Effect of Imide–Oxazolidinone Modification on the Thermal and Mechanical Properties of HTPB-Polyurethanes

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ABSTRACT: Imide- and oxazolidinone-incorporated polyurethanes, based on hydroxyterminated polybutadiene (HTPB), were synthesized and characterized. Reaction of the blocked isocyanate terminals of the HTPB prepolymer with diepoxy compounds, containing preformed imide groups, was the strategy followed. The diepoxy resins were derived through reaction of an aliphatic and an aromatic dicarboxylic acid with preformed imide groups with a diepoxy resin. The intermediates and the polyurethaneimide-oxazolidinone were characterized by chemical, spectral, and elemental analyses. Incorporation of these heterocyclic groups caused dramatic improvements in the thermal and mechanical properties and the thermomechanical profile of the system. The improvements in properties were proportional to the hard-segment content of the modified polyurethanes. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1731–1738, 1999

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INTRODUCTION

The thermal properties of polyurethanes (PUs) can be improved by the introduction of heterocyclic groups into the backbone. The improvement in the thermal and mechanical properties of PUs through incorporation of imide groups into the backbone has been reported by us and by others.¹⁻⁴ Different synthesis strategies have been adopted for realizing the imide-modified PU. The heterocyclic oxazolidinone group is also known to impart thermal stability to polymer systems. PUs have been modified with oxazolidinone groups through an isocyanate–epoxy reaction, resulting in improved thermal and physical properties. Roth reported isocyanurate–oxazolidinone (ISOX) systems through the reaction of isocyanate-terminated prepolymer with diepoxy compounds.⁵ Uribe and Hodd studied the linear polymers of isocyanurate–oxazolidinone, formed from 4,4'-methylene bis(phenyl isocyanate) and a diepoxy compound such as bisphenol A diglycidyl ether.⁶ It has been reported that by using suitable catalysts the competitive reaction leading to the formation of isocyanurate can be avoided during the isocyanate–epoxy reaction.⁷

The studies of Kinjo revealed that in such reactions an excess of isocyanate favors the formation of isocyanurate and that the relative proportion of isocyanurate and oxazolidinone units can be regulated by controlling the reaction parameters, particularly the catalyst.⁸ Yamaoka and Mizuno reported thermally stable epoxy resin laminates based on an isocyanate–epoxy reaction.⁹ Similarly, Sankaran and Chanda synthesized an oxazolidinone–urethane copolymer by the reaction of isocyanate-terminated polybutadiene with an aromatic diepoxy compound.¹⁰ Since both im-

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ide and oxazolidinone groups in PUs lead to the latter's enhanced performance, it was of interest to study the effect of both these groups together in PU.

This article describes the synthesis of PUs containing both imide and oxazolidinone groups in the backbone, realized through a new synthesis strategy. The thermal and mechanical properties of the resultant PU-imide-oxazolidinone, synthesized using hydroxy-terminated polybutadiene (HTPB) as the polyol, were compared with those of the base PUs and the PU-imides. The effect of the modifications on certain thermophysical properties of PU is also discussed

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA, Fluka, Switzerland) was freshly recrystallized from acetic anhydride. m-Aminobenzoic acid (MABA) and 4-aminobutyric acid (ABA) (both from SISCO Research, Bombay, India), tolylene diisocyanate (TDI, mixture of a 2,4- and a 2,6-isomer, Bayer, Germany), diaminodiphenyl ether (DDE, Aldrich, WI, USA), and hexamethylenetetramine (HEXA, SD Chemicals, Bombay) were used as received. Isophorone diisocyanate (IPDI, Rhenus Wtag, Germany) was purified by vacuum distillation and the purity checked by analysis of the isocyanate content using the dibutylamine method. Hydroxy-terminated polybutadiene (HTPB, number average molecular weight M_n 2800 of M/s NOCIL, Bombay), with a number-average functionality of 2.3, was used after drying by azeotropic distillation using benzene as the entraining solvent. The bisphenol A-based diepoxy resin, GY-252, with an epoxy equivalent of 5.2 equiv/kg, was procured from M/s CIBA (Bombay). All solvents were purified by distillation.

Instruments

Molecular weights were determined by a Knauer vapor pressure osmometer (VPO). Infrared (IR) spectra were recorded on a Nicolet FTIR, Model 510 P. Mechanical properties were evaluated using an Instron-UTM 4202. Differential scanning calorimetric analysis (DSC) was performed at a heating rate of 10°C/min using a Mettler DSC-20 apparatus. Thermal analyses were performed using a DuPont thermal analyzer, TGA-951, under $\rm N_2$ at a heating rate of 10°C/min. The glass transition temperature (T_g) was determined with a DuPont thermomechanical analyzer (TMA), Model 942.

Synthesis of Imide-Dicarboxylic Acids (IDA)

The amino acid (aminobutyric acid or aminobenzoic acid, 0.20 mol) taken as a 20% solution in dry dimethylacetamide (DMAc) was reacted with pyromellitic dianhydride (0.1 mol) at 60°C for 2 h. Sodium acetate (0.1 mol) and acetic anhydride (0.30 mol) were added to the mixture and stirring continued for 3 more hours at this temperature. The imide-diacid precipitated in the case of aminobenzoic acid. The aminobutyric acid-based one was separated from the solution by precipitation in water. The product, after filtration, was purified by repeated precipitation in water. The isolated products were dried at 60°C under a vacuum for 4 h. Characterization was done by estimation of the acid value and elemental analysis. The acid values of 226.5 mg KOH/g for the product from ABA (IDA-1) and 247.2 mg KOH/g for that from MABA (IDA-2) corresponded closely to the theoretical values of the IDAs, which confirmed the completeness of the imidization reaction.

Synthesis of Imide-Diepoxy (IDE) Compound

The above imide-diacid (10 g) was reacted with the diepoxy compound, GY-252, taken in a 1 : 2 acid/epoxy equivalent ratio in 10 mL DMAc in the presence of HEXA (1% by weight of the reactants) as a catalyst at 60°C for 2 h. The completeness of the esterification reaction was ensured from the disappearance of the acid from the medium. The product was isolated from the solution by precipitation in methyl alcohol. The filtered brown solid was washed with methyl alcohol and dried at 60° C for 4 h under a vacuum. It was characterized by elemental analysis, the epoxy value, and the acid value.

Synthesis of Isocyanate-terminated Polybutadiene

The isocyanate-terminated polybutadiene was synthesized by reacting HTPB with isophorone diisocyanate in a 1 : 2 (OH/NCO) ratio in bulk at 45°C.¹ The product was characterized by the NCO— content and was stored under N_2 until further use.



Synthesis of PU–Imide–Oxazolidinone (PU–IOX-1 and 2)

The isocyanate-terminated prepolymer was reacted with a stoichiometric amount of phenol in the presence of 1 wt % HEXA as a catalyst at 60°C in methyl ethyl ketone for 1 h. The completion of the phenol-isocyanate reaction was confirmed from the absence of isocyanate absorptions in the IR spectrum of the product. The blocked isocyanate prepolymer, thus formed, was isolated by evaporation of the solvent. It was then mixed with the IDE compound along with the catalyst (1% HEXA) in DMAc to form a 60 wt % solution which was poured into a Teflon mold. The solvent was allowed to evaporate slowly by heating the resulting film to 160°C in an oven in a flow of nitrogen and maintained at this temperature for 15 h for completion of the oxazolidinone formation. The progress of the reaction was monitored from the decrease in the intensity of the epoxy group at 829 cm⁻¹ in the IR spectrum (see Results and Discussion). The slabs thus cast were used for evaluation of the mechanical properties.

Synthesis of PU of HTPB

The PU for comparative purposes was synthesized by reacting HTPB and TDI in the presence of 5 mol % of trimethylol propane as a crosslinker at 60°Cfor 8 h, keeping the NCO–OH ratio as 1. The slabs were cast from the mixture on a Teflon mold and were used for the determination of the mechanical properties.

Synthesis of PU-Imide (PUI)

HTPB was end-capped with isocyanate groups by reacting it with IPDI in a 1:2 equivalent ratio at 45° C for 2 h.The product was characterized by estimation of the isocyanate content. The isocyanate-terminated prepolymer was reacted with DDE in a 1:2 equivalent ratio in DMAc to result in the amine-terminated PU–urea. The telechelic amine, in reaction with a stoichiometric amount of PMDA in DMAc, furnished the polyamic acid as a viscous solution (50% solid content). The polyamic acid was cast as thin sheets in a Teflon mold and were imidized by slowly heating from room

				Elemental Analyses (%)						
		Acid Value (mg KOH/g)		C		Н		N		Melt
Ref. No.	Ref. Synthesis No. From		Theoretical	Exp	Theoretical	Exp	Theoretical	Exp	Theoretical	(°C)
IDA-1 IDA-2	PMDA–ABA PMDA–MABA	$\begin{array}{c} 226.5\\ 247.2 \end{array}$	$228 \\ 246.5$	$\begin{array}{c} 55.1 \\ 63.8 \end{array}$	$\begin{array}{c} 55.6\\ 63.1 \end{array}$	$3.9 \\ 2.3$	$\begin{array}{c} 4.1 \\ 2.6 \end{array}$	$7.3 \\ 6.5$	$7.2 \\ 6.1$	$\begin{array}{c} 210\\ 245 \end{array}$

Table I Characteristics of the Imide-Diacids (IDA)

temperature to 160°C in a stream of nitrogen in an oven. The details of the synthesis and characterization of the PU, PUI, and its various intermediates were described in a previous article.¹

Determination of Sol Content

This was done by extracting the polymer with boiling toluene and finding the difference in weight.

RESULTS AND DISCUSSION

Synthesis and Characterization of PU–Imide–Oxazolidinone

A four-step synthesis strategy was followed to realize the PU-imide-oxazolidinone. In the first step, ABA and MABA were reacted with PMDA to form the imide dicarboxylic acids (IDA-1 and IDA-2, respectively) as shown in Scheme 1. The IDAs were characterized by spectral and elemental analyses and the acid value. The results of the acid value and elemental analysis, given in Table I, support the formation of the expected compounds. IR showed the characteristic absorption due to imide carbonyl at 1780 cm⁻¹ (in phase, weak) and 1728 cm⁻¹ (out of phase, strong) and an equally strong absorption due to the acid carbonyl at 1690 cm⁻¹. The IDE resins were synthesized from IDA. Reaction of the IDAs with the diepoxy resin, GY-252, taken in a 1 : 2 (acid– epoxy) equivalent ratio, generated the epoxy endcapped imide–ester resin (imide–diepoxy, IDE-1 and IDE-2, respectively). The progress and completion of this reaction was followed by the determination of the acid content of the reaction mixture.

This product was also characterized by elemental analysis and by estimation of the epoxy content (Table II). From the molecular weight as determined by VPO and the epoxy content, the epoxy functionalities were calculated to be around 1.9 as compared to the theoretical value of 2. The slight enhancement in molecular weight, causing a marginal decrease in the functionality, arises from the possibility of chain extension during the acid–epoxy reaction, causing formation of a minor amount of high molecular weight species. The IR of the compounds exhibited the characteristic epoxy absorption at 920 cm⁻¹ (weak) and 829 cm⁻¹ (strong). It retained the carbonyl absorptions of

					Elemental Analyses (%)						
Dof	IDE	Epoxy	Mol	F m		С		Н		N	Melt.
No.	on	(equiv/kg) ^a	(VPO) ^a	<i>r n</i> (av)	Exp	Theoretical	Exp	Theoretical	Exp	Theoretical	(°C)
IDE-1	IDA-1	1.47 (1.87)	1225 (1064)	1.90	68.5	70.0	5.1	5.8	2.8	2.6	115
IDE-2	IDA-2	1.35 (1.64)	$1325 \\ (1216)$	1.93	76.1	74.7	5.8	5.0	2.1	2.5	145

Table II Characteristics of the IDEs

^a Theoretical values in parentheses.



Figure 1 DSC thermogram of the IDE-2-isocyanate polymer system. Heating rate, 10°C/min.

the imide. On esterification, the acid carbonyl at 1690 cm^{-1} shifted to a higher frequency and merged with the carbonyl absorption of the imide at around 1730 cm^{-1} . The diepoxy compounds with preformed imide (IDE) were then reacted with the blocked isocyanate derived from HTPB to result in the PU-imide-oxazolidinone (PU-IOX-1 and PU-IOX-2 from IDE-1 and IDE-2, respectively). The blocking of the isocyanate was done to avoid or minimize the secondary reactions of isocyanate leading to the formation of isocyanurate. DSC analysis of the mixture showed an exotherm at 160°C corresponding to the formation of oxazolidinone (DSC shown in Fig.1). At this temperature, the blocked isocyanate decomposes to liberate the free isocyanate groups.¹¹ The presence of the HEXA catalyst and the blocking of the isocyanate are expected to minimize the secondary reactions of isocyanate and ensures the formation of oxazolidinone as the main product.6-10

The IR spectra of the products confirmed the reaction of the epoxy groups of IDE. The peak at 920 cm^{-1} was not distinct enough for monitoring, but that at 829 cm^{-1} diminished in intensity in oxazolidinone. Since there are some absorptions due to aromatic groups (C-H out-of-plane bending) appearing in the same region, this peak did not disappear completely. The carbonyl peak of the oxazolidinone, however, merged with those of the imide and the ester at around 1730-1740 $\rm cm^{-1}$ with the consequence that the absorption at this frequency became relatively stronger vis-àvis that of the precursor IDE. The IR spectrum of the cured product also showed a minor absorption at 1700 cm^{-1} attributable to the formation of some amount of isocyanurate.⁸ The imide absorption at 1780 cm^{-1} was retained in the product and the absorption at 2200 cm^{-1} due to any deblocked isocyanate was absolutely absent. All these confirmed the formation of PU–imide–oxazolidinone.

Due to the resinous and polymeric nature of the various products, the different carbonyl absorptions arising from the imide, ester, oxazolidinon, and urethane groups could not be resolved and they appeared as a broad band at around 1730-1740 cm⁻¹. The IR spectra of the IDA, IDE,



Figure 2 IR spectra of the various compounds: (A) IDA-2 (KBr); (B) IDE-2 (KBr); (C) PU–IOX-2 (neat).

Epoxy : Isocyanate	Tensile Strength	Elongation	Sol Content
Ratio (equivalent)	(MPa)	(%)	(%)
1:1	3.5	360	90
1:1.5	6.8	275	65
1:2	8.0	200	15

Table IIIEffect of Epoxy:Isocyanate Ratio on Mechanical PropertiesUsing IDE-2

and PUI–OX are shown together in Figure 2. It may be noted that all three compounds also exhibited the other characteristic absorptions, especially those due to the imide groups at around 1380, 1110, and 720 cm⁻¹ with some changes in their intensities of absorption. All of them showed peaks in the range 3200–3600 cm⁻¹ due to OH (IDA and IDE) and NH (PU–IOX) absorptions, supporting further the structure of the various compounds. Under the conditions employed, the cure reaction was completed in 15 h as evidenced from the mechanical properties of the polymer that attained the optimum values within this time. Scheme 1 illustrates the formation of the intermediates and the polymer.

Thermal and Mechanical Properties

Variation of Molar Ratio of Prepolymer and IDE Crosslinker

The molar ratio of the IDE to the isocyanate prepolymer was varied as 1:1, 1:1.5, and 1:2 using IDE-2. The mechanical properties of the resultant PU-imide-oxazolidinone were determined. It was found that the tensile strength reached a maximum value of 8.0 MPa at a 1:2 ratio. The results are given in Table III. This ratio ensures the complete reaction of both the hydroxyl and epoxy groups on the IDE with the isocyanate groups on the prepolymer, generating maximum crosslinks as evidenced also from the minimum sol content for the polymer at this ratio. Further studies were, hence, limited to this composition.

Effect of Imide–Oxazolidinone Modification on Mechanical and Thermal Properties

The changes in mechanical and thermal properties, effected by incorporation of imide and oxazolidinone units into the PU chain, were studied and the data are presented in Table IV. For the purpose of comparison, unmodified PU and Puimide (PUI) were also studied. The modification of PUs by imide and oxazolidinone improves the mechanical properties of PUs. The heterocyclic groups induce a decrease in elongation and an increase in the modulus. The comparative values of the mechanical and thermal properties for the various PU systems show that the modification of the polybutadiene-based urethane backbone with imide and imide-oxazolidinone has led to a sharp improvement in the tensile properties. There is a four- to fivefold increase in the tensile strength as

Table IV	Mechanical and Thermal Properties of Various PUs

Polymer Type	Hard- segment Content (wt %)	Tensile Strength (MPa)	Elongation (%)	Modulus (MPa)	T_g (°C)	IDT (°C)	Residue at 600°C	Char Yield (%) at 800°C
PU	7.5	1.8	410	1.1	-60	275	0	0
PUI	19.3	5.3	325	2.3	-30	290	30	15
PU-IOX-1 PU-IOX-2	$31.3 \\ 33.7$	$7.6\\8.0$	$\begin{array}{c} 225 \\ 195 \end{array}$	$\begin{array}{c} 3.2 \\ 4.2 \end{array}$	-35 	$\begin{array}{c} 315\\ 315\end{array}$	$\frac{38}{40}$	$\begin{array}{c} 20\\ 25 \end{array}$



Figure 3 Thermograms of various PUs: (—) PU (unmodified); (---) PUI; (—•-•-) PU–IOX-1; (—x—x—) PU–IOX-2.

a result of the incorporation of the imide&ndash oxazolidinone groups. The effect of the aromatic group is evident from the superior properties of the PU containing MABA (PU–IOX-2) to that containing ABA (PU–IOX-1). As the oxazolidinone group is introduced into a PUI, there is a further 50% increase in tensile strength. The elongation has correspondingly decreased. The enhanced cohesive forces promoted by the polar heterocyclic groups must be responsible for the observed improvement in the properties.

The imide-oxazolidinone modification brings about improvements also in the thermal characteristics of PU. The initial decomposition temperature (IDT) of the PU-IOX increases by 25°C relative to the PUI and by 40°C relative to the unmodified PU. The anaerobic char yield also registers a proportional increase when the chain accommodates imide-oxazolidinone groups. The thermograms of the various PUs shown in Figure 3 show that the presence of heterocyclic groups is conducive both for enhancing the IDT and for reducing the rate of thermal erosion of the polymers. Their presence is reflected in an enhanced char residue at any given temperature in comparison to the neat PU. It is also evident that the improvement in thermal characteristics is proportional to the number of hard segments, which increase in the order PU < PUI < PU-IOX-1< PU–IOX-2. Additional crosslinks generated through the reaction of the hydroxyl groups on the IDE with the isocyanate may also be a contributing factor in rendering the PU-IOX systems superior. Among the two PU-IOXs studied, the polymer formed from the IDE-2, containing the

aromatic group, that is, PU–IOX-2, gave the superior strength and thermal properties. This is due to the chain-stiffening effect of the aromatic rings present in it.

The relative increase in tensile strength and the char residue at 600°C of the various PU with their hard-segment content (a combination of urea, aromatic, imide, and oxazolidinone groups, calculated based on the molecular formula; refer to Table IV) is shown in Figure 4. The figure demonstrates the effect of the imide and oxazolidinone groups in improving the thermal and mechanical properties of PU. The almost linear nature of the plot shows that these improvements are more a function of the hard-segment content than that of the crosslinks. This is because the nature and number of crosslinks do not vary uniformly for the different polymers. The introduction of heterocyclic groups resulted also in an elevation in the glass transition temperature. However, the increase is well within the limits, not adversely affecting the low-temperature performance of the resultant polymers significantly. In general, the thermal and mechanical properties increase in the order PU < PUI < PU-IOX-1< PU–IOX-2.

Isothermal Aging Studies

The mechanical properties and mass loss of PU–IOX-2, aged for 20 h at 210 and 225°C in a N_2 atmosphere, were monitored. For comparison, PU and PUI were also studied. The properties for the three systems are compiled in Table V. PU–IOX-2



Figure 4 Dependency of increase in the (\blacksquare) tensile strength and (\bullet) anaerobic char yield at 600°C on hard-segment content of the PUs.

Polyurethane	Temperature (°C)	Tensile Strength (MPa)	Loss in Tensile Strength (%)	Elongation (%)	Loss in Elongation (%)	Mass Loss (%)
	30	1.8	0	410	0	0
PU	210	1.6	11	325	20	25
	225	1.1	39	285	30	30
	30	5.3	0	325	0	0
PUI	210	4.8	9	305	7.1	10
	225	4.2	20	290	16	13.5
	30	8.5	0	195	0	0
PU-IOX-2	210	7.8	8.2	190	2.5	5.5
	225	7.1	17.5	180	2.8	8.5

Table VEffect of Thermal Aging on Mechanical Properties for Various Polyimides(Exposure Time, 20 h)

shows a better retention of the mechanical properties (both tensile strength and elongation) over the PUI or PU. PUI is, in turn, superior to PU. The mass loss at this temperature also decreases in the order PU–IOX-2 < PUI < PU. These results additionally support the thermal stabilizing effect of the imide–oxazolidinone combination in the PU chain.

CONCLUSIONS

HTPB-based PUs could be modified through incorporation of imide and oxazolidinone groups into the backbone, through a novel synthesis strategy. The mechanical and thermal properties could be significantly improved through this modification. The results of the studies conducted on PU-imide-oxazolidinone indicate that a combination of imide and oxazolidinone in a PU chain is very effective in improving the thermal and mechanical properties of the system. The improvement results from the enhanced cohesive interactions caused by the polar heterocyclic groups. It could be concluded that the improvement in properties is caused by the rigidity and enhanced cohesive interactions of the aromatic rings and polar heterocyclic groups rather than by the crosslinks inadvertently introduced into the matrix during the modification. The improvements in mechanical and thermal properties were proportional to the hard-segment content of the polymers that could be altered through the selection of appropriate reactants during the synthesis.

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