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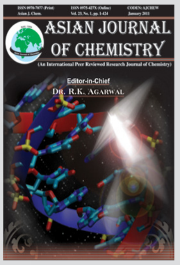

Synthesis and Surface Properties of Hydroxy Terminated Polybutadiene-Based Polyurethane Elastomers by Varying Aliphatic Alkane Diols

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A series of hydroxy terminated polybutadiene (HTPB) based polyurethane elastomers (PUEs) were synthesized by using tolylene diisocyanate *via* prepolymer methodology. The chains of prepolymers were extended with aliphatic diols (ethane-1,2-diol, propane-1,3-diol, butane-1,4-diol, pentane-1,5-diol and hexane-1,6-diol). The final polyurethane elastomers were analyzed by using fourier transformed infrared spectroscopy while solubility, contact angle measurement and evaluation of water absorption percentage (%) were executed to analyze the surface as well as the nature of polymers. Spectroscopic study confirmed the synthesis of polyurethane elastomers while surface characterization and solubility revealed that these polymers were hydrophobic and crosslinked. Furthermore, their hydrophobicity was depended on the number of methylene units of aliphatic alkane diols.

Key Words: polyurethane elastomers, prepolymer, tolylene diisocyanate, surface properties, contact angle.

INTRODUCTION

Polyurethanes have been widely used in industry due to their versatile properties[1-3]. Polyurethanes, which are normally based on alternate fashion of hard segments and soft segments, are known as segmented block copolymers. Chemically, hard segments are produced by the reaction of an isocyanate and chain extender which is low molecular weight (LMW) diamines or diols. On the other hand, soft segments are typically derived from a macrodiol/polyol. Polyurethanes are useful thermoplastic elastomers due to their superior mechanical strength and elastomeric behaviour that are derived from microphase separation and hydrogen bonding[4,5].

On the other hand, the characteristics of polymeric materials are also affected by a number of factors such as polymerization environment, relative reactivity, compatibility and proportion of the polyols, isocyanates and low molecular weight diols or diamines[6-12]. Finally, thermal treatment and mechanical handling have significant affect on curing of the final product[13].

When the soft segment of polyurethane elastomers (PUEs) is polybutadiene in spite of polyether or polyester, some new characteristics are appeared in the polyurethane samples. These are resistant to hydrolysis even under acidic or basic environments, good adhesion properties and significantly their elestometric performance at low temperature. Moreover, these are absolutely hydrocarbon in nature and only show the intersegmental hydrogen bonding, which is responsible for good mechanical properties usually present in polyether or polyester based soft segments of polyurethane[12,14]. Role of functionality of hydroxy terminated polybutadiene (HTPB) is another important feature. When hydroxy terminated polybutadiene is typically difunctional, linear segmented polyurethane elastomers are resulted while their functionality more than two generates crosslinked polyurethanes[12,15-20].

Polyurethane derived from hydroxy terminated polybutadiene have found wide use as solidified fuel in rockets, as adhesives, coatings, sealants, binders and potting compounds[21-28].

In different attempts[6,7], it has been studied that the surface properties of linear polyurethane can be modified using monofunctional polyhedral oligomeric silsesquioxane (POSS) which enhances the surface hydrophobicity and reduces the surface energy. Recently, Liu *et al.*[29] also reported the surface nature of crosslinked polyurethane network which display a significant enhancement in hydrophobicity.

Zia *et al.*[30] studied the water wettability of polyurethane surface which is an important issue now a days. Majority of the polymeric materials have relatively hydrophobic surface because of the nature of structural units. It is possible to change the extent of hydrophobicity by modifying the composition of polyurethanes which is linked with its end use. Zia *et al.*[31] also pointed out the decline of hydrophobicity of polyurethane elastomers based on caprolactone, tolylene diisocyanate along the variation of different low molecular weight α,ω-alkane diols.

In the present study, hydroxy terminated polybutadiene capped with tolylene diisocyanate has been used as the prepolymer for polyurethane elastomers which were extended with aliphatic alkane diols carrying different number of methylene units to determine the influence of chain extenders on the surface properties of the resulted polyurethane elastomers.

EXPERIMENTAL

Tolylene diisocyanate (TDI), (a mixture of 80 % w/w of the 2,4 isomer and 20 % w/w of 2,6 isomer); 1,2-ethane diol (1,2-EDO), 99 % pure; 1,3-propane diol (1,3-PDO), 99 % pure; 1,4-butane diol (1,4-BDO), 98 % pure; 1,5-pentane diol (1,5-P′DO), 98 % pure; 1,6-hexane diol (1,6-HDO), 97 % pure; were purchased from Sigma Chemical Co. (Saint Louis MO, USA). Hydroxy terminated polybutadiene (HTPB) having molecular mass 3000 was collected locally. Dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), *n*-methyl-2-pyrrolidone (NMP) and N,N-dimethyl acetamide (DMAc) from Merck Chemicals (Darmstadt, Germany). HTPB and chain extenders were evacuated at 80 ºC for 24 h to dryness prior to employing in the polymerization. Tolylene diisocyanate was used as received. All the chemicals used were of analytical grade.

Polymerization: Condensation polymerization was employed to prepare these polyurethane elastomers by using macrodiol, diisocyanate and chain extension with aliphatic alkane diols *via* prepolymer methodology following Barikani & Hepburn[32,33]. Entire polymerization reaction was carried out in a four-necked reaction kettle equipped with mechanical stirrer, reflux condenser, dropping funnel, N_2 inlet outlet *via* pyrogallol solution to make O_2 free and heating oil bath. Polyol was placed (*e.g.*, HTPB: 21.72 g, 0.0072 mol) in the reaction kettle and heated to 60 °C. Subsequently, tolylene diisocyanate (*e.g.*, TDI: 3.78 g; 0.0217 mol) was added and thermally treated at 100 °C for 1 h on an heating oil bath under the blanket of dry N_2. A small portion of the reacting material was taken out to ensure the completion of the prepolymer synthesis by FTIR spectroscopy. When isocyanate (NCO) terminated polyurethane prepolymer was prepared then already degassed chain extender (*e.g.*, 1,2-EDO: 0.88 g; 0.0142 mol) was added during the vigorous stirring of prepolymer to convert it into the final polyurethane. Subsequently the liquid polymers were cast into Teflon molds and then cured at 100 °C for 24 h in hot air circulating oven. Typical polyurethane synthesis is shown schematically in Fig. 1. The recipes of these polymers are given in the Table-1.

TABLE-1
SAMPLE CODES WITH DIVERSE FORMULATION ON THE BASIS OF CHAIN EXTENDERS FOR HTPB BASED PUEs

Sample code	Polyol (0.0072 mol)	Diisocyanate (0.0217 mol)	Chain extender (0.0142 mol)
E1	HTPB (21.72 g)	TDI (3.78 g)	EDO (0.88 g)
E5	HTPB (21.72 g)	TDI (3.78 g)	PDO (1.08 g)
E6	HTPB (21.72 g)	TDI (3.78 g)	BDO (1.28 g)
E7	HTPB (21.72 g)	TDI (3.78 g)	P'DO (1.48 g)
E8	HTPB (21.72 g)	TDI (3.78 g)	HDO (1.68 g)

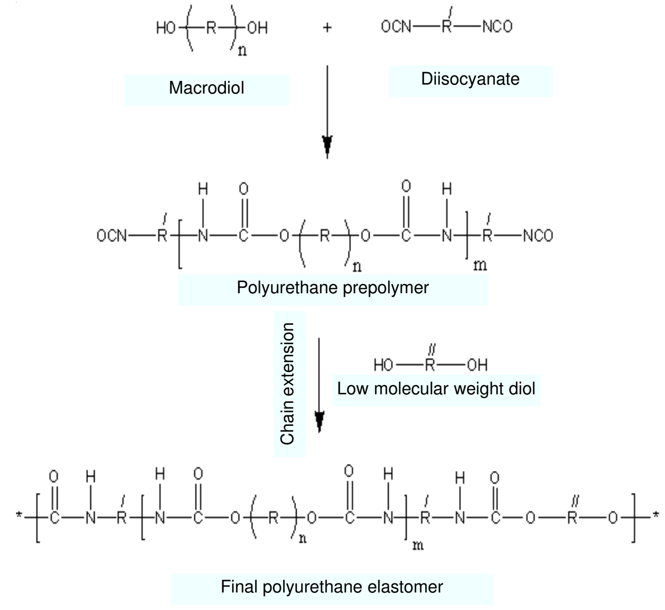

Fig. 1. Schematic route for the synthesis of polyurethane

Characterization

Fourier transform infrared spectroscopy: Thin films of polyurethane elastomers were subjected to Fourier transform infrared spectrometer IR prestige-21 Shimadzu, Japan at transmittance mode (4000-500 cm^{-1}) region.

Contact angle measurement: Contact angles were measured to determine the interfacial relation between the two surfaces *e.g.* between a solid and a liquid. These measurements were achieved by sessile-drop experiment using DSA G-10 goniometer (Kruss GmbH, Germany). This instrument utilizes precision optics and computer control discs (CCD) cameras along with image producing hardware and software to analyze and determine the contact angle. In practice a droplet of liquid *e.g.* water was placed onto the surface of sample, then a CCD camera scan the droplet and displays its profile on the computer monitor. All these measurements were average of ten analyses.

Evaluation of water absorption percentage (%): Hydrophobicity of the polyurethanes was evaluated by measuring the mass of each polymer after the absorption of water at 37 °C. For this purpose, sample films having dimensions (10 mm × 10 mm × 1 mm) were placed in 100 cm^3 conical flasks, containing triply distilled and degassed water and kept for consecutive 4 days in an incubator at 37 ± 2 °C. The samples were taken out from water according to predetermined intervals, swabbed with filter paper and weighed instantly by an analytical balance. The difference in the mass of sample was due to the water absorption. The water absorption percentage was calculated according to the following formula[30].

$$\text{Water absorption (\%)} = \frac{(m_w - m_d)}{m_d} \times 100$$

The masses of dry and wet samples are designated as m_d. and m_w, respectively.

Determination of solubility: Polyurethane elastomers (E1, E5-E8) were subjected to determine their solubility in different solvents and their combinations at various temperatures to recognize their crosslinking[34].

RESULTS AND DISCUSSION

Fourier transformed infrared studies of HTPB based polyurethane elastomers: Fourier transformed infrared spectra of final PUEs based on TDI, HTPB and different chain extenders (1,2-EDO; 1,3- PDO; 1,4-BDO; 1,5-PDO and 1,6-HDO) are shown in Fig. 1(a-e) and corresponding and significant absorption peaks of the final PUEs are tabulated in the Table-2.

TABLE-2
INFRARED CHARACTERISTIC ABSORPTION PEAKS (cm^{-1}) RELATED TO FINAL PUEs (a) E1, (b) E5, (c) E6, (d) E7 AND (e) (E8) BASED ON HTPB, TDI AND DIFFERENT CHAIN EXTENDERS 1,2-EDO, 1,3- PDO, 1,4-BDO, 1,5-PDO AND 1,6-HDO, RESPECTIVELY

Key absorption peaks (cm^{-1})	Sample E1	Sample E5	Sample E6	Sample E7	Sample E8
ν(NH)	3292	3298	3314	3314	3313
$\nu_s(CH_2)$	2916	2912	2914	2914	2914
$\nu_{as}(CH_2)$	2847	2843	2843	2843	2843
ν(C=O) Free	1716	1707	1707	1705	1705
ν(C=O) H-bonded	1649	1648	1643	1642	1645
δ(NH)	1599	1598	1599	1595	1597
δ(C-N)	1536	1536	1533	1533	1535
$\delta_s(CH_2)$	1445	1438	1440	1439	1438
$\delta_{as}(CH)$	1418	1420	1421	1419	1420
ν(C=C)	1223	1223	1225	1225	1223
ν_s(C-O-C)	1037-1018	1140-1070	1131-1057	1180-1059	1150-1053

ν = Stretching vibration; ν_s = Symmetric stretching vibration
ν_{as} = Asymmetric stretching vibration; δ = deformation/bending
δ_s = Symmetric bending vibration; δ_{as} = asymmetric bending vibration

FTIR spectrum in Fig. 2(c) is of polyurethane elastomer (E6) showed typical stretching band due to urethane groups at 3314 cm^{-1} (N-H stretching). The other absorption peaks of the spectrum at 2914 and 2843 cm^{-1} were assigned to CH symmetric and asymmetric stretching vibrations of CH_2 groups, respectively. While other absorption peaks were designated as: 1707, 1643 cm^{-1} (C=O bond); 1599 cm^{-1} (NH deformations); 1533 cm^{-1} (aromatic ring) 1440 cm^{-1} (CH_2 bending vibration) and 1317 cm^{-1} (CH_2 wagging). FTIR spectrum of extended prepolymer with 1,4-BDO have absorption peaks corresponding to NH was observed at 3314 cm^{-1},while stretching peaks at 1707 cm^{-1} (non-hydrogen bonded) and 1643 cm^{-1} (hydrogen bonded) for C=O group and C-O stretching at 1225 cm^{-1}. These absorption bands indicate that the final polyurethane elastomers had urethane (NHCOO) group. While the N-H bending vibrations at 1598 cm^{-1}, C-O-C stretching absorption band corresponds the linkage between OH and NCO groups to form urethane bond in the range 1057-1130 cm^{-1} had also evident the synthesis of polyurethane.

It is also important to know that the N-H and C=O groups in polyurethane could develop the inter-hard segmental hydrogen bonding and act as physical crosslinks by restricting the movement of polymeric chains, Actually these physical crosslinking had also influenced the phase separation between the hard segments and soft segments of polymer chains and ultimately influence the mechanical properties, flexibility and solubility of polyurethanes[35,36].

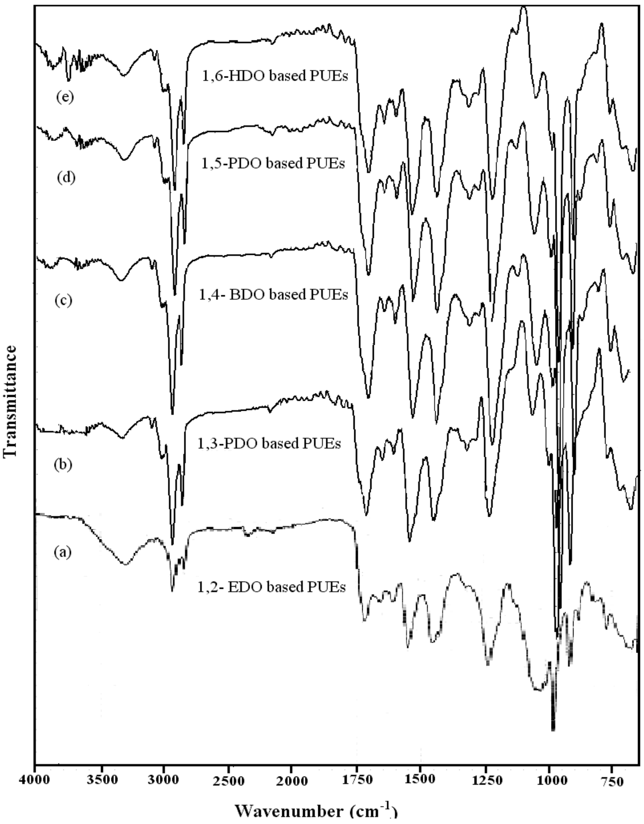

Fig. 2. FTIR spectra of final PUEs (a) E1; (b) E5; (c) E6; (d) E7; (e) (E8) based on HTPB, TDI and different chain extenders

Contact angle measurement: The surface hydrophobicity of polyurethane elastomers was determined by measuring the contact angle formed by water and the surface of the polyurethane films using contact angle measuring devices (G-10 KRUSS). In the present study the contact angle was determined by using water as a polar wetting liquid for polymer surfaces. The values of contact angle using water as test liquid for E1 was 70.6° and gradual increase of contact angle for the samples E5-E8 form 71.8° to 75.2°, as the number of methylene units in the PU backbone vary from 2 to 6 is reported in Table-3 and Fig. 3. There is slight increasing trend between the contact angle values of E1and E5 to E8 with water surface contact which shows that E8 is least hydrophilic. This means hydrophilicity of the final PU film decreases by increasing the chain extender length. This trend might be based on the fact that the hard segment carrying polar group is connected with chain extender and the movement of the hard segment also depends upon the degree of freedom of hard segment which is provided by the length of chain extender that make the surface hydrophilic[30]. On the other hand, these polymers are HTPB based, which is non-polar in nature and due to their higher percentage, soft segment covers more surface area than the hard segment and create hydrophobicity. Hydrophilicity of the polyurethane films was decreased with chain extender length because it diluted the polar groups and hydrophilicity decreases as in the case of E5 to E8. As these samples were HTPB (alkylene linkage) based which is non-polar than polyester and polyether based, therefore, chemical functional groups like C=O groups are not present in the backbone of HTPB which may be responsible for the decline of wettability. These polymers show only

TABLE-3
CONTACT ANGLE (θ), WATER ABSORPTION PERCENTAGE (%) OF PUEs BASED ON CHAIN EXTENDERS OF DIFFERENT NUMBER OF -CH_2-units (E1) 1,2-EDO, (E5)1,3-PDO, (E6) 1,4- BDO, (E7) 1,5- P'DO AND (E8) 1,6-HDO

Sample code	Temp. (°C)	Contact angle (θ)	Water absorption (%)			
			1st day	2nd day	3rd day	4th day
E1	23±2	70.6	0.55	0.55	0.56	0.56
E5	23±2	71.8	0.46	0.47	0.46	0.48
E6	23±2	72.2	0.35	0.36	0.36	0.36
E7	23±2	73.5	0.28	0.27	0.28	0.28
E8	23±2	75.2	0.22	0.22	0.23	0.23

Each value is expressed as mean ± standard error (n = 5).

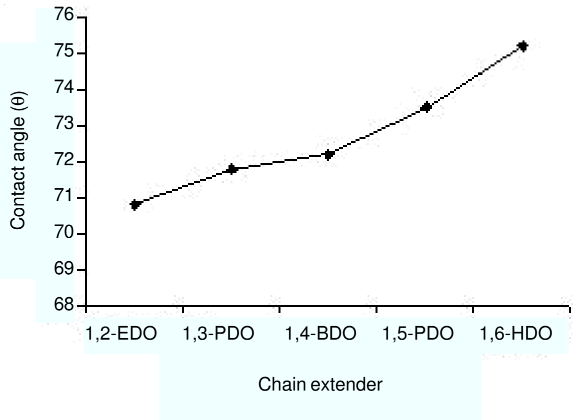

Fig. 3. Contact angles of PUEs (E1) 1,2-EDO, (E5)1,3-PDO, (E6) 1,4-BDO, (E7) 1,5- P′DO and (E8) 1,6-HDO as a function of chain extenders length

wettebility due to the polar contents (hard segment). But the lower wettebility of the polymers have high number of -CH_2-units in polymer chain provide more conformational freedom and better packing of chains which ultimately reduces the wettebility of polymers. It is known that the hydrophobic surface gives a low surface energy and gives a high contact angle while hydrophilic surfaces spread the drop of polar liquid and show a lower value of contact angle[37,38]. It is also found that there is no effect of crosslinking on the hydrophobicity of the surface.

Evaluation of water absorption percentage (%): The property like water absorption percentage (%) of polyurethane samples (E1, E5-E8) was determined as a function of time and is tabulated in Table-3. There is no significant change in the quantity of water absorption as a function of time. It is found that the water absorption capacity is decreased as the chain extender length in the main chain increased while it has been observed that the crosslinking in the polymeric chains has no effect on water absorption ability. The results obviously represented the enhancement in the hydrophobicity of polyurethane elastomers samples as the number of methylene units (-CH_2-) in the final polyurethane samples increased (Fig. 2).

Solubility of polyurethane elastomers: The solubilities of polyurethane samples (E1, E5-E8) were determined in different solvents like water and polar aprotic solvents such as DMSO, DMF, NMP, DMAc and also using their various combinations at different temperatures (30, 60, 80,100 and 120 °C). It has also been found that all of these sample are better resistant to water and polar aprotic organic solvent and their combinations which might be due to chemical crosslinking[34]. So, these polymers can be used in both indoor and outdoor atmosphere because they have hydrolytic resistant HTPB based soft segments in the polymeric chains. As these polymers are resistant to water absorption, it can be stated that these polymers exhibited more resistance to hydrolytic degradation.

Conclusion

Hydrophobic polyurethane elastomers were synthesized by step growth methodology using hydroxy terminated polybutadiene and tolylene diisocyanate, extended with aliphatic alkane diols. The spectroscopic analysis of the samples using FTIR spectroscopy was according to the proposed molecular structure of polyurethane. For all the samples the surface properties were studied and discussed by using contact angle measurement, water absorption capacity and solubility. All these studies revealed that the samples were hydrophobic and this property was increased as the chain extender length was increased. Investigation of these samples represented that the observed properties such as hydrophoboicity and insolubility were mainly due to physical and chemical crosslinking as well as the number of (-CH_2-) methylene units in the chain extender of the polyurethane backbone.

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