. Then the prepared (PEE1-3) were used as the starting material for the preparation of one component polyurethane coatings (ASTM type III polyurethane coatings).

## EXPERIMENTAL

### Materials

CO from SIGMA chemical company (St. Louis, MO) was dried at 80°C in a vacuum oven for 24 h before use. Three polyethylene glycols with average molecular weight 150 (PEG 150), 200 (PEG 200), and 300 (PEG 300) from MERCK (Whitehouse Station, NJ) were dried under vacuum at 80°C for 24 h. Toluene diisocyanate (TDI) (mixture of 80% 2, 4, and 20% 2,6 isomer) from MERCK was vacuum distilled before use. Postconsumer PET bottles with a number-average molecular weight ranging from 18,000–20,000 were cleaned, dried, and chipped. Dimethyl formamide (DMF) was distilled under vacuum over CaH<sub>2</sub>, and kept over 4 Å molecular sieves. Xylene was refluxed over sodium wire and then distilled and kept over 4 Å molecular sieves. Other materials and solvents were used as received.

### Characterization

FTIR spectra were obtained on a Bruker IF 548 instrument. <sup>1</sup>H NMR spectra were recorded on a Bruker instrument, model AVANCE DR X500, in CDCl<sub>3</sub> as solvent. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a Stanton STA780 with a heating rate of 10°C/min in air atmosphere. Tensile properties were determined from stress-strain curves with MTS tensile tester model 10/M at a strain rate 5 mm/min. The measurements were performed at 25°C with a film thickness of about 1 mm and stamped out with an ASTM D638 Die. Dynamic mechanical testing (DMTA) were carried out on a UK polymer lab dynamic mechanical ther-

mal analyzer model MKII over a temperature range of -100 to 300°C at a heating rate of 10°C/min, and frequency of 1 Hz. The dimensions of samples were 30 × 10 × 1 mm<sup>3</sup>. Molecular weight measurements were performed on a gel permeation chromatography instrument (GPC) model Waters 150 C in tetrahydrofuran (THF) as solvent. Evaluation of break down voltage was performed on a high voltage kite with 2 kV/s voltage increasing rate and a spherical electrode of 5 cm diameter and 50 Hz frequency. Dissipation factor (DF) and dielectric constant measurements were performed on one Schering bridge device Tettexag 2801 ZQ. Samples were cut into circular shape pieces of 5-cm diameter. The measurements were performed according to ASTM 149-94 and ASTM 150-94 under air atmosphere at 25°C. Pencil hardness of samples was evaluated according to ASTM D3363-92a. Adherence of coating to copper wire and solderability of coated magnet wire were evaluated according to CEI/IEC Standard, 2000, 60317-0-1, and CEI/IEC Standard, 2000, 60317-2, respectively. Density of samples was measured according to ASTM-D1817. Hydroxyl value and acid value measurements were conducted according to the procedure of ASTM D 4276-94 and ASTM D 4662-93, respectively.

### General procedure for preparation of PEE1-3

In a three-necked round-bottomed flask equipped with magnetic stirrer, reflux condenser, Dean-Stark trap, and N<sub>2</sub> gas inlet and outlet was placed crushed PET, PEG (with different molecular weight), glycerine, and zinc acetate. The mixture was stirred for 4 h at 220°C, and evolved ethylene glycol was collected in Dean-Stark trap. Then, an esterification reaction was performed with AA for 4 h at 220°C. Temperature was reduced to 190°C and required amount of CO was added to the flask. Dean-Stark trap was replaced with a vacuum inlet tube and the reaction was continued for another 2 h at 190°C under vacuum. The product was cooled to room temperature and filtered to remove any unreacted PET species.

The amounts of different starting materials for the preparation of PEE1-3 are collected in Table I.

TABLE I  
Different Formulations of PEE1-3

Polyol code	PEG150 (g)	PEG200 (g)	PEG300 (g)	Glycerine (g)	Caster oil (g)	PET (g)	Adipic acid (g)	OH No.	AC No.
PEE1	33	–	–	2.7	72	30	12	193.854	0.813
PEE2	–	44	–	2.7	72	30	12	161.54	1.71
PEE3	–	–	66	2.7	72	30	12	126.186	0.214

Zinc acetate (0.3 g) was added as catalyst to each formulation.

OH No., hydroxyl number (mg KOH/g polyol); AC No., acid number (mg KOH/g polyol).

**TABLE II**  
Molecular Weight Data of PEE1-3 Obtained from GPC

Polyol code	$M_n (\times 10^3)$	$M_w (\times 10^4)$	$D$
PEE1	5.86	1.16	1.98
PEE2	6.10	1.23	1.81
PEE3	6.25	1.41	1.87

### Synthesis of BIC curing agent

At first, TDI (26.1 g, 0.15 mol) was added to a four-necked glass reactor equipped with mechanical stirrer, reflux condenser, dropping funnel, and  $N_2$  inlet and outlet. Then, a solution of trimethylol propane (TMP; 6.74 g, 0.05 mol) dissolved in minimum amount of DMF was added dropwise to the reaction mixture via dropping funnel. The reaction kettle was maintained at  $45^\circ\text{C}$  for 2 h and then cooled to room temperature. *N*-methyl aniline (NMA; 16.4 g, 0.15 mol) was added to the reactor dropwise. The temperature was kept at  $45^\circ\text{C}$  and the reaction was continued until all the NCO groups were reacted. The end of reaction was detected by the disappearance of NCO peak at  $2270\text{ cm}^{-1}$  in FTIR spectrum of reaction mixture. The content of reactor was poured into the excess amount of distilled water and the precipitated white powder was filtered, washed with water, and dried in a vacuum oven at ambient temperature.

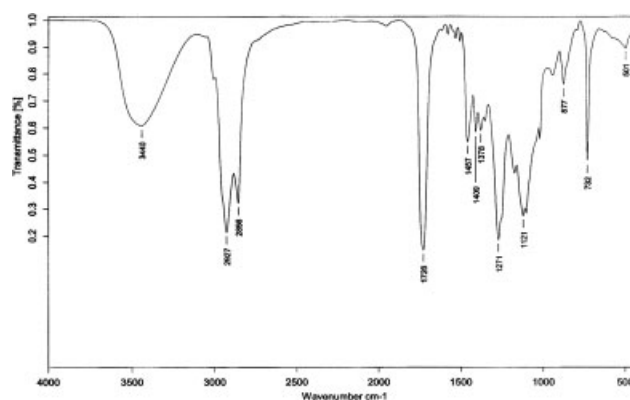
### Film casting

A 60% solid content solution of PEE1-3 and BIC in DMF/xylene (1/3 w/w) solvents mixture was prepared in an equivalent ratio of NCO and OH groups. Thin layer of solution was spread on a Teflon mould and heated at  $180^\circ\text{C}$  for 30 min.

The optimum temperature and time to reach maximum crosslinking were obtained via gel content measurements.

### Enamel wire coating

A 60% (w/w) solid content solution of PEE1-3 and BIC in DMF/xylene (1/3 w/w) solvents mixture was prepared, in such a way that equivalent ratio of NCO and OH groups present in the mixture. Then, an annealed, degreased copper wire (0.5 mm in diameter and 20 cm long) was dipped into the varnish bath and pulled through a small die (0.58 mm in diameter) at room temperature. Then, coated wire was placed in an air-circulated oven and heated at proper temperature and time. The procedure was repeated four times with the die slightly enlarged each time (0.60, 0.63, and 0.67 mm). The resulting polyurethane enamel wire had a diameter of 0.65 mm.



**Figure 1** FTIR spectrum of PEE1.

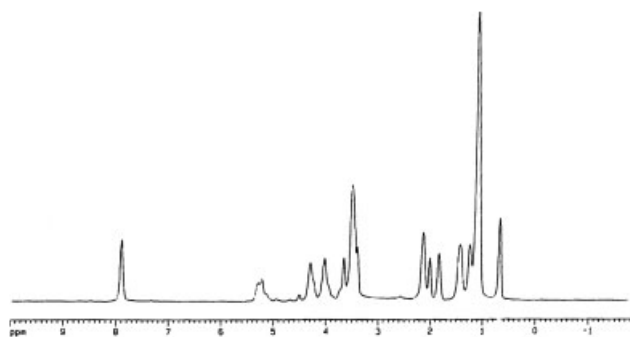
## RESULTS AND DISCUSSION

Preparation of PEE1-3 was conducted in three stages. At the first stage, excess amount of different molecular weight of PEG and glycerine were reacted with PET. At the second stage, esterification reaction of intermediate low molecular weight hydroxyl terminated PET oligomers was performed with AA. The product of this stage was hydroxyl-terminated polyester, which was participated in a transesterification reaction with CO.

The PEE1-3 polyols were subjected to hydroxyl value and acid value measurements as well as molecular weight determination by GPC method. The results are presented in Tables I and II.

The investigation of Tables I and II shows that the prepared polyols have low free acid, which are undesired, since they affect the desired and aspired hydrophobicity of the product. So, these polyols are excellent candidates for the preparation of polyurethane compositions especially for coatings and casting applications.

FTIR spectra of PEE1-3 compounds showed a broad peak at  $\sim 3400\text{ cm}^{-1}$  relating to hydroxyl functionality. Stretching vibration of ester carbonyl appeared at  $1726\text{ cm}^{-1}$ , ester bond appeared at  $1271\text{ cm}^{-1}$ , and ether bonds appeared at  $\sim 1120\text{ cm}^{-1}$ . Alkenyl stretching bond appeared at about  $3050\text{ cm}^{-1}$ .



**Figure 2**  $^1\text{H}$  NMR spectrum of PEE1.

TABLE III  
Composition of Final Formulations for Preparation of Cured Samples

Sample code	Polyol	NCO/OH	Polyol (g)	Curing Agent (g)	Xylene (g)	DMF (g)
XPEE1	PEE1	1/1	1	0.948	1.196	0.399
XPEE2	PEE2	1/1	1	0.734	1.064	0.355
XPEE3	PEE3	1/1	1	0.885	1.157	0.386

Symmetrical stretching vibration of methylene groups in the backbone of polyols appeared at about  $2856\text{ cm}^{-1}$ , and the unsymmetrical stretching vibration of these groups appeared at about  $2927\text{ cm}^{-1}$ . Peaks due to carbon-carbon double bonds from benzene rings were also appeared at about  $1580$ ,  $1460$ ,  $1060$ , and  $730\text{ cm}^{-1}$ . Representative FTIR spectrum of PEE1 is shown in Figure 1.

At  $^1\text{H NMR}$  spectra of PEE1-3 polyols, the terminal methyl groups of ricinoleate part of CO were appeared at  $0.71\text{ ppm}$ . Methylene groups in the part of aliphatic CO and middle methylene groups of adipate ester were appeared at  $1.13$ – $1.47\text{ ppm}$ . Allylic protons of seven carbon moieties of CO and allylic protons attached to CHOH groups of ricinoleate parts of CO were detected at  $1.8$  and  $2.02\text{ ppm}$ , respectively. Methylene groups connected to ester carbons of ricinoleate and adipate were appeared at  $2.17\text{ ppm}$ . Methylene groups of PEG moieties were detected as a strong peak at  $3.44$ – $3.7\text{ ppm}$ . Other methylene groups attached to ester oxygen atom were detected at  $4.06$ – $4.55\text{ ppm}$ . Protons of carbon-carbon double bonds of CO were appeared as two

multiplets at  $5.1$ – $5.33\text{ ppm}$ , and finally the aromatic C—H bonds were appeared at  $7.99$ – $8.5\text{ ppm}$ . Representative  $^1\text{H NMR}$  spectrum of PEE1 is shown in Figure 2.

The BIC was used as curing agent for PEE1-3 (Table III). Upon heating, the BIC was deblocked and crosslinking was occurred due to the reaction of deliberated isocyanate groups of BIC with hydroxyl groups of PEE1-3 (Fig. 3). FTIR spectrum of XPEE1 as a representative example is presented in Figure 4. The optimum temperature and time to reach maximum crosslinking were obtained via gel content measurements. The measurements were conducted at different timings ( $15$ ,  $30$ ,  $45$ , and  $60\text{ min}$ ) for different temperatures ( $150$ ,  $180$ , and  $210^\circ\text{C}$ ). The best curing condition (higher gel content at minimum possible time) obtained at  $180^\circ\text{C}$  for  $30\text{ min}$  heating.

Determination of crosslink density was performed according to the Flory-Rehner equation.<sup>42–45</sup> The results are shown in Table IV. The investigation of these data showed that increasing of molecular weight of PEG, resulted in the reduction of hydroxyl value of PEE and consequently decreasing, amount

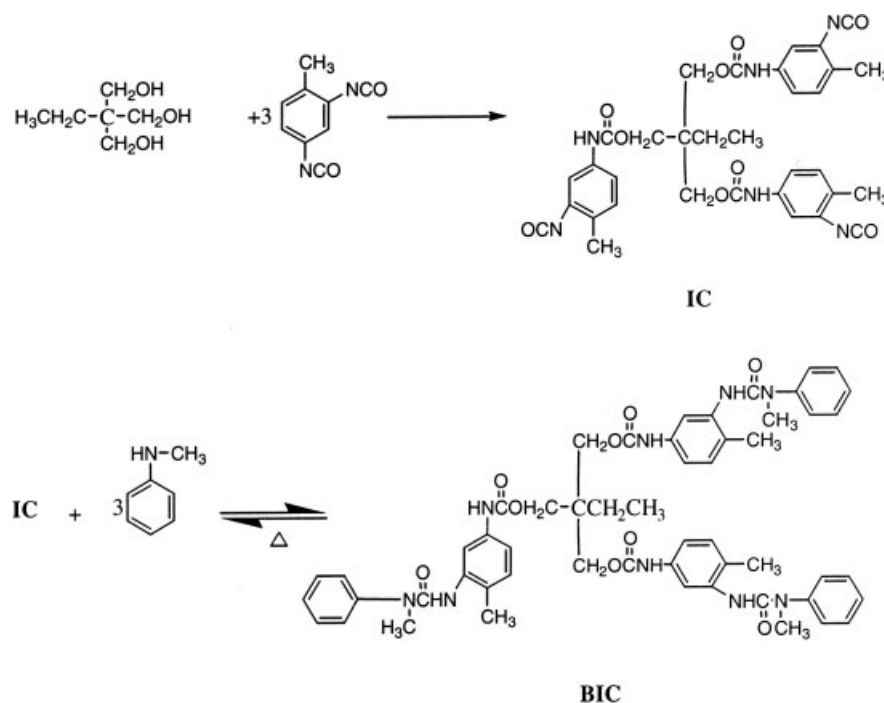
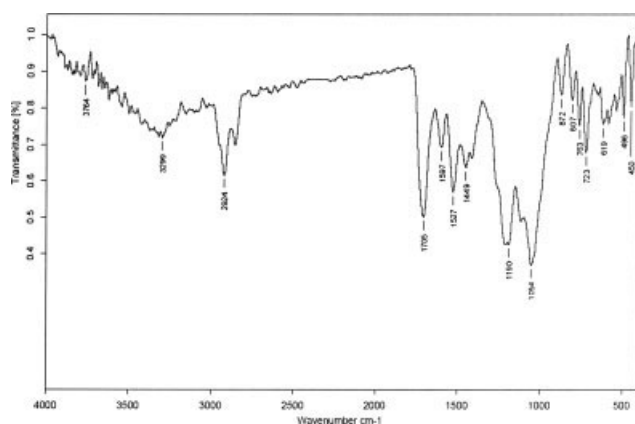


Figure 3 Synthetic route to BIC and deblocking of BIC upon heating.



**Figure 4** AT-FTIR spectrum (in reflectance mode) of XPEE1.

of available hydroxyl groups in a definite mass of PEE. Therefore, crosslink density of samples increased with increasing of hydroxyl value. Also,  $M_c$ , which is a measure of average molecular weight between crosslinked points, increased with decreasing of hydroxyl value of PEE.

Study of thermal stability of prepared coatings by TGA method (Table V) showed that regardless of the type of PEE, all samples undergo spontaneous decomposition at  $\sim 225^\circ\text{C}$ . The initial decomposition may correspond to aliphatic and etheric bonds, which are the weakest bonds of the prepared samples. The urethane linkage decomposes at  $\sim 275^\circ\text{C}$  leading to the formation of carbon dioxide, alcohols, and carbon monoxides. The decomposition beyond  $350^\circ\text{C}$  is related to castor oil with the formation of 10-undecanoic acid. The final decomposition may be related to the decomposition of ester bonds.

Mechanical property of the prepared films was determined by the analysis of stress-strain curves as shown in Figure 5, and tests data are collected in Table VI. According to the results, with the increasing of crosslink density, tensile strength, modulus, and elongation at break of samples were increased. Sample XPEE1 showed the behavior of a tough elastomers with yield point, followed with necking and drawing; however, the sample XPEE2 also showed the behavior of a tough elastomers but with weaker

**TABLE IV**  
Crosslink Density and Molecular Weight Between Crosslinked Point Data

Sample ID	$V_p$	$d_p$ (g/cm <sup>3</sup> )	$M_c$ (g/mol)	$v_c \times 10^3$ (mol/m <sup>3</sup> )
XPEE1	0.6092	1.0404	335.265	3.1032
XPEE2	0.5755	1.0534	351.347	2.9981
XPEE3	0.4398	1.4447	659.109	2.1919

$V_p$ , volume fraction of polymer in the swollen state;  $d_p$ , density of polymer;  $M_c$ , average molecular weight between two crosslinks;  $v_c$ , crosslink density.

**TABLE V**  
Thermal Stability Data of Cured Films

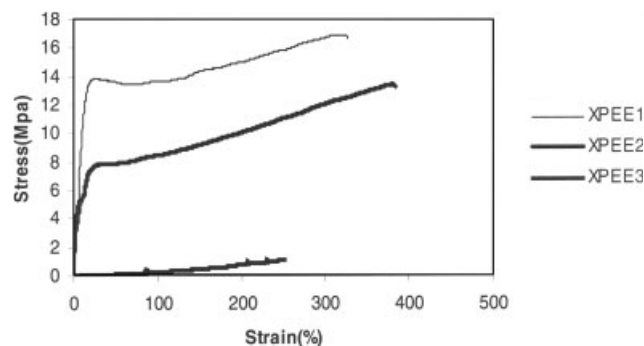
Samples	$T_{10\%}$ ( $^\circ\text{C}$ )	$T_{50\%}$ ( $^\circ\text{C}$ )	Char yield (%)
XPEE1	292	378	12
XPEE2	295	375	10
XPEE3	307	372	10

$T_{10\%}$ , temperature of 10% weight loss;  $T_{50\%}$ , temperature of 50% weight loss; Char yield (%), weight percent of remained polymer at  $600^\circ\text{C}$ .

characters and XPEE3 displayed a smooth transition in the stress-strain behavior from the elastic to plastic deformation regions similarly to lightly cross-linked weak rubbers.

Examination of DMTA curves (Figs. 6 and 7) of prepared samples showed that the modulus of plateau region increased with the decrease in PEG molecular weight (i.e., increase of crosslink density). Also,  $T_g$  peaks at  $\tan \delta$  curves shifted to higher temperature with the decrease in PEG molecular weight. Also, sharpness of  $\delta$  peaks, which is a criterion of phase separation, decreased with the decreasing PEG molecular weight (i.e., increasing of crosslink density).

Results of evaluation of electrical properties are collected in Table VII. In all electrical applications, it is desirable to keep the electrical losses at a minimum value. Electrical losses indicate the inefficiency of an insulator. The DF is a measure of such electrical inefficiency of insulating material. The DF indicates the amount of energy dissipated by the insulating material, when the voltage is applied. On the other hand, DF is a means of measuring dipole moment in a dielectric material. Dipole polarization occurs when normally oriented permanent dipoles of a molecule are aligned by an applied electric field. DF is an electrical characteristic that is related to the chemical structure and degree of crosslinking of polymers. For most polymers, DF decreases as the degree of crosslinking increase, because reactive polar groups are either neutralized or hindered by cross-

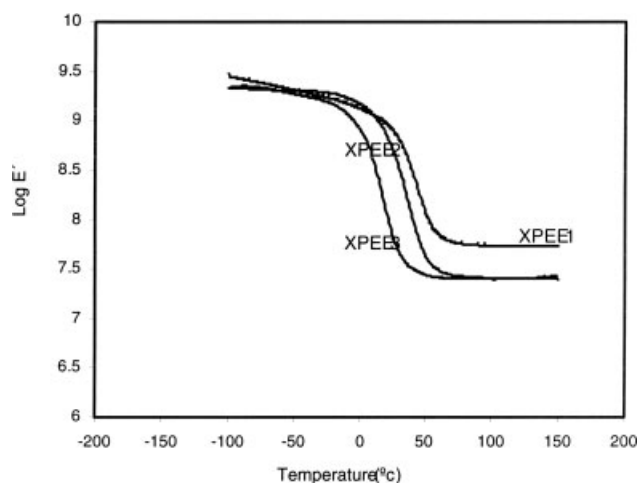


**Figure 5** Stress-strain curves of prepared cured films.

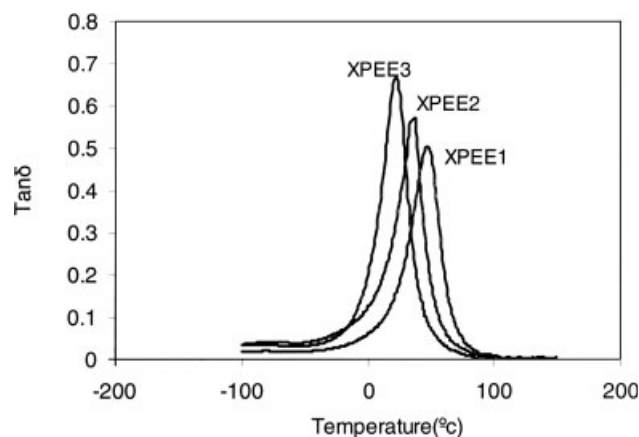
**TABLE VI**  
Mechanical Properties of Samples PEE1-3

Sample ID	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)
XPEE1	16.88	326.1	191.81
XPEE2	13.2	383.2	148.7
XPEE3	1.2	251.1	5.7

linking. Investigation of data collected in Table VI indicated that the DF values of prepared polymers were in the range of  $5.96 \times 10^{-5}$  to  $7.54 \times 10^{-5}$ , and by increasing of crosslink density, the value of DF decreased. Dielectric constant (permittivity) of an insulating material is defined as the ratio of the charge stored in an insulating material placed between two metallic plates to the charge that can be stored when the insulating material is replaced by air (or vacuum). Simply stated, the dielectric constant indicates the ability of an insulator to store electrical energy, and so it is desirable to have the capacitance of the insulating material as minimum as possible. The dielectric constant of prepared samples was in the range of 3.64–4.62, which is superior to common polyurethane insulator. The dielectric strength of an insulating material is defined, as the maximum voltage required producing a dielectric breakdown. Dielectric strength is expressed in volts per unit of thickness such as (V/cm). All insulators allow a small amount of current to leak through or around them. Only a perfect insulator, if there is such an insulator in existence, can be completely free from small current leakage. The small leakage generates heat, providing an easier access to more current. The process slowly accelerates with time and the amount of voltage applied until a failure in



**Figure 6** Storage modulus versus temperature curves for prepared cured films.



**Figure 7** Tan  $\delta$  versus temperature curves for prepared cured films.

terms of dielectric breakdown or what is known as puncture occurs. Obviously, dielectric strength, which indicates electrical strength of a material as an insulator, is a very important characteristic of an insulator. The higher the dielectric strength, the better the quality of an insulator. The measured value of  $\sim 31$  V/cm indicated the excellent insulating power of prepared polyurethane samples. Results of evaluation of electrical properties are collected in Table VII.

One desirable characteristic of polyurethane wire enamel is solderability without stripping. Solderability is a critical issue in automated processes. Measuring this factor for prepared samples indicated that the samples exhibited acceptable level of solderability at  $385^\circ\text{C}$  for 2 s that was examined via visual inspection of wire. The accepted specimens showed a continuous film of solder completely wetting the wire.

Investigation of chemical resistance by normal vision inspection of any change in appearance or loss of film integrity in different media confirmed that the samples showed excellent chemical resistance in acidic ( $\text{H}_2\text{SO}_4$ , 10%) and basic (NaOH, 1%) media. However, the samples underwent some degree of swelling in toluene and DMF media.

**TABLE VII**  
Electrical Properties of Samples

Sample	Thickness (cm)	Dissipation factor ( $\times 10^{-5}$ )	Dielectric constant (60 Hz)	Dielectric strength (V/cm)
XPEE1	0.85	5.96	3.64	32.2
XPEE2	0.95	6.59	4.06	31.1
XPEE3	0.9	7.54	4.62	30.8

DF, dissipation factor.

## CONCLUSION

A new category of cost feasible polyurethane insulating coating was prepared based one recycled materials (postconsumer bottle grade PET) and a renewable resource raw material (castor oil) via a simple synthetic method. The optimum curing condition as determined by gel content measurements indicated high degree of curing was achieved in 180°C for 30 min. Crosslink density measurements showed that with the decrease in the hydroxyl value of the PHC, crosslink density decreased. Evaluation of properties of final coatings showed that the prepared samples exhibited the combination of excellent mechanical properties as well as electrical insulation characteristics. Samples with higher crosslink density showed better electrical properties.

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