Novel Polyurethane Insulating Coatings Based on Polyhydroxyl Compounds, Derived from Glycolysed PET and Castor Oil

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ABSTRACT: To prepare versatile polyurethane material suitable as insulating coatings, novel kinds of polyhydroxy compounds (PHCs) were prepared via transesterification reaction of poly(ethylene terphthalate), different molecular weight of poly(ethylene glycol)s (PEGs), and castor oil. The final networks were prepared via crosslinking of PHCs with a novel blocked isocyanate curing agent (BPI) made from trimethylol propane (TMP), toluene diisocyanate (TDI), and *N*-methyl aniline (NMA). Polyols and curing agent were characterized by conventional methods and the curing condition was optimized via gel content measurements. Curing kinetic of the polyurethane network formation was investi-gated by differential scanning calorimetric method and the kinetic parameters were derived. Crosslink density of the samples was determined via equilibrium swelling method and by using Flory-Rehner equations. Effects of crosslink density on electrical, physical, mechanical, and dynamic mechanical (DMTA) properties of the polyurethane coatings were investigated. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1222–1233, 2006

Key words: polyurethane; insulating coating; crosslink density

INTRODUCTION

Because of special properties polyurethanes have found a wide range of applications as insulating materials in electrical industry. Coating of magnet wire with polyurethane varnishes is one of the most important uses of polyurethane insulating materials. The property, which has led to the popularity of polyurethane enameled magnet wire, is solderability at 360–425°C without the necessity of fluxing or stripping. Another feature of polyurethane insulated wire is its superior Q factor (reciprocal of dissipation factor (DF)).[1]

Desired levels of electrical insulation, environmental stability, and chemical resistance are all a function of the raw material building blocks chosen to formulate the polyurethane. Although the choice of isocyanate used will have various effects on the final performance of the polyurethane, by far the higher effect comes from the polyols. The polyol backbone can be completely hydrocarbon, polyether, polyester, or silicon in nature. Each of them have strong points, but rarely can they completely fulfill specific application requirements. Ricinoleate-based polyol, however, combines many of the strong points of the individual

polyols into the polyurethane compound.[2] castor oil (CO), which is a triglycerid of recinoleic acid, is one of the few commercially available glycerides. Its uniqueness stems from both unsaturation and nonconjugated hydroxyl functionality. There are several reports concerning the use of CO and its derivatives for the preparation of polyurethane compounds such as IPNs,[3–13] cast elastomers,[14–20] and polyurethane-insulating coatings.[21–23] In comparison with hydrocarbon and silicon-based polyurethanes, the ricinoleates give a better balance of chemical resistance and physical performance. They also outperform polyether-based compounds as an electrical insulator, have a better balance of chemical resistance, and have a better level of reactivity. 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.

On the other hand, many attempts have been made to decrease the cost of the polyurethane products by using inexpensive polyols. Polyester polyol made from glycolyzation of poly(ethylene terphthalate) (PET) wastes with different alcohols is one of the most important classes of low-cost polyol suitable for the production of different kinds of polyurethane products.[24–33]

In the present work novel kind of polyhydroxy compounds (PHCs) were developed by the glycolyza-

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tion and transesterification of a mixture of PET, different molecular weight of poly(ethylene glycol) (PEG), and CO. Prepared PHCs were then used as a starting material for the preparation of one component polyurethane coatings (ASTM type III polyurethane coatings). The synthesis and characterization of raw materials and final polyurethane coatings as well as physical, mechanical, and electrical properties of products were investigated.

EXPERIMENTAL

Materials and instruments

CO from Sigma chemical company was dried at 80°C in vacuum oven for 24 h before use. Triethylene glycol, polyethylene glycol 200 (PEG 200), and polyethylene glycol 300 (PEG 300) from Merck were dried under vacuum at 80°C for 24 h. toluene diisocyanate (TDI, mixture of 80% 2,4 isomer and 20% 2,6 isomer) from Merck was vacuum distilled before use. Postconsumed PET bottles with a number average molecular weight ranging from 18,000 to 20,000 were cleaned, dried, and chipped. Dimethyl formamide (DMF) was distilled under vacuum over CaH_2 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.

FTIR spectra were obtained on a Bruker IF 548 instrument. ^{1}HNMR spectra were recorded on a Bruker instrument, model AVANCE DR X500, using $CDCl_3$ as the solvent. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a Stanton STA 780, 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 of 5 mm/min. The measurements were performed at 25°C, with a film thickness of about 1 mm and stamped out with a ASTM D638 Die. Dynamic mechanical testing (DMTA) was carried out on a UK polymer lab dynamic mechanical thermal analyzer model MKII, over a temperature range of –100°C to 300°C, at a heating rate of 10°C/min and at a frequency of 1 Hz. The dimensions of the samples were $30 \times 10 \times 1$ mm^3. Molecular weight measurements were performed on a gel permeation chromatography instrument (GPC), model Waters 150C, using tetrahydrofuran as the 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 and dielectric constant measurements were performed using one Schering bridge device Tettexag 2801 ZQ. Samples were cut into circular shaped pieces of 5-cm diameter. The measurements were performed according to ASTM 149–94 and ASTM 150–94 under air atmosphere at 25°C. Hardness of the samples was evaluated with a pendulum hardness tester, using ERICHSEN instrument, according to ASTM D4366–94. 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, 60,317–0-1 and CEI/IEC Standard, 2000, 60,317–2, respectively. Density of the samples was measured on a six-column density measurement device of Davenport Company, with an accuracy of 0.0001 g/cm^3. Hydroxyl value and acid value measurements were taken according to the procedure of ASTM D 4276–94 and ASTM D 4662–93, respectively.

TABLE I
Different Formulations of PHC

Polyol	CO (g)	PEG (g)	PET (g)	Zinc acetate (g)
PHC-I	99	TEG (30)	30	0.3
PHC-II	99	PEG 200 (40)	30	0.3
PHC-III	99	PEG 300 (60)	30	0.3

PHC, polyhydroxy compound; CO, castor oil; PEG, poly-(ethylene glycol); PET, poly(ethylene terphthalate); TEG, Triethylene glycol.

General procedure for the preparation of PHCs

In a two-necked round-bottomed flask equipped with magnetic stirrer, reflux condenser, Dean-Stark trap, and N_2 gas inlet and outlet were placed crushed PET, polyethylene glycol, and zinc acetate. The mixture was stirred for 4 h at 220°C, and the evolved ethylene glycol was collected in Dean-Stark trap. Then temperature was reduced to 190°C and the 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 PHCs are listed in Table I.

Synthesis of BPI curing agent

In a four-necked glass reactor equipped with mechanical stirrer, reflux condenser, dropping funnel, and N_2 inlet and outlet was placed TDI (26.1 g, 0.15 mol). 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°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°C

TABLE II
Amount of Different Components Used for the Preparation of Polyurethane Samples

Sample ID	Polyol	NCO/OH	Polyol (g)	Curing agent (g)	DMF (g)	Xylene (g)	DBTDL (g)
Pu1	PHC-I	1.0	0.99	1.30	0.86	2.57	—
Pu2	PHC-I	1.1	0.99	1.43	0.9	2.72	—
Pu3	PHC-I	1.0	0.99	1.30	0.85	2.57	0.034
Pu4	PHC-II	1.0	1.01	1.30	0.86	2.59	—
Pu5	PHC-II	1.1	1.01	1.43	0.91	2.75	—
Pu6	PHC-II	1.0	1.01	1.30	0.86	2.60	0.034
Pu7	PHC-III	1.0	1.10	1.30	0.90	2.70	—
Pu8	PHC-III	1.1	1.10	1.43	0.95	2.85	—
Pu9	PHC-III	1.0	1.10	1.30	0.90	2.70	0.036

DMF, Dimethyl formamide; DBTDL, dibutyltin dilurate.

and the reaction was continued until all the NCO groups were reacted. The end of the reaction was detected by the disappearance of the NCO peak at 2270 cm^{-1} in FTIR spectrum of reaction mixture. The content of the 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 and curing

A 40% (w/w) solid content solution of PHC and BPI in DMF/xylene (1/3, w/w) solvent mixture was prepared in such a way that equivalent ratio of NCO and OH groups was present in the mixture. A layer of solution was spread over a Teflon mold and baked at a proper temperature for a given time. The free stand films obtained were used directly for subsequent physical property measurements.

In an attempt to investigate the effect of excess amount of NCO content (10% excess) and the effect of dibutyltin dilurate (DBTDL) catalyst on the curing condition, formulations concerning these two parameters were also prepared. The amount of different components for different formulations are shown in Table II.

Enamel wire coating

A 40% (w/w) solid content solution of PHC and BPI in DMF/xylene (1/3, w/w) solvent mixture was prepared in such a way that equivalent ratio of NCO and OH groups was 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 baked at a proper temperature for a particular time duration. 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.

RESULTS AND DISCUSSION

PHC was prepared in two stages. At the first stage excess amount of different molecular weight of PEG were reacted with PET and at the second stage CO was reacted with the glycolzed PET mixture. Several reactions may occur, which include (a) PEG hydroxyl with PET ester, forming PET hydroxyl, (b) Glycerol ester interchanges with PET hydroxyl to form a glycerol hydroxyl and a PET/CO copolymer, (c) CO hydroxyl and ester interchange, forming a glycerol hydroxyl and a fatty ester chain, (d) PET hydroxyl and ester interchange, forming higher molecular weight PET and difunctional hydroxyl compounds, and (e) Glycerol ester interchange with PEG hydroxyl to form a glycerol hydroxyl and PEG/CO copolymer.

The PHCs were subjected to hydroxyl value and acid value measurements as well as molecular weight determination by GPC method. The results are presented in Table III.

TABLE III
Characterization Data of PHC

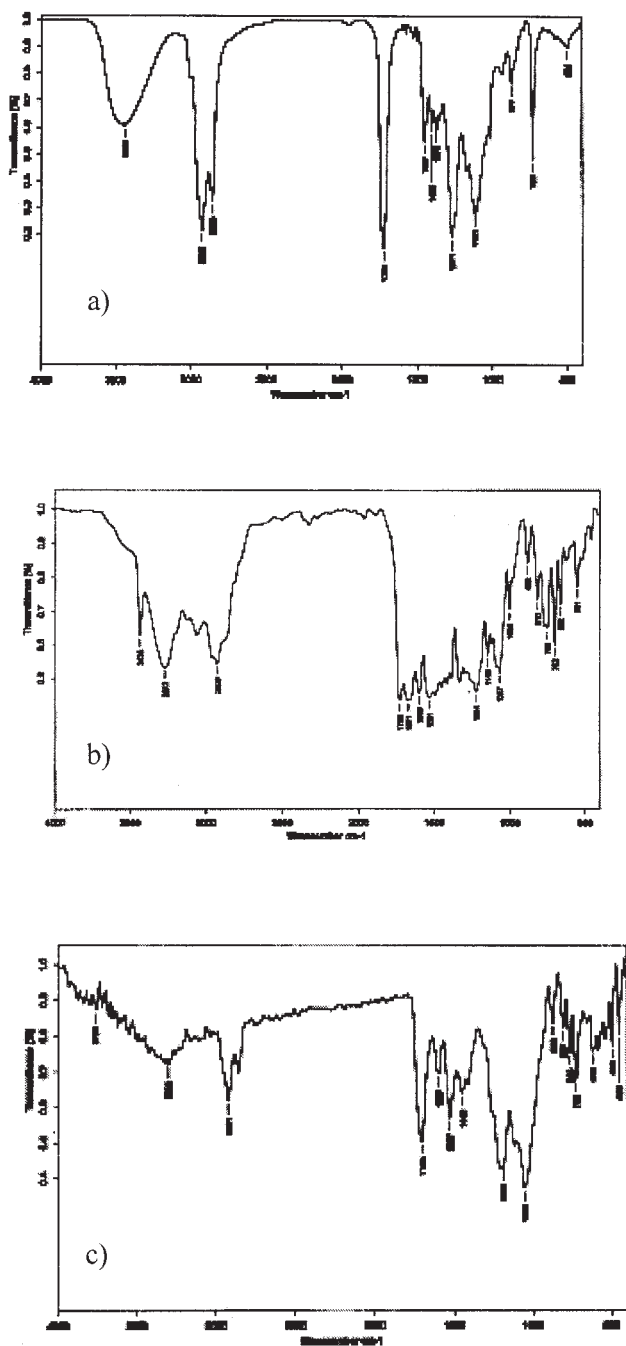| Polyol	OH value (mg KOH/g)	Acid Value (mg KOH/g)	OH equivalent weight	M_n (from GPC)
PHC-I	219.75	6.82	247.60	963
PHC-II	216.16	5.88	252.66	977
PHC-III	198.79	4.83	275.50	1004

**Figure 1** FTIR spectra of (a) PHC-I, (b) BPI, and (c) Pu-1.

The low molecular weight values indicated that the possibility of condensation reactions leading to high molecular weight compounds was low and the major reaction was transesterification reaction of different kinds of hydroxyl and ester groups present in the reaction mixture.

FTIR spectra of polyhydroxyl compounds showed a broad peak at ca. 3400 cm^{-1}, relating to hydroxyl functionality. Stretching vibration of ester carbonyl group appeared at 1726 cm^{-1} and that of etheric bonds appeared at ca. 1100 cm^{-1}. Alkenyl stretching bond appeared at about 3050 cm^{-1} [Fig. 1(a)].

^{1}HNMR spectra showed characteristic alkenyl protons at 5.41–5.54 ppm. Methylene moieties present in PEG, PET, and CO appeared at 0.87–4.47 ppm, depending on their vicinity to other functional groups present in the PHC structures. Aromatic protons corresponding to PET phenyl rings appeared at 8.1–8.13 ppm. Disappearance of the corresponding tertiary hydrogen of CO at 8.9 ppm is an indication that CO is being completely transesterified.

The synthetic route for the preparation of polyisocyanate is outlined in Scheme 1. The reaction of one equivalent TMP with three equivalents TDI leads to an intermediate compound (PI), which subsequently reacted with three equivalents of NMA to give BPI. FTIR spectrum of BPI showed a peak at 1729 cm^{-1} related to urethane carbonyl (NHCOO), and an intensive peak at 1671 cm^{-1} related to urea carbonyl (NHCONH) groups. A peak at 3272 cm^{-1} was related to hydrogen bonded urea/urethane N—H bonds, and another one at 3436 cm^{-1} was related to nonhydrogen bonded urea/urethane N—H bonds [Fig. 1(b)]. ^{1}HNMR spectrum of BPI showed two distinct triplet and quartet peaks at 0.91–0.94 ppm and 1.49–1.52 ppm due to ethyl group protons of TMP part. The methyl groups from TDI showed a singlet at 2.10 ppm and those from NMA showed a singlet at 2.40 ppm. The methylene groups attached to urethane linkage showed a singlet at 4.15 ppm. The aromatic C—H bond appeared as a multiplet at 6.76–7.80 ppm, and urea and urethane protons appeared at 6.1 and 8.02 ppm, respectively.

In blocked isocyanates chemistry, the charge difference between carbonyl carbon and blocking agent is of great importance. The greater the charge difference, the greater will be the strength of the bond, and if the blocking agent is less nucleophilic, the negative charge density of the blocking agent will be less, which makes the bond more liable. Such a charge separation is
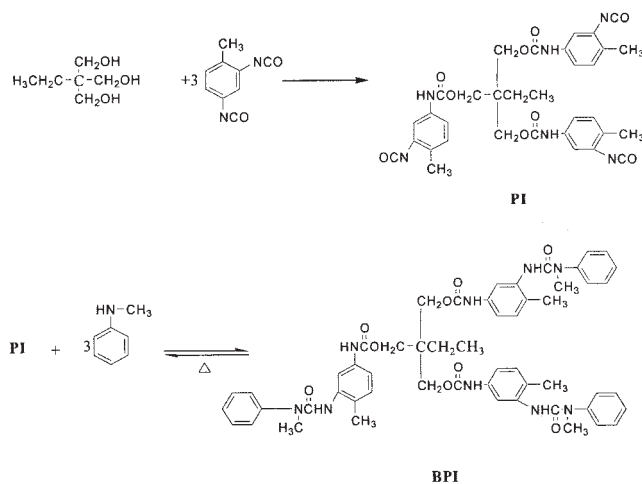
Scheme 1 Synthetic route for the preparation of curing agent.
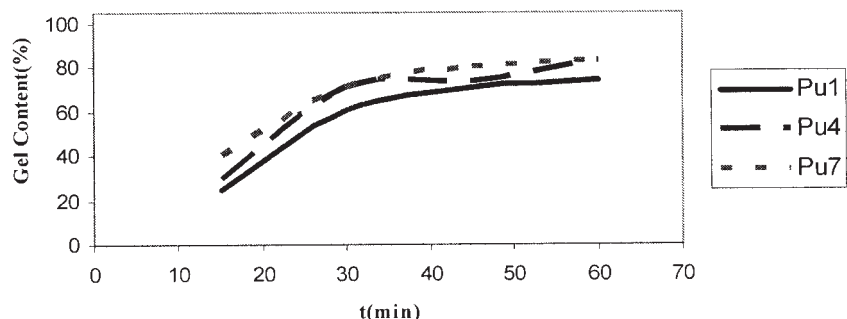
Figure 2 Gel content of the samples cured at different time at 150°C.

apparently more in the NMA-blocked system in comparison with the phenol-blocked system; the methyl group intensifies the negative charge. Hence, deblocking is expected to be difficult in NMA-blocked system. However, it was found that NMA-blocked isocyanate was deblocked at much lower time and temperature. A possible explanation to this phenomenon is that the tertiary nitrogen present in the NMA-blocked isocyanate autocatalyzes the deblocking through the formation of an intermolecular four-centered complex and, hence, reduces the reaction temperature and time.[35,36] Another feature of NMA-blocked polyisocyanate is that the released amine will catalyze urethane formation in subsequent reactions.

The BPI was used as the curing agent for PHC. Upon heating, the BPI was deblocked and crosslinking occurred because of the reaction of deliberated isocyanate groups of BPI with the hydroxyl groups of PHC. FTIR spectrum of Pu-1 as a representative example is presented in Figure 1(c). The optimum temperature and time to reach maximum crosslinking was obtained via gel content measurements.[37] Gel content measurements were performed in a soxhlet extractor, using acetone as solvent. As the noncrosslinked part of final coatings are soluble in acetone, the gel content is a measure of acetone insoluble content of final coatings. The measurements were conducted at different times (15, 30, 45, and 60 min) for different temperatures (150, 180, and 210°C). Results are illustrated in

Figures 2–4. The investigation of these figures showed that at 150°C insufficient degree of crosslinking was obtained. At 210°C, although high degree of crosslinking was achieved at lower time, after passing through definite time, degradation of samples occurred. Also, all the samples obtained at 210°C showed some degree of discoloration. The best curing condition (higher gel content at minimum possible time) was obtained at 180°C for 30 min of heating.

Using excess amount of curing agent led to the increase of gel content. This phenomenon is a result of the formation of extra allophanate bonds via the reaction of isocyanate groups of curing agent with urethane N—H groups. These samples (Pu2, Pu5, and Pu8) showed decreased flexibility. The results also indicated that the use of DBTDL catalyst could increase the rate of network formation during the initial heating period. However, prolonged heating of these samples (Pu3, Pu6, and Pu9) led to the decrease of gel content. It seems that DBTDL can also activate the depolymerization reaction of urethane bonds at elevated temperature (Figs. 5–7).

Determination of crosslink density was performed according to the Flory-Rehner equation.[37–39] The equilibrium degree of swelling (Q), which is the reciprocal of volume fraction of polymer in the swollen state (V_P), was calculated from the swelling data of polyurethane samples in various solvents, using the following relations:
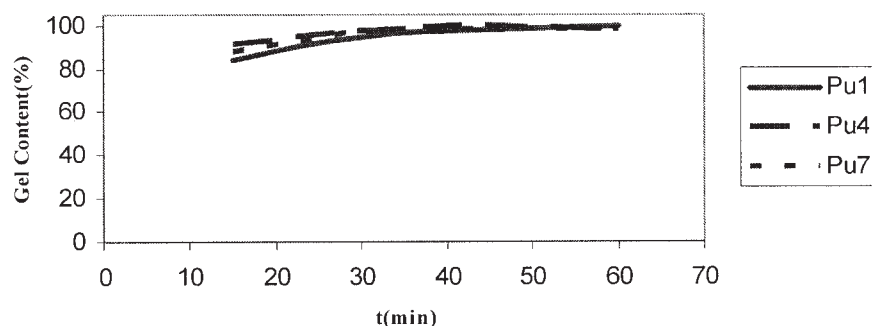

Figure 3 Gel content of the samples cured at different time at 180°C.
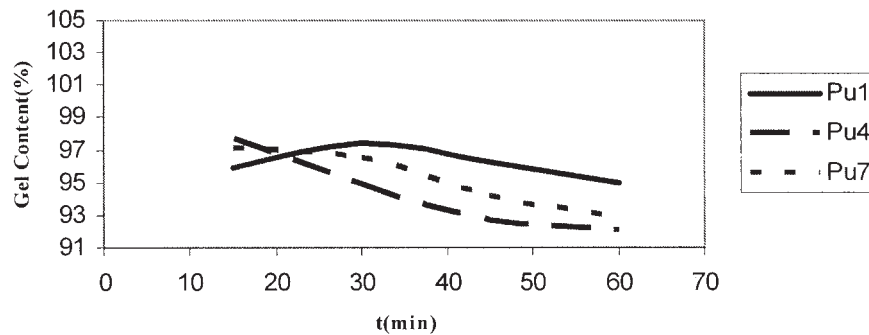
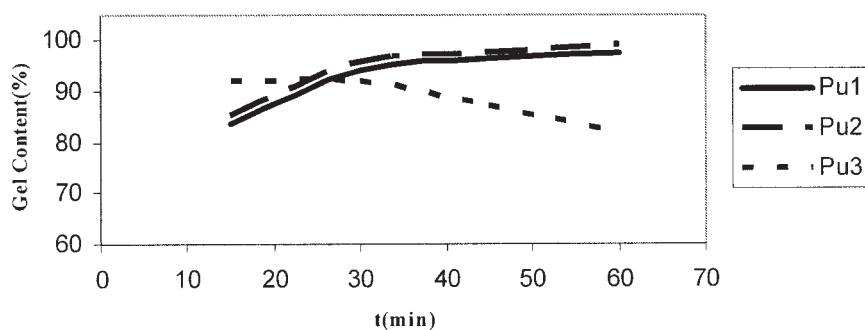**Figure 4** Gel content of the samples cured at different time at 210°C.

Figure 5 Gel content of the samples prepared using excess amount of isocyanate curing agent and DBTDL catalyst at 180°C for PHC-I.
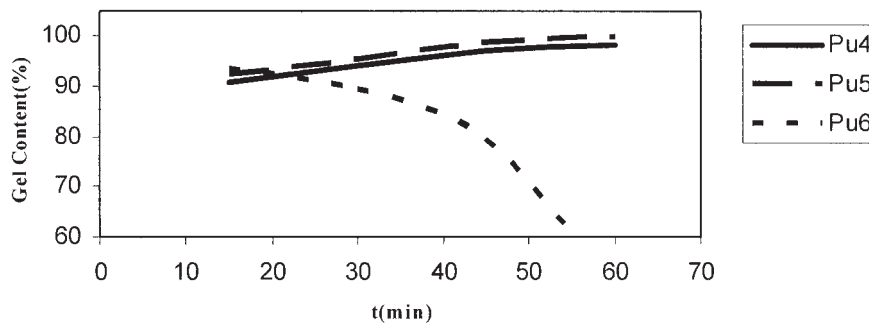

Figure 6 Gel content of the samples prepared using excess amount of isocyanate curing agent and DBTDL catalyst at 180°C for PHC-II.
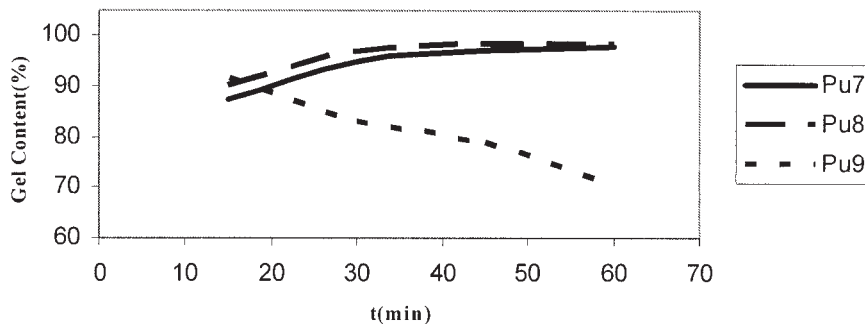

Figure 7 Gel content of the samples prepared using excess amount of isocyanate curing agent and DBTDL catalyst at 180°C for PHC-III.
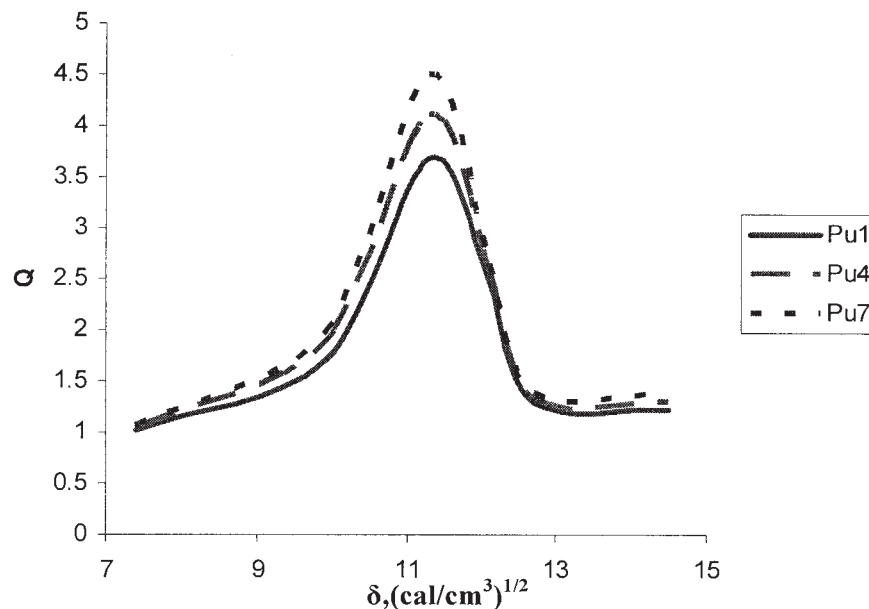
Figure 8 Equilibrium degree of swelling vs. solubility parameter of the solvents.

$$V_P = \frac{W_P/d_P}{W_P/d_P + W_S/d_S} \quad (1)$$

$$Q = \frac{1}{V_P} \quad (2)$$

where, W_P is the weight of dry polymer; W_S, weight of the solvent taken up at equilibrium; d_p, density of the polymer; d_s, density of the solvent; and Q is the equilibrium degree of swelling.

To determine the solubility parameter of polyurethane samples, Q was plotted against solubility parameter (δ) of different solvents. From the plot it was found that N-methyl pyrrolidone gave a maximum value of Q at 11.3 $(cal/cm^3)^{1/2}$ for all the samples (Fig. 8).

Measurements of crosslink density were performed using toluene as the solvent at 25°C, according to Flory-Rehner equation:

$$M_C = \frac{v_S d_P(V_P^{1/3} - V_P/2)}{\ln(1 - V_P) + V_P + \chi_{12} V_P^2} \quad (3)$$

$$v_C = \frac{d_P}{M_C} \quad (4)$$

where, v_c is the crosslink density; M_c, the average molecular weight between crosslinks; and χ_{12}, the polymer–solvent interaction parameter that was calculated using

$$\chi_{12} = 0.34 + \frac{V_S(\delta_P - \delta_S)^2}{RT} \quad (5)$$

where, V_S is the molar volume of solvent; δ_p, the solubility parameter of polymer; δ_s, the solubility parameter of solvent; R, gas constant; and T is the absolute temperature.

The results are shown in Table IV. The investigation of these data showed that increasing molecular weight of PEG resulted in the reduction of hydroxyl value of PHC and consequently decreases the amount of available hydroxyl groups in a definite mass of PHC. So, crosslink density of samples increased with increasing hydroxyl value. Also M_c, which is a measure of aver-

TABLE IV
Crosslink Density and Molecular Weight Between Crosslinked Point Data

Sample ID	NCO/OH molar ratio	V_p	d_p (g cm^{-3})	M_c (g mol^{-1})	v_c (mol ml^{-1}) $\times 10^3$
Pu1	1.0	0.61	1.1771	380	3.10
Pu4	1.0	0.55	1.1862	412	2.88
Pu7	1.0	0.50	1.1900	459	2.60
Pu2	1.1	0.65	1.1780	377	3.12
Pu5	1.1	0.60	1.1870	386	3.07
Pu8	1.1	0.55	1.1950	415	2.88

TABLE V
Mechanical Properties of Samples Pu1, Pu4, and Pu7

Sample ID	Tensile strength (MPa)	Elongation at break (%)	Modulus (MPa)	Pendulm hardness (s)	Pencil hardness
Pu1	46.90	8.00	1012.69	(148 ± 2)	HB
Pu4	28.00	11.20	903.37	(120 ± 2)	B
Pu7	19.45	23.83	634.89	(70 ± 2)	2B

age molecular weight between crosslinked points, increased with decreasing hydroxyl value of PHC.

The measurements showed that the use of excess amount of isocyanate curing agent resulted in the increase of crosslink density in comparison with that of the other samples. Results are listed in Table IV.

Mechanical property data as determined by stress–strain analysis were summarized in Table V. According to the results, with increasing crosslink density, tensile strength and modulus of samples were increased and in turn the elongation at break of samples was decreased. Hardness of the samples was evaluated by two methods: (a) pencil hardness and (b) pendulum hardness. The pendulum-damping test has been found to have good sensitivity in detecting the differences in coating hardness, where hardness is defined as resistance to deformation. It can be concluded that the increasing crosslink density caused an increase of sample hardness (Table V).

Segmented polyurethanes show phase-separated morphology. For these materials, better phase separation and more developed reinforcing hard domain structures will improve the physical and mechanical properties. However, introduction of nodes destroy phase-separation morphology. An important consideration in the interpretation of this behavior is the actual site of crosslinking. Cooper[40] confirmed that, in small amount of degree of crosslinking, whenever crosslinking occurred through hard segments, kinetic theory of elasticity was not obeyed. On the other hand, plateau modulus decreased with increasing crosslink density. However, with increasing crosslinking level, predicted behavior of rubber elasticity was observed. The phenomenon can be attributed to the poor association of hard segments, since packaging of the segments is disrupted in all crosslink points. The study of DMTA curves of prepared samples (Fig. 9) showed that modulus of plateau region increased with increasing crosslink density. This phenomenon indicated that the level of crosslinking was high enough to observe the behavior predicted by the kinetic theory of rubber elasticity. It is not unusual to see a peak or hump on the storage modulus directly preceding the drop that corresponds to T_g. The hump seen in Figure 8 in the T_g region is related to a rearrangement in the molecule so as to releive stresses frozen below the T_g by the processing method.[41] Also, width of plateau regions increased with increasing crosslink density. Investigation of loss tangent curves (Fig. 10) showed that tan δ curves of the samples increased with temperature. As the crosslink density increased, the α-type transition peak shifted to higher temperatures. Also, sharpness of tan δ peaks, which is an indication of the amount of phase separation, decreased with increasing crosslink density.[42]
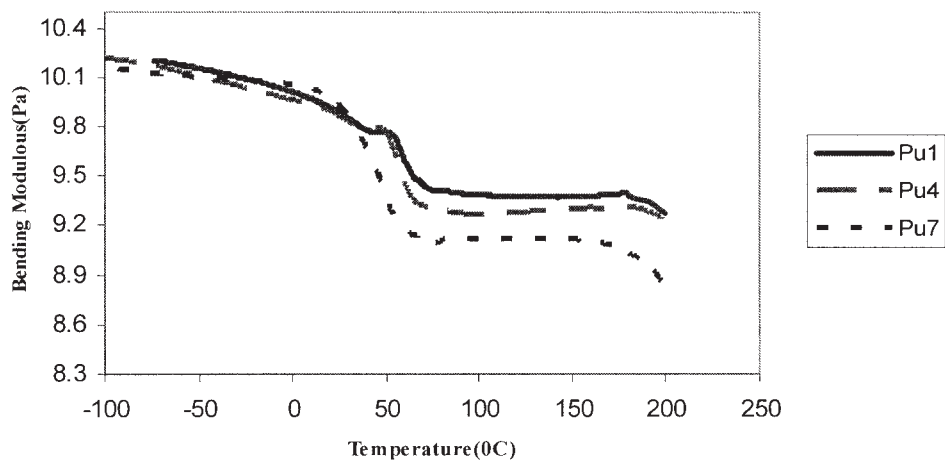

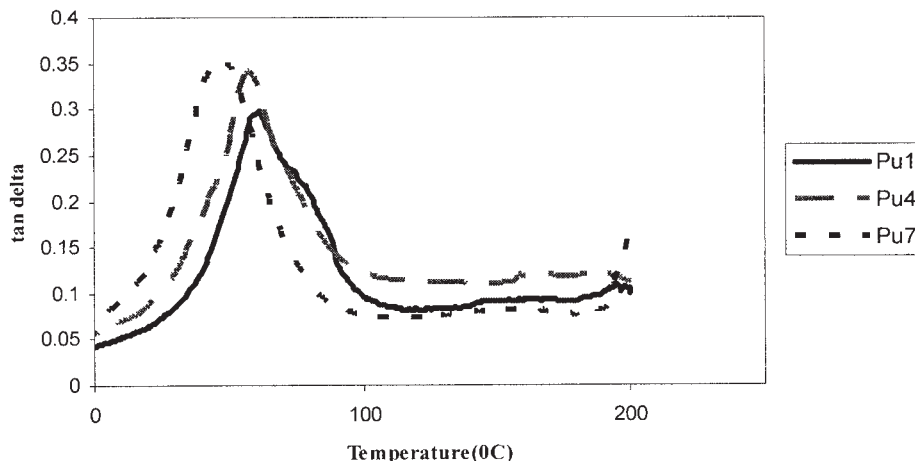**Figure 9** Storage modulus vs. temperature of samples Pu1, Pu4, and Pu7.

Figure 10 Tan δ vs. temperature of samples Pu1, Pu4, and Pu7.

TGA study showed that regardless of the type of PHC, all samples undergo spontaneous decomposition at ~250°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 ~270°C, leading to the formation of carbon dioxide, alcohols, amines, and carbon monoxides. The decomposition beyond 350°C is related to castor oil, with the formation of 10-undecanoic acid. The final decomposition may be related to decomposition of ester bonds. Results are presented in Table VI.

Determination of kinetic parameters of curing reaction was performed by DSC analysis. A model based on autocatalytic reaction was used to describe the curing behavior of the system.[43–44] The rate equation is given by

$$d\alpha/dt = A\exp\left(\frac{-E}{RT}\right)\alpha^m(1-\alpha)^n \qquad (6)$$

where, α is the conversion; A, the preexponential factor; E, the activation energy; R, universal gas constant; T, absolute temperature; and m and n are orders of the reaction.

The heat evolved during the curing reaction, which is measured by the dynamic DSC method, can be related to the conversion and conversion rate by

TABLE VI
Thermal Properties of Samples Pu1, Pu4, and Pu7

Sample ID	T_g (°C)	T 10% (°C)	T 50% (°C)	Char yield at 600 °C (%)
Pu1	61	262	345	8.0
Pu4	57	267	326	3.8
Pu7	47	272	320	8.7

$$Qt = \int_o^t \frac{dH}{dt}dt = \frac{1}{\beta}\int_{T_z}^T \frac{dH}{dt}dT \qquad (7)$$

$$\alpha = \frac{Qt}{\Delta H} \qquad \frac{d\alpha}{dt} = \frac{1}{\Delta H}\frac{dQt}{dt} \qquad (8)$$

where, Qt is the reaction heat up to time t or temperature T; dH/dt, the rate of heat evolution per unit mass of resin at time t (which is related to the scanspeed $\beta = dT/dt$); and ΔH is the total heat of reaction for 100% conversion.

It should be noted that the polymerization starts after the complete depletion in the system ($t = 0$ correspond to $T = T_z$). Equation (6) can be expressed in logarithmic form as follows:

$$\ln\frac{d\alpha}{dt} = \ln A - \frac{E}{RT} + m\ln\alpha + n\ln(1-\alpha) \qquad (9)$$

By integrating the DSC curve (Fig. 11), the total reaction heat $\Delta H = 39.52$ cal/g was calculated. Multiple regression technique was used to derive coefficients of eq. (9). Results are shown in Table VII. Figures 12 and 13 illustrate the conversion and conversion rate vs. temperature for the curing reaction at a scan rate of 10°C/min. The dashed lines represent the calculated values obtained from eq. (9) with aforementioned kinetic parameters, whereas the solid lines are obtained directly from the DSC curve data by using eqs. (7) and (8). According to the results, it can be concluded that experimental data agree very well with the theoretical prediction.

Results obtained by evaluating the electrical properties are given in Table VIII. In all electrical applications, it is desirable to keep the electrical losses at a minimum value. Electrical losses indicate the ineffi-
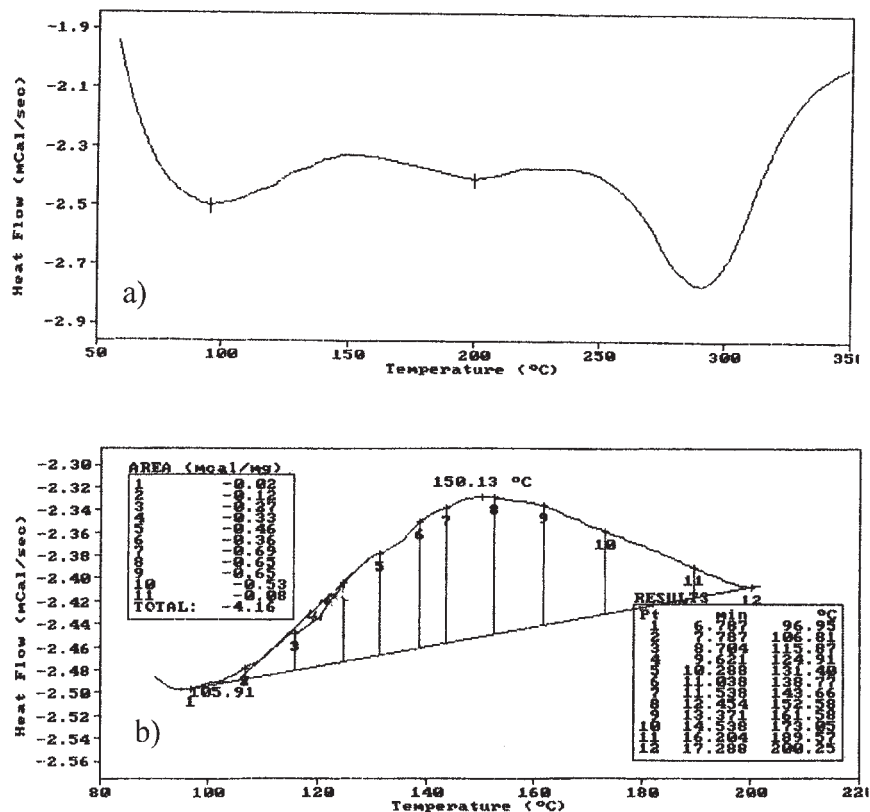
Figure 11 (a) DSC curve of curing reaction and (b) integrated curing exotherm.

ciency of an insulator. The DF is a measure of such an electrical inefficiency of the 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 the degree of crosslinking of polymers. For most polymers, DF decreases as the degree of crosslinking increases, because reactive polar groups are either neutralized or hindered by crosslinking. Investigation of data given in Table VIII indicated that the DF values of prepared polymers were in the range of (0.0082–0.0283), and by increasing the 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 the prepared samples was about 5, which is superior to that of the common polyurethane insulator. The dielectric strength of an insulating material is defined as the
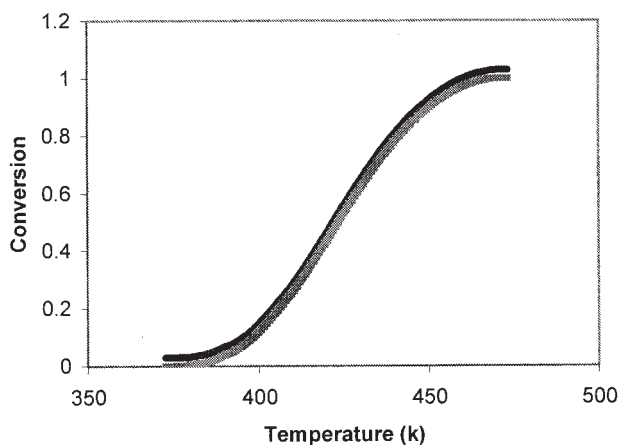
TABLE VII
Curing Kinetic Parameters of sample Pu7

Sample ID	m	n	E (cal/mol)	$\ln A$	r^2
Pu7	0.41	0.94	7846	4.66	0.97

Figure 12 Conversion (α) vs. temperature for experimental (solid line) and theoretical (dashed-line) data.

maximum voltage required to producing a dielectric breakdown. Dielectric strength is expressed in volts per unit of thickness such as (V/mil). 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 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 ca. 2000 V/mil indicated the excellent insulating power of the prepared polyurethane samples.[1,45]

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

Another important characteristic of polyurethane wire enamels is the adherence of coating to the substrate. The samples showed good adherence to copper wire. On the other hand, flaking of samples upon stretching was not observed.

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 (H_2SO_4, 10%) and basic (NaOH, 1%) media. However, the samples underwent some degree of swelling in toluene and DMF media.[46]
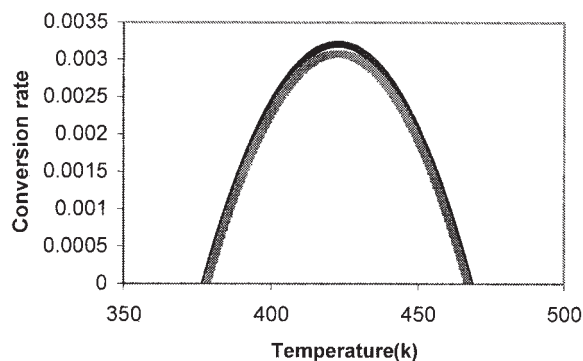
TABLE VIII
Electrical Properties of Samples Pu1, Pu4, and Pu7

Sample ID	Thickness (mil)	Dissipation factor (60 Hz)	Dielectric constant (60Hz)	Q factor	Dielectric strength (V/mil)
Pu1	17	0.0082	5.00	121.95	2159
Pu4	17	0.0226	5.45	44.24	2117
Pu7	17	0.0283	5.10	35.33	1926

1 mil = 1/1000 inch.

CONCLUSIONS

A new category of cost feasible one component polyurethane insulating coating was prepared via transesterification reaction of PET, PEG, and CO and subsequent crosslinking of the polyol by blocked triisocyanate. The optimum curing condition as determined by gel content measurements indicated that high degree of curing was achieved by maintaining the samples at 180°C for 30 min. Kinetic studies showed that theoretical values predicted by autocatalytic kinetic model agreed very well with the experimental ones. Crosslink density measurements showed that with decreasing hydroxyl value of the PHC, crosslink density decreased. The investigation of mechanical properties showed that with increasing crosslink density, tensile strength increased and the elongation at break decreased. Also, hardness of the samples increased with increasing crosslink density. Evaluation of the electrical properties confirmed excellent insulating power of the prepared samples. Samples with higher crosslink density showed better electrical properties.

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Figure 13 Conversion rate ($d\alpha/dt$) vs. temperature for experimental (solid line) and theoretical (dashed-line) data.

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