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Synthesis and characterization of calcium containing poly(urethane-ether)s

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Abstract

Calcium containing poly(urethane-ether)s (PUEs) were synthesized by the reaction of hexamethylene diisocyanate or toluylene 2,4-diisocyanate (HMDI or TDI) with a mixture of calcium salt of mono(hydroxybutyl)phthalate [$Ca(HBP)_2$] and polyethylene glycol (PEG_{200} or PEG_{400}). A series of calcium containing PUEs having different composition were synthesized by taking the mole ratio of $Ca(HBP)_2$:PEG_{200} or PEG_{400}:diisocyanate (HMDI or TDI) as 3:1:4, 2:2:4 and 1:3:4 to study the effect of calcium content on the properties of the copolymer. The structure of the polymers were confirmed by IR, ^{1}H-NMR, ^{13}C-NMR, and solid state ^{13}C-CP-MAS NMR. The polymers were soluble in dimethyl sulfoxide and dimethyl formamide. The initial decomposition temperature of the polymers decreases with increase in calcium content. The T_g value of PUEs increases with increase in calcium content and decreases with increase in soft segment content and length. A single T_g value is observed for the calcium containing PUEs based on PEG_{200} shows the presence of homogeneous phase. However, two T_g values for the PUEs based on PEG_{400} for various composition of $Ca(HBP)_2$, PEG_{400} and diisocyanate (HMDI or TDI) shows the presence of heterogeneous phase. The viscosity of the calcium containing PUEs increases with increase in the soft segment content as well as its length and decreases with increase in calcium content. X-ray diffraction patterns of the polymers show that the HMDI based polymers are partially crystalline and TDI based polymers are amorphous in nature. The dynamic mechanical analysis of the calcium containing PUEs based on HMDI shows that at any given temperature modulus (g' and g'') increases with increase in the ionic content in the polymers.

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1. Introduction

Polymers containing metals in the main chain are known for its importance in the scientific and industrial viewpoints. Incorporation of metal into the polymers have emerged that possess wide application as aqueous thickeners, impregnates, textile seizers, adhesives [1,2], additives [3], resins [4,5], catalysts [6] and in the biomedical fields [7,8]. Matsuda [9,10] synthesized a series of polyurethanes and poly(urethane-urea)s containing ionic links in the polymer chain using Ca and Mg salts of mono(hydroxyethyl)phthalate for the first time. Poly(urethane-ether)s have been proven to have sufficient biocompatibility and biodegradability for short-term use in a variety of blood contact applications, such as leaf-ventricular-assist devices for experimental artificial hearts and blood pumps [11]. We have reported the synthesis and characterization of series of polyurethanes

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and poly(urethane-urea)s based on divalent (Ca^{2+}, Mn^{2+}, Pb^{2+} and Zn^{2+}) salts of mono(hydroxybutyl)phthalate [12–14]. In continuation of our earlier work we report here the synthesis, spectral, thermal and viscoelastic properties of a new series of calcium containing poly(urethane-ether)s (PUEs) by the reaction of diisocyanate (HMDI or TDI) with a mixture of $Ca(HBP)_2$ and polyethylene glycol (PEG_{200} or PEG_{400}).

2. Experimental

2.1. Materials

Phthalic anhydride (Ranboxy), calcium acetate (Merck), 1,4-butanediol (Merck), polyethylene glycol of average molecular weight 200 and 400 (Merck), hexamethylene diisocyanate (HMDI) [Merck], toluylene 2,4-diisocyanate (TDI) [Merck] and di-*n*-butyltin-dilaurate (DBTDL) [Aldrich] were used as received. Solvents such as acetone, benzene, chlorobenzene, carbon tetrachloride, chloroform, dichloromethane, ethyl acetate, ethyl methyl ketone, methanol, ethanol, 1,4-dioxane, *n*-hexane, toluylene, xylene, tetra hydrofuran (THF), dioxane, dimethyl sulphoxide (DMSO), *N*,*N*′-dimethyl formamide (DMF) and dimethyl acetamide (DMAc) were purified by standard methods.

2.2. Synthesis of calcium containing poly(urethane-ether)s

Calcium salt of mono(hydroxybutyl)phthalate [$Ca(HBP)_2$] was synthesized as reported in our previous study [12]. In a 250-ml three necked round bottom flask fitted with an argon inlet, a condenser and a dropping funnel, $Ca(HBP)_2$ (0.008 mol), PEG_{200} or PEG_{400} (0.008 mol) and DMF (200 ml) were taken. Approximately three drops of DBTDL was added as a catalyst. The reaction mixture was heated to 80 °C over an oil bath under argon atmosphere with constant stirring using a magnetic stirrer. Then HMDI or TDI (0.016 mol) dissolved in 20 ml of DMF was taken in a dropping funnel and this solution was added slowly to the reaction mixture over a period of 30 min. After the addition the reaction temperature was raised to 90 °C and the reaction mixture was stirred at the same temperature for 8 h. Then the reaction vessel was taken out of the oil bath and set aside over night in argon atmosphere. Then DMF was added to the mixture in excess to provide the viscosity of the solution suitable for filtration. The filtrate was poured into an excess quantity of vigorously stirred acetone to precipitate the polymer. The polymer was washed several times, first with water, then with acetone and finally with by chloroform. The product was dried in vacuum at 80 °C for 24 h. Poly(urethane-ether)s having different composition were prepared by taking the mole ratio of $Ca(HBP)_2$:PEG_{200} or PEG_{400}: HMDI or TDI as 3:1:4, 2:2:1 and 1:3:4.

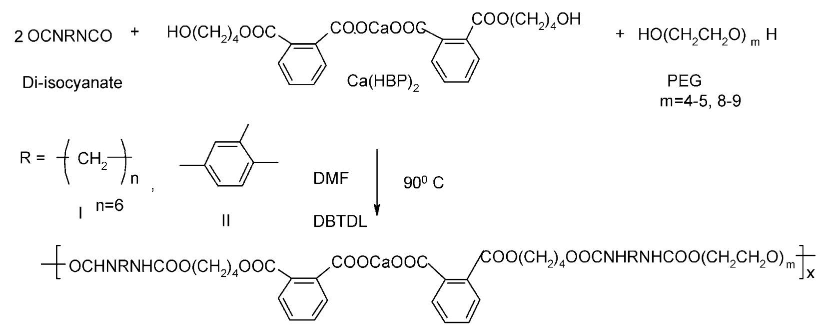
2.3. Instrumentation

IR spectra were recorded in a Perkin-Elmer Model 598 spectrophotometer using potassium bromide (KBr) pellet method. ^{1}H-NMR and ^{13}C-NMR spectra were recorded with Brucker MSL 75 MHz spectrometer and in Brucker MSL 300 MHz spectrometer. Solid state ^{13}C-CP-MAS-NMR spectra were carried out using Brucker MSL 75 MHz spectrometer with adamantine as chemical shift reference. Thermogravimetric analysis was carried out using Mettler TA-300-thermal analyzer in air atmosphere at the heating rate of 10 °C/min. DSC measurements have been performed with the cooling and heating rate of 10 °C/min using a Mettler 30 calorimeter with a cell purged with nitrogen. Solubility of the polymers was tested in various polar and non-polar solvents. About 5–10 mg of the polymer was added to about 2 ml of different solvents and kept over night. The inherent viscosity, η_{inh} of the polymers was determined using Ubbelohde-Viscometer in DMSO at 40 °C. The flow time for the solvent as well as the polymer solution [1 g/dl] was determined. X-ray diffractograms were recorded according to powder method with a Philips PW 1710 diffractrometer using Cu Kα radiation. Dynamic mechanical measurements were performed by means of rheometric mechanical spectrometer (RMS 800).

3. Result and discussion

3.1. Synthesis of polymers

The calcium containing PUEs were prepared by heating diisocyanate (HMDI or TDI) dissolved in DMF with a mixture of $Ca(HBP)_2$ and PEG_{200} or PEG_{400} in the same solvent at 90 °C for 8 h using di-*n*-butyltin laurate (DBTDL) as catalyst. Then DMF was added in excess to the mixture to dissolve the linear polymer and filtration is carried out to remove any crosslinked polymer formed. Then pouring the filtrate into an excess quantity of vigorously stirred acetone reprecipitated the polymer. The polymer was washed with water, to remove the unreacted $Ca(HBP)_2$, and then with acetone to remove the unreacted diol and finally with chloroform. The polymer was dried in vacuum at 80 °C for 24 h. The yields of the polymers were high (70–76%). By taking the mole ratio of $Ca(HBP)_2$:PEG_{200} or PEG_{400}:diisocyanate as 2:2:4, 3:1:4 and 1:3:4, calcium containing PUEs having different composition were prepared. Using the monomers $Ca(HBP)_2$ and PEG_{200} or PEG_{400} in different mole ratios six PUEs were prepared based on TDI and another six based on HMDI. Scheme 1 shows the reaction involved in synthesis of PUEs. These polymers are coded as



Polymer	1	2	3	4	5	6	7	8	9	10	11	12
$Ca(HBP)_2$:PEG:Diiscyanate	2:2:4	3:1:4	1:3:4	2:2:4	3:1:4	1:3:4	2:2:4	3:1:4	1:3:4	2:2:4	3:1:4	1:3:4
R	I	I	I	II	II	II	I	I	I	II	II	II
m	4-5	4-5	4-5	4-5	4-5	4-5	8-9	8-9	8-9	8-9	8-9	8-9

Scheme 1. Synthesis of calcium containing poly(urethane-ether)s.

$Ca(HBP)_2$–PEG_{200}–HMDI (2:2:4) **(1)**, $Ca(HBP)_2$–PEG_{200}–HMDI (3:1:4) **(2)**, $Ca(HBP)_2$–PEG_{200}–HMDI (1:3:4) **(3)**, $Ca(HBP)_2$–PEG_{200}–TDI (2:2:4) **(4)**, $Ca(HBP)_2$–PEG_{200}–TDI (3:1:4) **(5)**, Ca-$(HBP)_2$–PEG_{200}–TDI (1:3:4) **(6)**, $Ca(HBP)_2$–PEG_{400}–HMDI (2:2:4) **(7)**, $Ca(HBP)_2$–PEG_{400}–HMDI (3:1:4) **(8)**, $Ca(HBP)_2$–PEG_{400}–HMDI (1:3:4) **(9)**, $Ca(HBP)_2$–PEG_{400}–TDI (2:2:4) **(10)**, $Ca(HBP)_2$–PEG_{400}–TDI (3:1:4) **(11)** and $Ca(HBP)_2$–PEG_{400}–TDI (1:3:4) **(12)**. The synthesis data for calcium containing PUEs are given in Table 1.

Blank PUEs without $Ca(HBP)_2$ were also synthesized for the purpose of comparing the properties of the metal containing polymers by adopting the above procedure. Four blank PUEs coded as PEG_{200}–HMDI **(13)**, PEG_{200}–TDI **(14)**, PEG_{400}–HMDI **(15)** and PEG_{400}–TDI **(16)** were prepared. The synthesis data for PUEs are given in Table 1.

3.2. Characterization of polymers

IR spectra of calcium containing PUEs (polymers **1**, **4**, **7** and **10**) are shown in Fig. 1. PUEs show a broad band between 3335 and 3300 cm^{-1} which is attributed to N–H stretching. The absorption bands at 2958–2914 and 2922–2824 cm^{-1} are due to the asymmetrical and symmetrical C–H stretching of methylene and methyl groups. The peaks around 1714–1686 cm^{-1} are attributed to the carbonyl stretching of urethane and ester groups. The two broad bands at 1580–1528 and 1400–1388 cm^{-1} confirm the presence of static linkages between COO^- and Ca^{++} in the PUEs. The peak at 1094–1065 cm^{-1} is due to the C–O stretching of the ether group.

The ^{1}H-NMR spectra of PUEs (polymers **1**, **4**, **7** and **10**) are shown in Figs. 2 and 3. The PUEs show peaks

Table 1
Synthesis and viscosity data for poly(urethane-ether)s

Polymer no.	Polymer code	External appearance	Yield (%)	η_{inh}
1	$Ca(CHBP)_2$–PEG_{200}–HMDI (3:1:4)	White	70	0.0854
2	$Ca(HBP)_2$–PEG_{200}–HMDI (2:2:4)	White	72	0.1002
3	$Ca(HBP)_2$–PEG_{200}–HMDI (1:3:4)	White	73	0.1223
4	$Ca(HBP)_2$–PEG_{200}–TDI (3:1:4)	Yellowish White	72	0.0765
5	$Ca(HBP)_2$–PEG_{200}–TDI (2:2:4)	Slightly yellowish white	74	0.0972
6	$Ca(HBP)_2$–PEG_{200}–TDI (1:3:4)	Yellowish white	73	0.1054
7	$Ca(HBP)_2$–PEG_{400}–HMDI (3:1:4)	White	74	0.0919
8	$Ca(HBP)_2$–PEG_{400}–HMDI (2::2:4)	White	74	0.1134
9	$Ca(HBP)_2$–PEG_{400}–HMDI (1:3:4)	White	70	0.1393
10	$Ca(HBP)_2$–PEG_{400}–TDI (3:1:4)	Yellowish white	75	0.0854
11	$Ca(HBP)_2$–PEG_{400}–TDI (2:2:4)	Slightly yellowish white	76	0.1278
12	$Ca(HBP)_2$–PEG_{400}–TDI (1:3:4)	Yellowish white	73	0.1245
13	PEG_{200}–HMDI	White	76	0.1772
14	PEG_{200}–TDI	Slightly yellow	73	0.1567
15	PEG_{400}–HMDI	White	81	0.2038
16	PEG_{400}–TDI	Slightly yellow	80	0.1897

All the polymerization has done in dry DMF solvent at 80–90 °C.

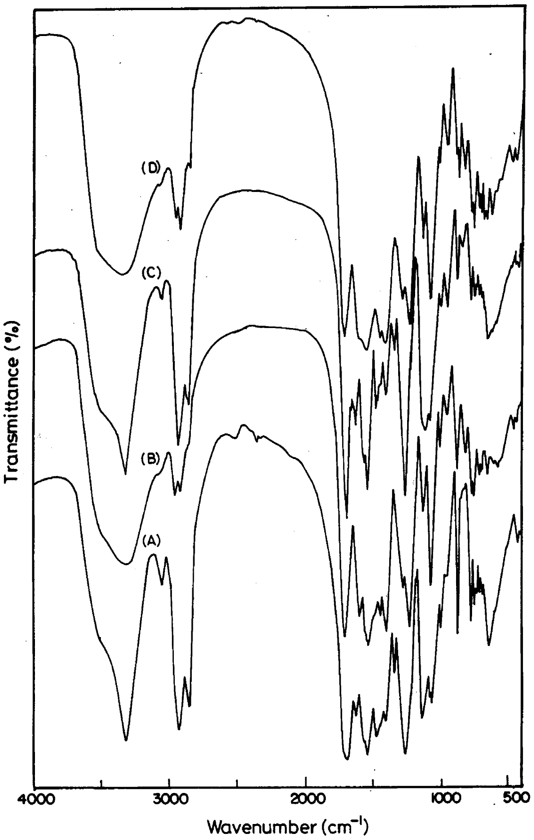


Fig. 1. IR spectra of (A) Ca(HBP)$_2$–PEG$_{200}$–HMDI (2:2:4) (B) Ca(HBP)$_2$–PEG$_{200}$–TDI (2:2:4), (C) Ca(HBP)$_2$–PEG$_{400}$–HMDI (2:2:4) and (D) Ca(HBP)$_2$–PEG$_{400}$–TDI (2:2:4).

around 9.47–9.10 and 8.43–8.38 ppm due to the urethane N–H proton of TDI based PUEs. The peak at 6.65–6.35 ppm is due to the urethane N–H proton of HMDI based PUEs. The aromatic protons show peak around 7.85–6.95 ppm. The methyleneoxy group attached to –COPh and –CONH shows signal around 4.25–4.05 ppm. The oxymethylene group attached to –CH$_2$OOCNH shows peak at 3.99–3.65 ppm. The signal around 3.57–3.52 ppm is due to the methyleneoxy group of the PEG$_{200}$ or PEG$_{400}$ unit in the polymeric chain. In the case of HMDI based PUEs the methylene group attached to –NH shows signal around 3.00–2.95 ppm. In TDI based PUEs the peak at 2.15–2.14 ppm is due to the methyl group attached to the aromatic ring. The peaks around 1.81–1.57 ppm are due to the methylene groups attached to –CH$_2$OCOPh and –CH$_2$OCONH. The other methylene groups attached to –(CH$_2$)$_2$NHCOO show peaks around 1.52–1.22 ppm.

The proton decoupled ^{13}C-NMR spectra of PUEs (polymers **1** and **7**) are shown in Figs. 4 and 5. The carboxylate carbon and ester carbonyl carbon of PUEs show peaks around 171.24–167.61 ppm. The urethane carbon gives signal around 155.81–153.17 ppm. The aromatic carbon signals are seen between 136.84 and 113.64 ppm for the TDI based PUEs while they are seen around 136.84–125.43 ppm for the HMDI based PUEs. The signal at 69.53–68.36 ppm is attributed to the methyleneoxy carbon of PEG$_{200}$ or PEG$_{400}$ unit in the PUEs. The methyleneoxy carbon attached to –CONH and –COPh show peaks around 63.58–62.44 ppm. The methylene group attached to –CH$_2$OCONH and the methylene group flanked between two –CH$_2$NHCOO groups in the case of HMDI based PUEs show peak around 29.47–28.40 ppm, while the other methylene groups are seen around 25.59–24.36 ppm. The methyl group attached to the aromatic ring of TDI based PUEs show peak around 16.62–16.32 ppm.

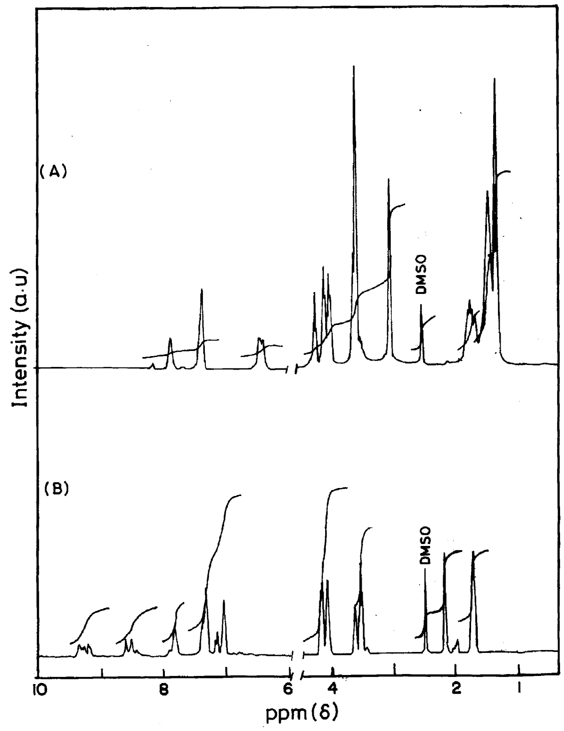


Fig. 2. ^{1}H-NMR spectra of (A) Ca(HBP)$_2$–PEG$_{200}$–HMDI (2:2:4) and (B) Ca(HBP)$_2$–PEG$_{200}$–TDI (2:2:4).

Fig. 6 shows the solid state ^{13}C-CP-MAS-NMR spectra of the polymers Ca(HBP)$_2$–PEG$_{200}$–HMDI (2:2:4) and Ca(HBP)$_2$–PEG$_{400}$–HMDI (2:2:4). The solid state ^{13}C-CP-MAS-NMR spectra of PUEs show a broad peak at 173.32–171.05 ppm corresponding to the carboxylate carbon and ester carbonyl carbon of the polymer. The urethane carbon shows broad peak at 157.68–154.61 ppm. The TDI based PUEs show broad resonance peak due to the aromatic carbons at 135.82–112.47 ppm while HMDI based PUEs show the aromatic carbon signals at 130.02–129.50 ppm. The peak at

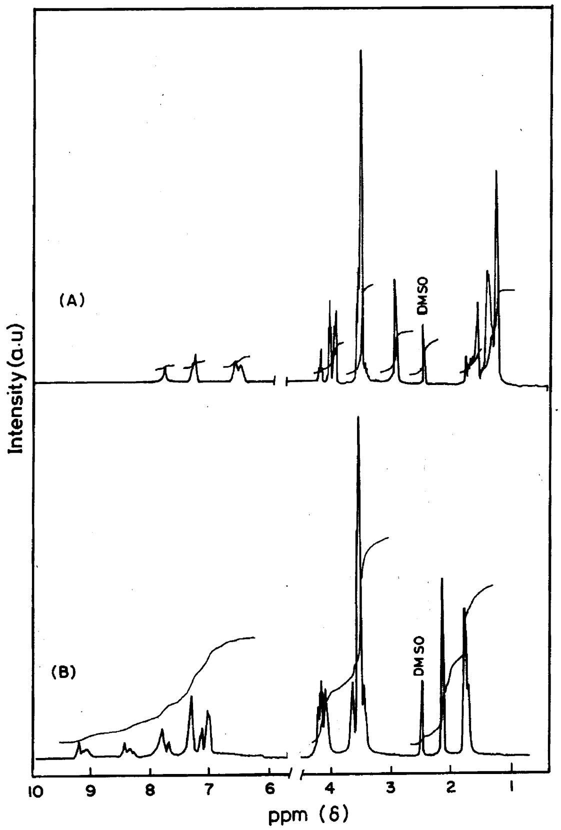


Fig. 3. ^{1}H-NMR spectra of (A) Ca(HBP)$_2$–PEG$_{400}$–HMDI (2:2:4) and (B) Ca(HBP)$_2$–PEG$_{400}$–TDI (2:2:4).

70.87–69.52 ppm is attributed to the methylenoxy carbon of PEG$_{200}$ or PEG$_{400}$ unit in PUEs. The methyleneoxy carbon attached to –OCOPh and –OCONH in the polymer show peak around 66.25–65.18 ppm. The methylene group attached to –NH group shows peak around 43.17–42.69 ppm in the case of HMDI based polymers. The broad peak around 30.98–29.57 ppm is due to the other methylene group in the polymer chain. The methyl group of TDI based polymers shows peak around 20.11–20.00 ppm.

3.3. Solubility

The calcium containing PUEs were insoluble in methanol, ethanol, acetone, CHCl$_3$, CCl$_4$, EMK, ethylacetate, *n*-hexane, benzene, toluene and xylene. However they were soluble in highly polar solvents such as DMF, DMSO and DMAc at 40 °C.

3.4. Viscosity studies

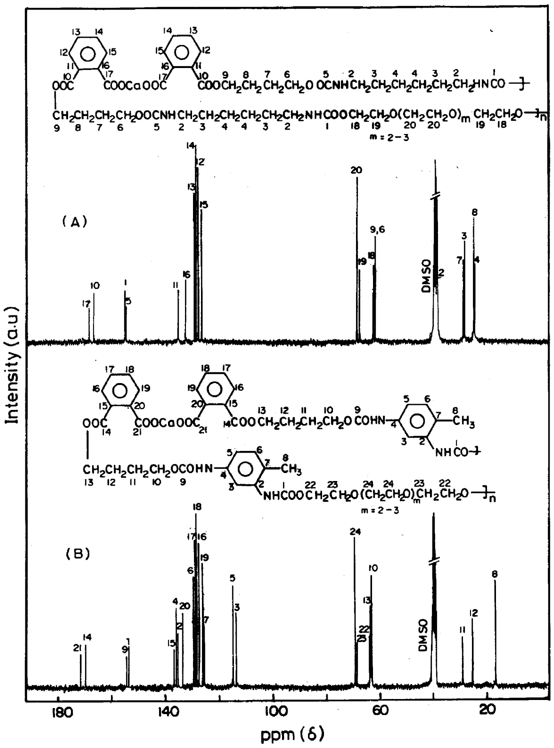


Fig. 4. ^{13}C-NMR spectra of (A) Ca(HBP)$_2$–PEG$_{200}$–HMDI (2:2:4) and (B) Ca(HBP)$_2$–PEG$_{200}$–TDI (2:2:4).

The inherent viscosity data for PUEs in DMSO at 40 °C are presented in Table 1. The inherent viscosity was found to be low when compared with its blank PUEs. Similar results were reported earlier for polymers containing ionic bonds in the backbone [14]. However, the viscosity of the calcium containing PUEs increases with increase in soft segment content as well as its length and decreases with increase in calcium content. Thus higher the amount of calcium content and lower the amount of soft segment length higher will be the amount of ionic linkages in the polymeric backbone, resulting in the dissociation into small molecular weight fragments in DMSO [3,15] thereby lowering the viscosity. With increases in the soft segment content and its unit length and decrease in calcium content in the polymer, the viscosity increases due to the presence of lower number of ionic linkages. Thus the PUEs based on PEG$_{400}$ show higher viscosity than PUEs based on PEG$_{200}$. Also, the HMDI based PUEs showed higher viscosity than TDI based PUEs because the hydrodynamic volume of the HMDI based polymers in DMSO are expected to be higher due to their increased unit chain length. From the low viscosity values of the polymers it cannot be inferred that there is no polymer formation. It is to be remembered that under the reaction conditions, even if the ionic diol does not react with the diisocyanate, the polyethylene glycol (PEG$_{200}$ and PEG$_{400}$) can react and give a high molecular weight polymer with higher viscosity. The low viscosity in this copolymer system

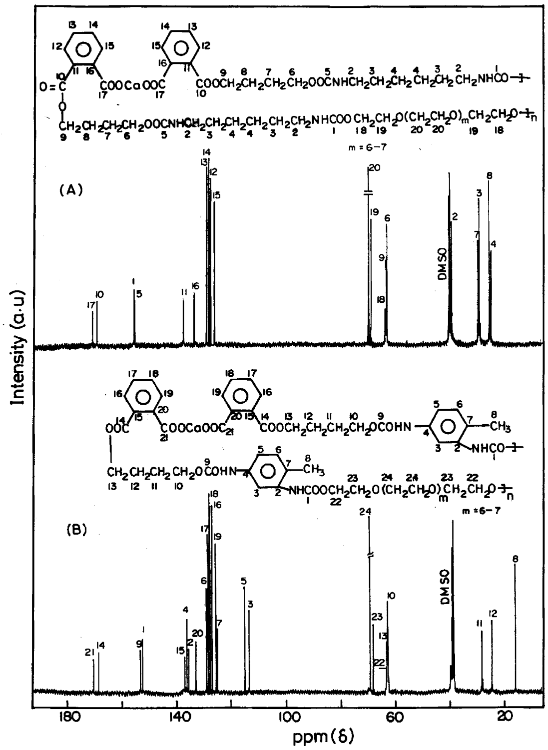


Fig. 5. ^{13}C-NMR spectra of (A) Ca(HBP)$_2$–PEG$_{400}$–HMDI (2:2:4) and (B) Ca(HBP)$_2$–PEG$_{400}$–TDI (2:2:4).

therefore is due to the chain fragmentation in a polar solvent like DMSO.

3.5. Thermogravimetric analysis

TGA traces of calcium containing PUEs (polymers **1**–**12**) along with blank PUEs (polymers **13**–**16**) are shown in Figs. 7 and 8. HMDI based PUEs show three-stage decomposition, while TDI based PUEs show two-stage decomposition. The blank PUEs show single stage decomposition. The IDT of the PUEs decreases with increase in calcium content but the rate of decomposition of these polymer decreases with increase in calcium content. This may be due to the fact that the metal catalyses the first stage decomposition and retards the further stages of decompositions. The blank PUEs show slightly higher IDT than calcium containing PUEs, but their rates of decomposition are higher than that of the calcium containing PUEs. Matsuda [16] has already reported that the thermal stability of metal containing polyesters decreases with increase in metal salt content in the feed. The TDI based PUEs showed higher decomposition temperature than HMDI based PUEs due to the presence of stiff phenylene group in the backbone of the polymer. Also, the PUEs based on PEG$_{400}$ showed higher decomposition temperature than

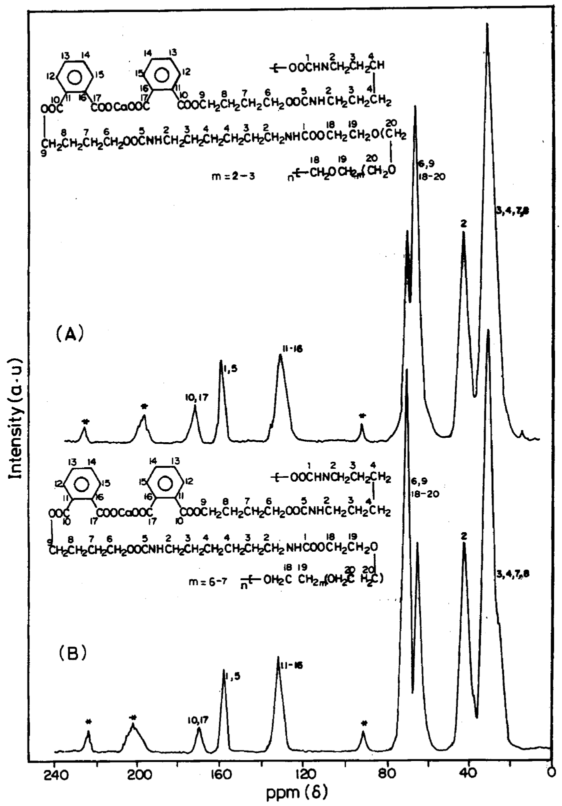


Fig. 6. Solid state ^{13}C-CP-MAS NMR spectra of (A) Ca(HBP)$_2$–PEG$_{200}$–HMDI and (B) Ca(HBP)$_2$–PEG$_{400}$–HMDI.

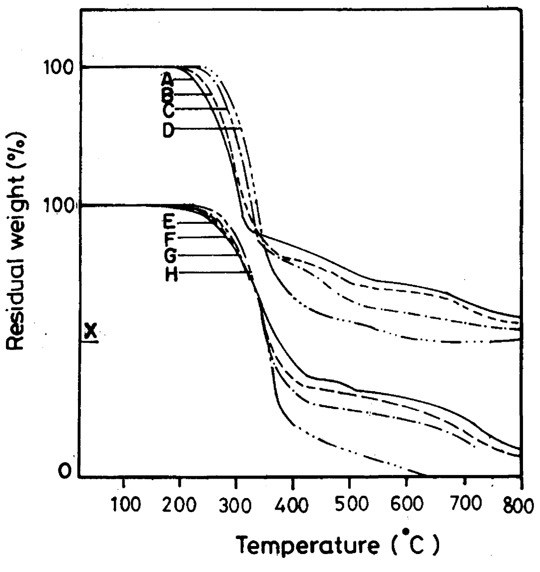


Fig. 7. TGA traces of (A) Ca(HBP)$_2$–PEG$_{200}$–HMDI (3:1:4), (B) Ca(HBP)$_2$–PEG$_{200}$–HMDI (2:2:4), (C) Ca(HBP)$_2$–PEG$_{200}$–HMDI (1:3:4), (D) PEG$_{200}$–HMDI, (E) Ca(HBP)$_2$–PEG$_{200}$–TDI (3:1:4) (F) Ca(HBP)$_2$–PEG$_{200}$–TDI (2:2:4), (G) Ca(HBP)$_2$–PEG$_{200}$–TDI (1:3:4) and (H) PEG$_{200}$–TDI.

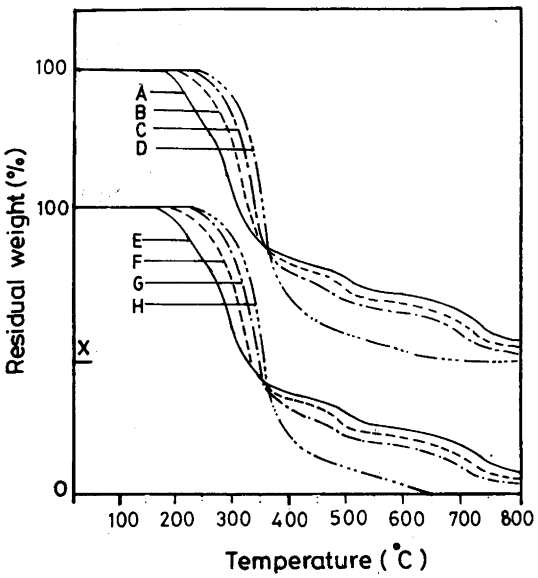


Fig. 8. TGA traces of (A) $Ca(HBP)_2$–PEG_{400}–HMDI (3:1:4), (B) $Ca(HBP)_2$–PEG_{400}–HMDI (2:2:4), (C) $Ca(HBP)_2$–PEG_{400}–HMDI (1:3:4), (D) PEG_{400}–HMDI, (E) $Ca(HBP)_2$–PEG_{400}–TDI (3:1:4), (F) $Ca(HBP)_2$–PEG_{400}–TDI (2:2:4), (G) $Ca(HBP)_2$–PEG_{400}–TDI (1:3:4) and (H) PEG_{400}–TDI.

PUEs based on PEG_{200}. In all the polymers the first stage decomposition takes place at the urethane linkage and the number of urethane linkages are more in the PEG_{200} based PUEs than that in PEG_{400} based PUEs. Also PEG_{200} based polymers may have higher percentage of calcium ions which act as catalysts for the first stage decomposition. Tables 2 and 3 give the thermal data for PUEs.

3.6. Glass transition temperature

DSC trace of calcium containing PUEs (polymers **1**, **4**, **7** and **10**) and blank PUEs (polymers **13**–**16**) are shown in Fig. 9. Table 2 shows the T_g values of all the polymers. It is found that the PUEs based on PEG_{200} show a single T_g value. The T_g of the PUEs decreases with decrease in calcium content of PUEs and increase in the soft segment content (PEG_{200}). Low T_g values of −22.5 and −11.4 °C are observed for the blank PUEs based on HMDI and TDI respectively. When the feed composition of $Ca(HBP)_2$:PEG_{200}:diisocyanate (HMDI or TDI) was 3:1:4 higher T_g values of 52.9 and 65.3 °C are observed for the PUEs based on HMDI and TDI respectively. Thus, increase in calcium content increases the hard segment and hence increases the T_g of the polymer.

The PUEs derived by PEG_{400} and HMDI show two T_g values for the polymer formed when the feed composition of $Ca(HBP)_2$:PEG_{400}:HMDI was 3:1:4 (10.9 and 105.8 °C) and 2:2:4 (−22.7 and 97.7 °C). Similarly two T_g values are observed when the composition of $Ca(HBP)_2$:PEG_{400}:TDI in the feed was 3:1:4 (15.8 and 110.3 °C) and 2:2:4 (−11.2 and 102.1). But only one T_g was observed when the feed composition of $Ca(HBP)_2$:PEG_{400}:HMDI was 1:3:4 and the composition of $Ca(HBP)_2$:PEG_{400}:TDI was 1:3:4. T_g values of −37.1 and −26.7 °C were observed for the blank PUEs formed from HMDI and TDI respectively with PEG_{400}. It is observed that T_g decreases with increase in soft segment content and its length.

In general, it is found that TDI based PUEs showed higher T_g value [17] than HMDI based PUEs. From the data in Table 3, it is clear that with increase in the calcium content of PUEs the T_g value increases and with increase in the soft segment contents the T_g value decreases. In the case of PUEs based on PEG_{200}, single T_g value was observed due to homogeneous phase, which can be due to phase mixing of soft segment (PEG_{200}) with ionic species (calcium carboxylate) and hard segment (urethane). In the case of PUEs based on PEG_{400}, two T_g values were observed for the polymers when the feed composition of $Ca(HBP)_2$:PEG_{400}:diisocyanate (HMDI or TDI) was 3:1:4 and 2:2:4. The heterogeneous phase might be due to longer soft segment length with different amount of $Ca(HBP)_2$ units. The lower T_g value can be considered for soft segment phase and the higher T_g value can be considered for the phase mixing due to soft segment, ionic species and hard segment.

Table 2
Thermal data of poly(urethane-ether)s based on PEG_{200}

Polymer	T_{g1} (°C)	IDT (°C)	Temperature at weight loss (°C)					Weight loss at 800 °C (%)
			20%	40%	60%	80%	90%	
$Ca(HBP)_2$–PEG_{200}–HMDI (3:1:4)	52.9	215	260	293	319	598	741	90.6
$Ca(HBP)_2$–PEG_{200}–HMDI (2:2:4)	17.4	226	266	299	325	533	728	93.0
$Ca(HBP)_2$–PEG_{200}–HMDI (1:3:4)	6.8	248	286	306	332	462	598	95.5
PEG_{200}–HMDI (1:1)	−22.5	257	293	319	332	377	455	100
$Ca(HBP)_2$–PEG_{200}–TDI (3:1:4)	65.3	187	298	341	400	708	780	90.4
$Ca(HBP)_2$–PEG_{200}–TDI (2:2:4)	24.7	198	302	334	374	662	746	92.4
$Ca(HBP)_2$–PEG_{200}–TDI (1:3:4)	12.1	223	308	334	334	616	728	94.5
PEG_{200}–TDI (1:1)	−11.4	242	312	338	356	393	492	100

Table 3
Thermal data of poly(urethane-ether)s based on PEG_{400}

Polymer	T_{g1} (°C)	T_{g2} (°C)	IDT (°C)	Temperature at weight loss (°C)					Weight loss at 800 °C (%)
				20%	40%	60%	80%	90%	
$Ca(HBP)_2$–PEG_{400}–HMDI (3:1:4)	10.9	105.8	223	248	284	344	661	747	92.0
$Ca(HBP)_2$–PEG_{400}–HMDI (2:2:4)	−22.7	97.7	236	278	296	324	562	721	93.3
$Ca(HBP)_2$–PEG_{400}–HMDI (1:3:4)	−29.7	–	258	298	317	340	496	694	95.2
PEG_{400}–HMDI (1:1)	−37.1	–	269	311	331	347	390	463	100
$Ca(HBP)_2$–PEG_{400}–TDI (3:1:4)	15.8	110.3	179	300	330	367	600	767	90.5
$Ca(HBP)_2$–PEG_{400}–TDI (2:2:4)	−11.2	102.1	203	320	357	403	567	673	93.2
$Ca(HBP)_2$–PEG_{400}–TDI (1:3:4)	−18.5	–	230	333	370	407	457	607	96.7
PEG_{400}–TDI (1:1)	−26.7	–	249	343	377	393	420	460	100

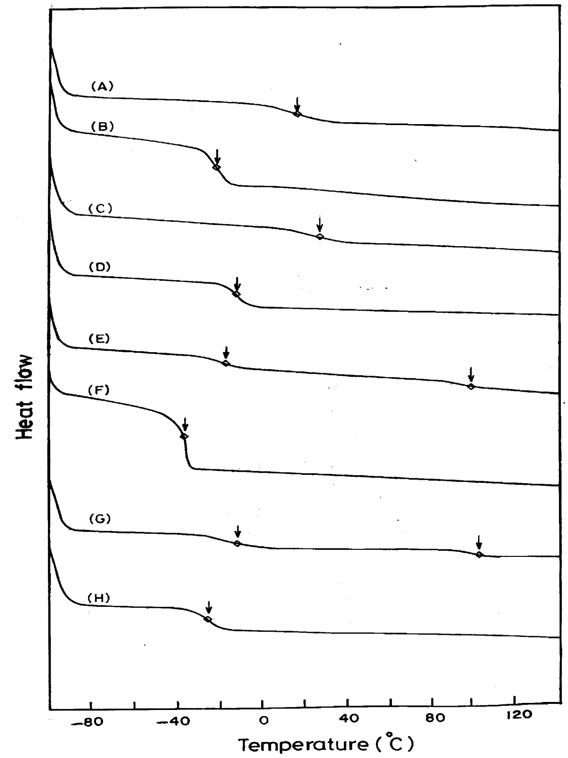


Fig. 9. DSC traces of (A) $Ca(HBP)_2$–PEG_{200}–HMDI (2:2:4), (B) PEG_{200}–HMDI, (C) $Ca(HBP)_2$–PEG_{200}–TDI (2:2:4), (D) PEG_{200}–TDI, (E) $Ca(HBP)_2$–PEG_{400}–HMDI (2:2:4), (F) PEG_{400}–HMDI, (G) $Ca(HBP)_2$–PEG_{400}–TDI (2:2:4) and (H) PEG_{400}–TDI.

3.7. X-ray diffraction studies

X-ray diffraction pattern of PUEs showed that the HMDI based PUEs are partially crystalline in nature as it showed some sharp peaks with strong broad peak around $2\theta = 20$–25. The TDI based PUEs do not show any sharp peaks which can be considered as amorphous in nature. The HMDI based polymers owe their tendency to crystallize to the presence of $–(CH_2)_6–$ units in the backbone of the polymers. Fig. 10 shows the XRD pattern of $Ca(HBP)_2$–PEG_{400}–HMDI (2:2:4) and $Ca(HBP)_2$–PEG_{400}–TDI (2:2:4).

3.8. Molecular weights

The molecular weight of calcium containing polymers could not be determined by GPC due to the possible deposition of the calcium salt in the GPC column, but the number and weight average molecular weight ($\overline{M}_n$ and $\overline{M}_w$) and polydispersity indices of blank PUEs were recorded using GPC.

Polymer **13** gives $\overline{M}_n = 0.9763 \times 10^4$;
$\overline{M}_w = 1.7545 \times 10^4$;
$\overline{M}_w/\overline{M}_n = 1.7964$,

Polymer **14** gives $\overline{M}_n = 0.9371 \times 10^4$;
$\overline{M}_w = 1.7164 \times 10^4$;
$\overline{M}_w/\overline{M}_n = 1.8317$,

Polymer **15** gives $\overline{M}_n = 0.9439 \times 10^4$;
$\overline{M}_w = 2.4580 \times 10^4$;
$\overline{M}_w/\overline{M}_n = 2.6040$,

Polymer **16** gives $\overline{M}_n = 0.9258 \times 10^4$;
$\overline{M}_w = 2.4546 \times 10^4$;
$\overline{M}_w/\overline{M}_n = 2.6413$.

3.9. Viscoelastic properties

Fig. 11 shows the effect of temperature on the storage modulus (g') and loss modulus (g'') for PUEs (polymers **1**–**3** and **13**) derived from $Ca(HBP)_2$, PEG_{200} and HMDI and that of blank PUEs. Fig. 11(A)–(D) shows the plot of temperatures vs. modulus for the PUEs when the feed composition of $Ca(HBP)_2$:PEG_{200}:HMDI was 3:1:4,

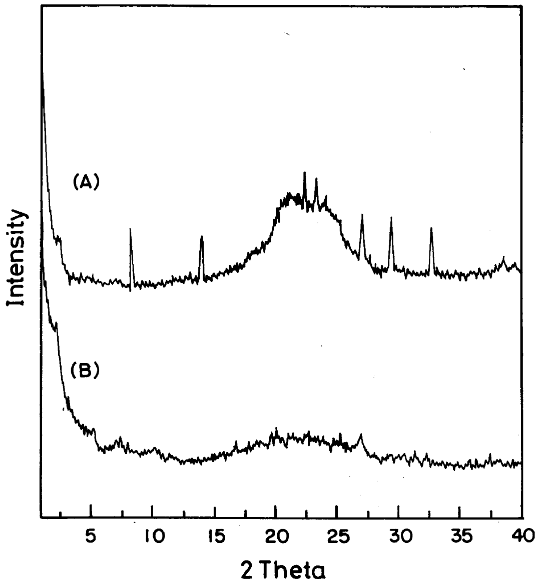


Fig. 10. XRD pattern of (A) $Ca(HBP)_2$–PEG_{400}–HMDI (2:2:4) and (B) $Ca(HBP)_2$–PEG_{400}–TDI (2:2:4).

2:2:4, 1:3:4 and 0:1:1 respectively. At any given temperature, the PUEs with higher amount of ionic content [Fig. 11(A)] show higher modulus (g' and g''). The decrease in the modulus (g' and g'') with increase in temperature for the polymer formed when the initial molar feed ratio of Ca(HBP):PEG_{200}:HMDI was 3:1:4 is less when compared with that of PUEs formed when the composition was 2:2:4 [Fig. 12(B)], 1:3:4 [Fig. 12(C)] and 0:1:1 [Fig. 12(D)]. At any given temperature the PUEs without the calcium salt shows lower modulus when compared to PUEs having ionic species. At any given temperature the PUEs with less ionic content shows less modulus when compared with PUEs with higher amount of ionic content. Relatively higher values of the storage modulus (g') for the polymers with higher amount of ionic content are probably related to the physical crosslinks in the copolymer system. As the ionic concentration in the polymer increases the ionic cluster forming capacity also increases which in turn increases the modulus [18].

It is observed from Fig. 12 that at temperatures above the T_g, the plateau due to the rubbery state is noted for all the PUEs. The compositions of the ionic and soft segment content in these copolymer systems have marked influence on the plateau height in the rubbery state at different temperatures. Soft rubbery state with lower plateau value of g' is observed for the system with higher amount of soft segment/or without ionic species. Hard rubbery state with higher plateau value of g' is observed for the system with higher ionic content [Fig. 12(A)]. Thus at higher amount of ionic content the polymer shows higher modulus.

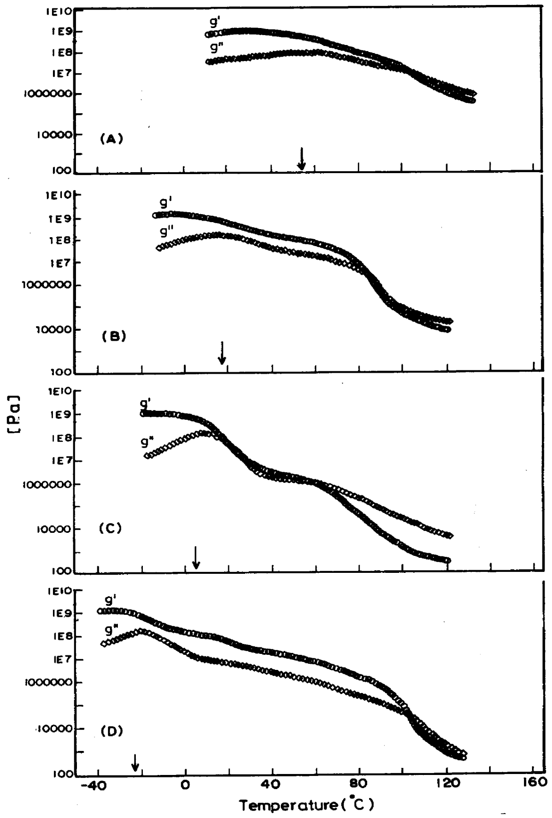


Fig. 11. Plot of storage modulus and loss modulus vs. temperature for (A) $Ca(HBP)_2$–PEG_{200}–HMDI (3:1:4), (B) $Ca(HBP)_2$–PEG_{200}HMDI (2:2:4), (C) $Ca(HBP)_2$–PEG_{200}–HMDI (1:3:4) and (D) PEG_{200}–HMDI (blank PUEs).

The T_g of the copolymer can be considered from the dynamic mechanical analysis (DMA) as the temperature at which the loss modulus (g') is maximum on the curve obtained by plotting loss modulus versus temperature [19]. Thus from Fig. 11, the T_g for the PUEs formed from equal quantity of $Ca(HBP)_2$ and PEG_{200} was found to be 17.4 °C [Fig. 11(B)]. T_g for the PUEs with lesser amount of ionic content and/or higher amount of soft segment was found to be 6.8 °C (Fig. 11(C)]. T_g for the blank PUEs [Fig. 11(D)] that has no ionic species was found to be −22.5 °C. From the above observation it is noted that increase in ionic content increases the T_g of the PUEs. It is seen from Fig. 11(B) that the peak of the loss modulus curve broaden very much with increase in ionic content of the PUEs. In contrast, the peak of the loss modulus curve for the polymer with less ionic content and/or higher soft segment is sharp [Fig. 11(C) and (D)]. The T_g of copolymers measured from DSC is shown by arrow mark in Fig. 11. It is observed that T_g of the PUEs determined by DSC as well as DMA is very close.

From Fig. 11 it is inferred that a homogeneous melt is formed for the PUEs formed at various composition

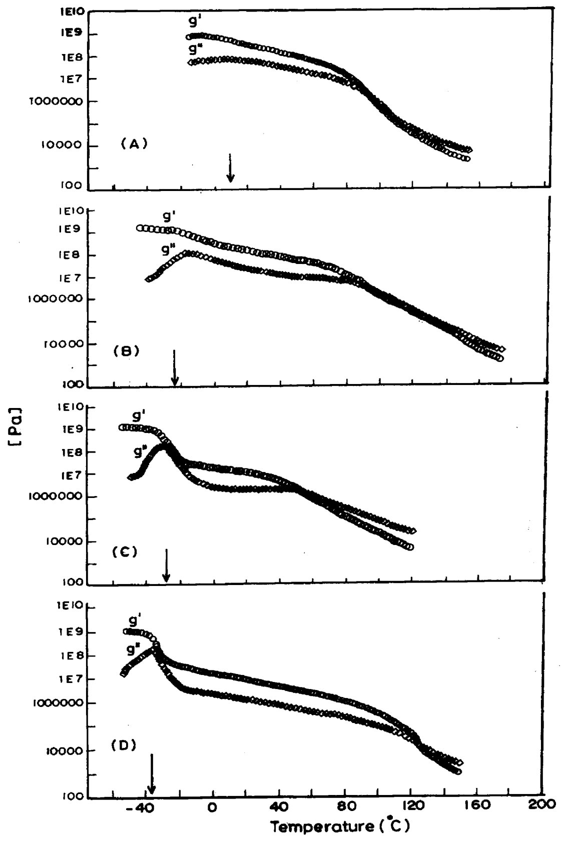


Fig. 12. Plot of storage modulus and loss modulus vs. temperature for (A) $Ca(HBP)_2$–PEG_{400}–HMDI (3:1:4), (B) $Ca(HBP)_2$–PEG_{400}HMDI (2:2:4), (C) $Ca(HBP)_2$–PEG_{400}–HMDI (1:3:4) and (D) PEG_{400}–HMDI (blank PUEs).

of $Ca(HBP)_2$, PEG_{200} and HMDI, and they exhibit a single value of T_g. The T_g shifts to higher value when the soft segment (PEG_{200}) was replaced by the more rigid [$Ca(HBP)_2$] ionic species. Thus in the PUEs the soft segments have dissolved or mixed with ionic (–COO-CaOOC–) and hard segment (–NHCOO–) and thus phase mixing was observed. A steep decrease in the value of modulus was observed for the blank PUEs at melting temperature whereas a gradual drop in the modulus was observed for the PUEs with ionic content.

Fig. 12 shows the effect of temperature on the storage modulus (g') and loss modulus (g'') for the PUEs (polymers **7**–**9** and **15**) derived from $Ca(HBP)_2$, PEG_{400} and HMDI. Fig. 12(A)–(D) corresponds to the copolymers formed when the feed composition of $Ca(HBP)_2$:PEG_{400}:HMDI were 3:1:4, 2:2:4, 1:3:4 and 0:1:1 respectively. At any given temperature the PUEs with higher content of ionic species [Fig. 12(A)] show higher modulus (g' and g''). The slightly lower values of modulus (g' and g'') were observed for the copolymer formed [Fig. 12(B)] from 50% of the ionic monomer, $Ca(HBP)_2$ and 50% soft segment containing monomer, PEG_{400}. The PUEs [Fig. 12(C)] with lower amount of ionic species and higher amount of soft segment shows lesser modulus than the above said PUEs system. The blank PUEs show less modulus than all the above said PUEs that have ionic species.

Fig. 12(A)–(D) shows that all the PUEs exhibit a rubbery plateau after their first T_g. The composition of ionic and soft segment in the PUEs system shows an influence on the plateau height/length in the rubbery state. A hard rubbery plateau with a higher value of g' is observed for the system with higher ionic content. The copolymers with increasing order of g' value is given as $Ca(HBP)_2$:PEG_{400}:HMDI (3:1:4) > $Ca(HBP)_2$:PEG_{400}:HMDI (2:2:4) > $Ca(HBP)_2$:PEG_{400}:HMDI (1:3:4).

A soft rubbery state with lower plateau value of g' is noted for the system with blank PUEs [Fig. 12(D)] i.e., for PUEs without ionic species. It is understood that at any given temperature the higher the amount of ionic species in the system higher will be the modulus at any given temperature the higher the amount of soft segment in the system lower would be the modulus.

PUEs shows two T_g values when the feed composition of $Ca(HBP)_2$:PEG_{400}:HMDI was 3:1:4 and 2:2:4. Fig. 12(A) shows a lower T_{g1}, value of 10.9 °C and higher T_{g2} value of 105.8 °C (from DSC trace). Fig. 12(B) shows a lower T_{g1} value of −22.7 °C and a higher T_{g2} value of 97.7 °C (from DSC trace). PUEs exhibited a single T_g value when the feed composition of $Ca(HBP)_2$:PEG_{400}:HMDI was 1:3:4 [Fig. 12(C)] and 0:1:1 [Fig. 12(D)]. From this observation it is clear that T_{g1} decreases with increase in the soft segment content (PEG_{400}) and increases with increase in the ionic content [$Ca(HBP)_2$]. The peak of the loss modulus–temperature curve broaden with increase in the ionic content [Fig. 12(A)] of the PUEs, while that for the PUEs with higher soft segment content and lower ionic content (Fig. 12(C)] becomes narrow. The T_g values measured from DSC are shown by arrow marks in Fig. 12(A)–(D), which shows that the T_g values determined from DSC and DMA are almost the same for the first T_g values.

Two T_g values observed for the copolymers when the feed composition of $Ca(HBP)_2$:PEG_{400}:HMDI was 3:1:4 and 2:2:4 indicates that a heterogeneous two phase system occurred on the copolymer system. The lower T_{g1} can be considered to be that of the phase with higher soft segment with little dissolved hard segment and ionic species while the T_{g2} can be considered due to that of the phase with higher hard and ionic segment with little dissolved soft segment. The mixing of the soft segment, ionic and hard segments to have a homogeneous phase was observed for the copolymer formed at different feed composition of $Ca(HBP)_2$, PEG_{200} and HMDI [Fig. 12]. The copolymer system $Ca(HBP)_2$–PEG_{400}–HMDI shows a heterogeneous phase due to phase segregation. Thus, the copolymer systems with PEG_{200} units have a shorter soft segment length and hence increase the hard segment content and glass transition temperature, indicating the restriction of freedom of soft segment rotation [20]. PUEs made from PEG_{200} with higher hard segment content have higher phase miscibility between hard and soft segment [21], apart the PUEs contain ionic species which intern increases miscibility of hard-ionic segment.

4. Conclusion

A series of calcium containing PUEs having different composition were synthesized by taking the mole ratio of $Ca(HBP)_2$:PEG_{200} or PEG_{400}:diisocyanate (HMDI or TDI) as 3:1:4, 2:2:4 and 1:3:4. Blank PUEs were synthesized by the reaction of PEG_{200} or PEG_{400} with diisocyanate (HMDI or TDI). The calcium containing PUEs and blank polymers were characterized by IR, ^{1}H-NMR, ^{13}C-NMR and solid state ^{13}C-CP-MAS NMR for structural confirmation. Molecular weights of blank polymers were determined by GPC.

Calcium containing PUEs are insoluble in most of the organic solvents and soluble in high polar solvents, which infer the presence of ionic linkages. The inherent viscosity of calcium containing PUEs are found to be low when compared with that of blank polymers which reveals that the static linkages between COO^- and Ca^{++} in the polymer chain dissociate into small fragments of low molecular weight. The HMDI based PUEs show slightly higher viscosity than TDI based polymers. The viscosity of the calcium containing PUEs increases with increase in the soft segment content as well as its length and decreases with increase in calcium content. The PUEs based on PEG_{400} has higher viscosity than those based on PEG_{200}. The IDT of the calcium containing PUEs increases with decrease in calcium content. The blank polymers show slightly higher IDT than calcium containing polymers, but their rate of decomposition is higher than that of calcium containing polymers. The PUEs based on PEG_{400} has higher IDT than PUEs based on PEG_{200} as the initial decomposition take place at the urethane linkages and the number of urethane linkages are more in the PUEs based on PEG_{200} than PUEs based on PEG_{400}. The PUEs based on PEG_{200} exhibit lower IDT than those derived from PEG_{400} this may be due to the presence of higher percentage of calcium ions in the former which catalyses the first stage decomposition. The T_g value of PUEs, increases with increase in calcium content (ionic content) and decrease with increase in soft segment content and its length. A single T_g value is observed for the PUEs based on PEG_{200} for various composition of $Ca(HBP)_2$: PEG_{200}:diisocyanate, indicating phase mixing of the soft segment with the ionic species and the hard segment. Two T_g values observed for the PUEs based on PEG_{400} for various composition of $Ca(HBP)_2$: PEG_{400}:diisocyanate (HMDI or TDI) indicates the presence of heterogeneous phase. The first T_{g1} value can be considered for soft segment and second T_{g2} value can be considered for the phase mixing due to soft segment, ionic species and hard segment. X-ray diffraction pattern of the polymers show that the HMDI based polymers are partially crystalline and TDI based polymers are amorphous in nature.

The dynamic mechanical analysis of the calcium containing PUEs based on HMDI show that with increase in the ionic content of polymer, increase in modulus (g' and g'') is observed at any given temperature. The magnitude of decrease in the modulus (g' and g'') with increase in temperature is found to be less for polymers with higher ionic content. At any given temperature the polymers without calcium content show lower modulus. The higher value of the storage modulus (g') observed for polymers having higher amount of ionic content are probably related to the formation of physical crosslinks in the copolymer system. As the ionic concentration in the polymer increases the ionic cluster forming capacity also increases which in turn increases the modulus. A rubbery plateau is noted for all the PUEs above the first T_g. The composition of ionic and soft segment content in the polymer system has influence on the plateau height in the rubbery state. Soft rubbery state with lower plateau value of g' is observed for the system with higher amount of soft segment or without ionic species. A hard rubbery state with higher plateau value of g' is observed for the system with higher ionic content.

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