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Effect of HTPB structure on prepolymer characteristics and on mechanical properties of polybutadiene-based polyurethanes

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ABSTRACT

Oligobutadiene-based prepolymers and polyurethanes (PU) were prepared from hydroxyl terminated polybutadiene (HTPB), three diisocyanates (aromatic, alicyclic and aliphatic) and two chain extenders (containing hydroxyl or amino groups). The free NCO content in the prepolymers varied systematically and the characteristic of these products were interpreted in terms of NCO group reactivity, propagation reactions and HTPB functionality. The mechanical properties of the polyurethane elastomers derived from the prepolymers were discussed in terms of hard and soft segment structures.

INTRODUCTION

Polybutadiene based-polyurethanes are used in a wide range of applications such as sealants, binders, adhesives, waterproof and anticorrosion coatings, foams, electrical insulation, elastomers, etc. Compared with usual polyether or polyester based polyurethanes, they present better hydrolytic resistance and higher flexibility at low temperatures. These properties are derived from the hydrophobic character and low Tg of the polybutadiene segments[1]. On the other hand the room temperature mechanical properties of these polyurethane elastomers such as tensile strength, abrasion and tear resistance are not as high as those found for polyether or polyester containing polyurethanes[2-4].

Hydroxyl terminated polybutadienes (HTPBs) used in the preparation of polyurethanes are commercially prepared by anionic or free radical processes[5]. In the first case the products contain functionality close to two (mainly difunctional and a minor amount of monofunctional species), with high 1,2 butadiene content[6]. The properties and morphology of polyurethanes prepared with anionic HTPBs have been explored[7-10].

In the free radical process, 1,4 addition is predominant, and HTPB functionality is always greater than two, due to transfer reactions occurring during polymerization[11]. The characterization of free radical produced HTPB has also been reported[12,13]. When hydrogen peroxide is used as initiator and an alcohol as solvent the resulting polymer is composed mainly of difunctional macromolecules and small amounts of mono and polyfunctional species[14,15].

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The morphology and properties of the HTPB containing polyurethane elastomers have been the subject of a number of publications[2-4,8-10,16-20], but the effects caused by the presence of polyfunctional molecules upon the polymerization process on the final product properties are still not clear.

It is known that the two step procedure for the preparation of polyurethanes is preferable to a "one shot" process due to the better properties that can be achieved with the prepolymer technique. This is probably due to a more homogeneous distribution of the soft and hard segments. The two step procedure is also important when the reactivities of the polyol and chain extenders differ as in polyurethane/urea elastomers.

It is important to know how the structural characteristics of HTPB affect the properties of the prepolymer produced in the first step of the polymerization, and subsequently the properties of the final polyurethane material. In this communication we report some results concerning polyurethane elastomers prepared in a two step procedure, and discuss the effect of the HTPB functionality on prepolymer characteristics and mechanical properties of the derived polyurethanes. The prepolymers were prepared by reacting HTPB with tolylene diisocyante (TDI 80/20 and TDI 65/35, corresponding mixtures of isomers 2,4/2,6 respectively); hexamethylene diisocyanate (HDI); or [5-isocyanate-1-(isocyanatemethyl)-1,3,3-trimethylcyclohexane] (IPDI - isophorone diisocyanate). In the second step they were cured with 4,4'-methylene-bis-orthochloroaniline (MOCA) or di(2-hydroxypropyl)-N-aniline (DHPA).

2 EXPERIMENTAL

Materials - **TDI 80/20, TDI 65/35** (Pronor Petroquímica, Brazil), **HDI** (Rhone-Poulenc, Inc.) and **IPDI** (Nuodex Inc.) were used as received. **MOCA** (MRV Corp.) and **DHPA** (Upjohn Co.) were dried at 120°C (10 mm Hg) for one hour. The **HTPB** commercial sample was Petroflex[21] Liquiflex-H which was dried at 100°C (10 mm Hg) for 30 minutes. Characterization data of HTPB were: hydroxyl number 0.83 meq/g; Brookfield viscosity 5800 cP at 25°C; M_n=2710 (determined by VPO analysis); number average functionality f_n=2.19; polydispersity D=1.66 (determined by GPC) and microstructure: 20.7% of 1,2 addition (vinyl enchainment), 59.6% of 1,4 trans and 19.7% of cis structures (determined by ^1H and ^{13}C NMR)[13]. **Syntheses** - **Prepolymers:** To a nitrogen purged reactor the HTPB, the required amount of diisocyanate and 0.06% benzoyl chloride (stabilizer) were added with stirring. After two hours at 60°C the mass was poured into a preweighted nitrogen-purged flask. The free NCO content and Brookfield viscosity were measured. **Polyurethane elastomers:** To a vessel, the dry and degassed prepolymer and the required amount of chain extender were added (NCO/OH or NCO/NH_2 = 1.05). When necessary 0.03% of dibutyl tin dilaurate was also added. The mixture was slowly stirred and cast into a vertical stainless steel mold, preheated to 100°C. After one hour at 100°C the mold was allowed to cool to ambient temperature and the rubber sheets were withdrawn. Before testing the specimens remained at room temperature for one week to complete curing. **Tensile and hardness** measurements were performed according to ASTM D412 and D2240 respectively.

RESULTS AND DISCUSSION

The results concerning the NCO content and the viscosity of the HTPB prepolymers prepared with TDI 80/20, TDI 65/35, HDI and IPDI are presented in Table 1.

Table 1 - Prepolymers from HTPB, TDI 80/20, TDI 65/35, HDI and IPDI

Diisocyanate	Prepolymer Characteristics	
	NCO content (%)	Brookfield Visc.(cP) 25 °C
IPDI	4.61	66000
	6.88	25000
	9.04	14000
HDI	4.68	66000
	6.58	20000
	8.89	10000
TDI 65/35	4.93	22000
	6.66	16000
	8.67	9000
TDI 80/20	4.81	23000
	6.73	16000
	8.61	8000

From the data it may be observed that viscosity values decrease with increasing free NCO content. This is due to two effects. The first is the dilution attributed to the excess diisocyanate and the second is that higher NCO/OH ratios in prepolymer synthesis decrease the number of intermacromolecular reactions, resulting in lower molecular weight and less viscous products.

It was also observed that at low free NCO content the viscosities of the TDI prepolymers are lower than those of the HDI or IPDI prepolymers. This can be explained in terms of reactivity differences between the NCO groups in the aromatic ring of TDI, where the $\underline{2}$ or $\underline{6}$ position is less reactive than the $\underline{4}$ position. The kinetic constants are: k_2=k_6=0.25 x 10^{-4} l.mol^{-1}.s^{-1} and k_4=2.62 x 10^{-4} l.mol.$^{-1}$.s^{-1} for the reaction of TDI with n-butanol in xylene, 25°C, NCO/OH = 1.0 $[NCO]_0$ = 0.5 N[22].

In the one step process, when stoichiometric amounts of reactants are used, the free NCO content is very low and the ratio between diisocyanate and polyol is the same as between equivalent weights. In the two step process when the diisocyanate/polyol ratio of 2/1 equivalents is used in the first step, all the terminal hydroxyls would be replaced by terminal NCO groups and theoretically there will not remain unreacted diisocyanate. In practice this can only occur if the reactivities of the two NCO groups are quite different, and the terminal NCO group will be the less reactive. When the reactivities are the same the terminal NCO groups of the prepolymer and the monomeric NCO have the same probability for reacting with the hydroxyls of the polyol, resulting in higher polydispersities and unreacted diisocyanate.

Using an equivalent NCO/OH ratio of 2/1 for calculating the free NCO content of HTPB prepolymers made with TDI, IPDI and HDI, the resulting values were 3.04%, 2.14% and 3.06%, respectively. However it was not possible to employ such values in the syntheses due to the extremely high viscosities produced. The prepolymers listed in Table 1 were prepared with equivalent NCO/OH ratios of 2.8, 3.6 and 4.5 for obtaining the approximate free NCO values of 5%, 7% and 9% for TDI, IPDI and HDI prepolymers, respectively. The minimum limiting value NCO/OH = 2.8 was set in practice by the resulting extremely viscous products. This effect is explained as follows: in addition to the factors already mentioned prepolymer viscosity is affected by HTPB functionality. As stated above low NCO/OH ratios favor propagation, and polyfunctional molecules give rise to branched and crosslinked prepolymers under these conditions, causing viscosity to increase.

In the second step of polyurethane or polyurethane/urea preparation, DHPA or MOCA curing agents were used with NCO/OH or NCO/NH_2 equivalent ratios of 1.05. With MOCA it was not possible to prepare polyurethane/urea elastomers from prepolymers with free NCO content above 5% due to a very short pot life. In addition to these factors, in this case the reaction was accelerated by the high reactivity of the amino group in MOCA towards the prepolymer NCO end group. For TDI prepolymers the pot life was shorter (approximately 4 minutes) than for the corresponding HDI and IPDI prepolymers (6-7 minutes). This was attributed to the lower reactivity of the aliphatic NCO groups relative to the aromatic NCO groups.

A interesting feature of HTPB prepolymers is the low pot life of the reaction mixture prior to mold casting polyurethane/urea elastomers. Two factors that can be responsible for this behavior are: first, since it is not possible to prepare HTPB based prepolymers with low free NCO contents (less than 5%) as explained, the use of greater amounts of chain extenders (curing agents) are required; and second, the polyfunctional prepolymers rapidly form crosslinked segments when the curing agents are added in the second polymerization step.

The mechanical properties of the polyurethane elastomers prepared from the prepolymers listed in Table 1 are shown in Table 2.

Table 2. Mechanical properties of PUs prepared from prepolymers listed in Table 1.

Isocyanate	Curing agent	Hard segment content^a %	Tensile strenght^b Kgf/cm^2	Ultimated elongation^b %	Modulus 100%^{b} Kgf/cm^2	Hardness Shore A
IPDI	DHPA	29.0	80	480	20	69
		36.4	146	470	46	86
		43.1	175	440	58	97
	MOCA	31.1	220	360	100	99
HDI	DHPA	25.4	21	260	13	55
		31.2	46	300	16	62
		37.4	53	360	20	65
	MOCA	21.6	121	280	63	86
TDI 80/20	DHPA	26.1	70	390	24	73
		32.2	103	380	44	85
		38.2	123	400	60	88
	MOCA	38.4	190	240	130	89
TDI 65/35	DHPA	26.1	68	370	25	72
		32.2	99	360	37	84
		38.2	118	370	59	88

a - (mass diisocyanate + mass curing agent) x 100 ÷ total mass; b - ASTM D412; c- ASTM D2240

It is well known that the balance between the hard and soft segments greatly affects the physical properties of segmented polyurethanes, and in fact the data in Table 2 show that increases in the free NCO content in prepolymers correspond to systematic increases in tensile strength and 100% modulus. In respect to elongation, only HDI polymers showed a small increase with increasing hard segment content.

IPDI or TDI elastomers had higher mechanical properties than those prepared from HDI. The aromatic or alicyclic structures of TDI or IPDI can give rise to better phase separated materials, due to their higher incompatibility with HTPB than HDI hard segments. Higher values for mechanical properties with increasing hard segment content are attributed to higher concentrations of rigid in relation to flexible segments, thus increasing the intermolecular secondary forces, which are hydrogen bonding and π interactions between aromatic rings.

The fact that elongation at break did not follow this general trend may be attributed to the existence of crosslinks between the polyfunctional HTPB chains. In linear polyurethanes, when mechanical forces are applied, changes in the orientation and mobility within the hard segments can occur, depending on the temperature. The initial hydrogen bonds can be disrupted and new, energetically more favorable bonds are formed, while structural changes occurs along the direction of the applied force. The tensile stress is better distributed and as a result the overall resistance increases. For crosslinked polyurethanes the extent to which such changes can occur depend on the crosslink density. The fact that elongation did not increase with increasing hard segment content may be attributed to crosslinks that hinder chain realignment in the direction of the applied force.

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