

Synthesis and characterization of polyurethane based on aliphatic diisocyanate and stiff chain extenders

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Abstract—The present research work was performed to study the properties of polyurethanes (PU) based on aliphatic diisocyanate and the effect of chemical structure of chain extenders. Two series of PUs were synthesized via two steps polymerization technique. The PU samples constituted on hexamethylene diisocyanate (HDI), hydroxy-terminated polybutadiene (HTPB) and blends 1, 4 butanediol (BDO)/bisphenol A (BPA) and or 1, 4 butanediol (BDO)/bisphenol S (BPS) were prepared. Structural characterization was done using Fourier transform infrared spectroscopy during and after the synthesis. The FTIR analysis confirmed the existence of proposed bisphenol A (BPA) and bisphenol S (BPS) based PU structures. Differential scanning calorimeter (DSC) analysis gives information about the thermal transition of all the polymer samples. Because of the difference of polarity between hard and soft segments of PU, microphase separation can occur. The degree of phase separation in the prepared PU was confirmed using scanning electron microscope (SEM) technique. The SEM techniques present a distinctive chance to directly visualize the morphology of the polyurethanes.

Keywords: Polyurethane, Bisphenol S, Bisphenol A, FT-IR, DSC, SEM

INTRODUCTION

Polyurethanes (PUs) are a novel class of polymers used in every field of life. Polyurethanes are famous for their easy processing and versatile applications in textiles, plastics, coatings, foams, rubbers, insulations, and applications in construction and automotive industries [1]. Polyurethane elastomers (PUEs) are possibly the most versatile classes of polymers as they can be molded, injected, extruded, recycled [2] and can be easily modified by varying the diisocyanate structure [3] and chain extender (CE) length using α , ω -alkane diols [4,5]. Synthesis, characterization of UV-curable and waterborne polyurethane dispersions [6,7], effect of blocked polyisocyanate based PU composites [8] and PU/natural rubber blends [9, 10] have been studied comprehensively. Bio-based hyperbranched PU [11-14], PLA-based hybrid bio-composite [15], PP/ nitroxide-mediated radical graft polymerization of styrene [16] and influences of clay type, content and dispersion state on PET/clay nanocomposites [17,18] have been documented in the established literature. Polyurethanes are specialized types of polymers which have pivotal role in material formulation for human applications. They are characterized by distinctive features with respect to their physical and chemical behavior by virtue of their structural chemistry and molecular arrangements. On the basis of structural chemistry

and variation of its structural components, their properties can be changed as per requirement [19,20]. Customized manufacturing of PU in association with different structural arrangement render the required properties to the PU materials for various application such as aerospace, automotive industries, foams, fibers, surface coatings, adhesives, varnishes, elastomers and sealants [21,22]. Different polyurethane systems have been studied which exhibit amorphous, semi-crystalline structure [23]. The specialized molecular arrangements of diols and diisocyanates provide the basis for the PU shape, flexibility, and miscibility. The PU, having structurally different phases, is temperature-sensitive and is converted by heating into a single (isotropic) phase. Two-phase structure gives rise to the mechanical durability and special physical and chemical properties of PUs [24]. Polyurethane chemical modifications based on increasing number of methylene units in alkane diol chain extender have a remarkably acknowledged method which not only creates an impact for the PU bulk but also has a substantial effect on the surface properties of the PUs [25]. It is factually perceived that soft segments constitute the crystalline structure in the segmented polyurethane by virtue of their elongated and systematic structure [20,26].

The PUs were synthesized via a standard two-step reaction procedure to study the effect of the nature of the chain extender. A PU prepolymer based on hydroxy-terminated polybutadiene (HTPB, MW=2,912 g/cm³) and 1,6 hexamethylene diisocyanate (HDI) was extended with the series of blends of 1,4 butanediol (BDO) and bisphenol S (BPS) following the formulation given in Table 1. Similarly, another series of PUs was prepared by extending the same

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Table 1. Sample code designation and formations of polyurethanes based on blends of bisphenol-S and 1,4-BDO

Sample code	HDI ^a	HTPB ^b	BP-S ^c	BDO ^d	Tg (°C) ^e
SPU0 ^f	1.2 m; 1.02 g	0.7 m; 7.27 g	0.00 m; 0.000 g	0.7 m	-24.0
SPU1 ^g	1.2 m; 1.02 g	0.7 m; 7.27 g	0.3 m; 0.370 g	0.4 m; 0.180 g	21.037
SPU2	1.2 m; 1.02 g	0.7 m; 7.27 g	0.4 m; 0.492 g	0.3 m; 0.135 g	22.066
SPU3	1.2 m; 1.02 g	0.7 m; 7.27 g	0.5 m; 0.625 g	0.2 m; 0.090 g	22.337
SPU4	1.2 m; 1.02 g	0.7 m; 7.27 g	0.6 m; 0.750 g	0.1 m; 0.045 g	24.733
SPU5	1.2 m; 1.02 g	0.7 m; 7.27 g	0.7 m; 0.875 g	0.0 m; 0.000 g	38.066

^aHexamethylene diisocyanates^bHydroxy terminated polybutadiene^cBisphenol-S^d1,4-Butane diol^eGlass transition temperature measured from DSC curves^fValue reported in the established literature [31]^gBisphenol-S based PU**Table 2. Sample code designation and different formations of PUs based on blends of bisphenol-A and 1,4-BDO**

Sample code	HDI ^a	HTPB ^b	BP-A ^c	BDO ^d	Tg (°C) ^e
APU1 ^f	1.2 m; 1.02 g	0.7 m; 7.27 g	0.00 m; 0.00 g	0.7 m	-24.00
APU1 ^g	1.2 m; 1.02 g	0.7 m; 7.27 g	0.3 m; 0.342 g	0.4 m; 0.180 g	21.737
APU2	1.2 m; 1.02 g	0.7 m; 7.27 g	0.4 m; 0.456 g	0.3 m; 0.135 g	26.400
APU3	1.2 m; 1.02 g	0.7 m; 7.27 g	0.5 m; 0.570 g	0.2 m; 0.090 g	24.700
APU4	1.2 m; 1.02 g	0.7 m; 7.27 g	0.6 m; 0.685 g	0.1 m; 0.045 g	22.066
APU5	1.2 m; 1.02 g	0.7 m; 7.27 g	0.7 m; 0.799 g	0.0 m; 0.000 g	31.066

^aHexamethylene diisocyanates^bHydroxy terminated polybutadiene^cBisphenol-A^d1,4-Butane diol^eGlass transition temperature measured from DSC curves^fValue reported in the established literature [31]^gBisphenol-A based PU

NCO-terminated PU prepolymer with various blends (Table 2) of 1,4 butanediol (BDO) and bisphenol A (BPA). The effect of the chemistry of chain extender on the structural and thermal properties of PUs has been comprehensively studied and discussed using FTIR and differential scanning calorimetry (DSC).

EXPERIMENTAL

1. Chemicals and Reagents

Hydroxy-terminated polybutadiene (HTPB, MW=2,912 g/cm³) and 1,6 hexamethylene diisocyanate (HDI) and potassium hydroxide (KOH) were purchased from Sigma-Aldrich Chemical Co, USA. The 1, 4 butanediol (BDO) was procured from Merck Chemicals. Pure bisphenol A (BPA) and crude 70% pure bisphenol S (BPS) were purchased from local industry and purified to 99.0% by successive crystallization. All the other chemicals, such as concentrated HCl, NaOH and dimethyl sulfoxide (DMSO), were of analytical grade and used without further purification.

2. Purification of Bisphenol S

The 70% crude bisphenol S was purified in the laboratory to get

99% pure bisphenol S. For this purpose the crude BPS was dissolved in 500 ml demineralized water by adding a caustic solution to increase the dilution in water at higher pH and boiled for 15 minutes by adding activated carbon. After boiling, the solution was cooled to warm and filtered in a beaker. The pH of the solution was decreased by the addition of some drops of concentrated HCl. The filtrate was dried in an oven at 100 °C. The dried powder form of bisphenol-S was dissolved in methanol to crystallize the powder, then filtered and the filtrate kept for crystallization. After two days, the crystallization was completed and the crystallized bisphenol S was separated from the filter paper and preserved in reagent bottle for further reaction.

3. Synthesis of PU Prepolymer

A 500 ml round-bottom, four-necked separable flask equipped with a mechanical stirrer, nitrogen gas inlet, thermometer and condenser was used as a reactor. The main purpose of N₂ gas was to provide the inert media during the reaction. The PU prepolymer was synthesized according to a recommended procedure [27]. The diisocyanate like hexamethylene diisocyanate (HDI) was reacted with diol e.g., hydroxy-terminated polybutadiene (HTPB) to obtain

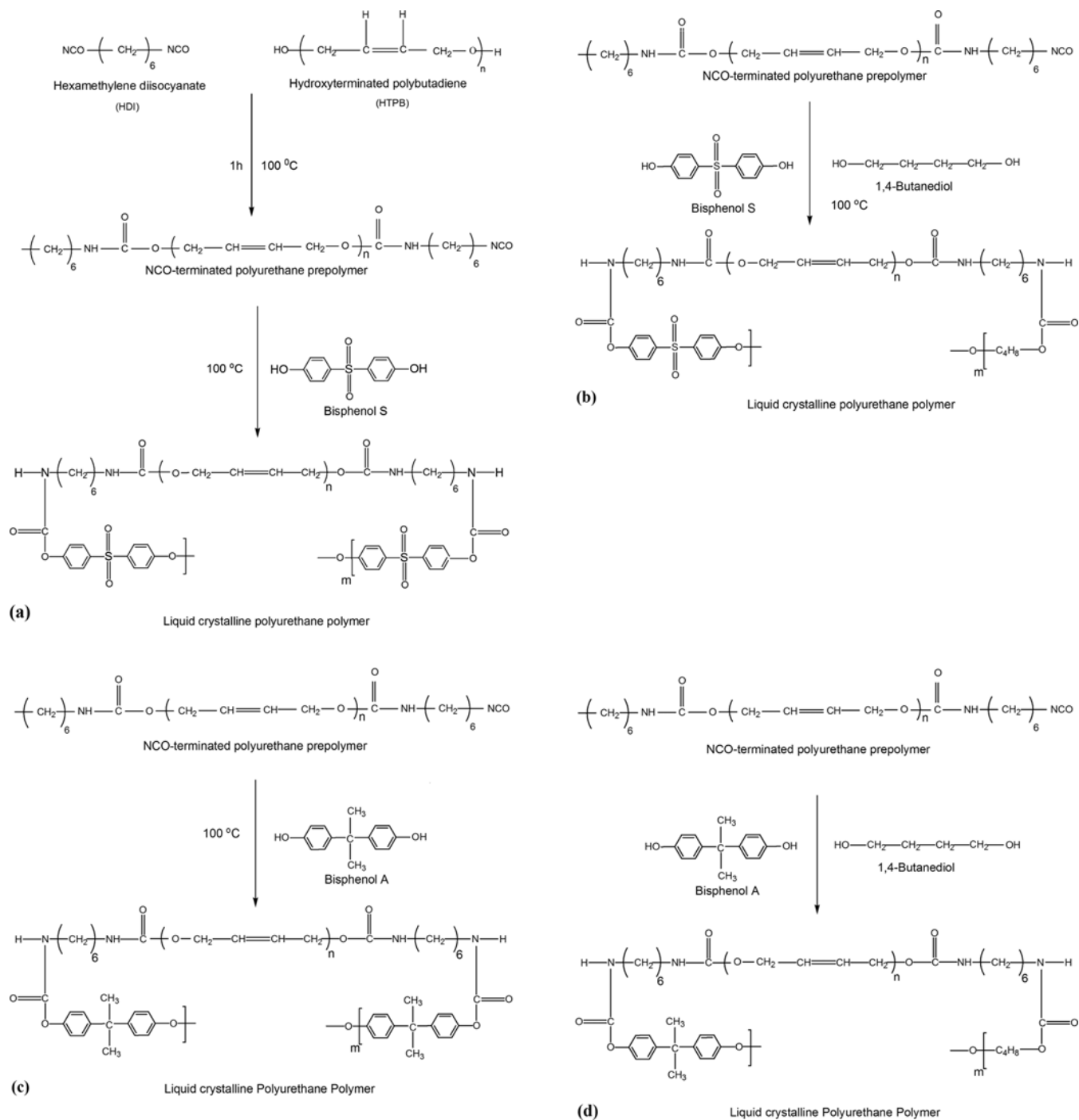


Fig. 1. (a) Synthetic route for the preparation of polyurethane (PU) using bisphenol S (BPS); (b). Preparation of PU using blends of BPS and 1,4-butane diol (BDO); (c). Preparation of PU using bisphenol A (BPA); (d). Preparation of PU using blends of BPA and BDO.

NCO-terminated polyurethane (PU) prepolymer. For this purpose the weighed amount of hydroxy-terminated polybutadiene was taken in the reaction kettle and the temperature of the oil bath was slowly raised to 60 °C; then the diisocyanate was added with a syringe and the temperature was further increased to 100 °C. Continuous mixing was carried out by using a mechanical stirrer in the presence of N₂ gas. Almost after 1.0 h the NCO terminated PU prepolymer was formed.

4. Synthesis of Polyurethane (PU)

The PU prepolymer was reacted with chain extenders to complete the polymerization reaction. Two series of PUs were synthesized: one with blends of 1,4-BDO/bisphenol-S (BPS) and the other with blends of 1,4-BDO/bisphenol-A (BPA) varying mole ratio of the blends. Sample code designation and various formulations of both the series are presented in Table 1 and Table 2, respectively. Prior to use, both the bisphenol A (BPA) and bisphenol S (BPS)

were dissolved in dimethyl sulfoxide (DMSO) and then injected to the reaction vessel to complete the polymerization reaction. After complete mixing, the prepared polymer was poured on a Teflon plate and kept at 90 °C in an oven for 24 hours.

5. Characterization

The monomers and prepared PU samples were characterized by different techniques. Molecular structure of the monomers used in the synthesis, the intermediate compounds and the final material formed at the end of complete polymerization were confirmed using Fourier transform infrared (FT-IR) spectroscopy. FT-IR scans of the prepared polymer samples were obtained in the transmission mode using a Shimadzu Fourier transform infra-red (FT-IR) spectrometer and the scanning region was from 4,000 cm^{-1} to 500 cm^{-1} .

Differential scanning calorimetry (DSC) was used to measure the temperature and heat flow associated with the phase transitions of the material as a function of time and temperature in a controlled atmosphere. These measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic and exothermic processes or change in heat capacity. The samples were heated from -5.0 °C to 510 °C.

Scanning electron microscopy (SEM) studies of TDI-bentonite nano-clay based polyurethane were performed in a JSM-6490A analytical scanning electron microscope (JEOL JAPAN). The samples were auto coated in JFC-1500 in Ion Sputtering Device (JEOL JAPAN) with 290A gold coating.

RESULTS AND DISCUSSION

1. Structural Characterization

FTIR spectra of all the monomers and the prepared PU sam-

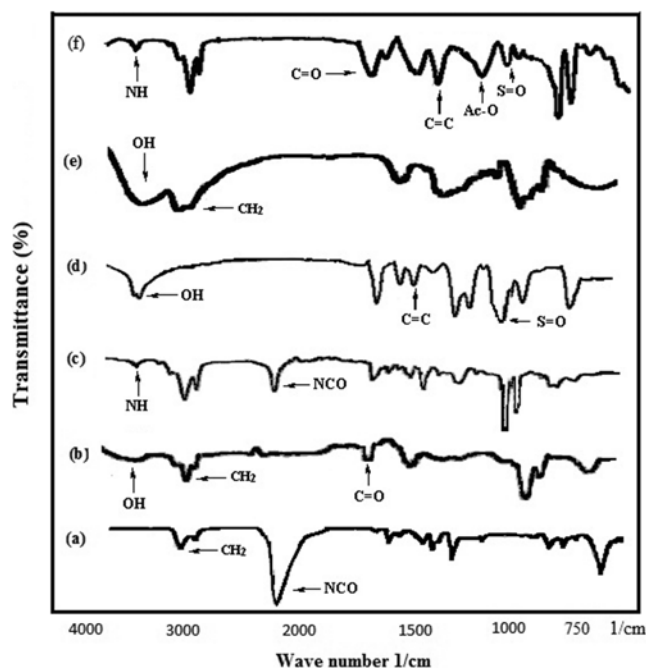


Fig. 2. FTIR spectra of the monomers, PU prepolymer and final PU polymers, (a) HDI, (b) HTPB, (c) PU prepolymer with free NCO groups, (d) BPS, (e) BDO (f) final PU polymer using blends BPS and BDO.

ples are shown in Fig. 2. FTIR spectra of hexamethylene diisocyanate (HDI) and hydroxy-terminated polybutadiene (HTPB) are shown in Fig. 2(a), (b). The PU prepolymer was obtained by the reaction of these two monomers, and the spectrum of the PU prepolymer is shown in Fig. 2(c). The spectrum of HDI is presented in Fig. 2(a). The HDI spectrum shows sharp peaks at 2,935.6 cm^{-1} and 2,860.0 cm^{-1} which are due to the $-\text{CH}_2$ antisymmetric stretching and $-\text{CH}_2$ symmetric stretching, respectively. A very strong peak at 2,249.0 cm^{-1} was also observed, attributed to the isocyanate ($-\text{NCO}$) group attached to the HDI.

The FTIR spectrum of HTPB is presented in Fig. 2(b). In the FT-IR spectrum a broad peak at 3,506.74 cm^{-1} was observed which corresponds to the OH stretching vibration. Similarly, peaks at 2,963 cm^{-1} and 2,810 cm^{-1} were observed which are due to asymmetric $-\text{CH}_2$ and symmetric $-\text{CH}_2$ stretching, respectively. In Fig. 2(c) the peaks observed at 3,365, 1,442, 1,280, and 1,136 cm^{-1} are attributed to OH stretching, C=C stretching due to aromatic, Ac-O stretching and S=O stretching vibrations, respectively, which support the structure of bisphenol S (BPS) having OH groups at the terminals. A broad peak at 3,400 cm^{-1} is observed which is due to the OH stretching in Fig. 2(d) which is attributed to the OH groups present in the 1, 4 butanediol (BDO). The FTIR spectrum of bisphenol A (BPA) is shown in Fig. 2(e). The characteristic absorptions at 3,365, 2,914, 2,845 and 1,442 cm^{-1} are assigned to the OH stretching, CH_2 asymmetric stretching and C=C aromatic stretching, respectively. The FTIR spectrum of NCO terminated PU prepolymer is depicted in Fig. 2(f) which shows the characteristic absorption at 3,324 cm^{-1} attributed to the NH stretching. The appearance of NH peaks confirms the reaction of the NCO group of 1,6 hexamethylene diisocyanate with that of OH groups of the HTPB. There is no OH peak in the FTIR spectrum of NCO terminated PU prepolymer, which confirms that the OH group of hydroxy terminated polybutadiene (HTPB) has been completely reacted with the NCO of the HDI. The NCO peak observed at 2,284 cm^{-1} in the spectrum confirms that the prepared polyurethane prepolymer is NCO terminated PU prepolymer. The other characteristic absorptions at

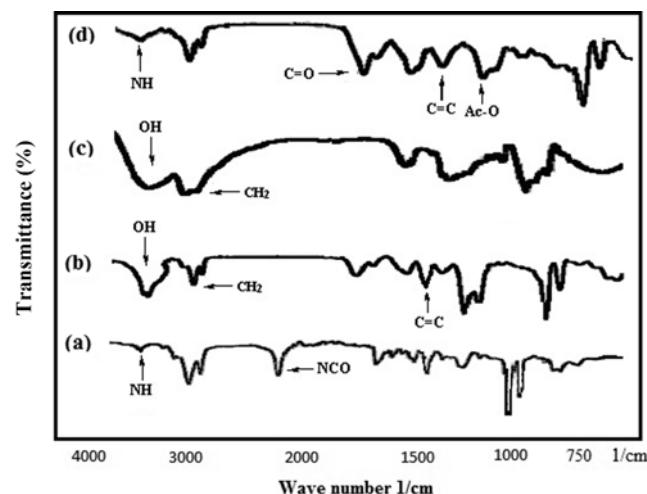


Fig. 3. FTIR spectra of the PU prepolymer and final PU (a) PU prepolymer with free NCO groups, (b) BPA, (c) BDO (d) final PU polymer using blends BPA and BDO.

2,913, 2,843 and $1,690\text{ cm}^{-1}$ are assigned to CH_2 asymmetric stretching, CH_2 symmetric stretching and C=O stretching vibrations, respectively. The chain extension was carried out by the reaction of the prepared PU prepolymer with the stiff chain extenders. Fig. 2(g) shows the FTIR spectrum of PU polymer based on blends of bisphenol S and 1,4 butanediol. After the completion of polymerization reaction of the chain extenders with PU prepolymer, the FTIR spectrum of PU is shown in Fig. 2(g). In this spectrum a peak observed at $3,330\text{ cm}^{-1}$ is attributed to the NH stretching. The NCO peak observed at $2,284\text{ cm}^{-1}$ in the FTIR spectrum of PU prepolymer completely disappeared, which confirms that NCO terminated PU prepolymer has reacted completely with the chain extenders. Similarly, characteristic absorptions at $2,912\text{ cm}^{-1}$, $2,845\text{ cm}^{-1}$ and $1,707\text{ cm}^{-1}$ are attributed to the CH_2 asymmetric stretching, CH_2 symmetric stretching and C=O stretching. The other peaks observed are assigned as: $1,514\text{ cm}^{-1}$, NH bending; $1,442\text{ cm}^{-1}$, C=C stretching; $1,244\text{ cm}^{-1}$, Ac-O stretching; $1,145\text{ cm}^{-1}$, asymmetric and symmetric and at $1,103\text{ cm}^{-1}$ stretching of O=S=O group [28]. Note that the insertion of sulfonyldiphenol units (bisphenol S, BPS) may lead to a more consistent improvement in T_g of polymers with respect to the use of BPA derivatives. This behavior has been attributed to the higher rigidity of the BPS unit since in this molecule it is not possible to bend the C-S-C bonds due to the presence of O=S=O double bonds [28].

Another series of PUs were prepared by extension of the PU prepolymer with blends of bisphenol A (BPA) and 1,4 butanediol (BDO). The characteristic absorptions at 3,319, 2,918, 2,846, 1,687, 1,533, 1,440, and at $1,257\text{ cm}^{-1}$ shown in Fig. 2(h) are due to NH stretching, asymmetric stretching of CH_2 , symmetric stretching of CH_2 , C=O stretching, NH deformation, -NH (urethane group) and Ac-O stretching, respectively. The peaks observed at 3,330, 1,707 and $1,442\text{ cm}^{-1}$ confirm that the synthesized sample has a urethane linkage -NHCOO [29]. There is a pronounced effect on the position of the C=O stretching peak towards higher energy level with the increase in BPS or BPA molar ratio in the blends of BPS/BDO based

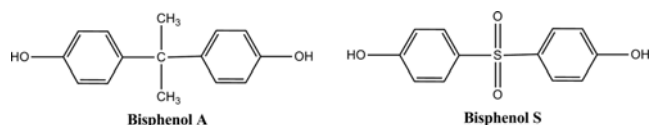


Fig. 4. Chemical structures of BPS and BPA.

PU or BPA/BDO based PU, respectively (Table 3, Table 4). All other position variation can also be observed for understanding (Table 3, Table 4).

2. Thermal Characterization

Differential scanning calorimetry (DSC) was used to measure the temperature and heat flow associated with the phase transitions of the material as a function of time and temperature in a controlled atmosphere. These measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic and exothermic processes or change in heat capacity. The differential scanning calorimetric analysis also gives information about the glass transition temperature T_g of the samples.

As reported in the above lines that in the first series, the blends of bisphenol S (BPS) and 1,4 butanediol (BDO) were used to make the final PU. It can be noticed from the DSC data that by increasing the amount of bisphenol S (BPS) in the blends, the glass transition temperature (T_g) is increased due to the increase in rigidity in the backbone of the PU samples. Note that bisphenol S (BPS) possesses a rigid and linear structure that exhibits a greater impact on glass transition temperature [30,31]. Further, bisphenol S (BPS) has the S=O group which resists twisting and bending of C-S-C due to the linear structure [28,30,31]. By virtue of the linear structure, polymer chain packing occurs in a much ordered form that facilitates to increase the glass transition temperature T_g which in turn gives rise to the high tensile strength of the polymer; hence the polymer formed would have greater durability [32,33]. Contrary to bisphenol S (BPS), the bisphenol A (BPA) has tetragonal

Table 3. Absorptions of the prepared PUs in FTIR spectra (cm^{-1}) based on blends of bisphenol-S and 1,4-BDO

Sample code	NH Stretch	CH_2 As. Stretch	CH_2 Stretch	C=O Stretch	NH Deform	C=C Stretch	Ac-O Stretch	S=O Stretch
SPU1	3330	2912	2845	1645	1514	1442	1244	1145
SPU2	3327	2918	2848	1697	1531	1444	1251	1147
SPU3	3331	2914	2845	1697	1531	1442	1257	1145
SPU4	3334	2916	2845	1697	1581	1442	1286	1145
SPU5	3334	2918	2845	1716	1583	1444	1288	1145

Table 4. Absorptions of the prepared PUs in FTIR spectra (cm^{-1}) based on blends of bisphenol-A and 1,4-BDO

Sample code	NH Stretch	CH_2 As. Stretch	CH_2 Stretch	C=O Stretch	NH Deform	C=C Stretch	Ac-O Stretch
APU1	3319	2918	2846	1687	1533	1440	1257
APU2	3327	2916	2845	1708	1504	1440	1213
APU3	3329	2914	2845	1708	1508	1442	1215
APU4	3329	2914	2845	1709	1512	1442	1217
APU5	3331	2918	2845	1714	1514	1444	1219

structure due to the presence of carbon in the middle of the structure which does not restrict twisting and the inherent structural bending due to the tetrahedral CH_2 centered carbon effect in the polymer packing, which ultimately decreases associated durability and tensile strength. Moreover, PU based on blends BPA/1,4-BDO has shown lesser value for T_g (Table 1) as compared to the PU based on blends of BPS/1,4-BDO (Table 2). Furthermore, 1,4 butanediol (BDO) acts as a part of a hard segment in the PU chain which has been used in the blends of bisphenol S (BPS) and bisphenol A (BPA) separately. It was observed that by increasing the percentages of bisphenol S (BPS) and bisphenol A (BPA), the T_g value increases; however, the percent increase of T_g is higher in the BPS based PU as compared to the BPA based PU. Moreover, by increasing the content of 1,4 butanediol (BDO) in the blends of both bisphenol S (BPS) and bisphenol A (BPA), the T_g decreases at a much higher rate.

3. Morphological Characterization

Microphase separation can occur due to the difference of polarity between hard and soft segments of PU. The degree of phase separation depends on many factors such as chemical structure, molecular weight, composition and arrangement of both kinds of segments. One of the simplest methods for observation of this phenomenon is an SEM micrograph. In SEM analysis, the surface of the specimen is scanned with a high-energy electron beam generating secondary electrons. The secondary electrons are collected by a detector, producing an image representing the intensity of secondary electron. The scattering of the electrons is also a function of the local surface contour, and the scanned image describes the surface morphology. The polymer chains are composed of carbon backbones, and the organic chain can be damaged by the energetic electrons hitting the surface [29]. The SEM images of polyurethane based BPS/BDO (SPU1) and BPA/BDO (APU1) are presented in Fig. 5(a) and Fig. 5(b), respectively. SEM images of the prepared PUs provide a detailed view of morphology in the polyurethane matrix. A continuous phase is visible in SEM micrographs, which is created by the amorphous part of the soft segment. The microstructure surface of the PU based on BPS/BDO or BPA/BDO shows a very compact multilayer net-work structure due to mutual networking of PU [29]. This multilayer structure will certainly help to give better mechanical and thermal properties of the prepared samples.

CONCLUSION

The present research work was carried out to study the properties of PUs based on blends of BPS:1,4-BDO and BPA:1,4-BDO. Spectroscopic data was collected from FT-IR analysis which confirmed the proposed PU structures. It was observed that the PUs based on blends of bisphenol S (BPS) and 1, 4 butanediol (BDO) have greater glass transition temperatures (T_g) as compared to the PUs based on blends of bisphenol A (BPA) and 1,4 butanediol (BDO). The main reason for the higher T_g in the former is the rigid and linear structure of the bisphenol S (BPS) for easy chain packing. Whereas, the latter has a tetragonal structure, so the packing of chains in the skeleton of the polymer is not proper. The 1,4 butanediol (BDO), which acts as part of the hard segment in the polymeric chains is also the reason to observe the decrease in T_g . The PU samples having pristine bisphenol S (BPS) and pristine bisphenol A (BPA) have the higher T_g than the blends. But contrarily, the PUs based on pristine bisphenol S (BPS) have much higher T_g than the PUs based on pristine bisphenol A (BPA). It can be concluded that the prepared polymeric material, i.e., bisphenol S (BPS)-based polyurethanes are very suitable materials where higher T_g and strength are required. The scanning electron microscope (SEM) technique verified the micro-phase separated structure in the PU.

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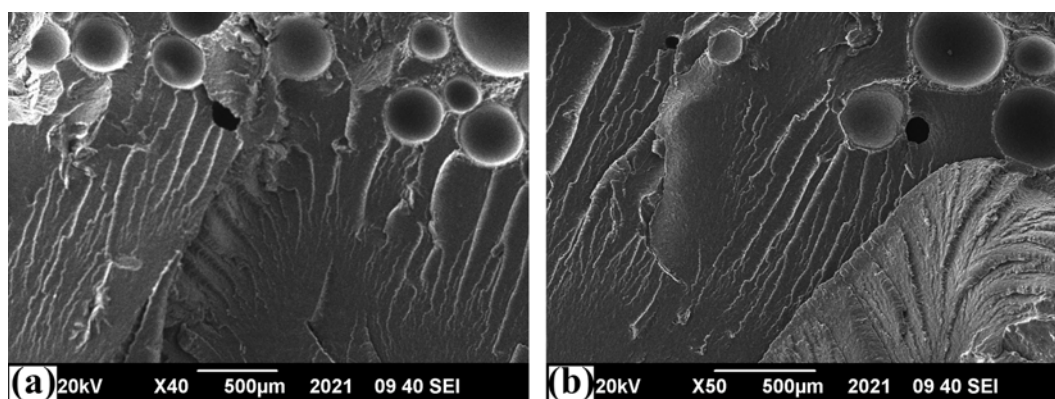


Fig. 5. SEM images of: (a) final PU polymer using blends BPS and BDO; (b) final PU polymer using blends BPA and BDO.

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