

Synthesis and Coating Characteristics of Novel Calcium-Containing Poly(urethane ethers)

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ABSTRACT: Calcium salt of mono(hydroxypentyl)phthalate [Ca(HPP)₂] was synthesized by the reaction of 1,5-pentanediol, phthalic anhydride, and calcium acetate. Calcium-containing poly(urethane ethers) (PUEs) were synthesized by the reaction of hexamethylene diisocyanate (HMDI) or toluylene 2,4-diisocyanate (TDI) with a mixture of Ca(HPP)₂ and poly(ethylene glycol) (PEG₃₀₀ or PEG₄₀₀) with di-*n*-butyltin dilaurate as a catalyst. We synthesized a series of calcium-containing PUEs with different compositions by taking the molar ratio of Ca(HPP)₂ : PEG₃₀₀ or PEG₄₀₀ : diisocyanate (HMDI or TDI) as 2 : 2 : 4, 3 : 1 : 4, and 1 : 3 : 4 to study the coating properties of the PUEs. Blank PUEs without a calcium-containing ionic diol were also prepared by the reaction of PEG₃₀₀ or PEG₄₀₀ with HMDI or TDI. The PUEs were well characterized by fourier transform infrared

spectroscopy, ¹H-NMR, ⁻¹³C-NMR, solid-state cross-polarity/magic-angle spinning ¹³C-NMR, viscosity, solubility, and X-ray diffraction studies. The thermal properties of the polymers were also studied with thermogravimetric analysis and differential scanning calorimetry. The PUEs were applied as a top coat on acrylic-coated leather, and their physicochemical properties were also studied. The coating properties of PUEs, including tensile strength, elongation at break, tear strength, water vapor permeability, flexing endurance, cold crack resistance, abrasion resistance, color fastness, and adhesive strength, were better than the standard values. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 710–721, 2004

Key words: polyurethanes; thermal properties; viscosity; glass transition; coatings

INTRODUCTION

Polyurethanes represent an important class of thermoplastic and thermoset polymers as their mechanical, thermal, and chemical properties can be tailored by the reaction of various polyols and polyisocyanates. Polyurethanes are becoming increasingly important as engineering materials because they have excellent abrasion resistance and properties of both elastomers and plastics.^{1–4} Polyurethanes are usually used as coatings, foams, different kinds of plastics and elastomers, and rocket motor liners for the securing of composite propellant grain within the rocket motor. The properties of polyurethanes can be varied in numerous ways according to their demand. It was found that diols containing an even number of carbon atoms adopt a lowest energy, fully extended confirmation, which allows hydrogen bonding in both the directions of the chain axis.⁵ Polyurethanes, in general, present

good adhesive properties due to their elastomer properties, enhanced by soft segments of the polyol and by the polar character of the urethane groups.⁶ The applications of polyurethane adhesives include substrates such as glass, wood, leather, plastics, rubber, metal, concrete, and ceramics.^{7–11}

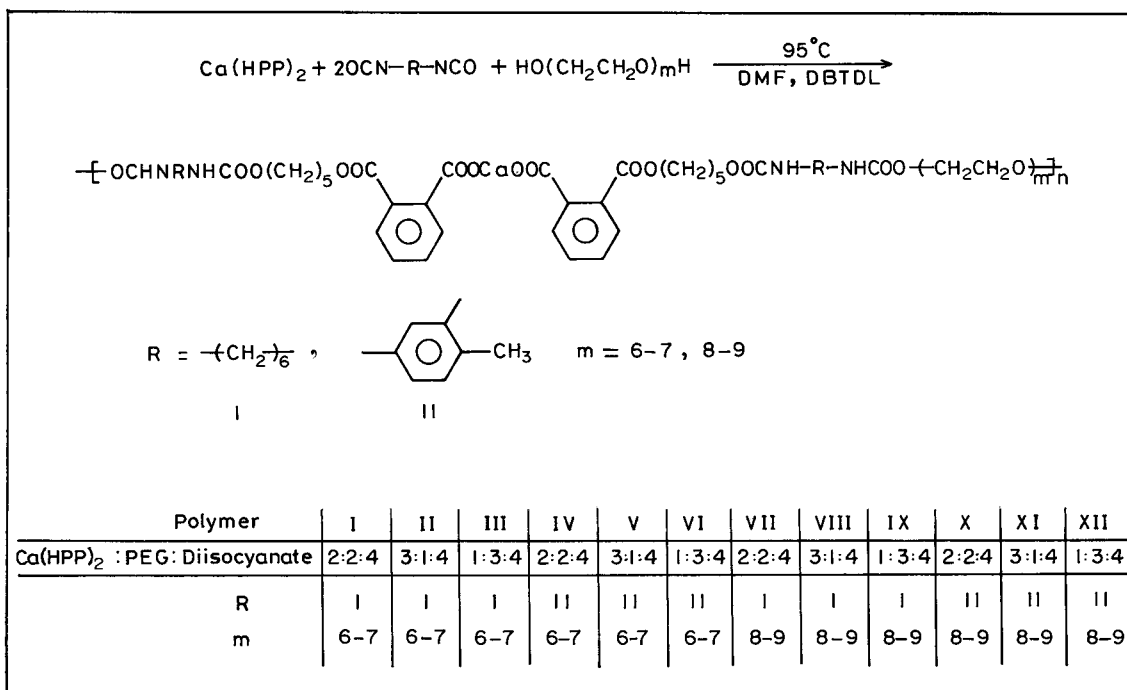
Polyurethanes are an important class of materials in the surface-coating industry. Their applications include construction, automotive, packing, transportation, electronics, textiles, tape, paper, and footwear areas.^{10–12} The incorporation of metal and functional groups into the polymers has led to wide application as aqueous thickeners, impregnates, textile sizings,^{13,14} resins,^{15–17} and catalysts.¹⁸ Ionic diols containing ionic linkages between COO⁻ and M⁺⁺ are of interest and are very important starting materials for the synthesis of ionic polymers in which the metal is firmly incorporated into the backbone of the polymer chain.^{19–24}

Leather finishing uses solvent-based systems predominantly in top coats. Solvent lacquers based on nitrocellulose, cellulose acetate butyrate, and polyurethanes are widely used in leather finishing operations. The finishing of leather enhances its aesthetic appeal and protects the leather surface against abrasion and chemical attack. Polyurethane coating serves these purposes by creating a film over the leather. Polyurethanes have good water resistance, color retention,

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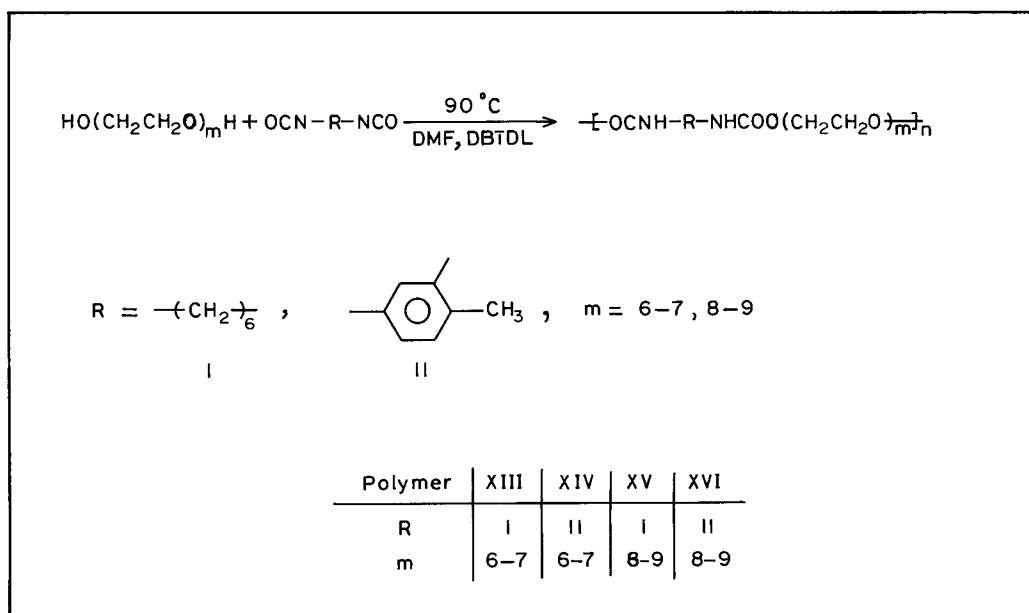
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Scheme I Synthesis of calcium-containing PUEs.

and weather resistance properties. Polyurethanes also show good abrasion resistance, soil resistance, low temperature flexibility, and excellent gloss. Also, they have good film adhesion and find applications in coating. A combination of both polyurethane (as a top coat) and acrylics (as a base coat) is anticipated to have synergistic effects with good water resistance, the ability to find a large amount of pigment, good wet rub

fastness, gloss film adhesion, low temperature flexibility, and toughness. To meet the increasing need of leather products, leather with defects, such as split leather, needs to be treated. The top coat masks the defects of the leather and makes it similar to good leathers in appearance and properties. Hence, the top coat not only improves the properties of the leather but also modifies defective leather.



Scheme II Synthesis of blank PUEs.

TABLE I
Synthesis and Viscosity Data of the Calcium-Containing PUEs

Polymer	Polymer composition	Yield (%)	η_{inh}	External appearance
I	Ca(HPP) ₂ -PEG ₃₀₀ -HMDI (2 : 2 : 4)	78	0.103	White
II	Ca(HPP) ₂ -PEG ₃₀₀ -HMDI (3 : 1 : 4)	70	0.094	White
III	Ca(HPP) ₂ -PEG ₃₀₀ -HMDI (1 : 3 : 4)	68	0.131	White
IV	Ca(HPP) ₂ -PEG ₃₀₀ -TDI (2 : 2 : 4)	73	0.101	Yellowish white
V	Ca(HPP) ₂ -PEG ₃₀₀ -TDI (3 : 1 : 4)	74	0.081	Yellowish white
VI	Ca(HPP) ₂ -PEG ₃₀₀ -TDI (1 : 3 : 4)	71	0.130	Yellowish white
VII	Ca(HPP) ₂ -PEG ₄₀₀ -HMDI (2 : 2 : 4)	79	0.142	White
VIII	Ca(HPP) ₂ -PEG ₄₀₀ -HMDI (3 : 1 : 4)	73	0.101	White
IX	Ca(HPP) ₂ -PEG ₄₀₀ -HMDI (1 : 3 : 4)	71	0.142	White
X	Ca(HPP) ₂ -PEG ₄₀₀ -TDI (2 : 2 : 4)	75	0.104	Slightly yellow
XI	Ca(HPP) ₂ -PEG ₄₀₀ -TDI (3 : 1 : 4)	70	0.086	Slightly yellow
XII	Ca(HPP) ₂ -PEG ₄₀₀ -TDI (1 : 3 : 4)	69	0.133	Slightly yellow
XIII	PEG ₃₀₀ -HMDI	78	0.192	White
XIV	PEG ₃₀₀ -TDI	72	0.176	Slightly yellow
XV	PEG ₄₀₀ -HMDI	84	0.202	White
XVI	PEG ₄₀₀ -TDI	82	0.190	Slightly yellow

In this article, we describe the coating characteristics and the synthesis of calcium-containing poly(urethane-ethers) (PUEs) derived from the calcium salt of mono(hydroxypentyl)phthalate [Ca(HPP)₂] and poly(ethylene glycol) (PEG₃₀₀ or PEG₄₀₀) with hexamethylene diisocyanate (HMDI) or tolylene 2,4-diisocyanate (TDI).

EXPERIMENTAL

Materials

Phthalic anhydride (Merck, India), 1, 5-pentanediol (Merck), PEG₃₀₀ and PEG₄₀₀ (Merck), di-*n*-butyltin dilaurate (DBTDL); (Fluka, Buchs, Switzerland), HMDI and TDI (Fluka), and calcium acetate (Merck) were used as received without any purification. The solvents, including acetone, methyl ethyl ketone, water, methanol, dimethyl formamide (DMF), dimethyl sulphoxide (DMSO), dimethyl acetamide (DMAc), tetrahydrofuran, benzene, toluene, *m*-cresol, and chloroform were purified by standard procedures. The acrylic binder (Acrilan MD), pigment paste, and filler (Lepton wax emulsion) were commercially received and then used. Ca(HPP)₂ was synthesized as reported in our previous article.²²

Synthesis of PUEs

Ca(HPP)₂ (4.34 g, 0.008 mol) and PEG₃₀₀ (2.6 mL, 0.008 mol) or PEG₄₀₀ (3.2 mL, 0.008 mol) were dissolved in 100 mL of DMF in a 500-mL, three-necked, round-bottomed flask equipped with a nitrogen inlet, a condenser, and a dropping funnel. Then, HMDI or TDI (0.016 mol) dissolved in 20 mL of DMF was added to the mixture, which was maintained at 95°C over a period of 30 min in the presence of 2–3 drops of

DBTDL as a catalyst. The reaction was completely carried out under a nitrogen atmosphere. Then, the reaction mixture was diluted with DMF and filtered. The filtrate was poured into an excess quantity of methanol being vigorously stirred. The separated product was washed several times with methanol and then with acetone. The precipitate was dried *in vacuo* at 80°C for 24 h. Scheme I shows the reactions involved in the synthesis of PUEs based on Ca(HPP)₂. The blank PUEs were also prepared by the same method without, a calcium-containing ionic diol. Scheme II shows the reactions involved in the synthesis of blank PUEs.

Preparation of the leather surface

Cow leather was buffed and snapped with 320- and 400-grit emery papers. Then, it was dusted off completely, as any dust would hinder the adhesion of the film. The leather was slightly pressed under a hydraulic press to impart flatness and also to suppress the nap. The leather was trimmed without any folds at the edges and cut into an area of 1 ft².

Preparation of the coating formulation for the base coat and top coat

An acrylic base coat was prepared according to the following formulation. The acrylic binder (Acrilan MD; 10 g) a pigment paste (4 g), and a filler (Lepton wax emulsion; 2 g) were mixed with 24 g of water (solvent). The formulation was stirred well and then applied uniformly on the leather surface with a spray gun. Then the base coat was allowed to dry for 3–4 h.

The solutions of PUEs (I–XII) in 1 : 3 mixtures of DMF and CHCl₃ were used as top coats on the acrylic-

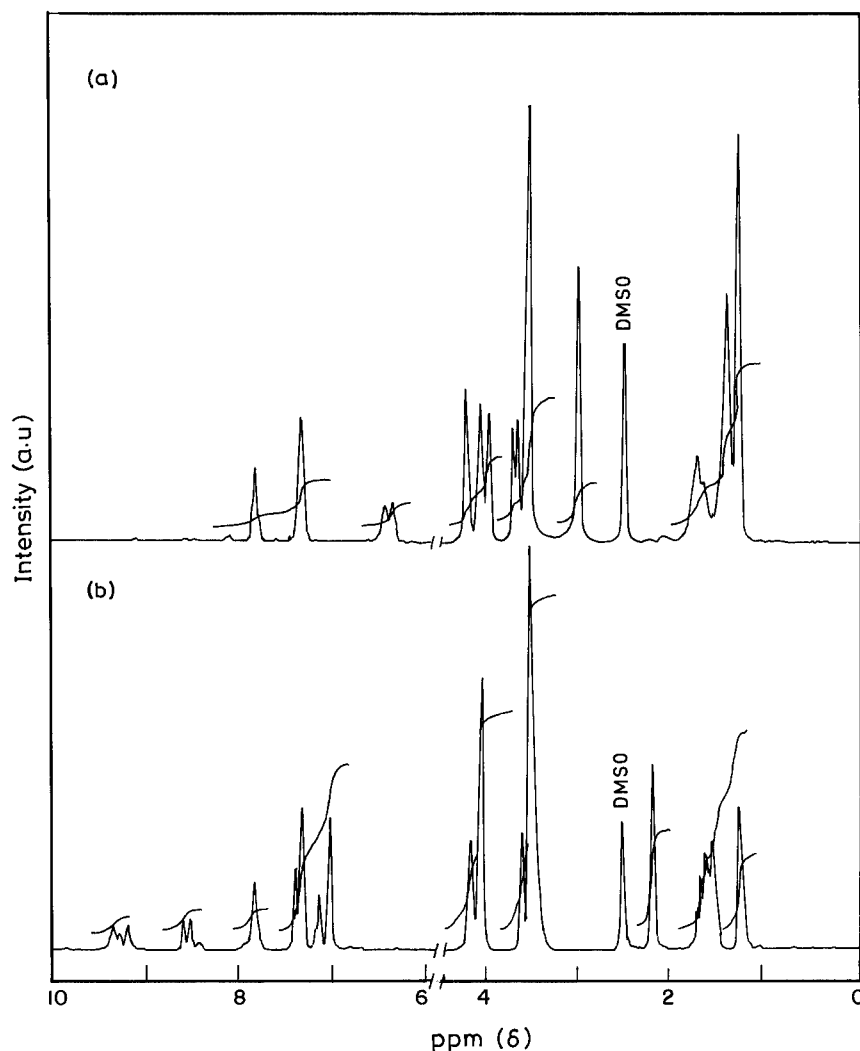


Figure 1 $^1\text{H-NMR}$ spectra of PUEs: (a) I and (b) IV.

coated leather. The 4% w/v polymer solution was applied uniformly as a top coat on the acrylic-coated leather with a spray gun. Then, the finished leather was allowed to dry for 4–6 h.

Measurements

The IR spectra of the polymers were recorded on a Shimadzu Testscan 8000 series Fourier transform infrared (FTIR) spectrophotometer (Japan) at room temperature with the KBr pellet method. $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and distortionless enhancement by polarization transfer spectra of the polymers were recorded on a Jeol GS \times 400-MHz spectrometer in $\text{DMSO-}d_6$ with tetramethylsilane as an internal standard. The solid-state cross-polarity/magic-angle spinning (CP-MAS) $^{13}\text{C-NMR}$ spectra were obtained with a Bruker MSL 75-MHz spectrometer (Switzerland) with adamantane as a chemical shift reference. The thermogravimetric analysis (TGA) was performed with a Mettler-3000

thermal analyzer (UK) with 2 mg of the sample at a heating rate of $20^\circ\text{C}/\text{min}$ in air. The differential scanning calorimetry (DSC) analysis was carried out with a DuPont 2100 DSC V4.OB model differential scanning calorimeter (Wilmington, DE) at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. The X-ray diffractograms were recorded according to a powder method with a Philips PW 1710 diffractometer with CuK_α radiation. The inherent viscosity (η_{inh}) of the polymers in DMSO was determined with an Ubbelohde viscometer (India) at 40°C . The flow times for the solvent and the polymer solution (1.0 g/dL) were determined. We tested the solubilities of the polymers in various polar and nonpolar solvents by taking 10 mg of the polymers in 2 mL of different solvents in a closed test tube and setting them aside for 1 day.

The tensile strength and elongation at break were determined with an Instron 4031 universal testing machine (UK) according to the SLP/IUP6 specifications. The tear strength was carried out on an Instron 4031

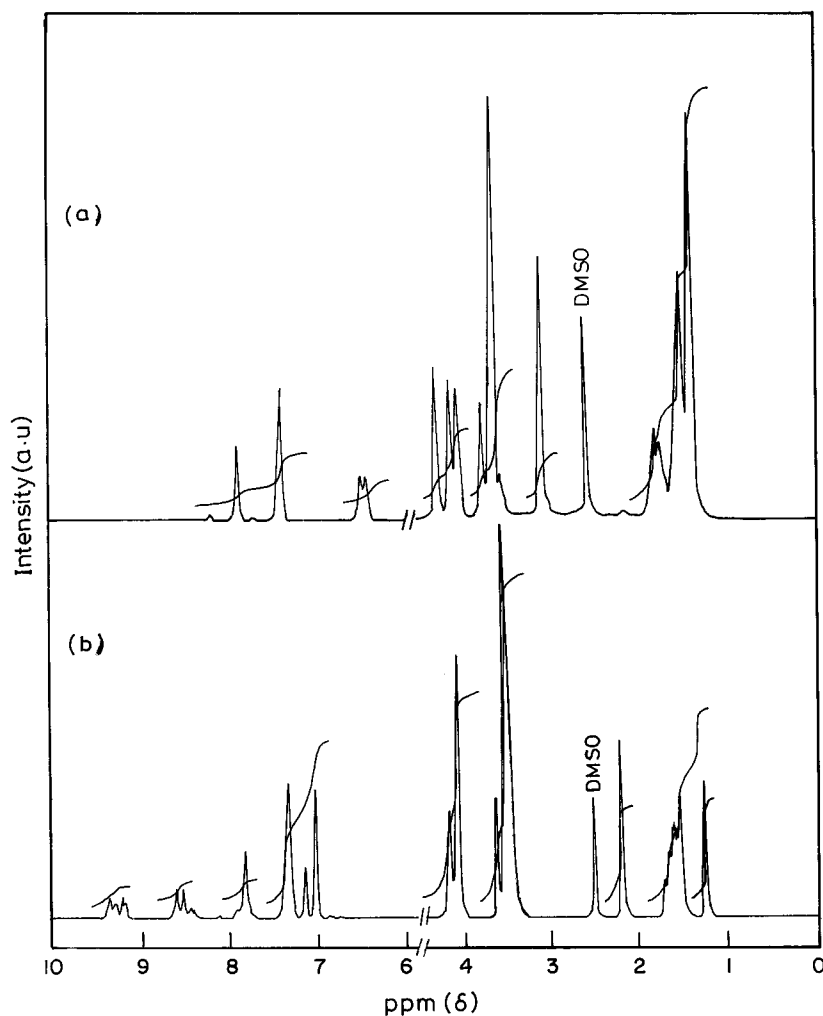


Figure 2 $^1\text{H-NMR}$ spectra of PUEs: (a) VII and (b) X.

universal testing machine by the SLP7/IUP8 method. The flexing endurance test was carried out on a Bally flexometer (India) according to SLP/IUP10 specifications. The cold crack resistance of the leather samples was carried out according to SLP34/IUP29 specifications with a freeze chamber made by SLEE (London). The abrasion resistance of the finished leather samples was measured according to BSEN 344 (5.14) standards in a Martindale abrasion tester (UK). The color fastness test was carried out with a SATRA rub fastness tester (India) according to the method given in SLF 5 of the official Methods of analysis of the Society of Leather and Technologists. The finished adhesion test was done according to IUP470 specifications. The water vapor permeability was tested according to SLP25/IUP15 specifications.

RESULTS AND DISCUSSION

Synthesis

We synthesized the calcium-containing PUEs were synthesized by heating the diisocyanate (HMDI or

TDI) dissolved in DMF with a mixture of $\text{Ca}(\text{HPP})_2$ and PEG_{300} or PEG_{400} in the same solvent at 90°C for 8 h with DBTDL as a catalyst. The reaction mixture was diluted with DMF and was then filtered and precipitated in methanol. The precipitated polymer was washed with water to remove the unreacted $\text{Ca}(\text{HPP})_2$, and then, it was washed with methanol and then with acetone. By the same method, we prepared twelve different PUEs were by varying the molar ratio of $\text{Ca}(\text{HPP})_2/\text{PEG}_{300}$ or $\text{PEG}_{400}/\text{HMDI}$ or TDI as 3 : 1 : 4, 2 : 2 : 4, or 1 : 3 : 4. The PUEs were encoded as $\text{Ca}(\text{HPP})_2\text{-PEG}_{300}\text{-HMDI}$ (2 : 2 : 4; I), $\text{Ca}(\text{HPP})_2\text{-PEG}_{300}\text{-HMDI}$ (3 : 1 : 4; II), $\text{Ca}(\text{HPP})_2\text{-PEG}_{300}\text{-HMDI}$ (1 : 3 : 4; III), $\text{Ca}(\text{HPP})_2\text{-PEG}_{300}\text{-TDI}$ (2 : 2 : 4; IV), $\text{Ca}(\text{HPP})_2\text{-PEG}_{300}\text{-TDI}$ (3 : 1 : 4; V), $\text{Ca}(\text{HPP})_2\text{-PEG}_{300}\text{-TDI}$ (1 : 3 : 4; VI); $\text{Ca}(\text{HPP})_2\text{-PEG}_{400}\text{-HMDI}$ (2 : 2 : 4; VII), $\text{Ca}(\text{HPP})_2\text{-PEG}_{400}\text{-HMDI}$ (3 : 1 : 4; VIII), $\text{Ca}(\text{HPP})_2\text{-PEG}_{400}\text{-HMDI}$ (1 : 3 : 4; IX), $\text{Ca}(\text{HPP})_2\text{-PEG}_{400}\text{-TDI}$ (2 : 2 : 4; X), $\text{Ca}(\text{HPP})_2\text{-PEG}_{400}\text{-TDI}$ (3 : 1 : 4; XI), and $\text{Ca}(\text{HPP})_2\text{-PEG}_{400}\text{-TDI}$ (1 : 3 : 4; XII). The blank PUEs were encoded as $\text{PEG}_{300}\text{-HMDI}$ (XIII), $\text{PEG}_{300}\text{-TDI}$ (XIV), $\text{PEG}_{400}\text{-HMDI}$ (XV), and $\text{PEG}_{400}\text{-$

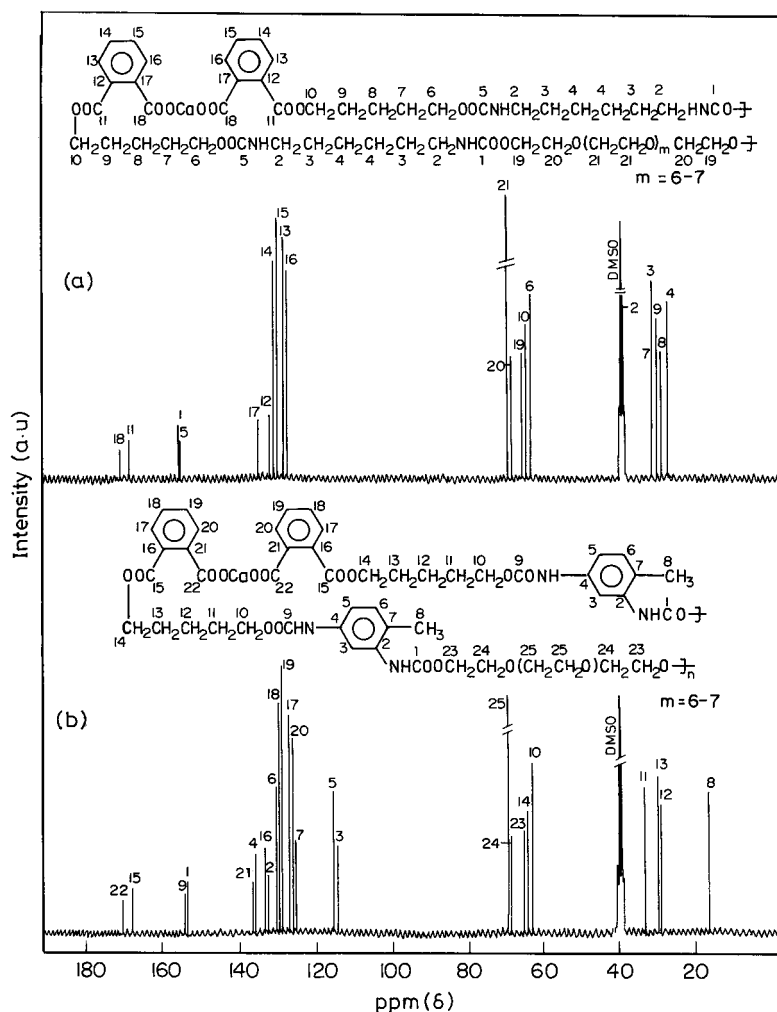


Figure 3 ^{13}C -NMR spectra of PUEs: (a) I and (b) IV.

TDI (XVI). The yields of the PUEs were good in all of the cases. The synthesis data of the PUEs and blank PUEs are given in Table 1. The PUEs were insoluble in methanol, ethanol, acetone, ethyl methyl ketone, carbon tetrachloride, ethyl acetate, *n*-hexane, benzene, toluene, tetrahydrofuran, and xylene. However, they were sparingly soluble in chloroform and soluble in highly polar solvents such as DMF, DMSO, and DMAc at 40°C.

Characterization of the PUEs

FTIR spectra

The PUEs showed a broad band between 3336 and 3289 cm^{-1} , which was attributed to N—H stretching. The absorption band at 3057–3028 cm^{-1} was due to aromatic C—H stretching. The peaks around 1704–1685 cm^{-1} were attributed to the carbonyl stretching of urethane and ester groups. The two broad peaks between 1600–1556 and 1412–1394 cm^{-1} confirmed the presence of ionic linkages between COO^- and

Ca^{++} in the PUEs. The peak at 1109–1076 cm^{-1} was due to C—O stretching of the ester group. The C—H out-of-plane bending vibrations of the aromatic ring were seen at 756–730 cm^{-1} .

^1H -NMR spectra

The ^1H -NMR spectra of PUEs containing PEG₃₀₀ or PEG₄₀₀ are shown in Figures 1 (I and IV) and 2 (VII and X), respectively. The HMDI-based PUEs showed a peak around 6.39–6.37 ppm due to the urethane N—H proton, but the TDI-based PUEs showed peaks at 9.39–9.37 and 8.45–8.42 ppm due to the N—H proton. The aromatic protons of the HMDI-based PUEs showed resonance signals at 7.82–7.30 ppm, whereas those of the TDI-based PUEs showed peaks at 7.85–6.95 ppm. The methyleneoxy groups attached to —COPh and —CONH groups showed signals around 4.24–4.01 ppm. The oxymethylene group attached to —CH₂OCONH showed a peak around 3.98–3.96 ppm. The peak at 3.57–3.54 ppm was due to the

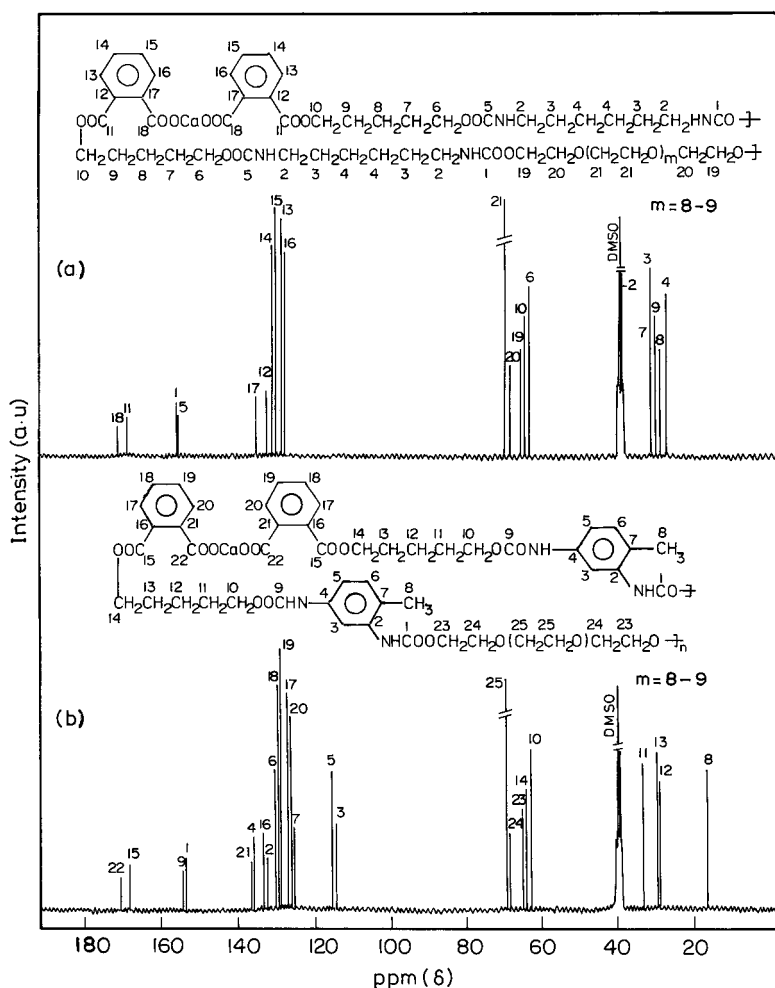


Figure 4 ^{13}C -NMR spectra of PUEs: (a) VII and (b) X.

— CH_2OCH_2 — group. For the HMDI-based PUEs, the methylene groups attached to —NH showed a signal around 3.01–2.99 ppm. For the TDI-based PUEs, the peak at 2.14–2.12 ppm was due to the methyl group attached to the aromatic ring. The peaks around 1.81–1.53 ppm were due to methylene groups attached to — CH_2OOC and — CH_2NH — groups. The other methylene groups were observed between 1.45 and 1.20 ppm.

^{13}C -NMR spectra

The proton-decoupled ^{13}C -NMR spectra of PUEs containing PEG_{300} or PEG_{400} are shown in Figures 3 (I and IV) and 4 (VII and X), respectively. The carboxylate carbon and ester carbonyl carbon of the PUEs showed peaks at 170.73–168.31 ppm. The urethane carbonyl carbon gave signals around 156.32–153.16 ppm. The signals at 136.48–125.47 and 136.42–115.21 ppm were due to aromatic signals for the HMDI-based PUEs and the TDI-based PUEs, respectively. The signal at 69.61–68.23 ppm was attributed to the methyleneoxy carbon

of the PEG_{300} or PEG_{400} unit. The peaks at 64.32–64.08 and 63.33–63.22 ppm were due to methylene carbons attached to — OCOPh — and — OCONH — groups, respectively. The signal due to the methylene carbon attached to the —NH group was overlapped with the DMSO peak. The other methylene carbons were observed at 33.75–26.40 ppm. The peak at 17.23–17.14 ppm was due to the methyl carbon attached to the aromatic ring.

Solid-state CP-MAS ^{13}C -NMR spectra

Figure 5 shows the solid-state CP-MAS ^{13}C -NMR spectra of the HMDI-based PUEs (I and VII). The PUEs showed a broad resonance signal at 173.33–171.35 ppm due to the carboxylate carbon and ester carbonyl carbon of the polymer. The peak at 157.68–154.69 ppm was due to the urethane carbonyl carbon. The HMDI-based PUEs showed a broad resonance peak due to the aromatic carbons at 135.08–129.60 ppm. The peak at 70.98–69.78 ppm was attributed to the methyleneoxy carbon of the PEG_{300} or PEG_{400} unit

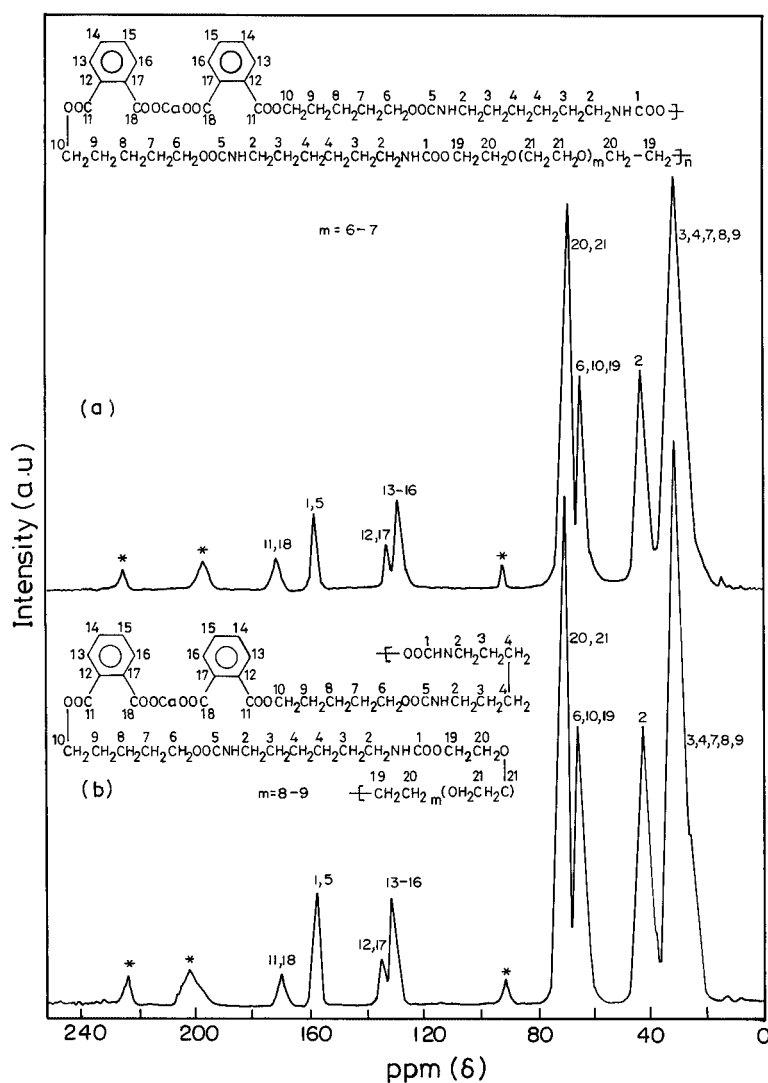


Figure 5 Solid-state CP-MAS ^{13}C -NMR spectra of PUEs: (a) I and (b) VII.

in the PUEs. The methyleneoxy groups attached to $-\text{COPh}$ and $-\text{CONH}$ groups showed a peak at 65.41–65.15 ppm. The methylene groups attached to the $-\text{NH}$ group showed a peak at 42.69–42.67 ppm. For the HMDI-based PUEs, the corresponding peak was not observed in the ^{13}C -NMR spectra of the liquid sample, as it was hidden with the DMSO peaks. The other methylene groups of the HMDI-based PUEs were observed at 30.88–29.70 ppm.

η_{inh}

The η_{inh} data for the PUEs in DMSO at 40°C are given in Table 1. The η_{inh} values of the calcium-containing PUEs were lower than those of the blank PUEs due to the presence of ionic linkages in the calcium-containing PUEs. However, the viscosity of the calcium-containing PUEs increased with the soft segment content and its unit length and decreased with the calcium

content. Thus, the PUEs containing larger amounts of calcium and smaller amounts of soft segment were more efficiently dissociated into low-molecular-weight fragments in DMSO^{15, 22–24} resulting in the decrease of the viscosity. With increasing soft segment content and unit length and decreasing in calcium content in the PUEs, the viscosity increased due to the lower number of ionic linkages. So, the PUEs based on PEG₄₀₀ showed higher viscosities than PUEs based on PEG₃₀₀. Also, the HMDI-based PUEs showed higher viscosities than the TDI-based PUEs.

TGA

The TGA curves of calcium-containing PUEs prepared from PEG₃₀₀ or PEG₄₀₀ are shown in Figures 6 (I–VI) and 7 (VII–XII), respectively. The HMDI-based PUEs showed three-stage decomposition, but the TDI-based PUEs showed two-stage decomposition. The blank

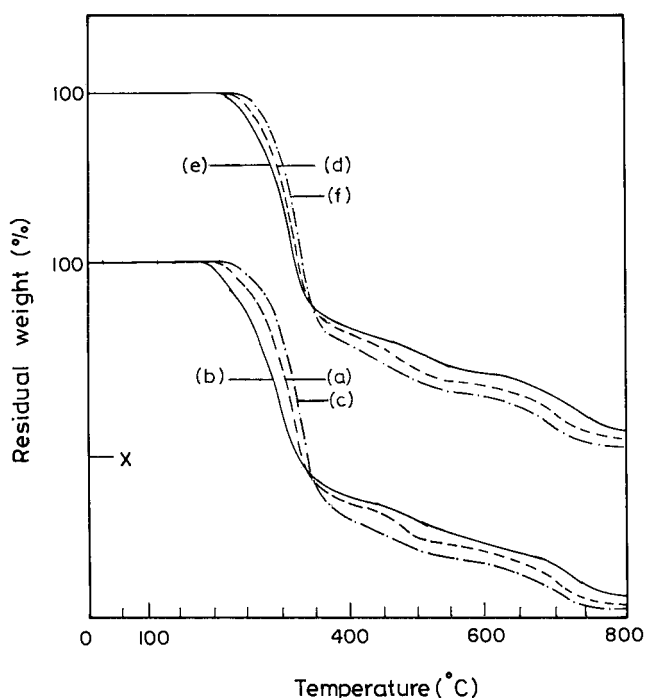


Figure 6 TGA traces of PUEs: (a) I, (b) II, (c) III, (d) IV, (e) V, and (f) VI. The baseline for d, e, and f were shifted to X.

PUEs showed single-stage decomposition. The initial decomposition temperatures (IDTs) of the PUEs ranged between 174 and 251°C. The IDT and decomposition rate of the PUEs decreased with increasing calcium content. The IDTs of the calcium-containing PUEs were slightly lower than those of the blank PUEs, but the decomposition rates were slower. The PUEs based on PEG₄₀₀ showed higher IDT values than PEG₃₀₀. The initial decomposition took place at the urethane linkages, and the number of urethane linkages was higher in the PEG₃₀₀-based PUEs than in the PEG₄₀₀-based PUEs. In general, the residual weight at 800°C corresponded to the amount of CaO formed at this temperature. The TDI-based PUEs showed higher IDTs than the HMDI-based PUEs due to their rigid aromatic rings. The TGA data of PUEs and blank PUEs are given in Table II.

Glass-transition temperature (T_g)

The T_g values of the PUEs and blank PUEs are given in Table II. The TDI-based polymers had higher T_g values than the HMDI-based PUEs. The T_g values of the PUEs decreased with the soft segment content (polyol) but increased with the metal content (hard segment unit). The blank PUEs had lower T_g values, which were -37.1 and -19.4°C for HMDI-based and TDI-based polymers, respectively. The PUEs derived from PEG₃₀₀, HMDI, and Ca(HPP)₂ showed two T_g values when the feed composition of Ca(HPP)₂-PEG₃₀₀-

HMDI was kept at 3 : 1 : 4. A similar observation was also made when the composition of Ca(HPP)₂-PEG₃₀₀-TDI in the feed was 3 : 1 : 4 and 2 : 2 : 4. When the composition ratio was 1 : 3 : 4 in the feed, the polymer showed a single T_g value. The PUEs based on PEG₄₀₀ also showed two T_g values when the feed composition of Ca(HPP)₂-PEG₄₀₀-HMDI or TDI were 2 : 2 : 4 and 3 : 1 : 4 and a single T_g value when the ratio of the composition was 1 : 3 : 4.

A single T_g value was observed for the homogenous phase systems due to the phase mixing of the soft segment (polyol) with ionic species (calcium carboxylate) and the hard segment (urethane unit). The reason for the two T_g values for the PUEs was that these systems exhibit heterogeneity, which might have been due to a phase with soft segments and another phase with different amount of soft and hard segments [urethane and Ca(HPP)₂ units] completely mixed together. The lower T_g value could be considered for the phase mixing due to the soft segment, ionic species, and the hard segment. In general, the TDI-based PUEs showed higher T_g values than the HMDI-based PUEs. The T_g values of the PUEs decreased with the soft segment length and increased with the calcium content.

X-ray diffraction

The X-ray diffraction patterns of the PUEs (I, IV, VII, and X) are shown in Figure 8. The X-ray diffraction

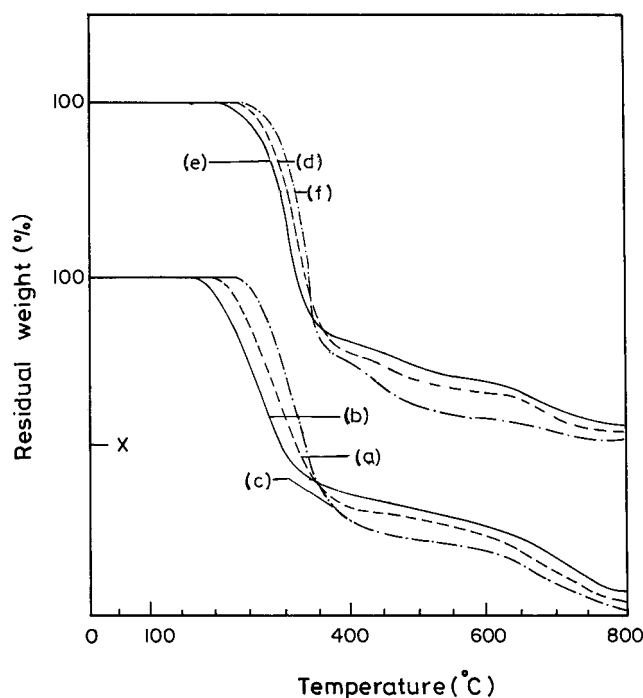


Figure 7 TGA traces of PUEs: (a) VII, (b) VIII, (c) IX, (d) X, (e) XI, and (f) XII. The baseline for d, e, and f were shifted to X.

TABLE II
TGA Data of the Calcium-Containing PUEs

Polymer	T_{g1} (°C)	T_{g2} (°C)	IDT (°C)	Temperature at weight loss (°C)					Weight loss at 800 °C (%)
				20%	40%	60%	80%	90%	
I	9.4	—	196	287	313	346	558	701	92.0
II	16.8	106.7	185	264	298	349	617	736	89.5
III	0.3	—	215	298	324	348	490	672	93.8
IV	12.9	—	222	298	318	350	503	699	92.7
V	21.3	113.8	212	285	312	350	633	742	90.4
VI	6.2	—	243	308	332	350	492	671	95.2
VII	-21.3	94.6	198	265	287	348	630	746	92.2
VIII	10.2	101.3	174	240	274	348	669	770	89.8
IX	-28.6	—	226	290	316	348	558	713	95.7
X	-10.2	99.2	233	289	319	347	472	701	92.3
XI	14.7	105.4	218	281	312	330	531	727	91.4
XII	-17.4	—	251	308	330	341	430	533	94.5
XIII	-30.2	—	234	313	339	365	427	531	100.0
XIV	-19.4	—	229	301	321	340	371	503	100.0
XV	-37.1	—	246	322	346	361	407	504	100.0
XVI	-26.7	—	241	320	343	357	401	483	100.0

patterns revealed that the HMDI-based PUEs were partially crystalline in nature, as they showed a few sharp peaks and a broad peak around $2\theta = 20\text{--}25^\circ$. The TDI-based PUEs did not show any sharp peak, and hence, we considered them to be amorphous in nature. The HMDI-based PUEs owed their tendency to form crystallinity to the presence of a flexible hexamethylene unit in the backbone. The crystallinity of the HMDI-based polymers was also evidenced by the solubility studies because they were less soluble in DMSO than the TDI-based PUEs.

Application of PUEs as top coats on acrylic-coated leather

Tensile strength, elongation at break, and tear strength

The tensile strength, elongation at break, and tear strength properties of the coated leathers were determined, and the results are given in Tables III and IV. There was an appreciable improvement in the tensile strength of the coated leather. This may have been due to the compactness of the fibrous structure in the leather. The tensile strengths of the TDI-based PUE coats were better than those of the HMDI-based PUE coats. This may have been due to the stiff phynelene rings present in the main chains of the TDI-based PUEs. The data revealed that the tensile strength increased with increasing hard segment (calcium salt and urethane linkage) content and decreases with increasing soft segment (polyol) content. The PUEs based on PEG₃₀₀ showed higher tensile strengths than PEG₄₀₀-based PUEs due to

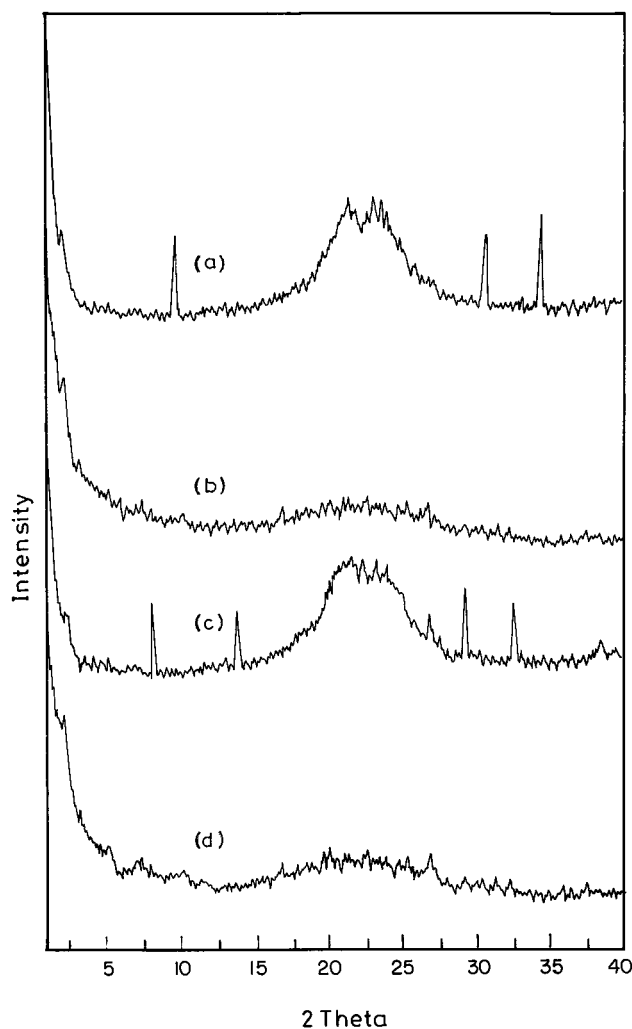


Figure 8 X-ray diffraction patterns of PUEs: (a) I, (b) IV, (c) VII, and (d) X.

TABLE III
Properties of Leather Coated with Calcium-Containing PUEs Based on PEG₃₀₀

Sample	Property	Polymer						Standard value
		I	II	III	IV	V	VI	
1	Tensile strength (kg/cm ²)	297	308	286	314	319	303	Minimum 200
2	Elongation at break (%)	48	44	54	43	40	49	45–75
3	Tear strength (kg/cm)	90	93	85	100	104	95	Minimum 80
4	Water vapor permeability (mg/cm ²)	2.1	1.9	2.4	1.7	1.5	1.9	1–2
5	Fluxing endurance (number of flexes in lakhs)							
	Dry	>1	>1	>1	>1	>1	>1	>1
	Wet	>0.5	>0.5	>0.5	>0.5	>0.5	>0.5	>0.5
6	Cold crack resistance (°C)	–20	–15	–20	–15	–15	–15	Minimum –15
7	Abrasion resistance (cycles)	No damage	No damage	Slight damage	No damage	No damage	No damage	Minimum 51,2000
8	Color fastness (gray scale)							
	Dry	3	3	3	4	4	4	3–4
	Wet	4	4	4	5	5	5	4–5
9	Adhesive strength (g/cm)	325	325	300	300	300	275	Minimum 250

the decrease in the soft segment length in the former.

The HMDI-based PUEs exhibited better elongation properties than the TDI-based PUEs due to the flexible hexamethylene units in the HMDI-based PUEs. Also, the elongation increased with increasing soft segment content. Thus, PUE coats obtained from PEG₄₀₀ showed a higher percentage elongation at break than those obtained from PEG₃₀₀. The TDI-based PUEs showed higher tear strengths than the HMDI-based PUEs due to the rigid aromatic rings in their backbones. The tear strength decreased with the soft segment content and its length but increased with the hard segment content. Thus PUEs based on PEG₄₀₀ showed lower tear strengths than those derived from PEG₃₀₀.

Water vapor permeability, flexing endurance, and cold crack resistance

The water vapor permeability, flexing endurance, and cold crack resistance data of PUEs are given in Tables III and IV, respectively. The water vapor permeability values were slightly more or less than the standard limits. They showed higher values when the soft segment content increased, but the values decreased with increasing hard segment content. All of the PUEs showed good flexing endurance. The PUEs did not show any damage before the standard flex values were reached. All of the samples showed more than 100,000 flexes (dry) and 50,000 flexes (wet) without showing any sign of damage. The cold crack resistance value decreased with increasing hard segment ratio. All of the PUE-coated leather samples gave very good cold crack resistance.

Abrasion resistance and color fastness

The PUEs-coated leather showed good abrasion resistance without showing any discoloration and peeling. None of the PUE-coated leathers showed any sign of damage before the standard values were reached except when the soft-to-hard segment ratio was high. Generally, the HMDI-based polymer coats showed less abrasion resistance than the TDI-based PUE coats due to the presence of the flexible hexamethylene group. All of the PUEs show good color fastness properties. The values were within standard values. The abrasion resistance and color fastness (dry and wet) data are given in Tables III and IV, respectively.

Adhesive strength

The adhesive strength values of the PUEs are shown in Tables III and IV. The HMDI-based PUEs showed better film adhesion than the TDI-based PUEs. Also, the PUEs based on PEG₄₀₀ showed a higher adhesion than those derived from PEG₃₀₀. The film adhesion increased with increasing hard segment molar ratio and decreased with increasing soft segment molar ratio. Hard segments served as pseudo crosslinking centers because of the hydrogen bonding of the urethane NH and the formation of ionic clusters in the calcium carboxylate salt. Hence, the increase in hard segments (urethane links) led to more hydrogen bonding, which subsequently led to good adhesion. In HMDI-based PUEs, the hard domains were compact due to its symmetric structure, which led to good hydrogen bonding. For the TDI-based PUEs, the aromatic ring disrupted the close packing of the hard domain, and hence, hydrogen bonding was less efficient. Hence, the HMDI-based PUEs showed better adhesion.

TABLE IV
Properties of Leather Coated with Calcium-Containing PUEs Based on PEG₄₀₀

Sample	Property	Polymer						Standard value
		VII	VIII	IX	X	XI	XII	
1	Tensile strength (kg/cm ²)	289	294	279	300	303	284	Minimum 200
2	Elongation at break (%)	52	49	58	48	43	54	45–75
3	Tear strength (kg/cm)	88	91	85	97	101	92	Minimum 80
4	Water vapor permeability (mg/cm ²)	2.2	1.9	2.6	1.6	1.4	1.9	1–2
5	Fluxing endurance (number of flexes in lakhs)							
	Dry	>1	>1	>1	>1	>1	>1	>1
	Wet	>0.5	>0.5	>0.5	>0.5	>0.5	>0.5	>0.5
6	Cold crack resistance (°C)	–20	–15	–20	–15	–15	–15	Minimum –15
7	Abrasion resistance (cycles)	Slight damage	No damage	Slight damage	No damage	No damage	No damage	Minimum 51,2000
8	Colour fastness (gray scale)							
	Dry	3	3	3	4	4	4	3–4
	Wet	4	4	4	5	5	5	4–5
9	Adhesive strength (g/cm)	375	350	325	400	375	350	Minimum 250

CONCLUSIONS

A series of calcium-containing PUEs with different compositions were synthesized with molar ratios of Ca(HPP)₂ PEG₃₀₀ or PEG₄₀₀HMDI or TDI as 3 : 1 : 4, 2 : 2 : 4, and 1 : 3 : 4. Blank PUEs were synthesized by the reaction of PEG₃₀₀ or PEG₄₀₀ with HMDI or TDI. The PUEs and blank PUEs were characterized by FTIR, ¹H-NMR, ¹³C-NMR, and CP-MAS ¹³C-NMR for structural confirmation. The viscosities of PUEs increased with the soft segment content and the unit length and decreased with the calcium content due to dissociation into low-molecular-weight fragments in DMSO solvent. The IDTs of TDI-based PUEs were higher than that of HMDI-based PUEs due to the presence of rigid aromatic rings. The *T_g* values of PUEs increased with the calcium content and decreased with the soft segment content and length. Two *T_g* values were observed for PUEs for certain compositions due to the presence of heterogeneity. The X-ray diffraction data showed that the HMDI-based PUEs were partially crystalline, whereas the TDI-based PUEs were amorphous in nature. The coating properties, such as tensile strength, elongation at break, tear strength, water vapor permeability, flexing endurance, cold crack resistance, abrasion resistance, color fastness, and adhesive strength of the PUEs were comparable to standard values. Thus, the PUEs were suitable for coating applications.

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