Synthesis and Characterization of Poly(urethane-ether)s from Calcium Salt of *p*-Hydroxybenzoic Acid

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ABSTRACT: The synthesis and characterization of calcium-containing poly(urethane-ether)s, having ionic links in the main chain, is reported. Calcium salt of *p*-hydroxybenzoic acid (HBA-Ca) was prepared from *p*-hydroxybenzoic acid (HBA) and used as the chain extender in the preparation of calcium-containing poly(urethane-ether)s. Poly(urethane-ether)s, having two different compositions, were prepared by varying the mole ratios of poly(tetramethylene glycol), hexamethylene diisocyanate, and HBA-Ca. The synthesized poly(urethane-ether)s were characterized by infrared spectroscopy, thermogravimetric analysis, and dynamic mechanical analysis. The presence of calcium in the polymer chain was confirmed by energy-dispersive X-ray analysis. The inherent viscosity of metal-containing polymers decreased with the increase in the metal content of the polymer. The introduction of metal into the polymer lowers the thermal stability of the polymers as indicated by the decreased initial decomposition temperature. The glass transition temperature (T_g) and the storage modulus of the metal-containing polymers increase with the increase in metal content presumably due to the formation of physical crosslink's in the polymer. From the mechanical studies of the polymer, it was observed that the metal-containing polymers exhibit high tensile strength and modulus. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 1946–1952, 2011

Key words: calcium salt of *p*-hydroxybenzoic acid; polyurethanes; DMA; modulus; viscosity

INTRODUCTION

Synthesis of polymers containing metals in the main chain or side chain is one of the most frontier areas of current chemical research.[1] Such polymers possess the merits of both organic and inorganic components.[2–4] Metals can be incorporated into the polymers by ionic bond or by covalent bonds. Diols containing ionic linkages between COO^- and M^{2+} are used as the starting material for the synthesis of ionic metal-containing polymers. Because of the combination of covalent hydrocarbon polymer chains and ionic salt species in the same molecule, these materials possess unusual properties and are widely used in scientific and industrial field. The metal-containing ionic polymers are widely used as adhesives, additives, resins, or catalysts.[5–10] These ionic polymers also have application in the biomedical field.[11,12] Klein et al.[13] synthesized metal-containing polyurethanes using bis(diacetylcarbinol)-beryllium. Matsuda and coworkers[7,14,15] synthesized a series of metal-containing polyureas and poly(urethane-urea)s using divalent metal salts of *p*-aminobenzoic acid and mono(hydroxyethyl)phthalate. A series of metal-containing poly(urethane-urea)s and polyurethanes based on divalent salts of mono(hydroxybutyl)-phthalate were synthesized by Arun et al.[16–18] Abraham et al.[19] has reported the synthesis of calcium-containing methacrylate resin.

Polyurethanes possess excellent mechanical and physical properties, high combustion resistance, high wear resistance, and have broad temperature range for use.[20] Because of their excellent blood compatibility and physical properties, polyurethanes find use in blood contacting devices like vascular grafts, catheters, and artificial heart-assisting devices.[21] It was observed that many of the commercially available polyurethanes are not quite appropriate for use in some blood-contacting applications like small diameter vascular grafts and the artificial heart due to rapid thrombus formation.[22] One of the methods to improve the blood-contacting property of polyurethane is by incorporating ion-containing groups onto a polymer backbone.[23–25] Besides enhancing the polymer's blood contacting properties, ion incorporation also affects the physical properties of the polymer. Usually, ionomers have higher tensile strength and modulus due to clustering of the ionic groups. These ionic aggregates act as physical crosslinks, thereby strengthening the polymer.[26] In this work, we report the synthesis and characterization of calcium-containing

monomer using *p*-hydroxybenzoic acid and a series of calcium-containing polyurethanes using this monomer.

EXPERIMENTAL

Materials

Calcium oxide (CaO; SD Fine Chemicals, Mumbai), *p*-hydroxybenzoic acid (HBA; SD Fine Chemicals), hexamethylene diisocyanate (HDI) (Merck, Mumbai), di-*n*-butyltin-dilaurate (DBTL; Sigma-Aldrich, MO), ethylene diaminetetraacetic acid (dihydrate) (disodium salt) (EDTA; SD Fine Chemicals), and eriochrome black T indicator (SD Fine Chemicals) were used without further purification. Poly(tetramethylene glycol) (PTMG; Terathane 1000; Sigma-Aldrich) was degassed for 24 h at 50°C under reduced pressure. Dimethyl formamide (DMF; SD Fine Chemicals) was distilled under reduced pressure and kept over 4 Å molecular sieves.

Measurements

FTIR spectra were recorded in a Thermo Nicolet 5700 spectrometer with a diffused reflectance sample holder (Thermo Scientific, Germany). ^{1}H-NMR and ^{13}C-NMR spectra were recorded using 300-MHz Brucker NMR Spectrometer in dimethyl sulfoxide, containing small amount of TMS as internal standard. Elemental analysis of monomer was carried out using Elemental Vario EL-III CHN analyzer. Thermal analysis was carried out using a TA Thermal Analyzer (TA Instruments, USA, Model SDT-2960) under nitrogen atmosphere at a heating rate of 20°C/min. Viscosities were determined at 30°C using a Ubbelohde viscometer in DMF. Energy-dispersive X-ray analysis (EDX) was carried out using Quanta 200 (Environmental SEM) FEI Company, the Netherlands. Polymer films were prepared using 10% solution in DMF. The polymer solution was poured into a glass dish and solvent evaporated at 60°C in an air oven. The films were dried in vacuum oven at 60°C for 2 days to remove traces of solvent and moisture and stored in dessicator. The thickness of the film is in the range 0.3 mm to 0.5 mm. Dynamic mechanical analysis (DMA) was carried out using Tritec 2000 DMA, Triton Technology Limited, UK. Rectangular strips of dimensions 10-mm length and 4-mm width were cut out from the polymer film and used for DMA analysis. The tensile properties of the polymer specimens were measured by using an Instron 3345 Universal Testing Machine. Tensile measurements were carried out on dumpbell-shaped specimens. The narrow portion of the specimen has a dimension of 30 mm length and 4 mm width. The thickness of each specimen was measured and recorded as the average of four measurements. The samples were conditioned at 23°C ± 2°C and at 50% relative humidity, and the test was performed at a crosshead speed of 100 mm/min.

Estimation of calcium

The calcium content in the monomer calcium salt of *p*-hydroxybenzoic acid (HBA-Ca) was determined by complexometric method.[27] A known weight of the monomer was dissolved in deionized water, and this solution was used for calcium determination. The monomer solution was titrated with standard EDTA solution using Eriochrome black T as the indicator. The end point is the color change from wine red to clear blue.

Synthesis of calcium salt of *p*-hydroxybenzoic acid

About 6.91 g (0.05 mol) of *p*-hydroxybenzoic acid and 65 mL of water were added into a round-bottomed flask equipped with a magnetic stirrer. To this, 1.402 g (0.025 mol) of CaO was added in one lot. The reaction mixture was stirred at ambient temperature for 15 min and then at 80°C for another 2 h. The clear solution obtained after the reaction was filtered. To the filtrate, 80 mL of acetone was added and allowed to stand overnight. The calcium salt was separated as white crystals, which was filtered and washed several times with acetone. The product dried at 50°C overnight in an air oven. HBA-Ca obtained by drying the product at 150°C for 2 h to remove the water of crystallization.

Synthesis of poly(urethane-ether)s

Poly(urethane-ether)s were prepared using HDI, PTMG, and HBA-Ca as chain extender. In a three-necked round-bottomed flask fitted with water cooled condenser, a nitrogen inlet tube, a mechanical stirrer, and an addition funnel, 1.5 mmol of HBA-Ca, 4.5 mmol of PTMG, and 30 mL of DMF were placed. To this solution, two to three drops of DBTL were added as catalyst. The flask was placed in an oil bath, and the reaction mixture was maintained at 80°C with continuous stirring. The diisocyanate HDI (6 mmol) dissolved in 15 mL of DMF was added through a pressure-equalized addition funnel over a period of 30 min. After the addition of diisocyanate was completed, the reaction mixture stirred continuously at the same temperature for 8 h. The reaction mixture was allowed to cool to room temperature and kept under stirring for another 18 h. The reaction mixture was poured into excess of water to precipitate the polymer. The polymer was washed several times with methanol. The product was dried in vacuum at 80°C for 24 h. Poly(urethane-ether)s having different compositions were prepared by taking the mole ratio of HBA-Ca : PTMG : HDI as 1 : 1 : 2 and 1 : 3 : 4. In a
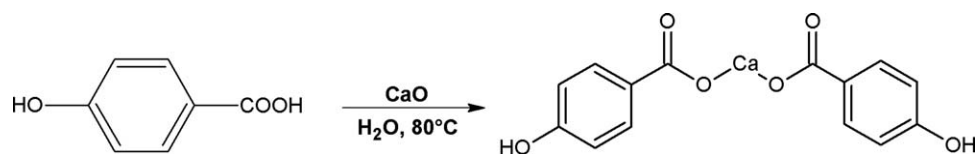
Scheme 1   Synthesis of HBA-Ca.

similar manner, polyurethane without calcium was also prepared using equimolar ratio of PTMG and HDI for comparative studies.

RESULTS AND DISCUSSION

### Synthesis of calcium salt of *p*-hydroxybenzoic acid

The calcium salt of *p*-hydroxybenzoic acid was prepared similar to the procedure reported for the synthesis of calcium salt of *p*-aminobenzoic acid by Matsuda and Shigetoshi.[4] The calcium salt of *p*-hydroxybenzoic acid prepared by neutralizing it with CaO in water (Scheme 1). The HBA and CaO distributed in water as insoluble particles at the beginning of the reaction. As the reaction proceeds, a clear solution was obtained. The product was separated as white crystals upon the addition of acetone. The water of crystallization present in the product was removed by drying the product at 150°C for 2 h. The yield of the product was 70%. The ^{1}H-NMR spectrum of HBA-Ca (Fig. 1) showed a chemical shift at 10.1 ppm due to hydroxyl protons. The signal at 7.8 ppm is due to two protons ortho to —OH group in each phenyl ring, and another signal at 6.7 ppm corresponds to two protons meta to —OH groups in each ring. The proton decoupled ^{13}C-NMR spectrum is shown in Figure 2. The resonance signal at 172.74 ppm corresponds to the two carboxylate carbon. The aromatic carbon gives peak at 127.67 (C2), 131.45 (C3), 114.00 (C4), and 159.70 (C5) ppm.

Elemental analysis of HBA-Ca showed that the percentage value of carbon and hydrogen is same as that of the calculated value. The calcium content in the monomer determined by complexometric method was 12%, which is same as that of the theoretical values.

Figure 3 shows the FTIR spectra of HBA-Ca. The absorption band at 3400 cm^{-1} corresponds to O—H stretching. The peak at 1607 cm^{-1} corresponds to the carbonyl stretching vibrations. Absorption band at 1400 cm^{-1} is the characteristics of carboxylate group.

Synthesis of poly(urethane-ether)s

Poly(urethane-ether)s was synthesized using HDI, PTMG, and HBA-Ca as chain extender (Scheme 2). The reaction was carried out in DMF solvent using DBTL as catalyst. The polymer was precipitated out from water and washed several times with methanol. The product was obtained in 90% yield. Poly-(urethane-ether)s of two different compositions were prepared by taking mole ratios of HBA-Ca and PTMG as 1 : 1 and 1 : 3 and they are respectively, coded as PUCa-HBA-11 and PUCa-HBA-13. The amount of metal-containing monomer in the polymer was varied to find the effect of metal incorporation on thermal and mechanical properties of polyurethanes. For comparative purpose, control polyurethane without metal was also prepared using PTMG and HDI and is denoted as PU-C.
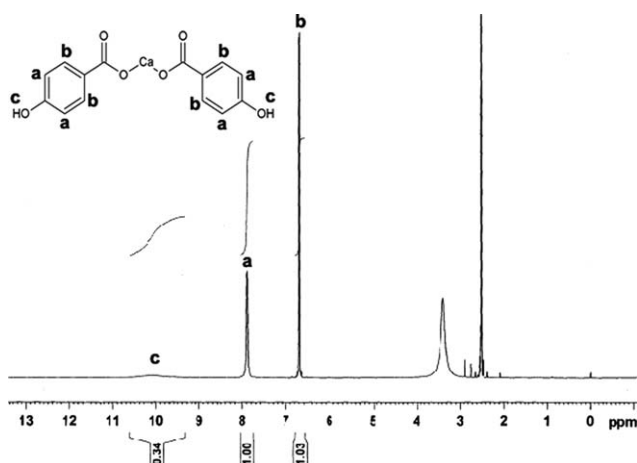
Figure 1 ^{1}H-NMR spectrum of HBA-Ca.
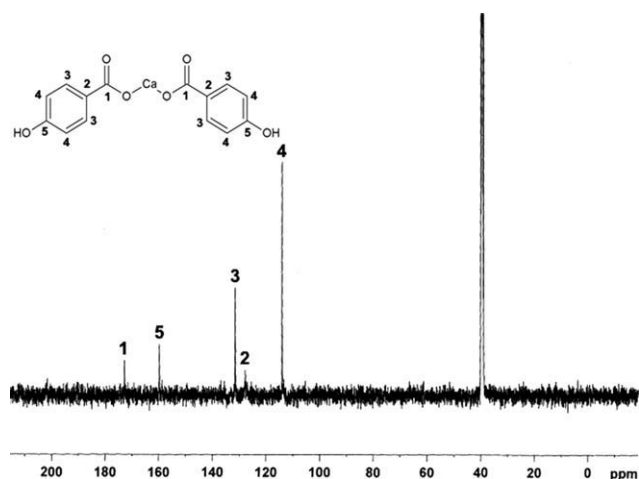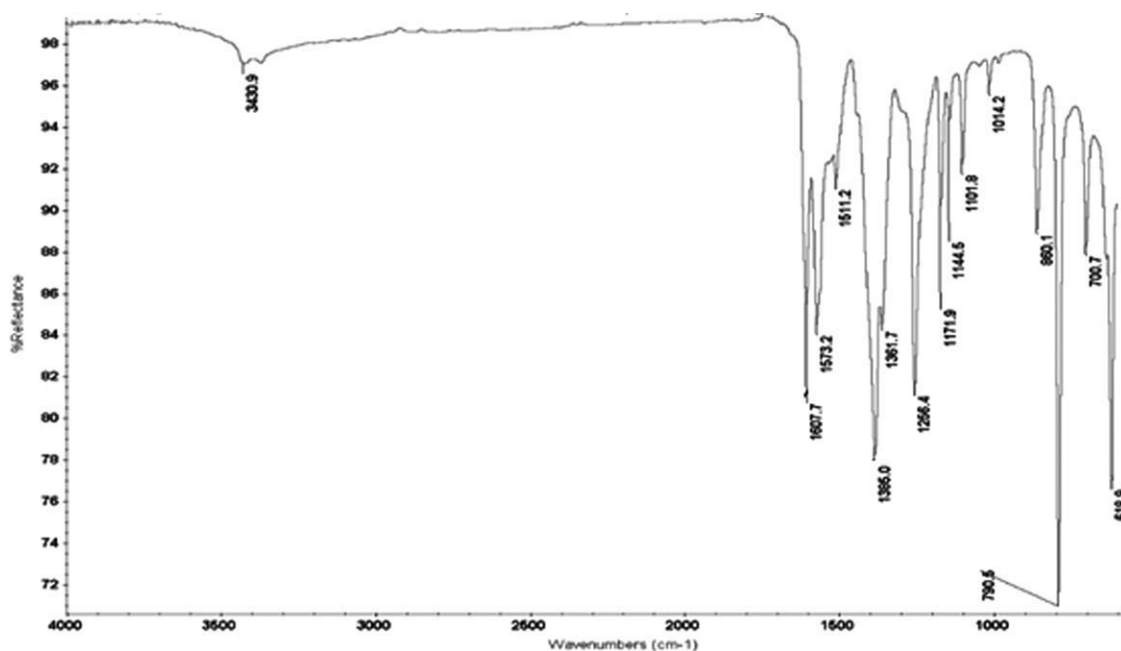

Figure 2 ^{13}C-NMR spectrum of HBA-Ca.

**Figure 3** FTIR spectra of HBA-Ca.

Characterization of polymer

Figure 4 shows the IR spectrum of poly(urethane-ether)s. A broad peak at 3317 cm^{-1} is attributed to N—H stretching. The peaks around 1680–1720 cm^{-1} correspond to the carbonyl stretching of urethane groups. The peak at 1620 cm^{-1} and around 1400 cm^{-1} corresponds to the carboxylate groups in the polymer.

Viscosity studies

The determination of molecular weight of metal-containing polymers by gel permeation chromatography (GPC) is complicated due to the interaction of charged materials with GPC column materials. So, viscosity studies of the polymers are only undertaken. The inherent viscosity data of calcium-containing polymers

and blank polymers are given in Table I. The inherent viscosities were determined at 30°C in DMF. It was found that the inherent viscosities of metal-containing polymers are low compared to blank polyurethane. Similar tendency has been observed for metal-containing polyurethanes and poly(urethane-urea)s based on divalent metal salts of mono(hydroxyethyl)phthalate.[15,28] This decrease in inherent viscosities is due to the dissociation of the ionic links in the polymer main chain into low-molecular weight fragments in a polar solvent. It was also observed that the inherent viscosity decreases markedly with the increase in calcium content in the polymer. On increasing the calcium content in the polymer, the ionic linkages present in the polymer increases, resulting in the formation of low-molecular weight polymer fragments, which decreases the viscosity.
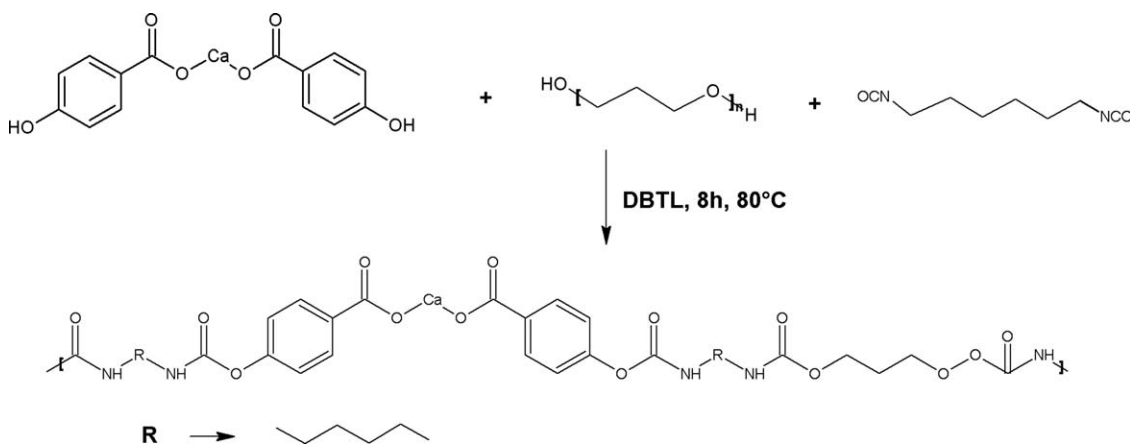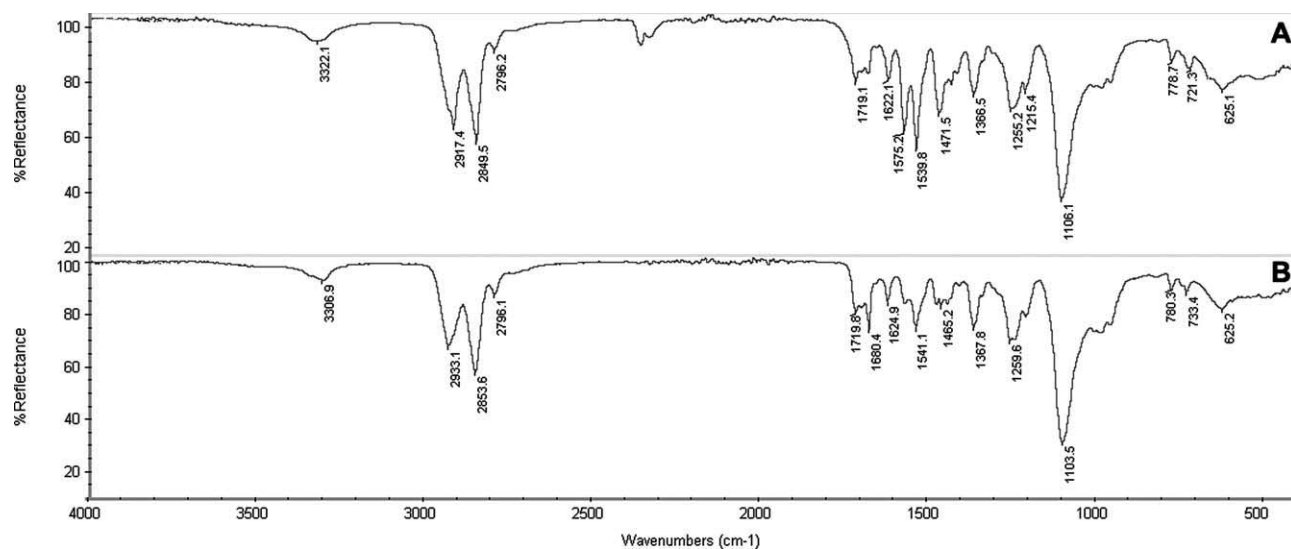

Scheme 2 Synthesis of poly(urethane-ether)s.

Figure 4 FTIR spectra of PUCa-HBA-11 (A) and PUCa-HBA-13 (B).

Thermogravimetric analysis

The TGA traces of metal-containing polymers and blank PUEs are shown in Figure 5. The initial decomposition temperature of metal-containing polymers is low compared to blank polyurethane. Also, it was observed that on increasing the metal content in the polymer, the initial decomposition temperature decreases. This decrease in initial decomposition temperature of metal-containing polymers is due to the catalytic action of metal to initial decomposition of the polymer.[16] TGA traces of PUEs showed two decomposition stages, while the blank PUEs showed single-stage decomposition. The polymer PUCa-HBA-13 is stable up to 231°C, and second-stage decomposition starts at 355°C. The residual weight at 800°C was 1.77%. The polymer PUCa-HBA-11 is stable up to 213°C and at 369°C, second-stage decomposition started. The weight remained at the end temperature of analysis was 2.74%. The initial decomposition of control polyurethane started at 284°C.

Dynamic mechanical analysis

The glass transition temperature (T_g) of the polymer was determined by DMA. DMA allows accurate and precise measurements of the thermal transitions in thermoplastics like polyurethanes. It is 10–100 times more sensitive to the changes occurring in T_g than the DSC. Thus, in this work, DMA is opted over DSC to study the thermal behavior and viscoelastic properties of the material. The viscoelastic properties like storage modulus, loss modulus, and damping factor (tan δ) were investigated over a temperature range of −100 to 20°C under tension mode following the standard technique under the following conditions; a scan rate of 1°C/min and a frequency of 1 Hz. Figure 6 shows the temperature dependence of tan δ. The temperature correspondent to the tan δ peak taken as the glass transition temperature (T_g) of the polymer. Table II shows the glass transition temperature and the initial decomposition temperature of polymers. The control polyurethane has a low T_g compared to the metal-containing polyurethane. The T_g values of metal-containing
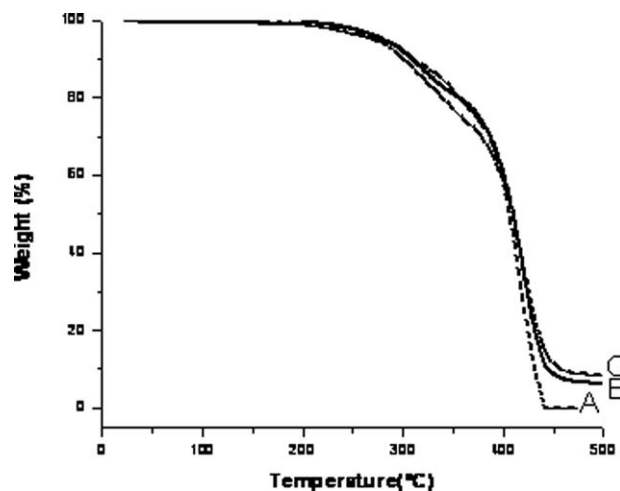
TABLE I
Inherent Viscosity of PUEs

Sample code	Inherent viscosity (dL/g)
PU-C	0.775
PUCa-HBA-13	0.50
PUCa-HBA-11	0.465

Figure 5 Thermogravimetric traces of PU-C (A), PUCa-HBA-13 (B), and PUCa-HBA-11 (C).

Figure 6 Dynamic mechanical analysis of PU-C (A), PUCa-HBA-13 (B), and PUCa-HBA-11 (C).
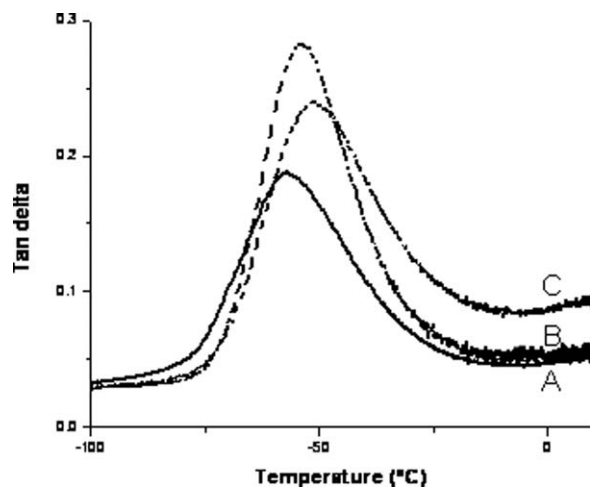

Figure 7 Storage modulus versus temperature of PU-C (A), PUCa-HBA-13 (B), and PUCa-HBA-11 (C).

polyurethane increases with increase in calcium content in the polymer. This increase in T_g is presumably due to ionic bonding. Similar trend was observed with various ionomers. In ionomers, ionic clustering occurs, which will result in the formation of physical crosslinks, that results in the increase in T_g.[29,30] The storage modulus of polymers as a function of temperature is shown in Figure 7. The storage modulus of metal-containing polymers is higher than the blank polyurethane. The polymer PUCa-HBA-13 shows only a slight increase in storage modulus compared to blank polyurethane, but on increasing the ionic content, that is, in the polymer PUCa-HBA-11, it shows a drastic increase in storage modulus. It was reported in one of the study[31] that at low ionic concentration, the ions form simple multiplets, which act as transient crosslink's, on increasing the ionic concentration cluster formation occurs causing an improvement in properties. The drastic increase in storage modulus in PUCa-HBA-11 may be due to this cluster formation.

Mechanical studies

Static mechanical properties of metal-containing poly(urethane-ether)s and blank polyurethane were measured by stress–strain tests and are summarized in Table III. Comparing the tensile strength of the polymers, it was observed that the metal-containing

polymers show high tensile strength than the control polyurethane. The improved tensile strength of metal-containing polymers compared to blank polymer is due to the presence of rigid phenyl group in the metal-containing monomer. Also, there was an increase in the tensile strength with the increase in the calcium content. This increase in tensile strength may be due to clustering of ionic groups present in the polymer.

The presence of calcium in the polymer was confirmed by EDX (Fig. 8). In the control, polyurethane peak corresponding to carbon and oxygen only was obtained. But the spectrum of calcium-containing polymer (spectrum of PUCa-HBA-11 only shown) showed extra peak in the area of around 4 KeV, which corresponds to the calcium atom. Thus, the presence of calcium in the polyurethane was confirmed.

CONCLUSIONS

Calcium-containing monomer was prepared using p-hydroxybenzoic acid. The monomer was characterized by spectroscopic methods. This calcium salt of p-hydroxybenzoic acid was used for the preparation of calcium-containing poly(urethane-ether)s. It was observed that the thermal properties and mechanical properties of calcium-containing polyurethanes were improved with the incorporation of calcium-containing monomer. The prepared polymers possess static ionic linkages in the main chain. It is also presumed that the presence of ionic

TABLE II
Thermal Data of PUEs

Sample code	T_g (°C)	Initial decomposition temperature (°C)
PU-C	−57	284
PUCa-HBA-13	−53.6	231
PUCa-HBA-11	−51.4	213

TABLE III
Mechanical Data of PUEs

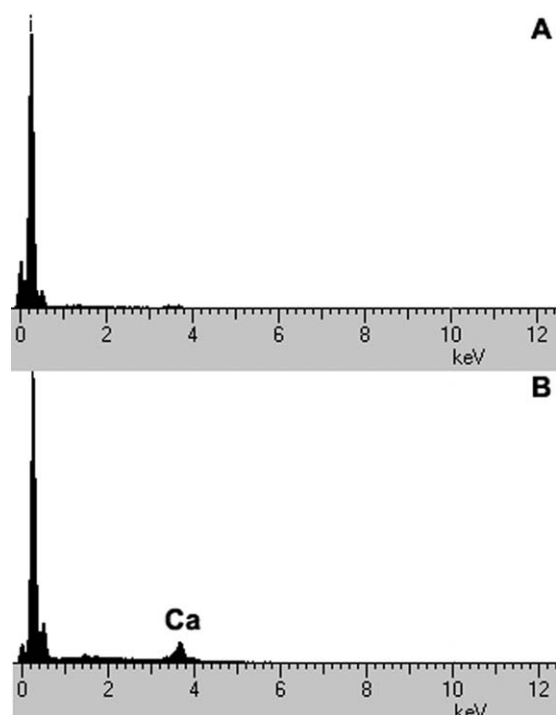| Sample code	Tensile strength (MPa)
PU-C	5.33 ± 0.643
PUCa-HBA-13	31.09 ± 1.10
PUCa-HBA-11	34.45 ± 1.67

Figure 8 EDX spectrum of polyurethanes PU-C (A) and PUCa-HBA-11(B).

linkages in the main chain gives improved blood compatibility to the polymers and thus can be used in biomedical applications.

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