Imide-Modified Polyurethanes, Syntheses, Thermal, and Mechanical Characteristics

P. RADHAKRISHNAN NAIR,¹ C. P. REGHUNADHAN NAIR,¹ D. J. FRANCIS²

¹Polymers and Special Chemicals Division, Vikram Sarabhai Space Centre, Trivandrum 695 022, India

²Hindustan Latex, R and D Centre, Akkulam, Trivandrum, 695017, India

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ABSTRACT: Polyurethanes based on polyethylene glycol and hydroxy-terminated polybutadiene, bearing pyromellitimide groups in the backbone, were synthesised via a sequential method. The diisocyanate and diamine telechelic precursor polymers, the polyamic acid intermediate and the polyimides were characterized by physicochemical and thermoanalytical techniques. The imide content could be varied in the chain through selection of the polyol of desired molecular weight or by a chain extension process of the diisocyanate precursor. The thermal and mechanical properties of the imide-modified polyurethane increased proportionate to the hard segment content, constituted by the imide and the urea groups. The presence of the imide group resulted in better thermomechanical profile and caused enhancement in glass transition temperature of the modified polyurethane vis-à-vis the unmodified resin. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1483–1491, 1998

Key words: polyurethane; imide-modified polyurethane; telechelic polymers; polyethylene glycol; hydroxy-terminated polybutadiene

INTRODUCTION

Polyurethanes generally exhibit poor resistance to heat. At around 100°C, the mechanical properties start to diminish, and beyond around 200°C, thermal degradation sets in, depending on the nature of the back bone. One accepted approach for improvement of thermal stability of polyurethanes is by way of chain modification with heterocyclic groups. The heterocyclic groups like imide, oxazolidone, triazine, phosphazene, etc., generally constitute the groups of choice for achieving this.¹ Among these, imide and oxazolidone have evinced some interest in recent years. The imide group is more interesting from the point of view of its known capability for conferring thermal stability to polymer systems and the availability of published literature pertinent to its chemistry. The synthesis of polyurethane-imides by a one-shot technique, through isocyanate-acid anhydride reaction and the consequent improvements in thermomechanical properties has been reported.²

The two-step method reported involves the reaction of a polyol with a polyimide prepolymer obtained from a dicarboxylic acid anhydride and a polyisocyanate. Corresponding improvements in mechanical and thermal properties have been claimed by several authors.^{3–8} The imide group, in conjunction with the rigid aromatic rings, contributes to increased thermal stability of the imide-modified urethanes.

The one-step method for the preparation of imide-polyurethanes is associated with the uncon-

Correspondence to: P. R. Nair.

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trolled release of carbon dioxide, which is usually exploited to make cellular polyurethane-imide. This method of direct imidization has the additional drawback of inducing secondary reactions involving isocyanate and urethane, like trimerization of isocyanate and formation of amide through its reaction with the acid impurity (present in the anhydride). Hence, the resultant polymers do not derive the full advantage of the presence of imide groups.

In this work, we have explored the possibility of introducing the imide function in polyurethane backbones through a different synthesis strategy. This involves reactions of an amine telechelic polyurethane prepolymer with dianhydride and the cyclodehydration of the intermediate polyamic acid in a sequential way The preliminary results have already been published.⁹ This article concerns detailed studies on the synthesis and characterization of the polyurethane-imide (PUI) using various combination of diamines and polyols, and investigations on their physical, mechanical, and thermal properties.

EXPERIMENTAL

Materials

Polyethylene glycol (PEG, of molecular weights 600 and 1000 from BDH, India), hydroxy-terminated polybutadiene (HTPB, M_n 2800 from M/s NOCIL, Bombay), were used after drying by azeotropic distillation using benzene as the entraining solvent. Diamino diphenvl sulphone (DDS), diamino diphenyl ether (DDE) (Aldrich, Madison, WI), and tolylene diisocyanate (TDI, mixture of 2,4 and 2,6 isomer, Bayer, Germany) were used as received. Isophorone diisocyanate (IPDI, Rhenus Wtag, Germany) was purified by vacuum distillation and purity checked by analysis of isocyanate content using the dibutylamine method. Pyromellitic dianhydride (PMDA, Fluka) was recrystallized from acetic anhydride after refluxing for 2 h. It was dried under vacuum at 60°C. Dimethyl acetamide (DMAc, Sisco Research, Bombay) was distilled prior to use.

Instruments

Molecular weights were determined by Gel Permeation Chromatography using Waters GPC, model Delta Prep 3000 μ styragel and by Knauer Vapour Pressure Osmometer (VPO). Infrared spectra were recorded on a Nicolet FTIR model 510 P. Mechanical properties were performed on a UTM 4202. Thermal analyses were carried out using a DuPont thermal analyzer, TGA-951. Glass transition temperature (T_g) was determined with a DuPont thermomechanical analyzer (TMA), model 942.

Synthesis of Isocyanate-Terminated Prepolymer (iso-PU)

The isocyanate-terminated prepolymers from various polyols were synthesized by reacting them with isophorone diisocyanate. In a typical reaction, 15 g of polyethylene glycol (mol wt 600) corresponding to an isocyanate-polyol molar ratio of 2:1 was added dropwise over a period of 1 h, to 10 g of IPDI containing two drops of benzoyl chloride. The reaction system was kept agitated at about 20°C under N₂ atmosphere. After complete addition of the glycol, the reaction mixture was maintained at 45°C for 2 h. The product was stored as such under N₂ until further use. The same procedure was adopted for the other polyols. It was characterized for isocyanate content and for molecular weight.

Synthesis of Polyurethane-diamine (PU-amine)

To 10 g of the diamine (DDE or DDS) dissolved in 25 mL of dimethyl acetamide, a calculated quantity of the isocyanate-terminated prepolymer (for isocyanate-amine equivalent ratio 1:2) taken as a solution in dimethyl acetamide was added dropwise with agitation, at $10^{\circ}C$ under N_2 atmosphere. After the addition, the reaction temperature was slowly increased to about 40°C and the contents kept stirred at this temperature for another 1 h to ensure the completion of the reaction, as evidenced from the disappearance of the peak at 2250 cm^{-1} in the IR spectrum. The polyurethane-diamine thus obtained was stored as a solution in dimethyl acetamide for further reaction. The polyurethane-diamine, for characterization, was isolated by precipitation in water, filtering, and drying in vacuum at 60°C.It was characterized for amine content and for molecular weight.

Synthesis of Polyurethane-amic Acid (PU-AA)

To about 20 g of the above polyurethane-diamine dissolved in 20 mL of anhydrous dimethyl acetamide at 30°C, stoichiometric quantity of finely



powdered pyromellitic dianhydride was added over a period of 1 h with thorough stirring and under N_2 . The viscosity of the reaction mixture increased considerably during reaction. The stirring was continued for a further period of 1 h. The amic acid solution was then preserved in moisture-free condition. The PU-amic acid, for characterization was isolated from solution by precipitation into methanol. The precipitated polymer was washed with methanol and dried under vacuum at 60°C for 2 h. It was characterized for acid content and for inherent viscosity.

Cyclodehydration of Polyurethane-amic Acids to the Imides (PU-I)

The polyurethane-amic acid solution in dimethyl acetamide was poured into a Teflon mold in thin layers and then heated in an oven in a current of nitrogen. The temperature was increased at the rate of about 5°C/min from room temperature to 160°C. The slow heating rate was maintained to avoid the formation of blow holes during imidization. The film so obtained was heated for a further period of 10 h at this temperature to complete the imidization. Thus, clear brown and transparent. polyurethane-imide films were obtained. Characterization was done by elemental analysis and by IR. The mechanical properties were determined using specimens cut from this slab.

Determination of Sol Content

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

RESULTS AND DISCUSSION

Polyurethane-imides, based on HTPB and polyethylene glycol of two different molecular weights (600 and 1000) were realized through transformation of the polyol to the isocyanate terminated prepolymers and subsequent end-capping with a diamine to derive the amine-terminated prepolymer. Reaction of the diamine with PMDA and subsequent thermal imidization furnished the required polymer. The general method of synthesis is shown in Scheme 1.

Because HTPB possessed functionality greater than 2, it was partially acetylated to bring down the functionality to around 1.8, in order to avoid the chances of crosslinking. IPDI was found to be

Polyol/Diisocyanate Combination	NCO Content	Viscosity (cps)	Mol Wt (VPO)	Functionality	Sol Content	Polym. Ref.
PEG-600/IPDI	7.80	12570	1120	2.08	98.5	P-600
PEG-600/TDI	4.90	18500	1525	1.77	91.5	
PEG-1000/IPDI	5.50	11260	1470	1.92	98.5	P-1000
PEG-1000/TDI	4.50	15650	1655	1.75	93.5	
HTPB/IPDI	2.60	15250	3850	1.92	97.5	HTCY
HTPB/TDI	1.75	18755	4135	1.72	91.5	—

Table I Comparison of Properties of IPDI- and TDI-Based Isocyanate-Prepolymers (isoPU)

Mol Wt of Polyol	Mol Wt of Isocyanate– Polymer (by VPO)	Isocyanate Content (wt %)	Functionality (Fn)	Viscosity (cps, 30°C)	Sol Content (wt %)
600 1000	$\begin{array}{c} 1120\\ 1470 \end{array}$	7.8 5.5	2.08 1.91	$12570 \\ 11260$	98.9 99.5

Table II Characteristics of Isocyanate-Terminated Prepolymers Based on PEG

better than TDI for generating the isocyanateterminated polymer, as the latter being more reactive, tended to cause chain extension and partial crosslinking, despite the favorable molar ratio of 1:2 (OH-isocyanate) for both systems. In the case of IPDI, the isocyanate-alcohol coupling took place as required without any significant molecular weight buildup. This compound has the advantage of possessing two isocyanate groups of differing reactivities. End-capping takes place through reaction with the primary isocyanate, and the chain terminates possibly with the less reactive secondary isocyanate group. Moreover, the reduced reactivity of the aliphatic isocyanate groups in IPDI is advantageous in minimizing the possibilities for chain extension and gelation. The difference in reactivities of the IPDI and TDI is evident from the properties of the resultant polymers, listed in Table I. Hence, for further studies only IPDI was used.

The isocyanate-terminated polymers were characterized by IR, which showed the characteristic absorption due to the isocyanate group at 2250 cm^{-1} and the urethane carbonyl at 1740 cm^{-1} . The characteristics of the prepolymers are given in Table II. From the isocyanate content and the molecular weight (by VPO) the average functionality was calculated and found to be around 2, as expected. Use of IPDI does not absolutely preclude chain extension, as is seen from the marginal increase in molecular weight of the prepolymers. The sol content shows that practically no secondary reaction leading to gel occurs in this case. The reverse trend in viscosity of the isocyanate-terminated polymer with increasing molecular weight of the polyol is attributable to the proportionately reduced content of the rigid and polar urethane groups in the polymer.

The diamines, obtained by reaction of the diisocyanate with two different types of aromatic diamines (diaminodiphenyl ether and diaminodiphenyl sulfone) were also characterized. The IR spectra gave indication of all isocyanate group having reacted to give the ureaamine, which showed further characteristic peaks at 1540 cm^{-1} (urea carbonyl) and at 3300 and 3600 cm^{-1} (NH-amine). The sol content was almost 100% when IPDI was used for end-capping in the preceding step. TDI terminals tend to produce gels on reacting the prepolymer with diamine, possibly due to the enhanced reactivity of its primary aromatic isocyanate groups towards the amines. Even with IPDI terminals,

Table III Characteristics of PU-amines (PU-A) and the Corresponding Polyurethane-amic Acid (PU-AA)

(PU-amine)	Amine Value (mg KOH/g)		Mol Wt		$\eta_{\rm inh}$ of PU-AA	Acid Value of PU-AA (mg KOH/g)	
Type (PU-A)	Exp.	Theor.	of PU-A (VPO)	Fn of PU-A	(dL/g) (DMAc)	Exp.	Theor.
P-600/DDS	71.8	72.9	1550	1.98	0.57	63.9	65.0
P-600/DDE	76.8	77.8	1665	2.20	0.54	67.5	67.5
P-1000/DDS	56.1	57.9	2115	2.10	0.47	52.1	53.2
P-1000/DDE	58.7	60.9	1950	2.04	0.42	54.4	55.0
HTCY/DDS	30.8	32.6	3615	1.98	0.38	30.7	31.2
HTCY/DDE	32.5	33.5	3210	1.95	0.37	31.5	32.0

	Ca	Carbon		Hydrogen		Nitrogen	
PU-imide Based on	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Gel Content (%)
P-600/DDS HTCY/DDS	$\begin{array}{c} 58.5\\ 86.4\end{array}$	$\begin{array}{c} 60.0\\ 88.2 \end{array}$	$\begin{array}{c} 6.9 \\ 9.1 \end{array}$	$7.1\\8.6$	$\begin{array}{c} 4.3\\ 1.7\end{array}$	$\begin{array}{c} 4.8\\ 1.5\end{array}$	93.8 91.7

Table IV Elemental Analyses and Gel Content of Polyurethane Imides

reaction with diamine led to partial chain extension, as evident from the molecular weights of the diamine (except for HTPB), as given in Table III. The average amine functionality, calculated from the amine content and molecular weight by VPO was close to the theoretical value of two within experimental error.

Reaction of the diamines with pyromellitic dianhydride resulted in the corresponding polyurethane-polyamic acid (PU-AA) whose acid values (Table III) corresponded well to the amine values of the precursors, indicating completion of amineanhydride reaction.

Polyurethane-imides (PUI) were formed by thermal imidization of the polyamic acid. Thermal imidization also facilitated molding the resin directly from the amic acid. The elemental analysis results of the imides, given in Table IV, confirmed the formation of the expected structure. The PUI derived from higher molecular weight polyols were soluble in DMAc due to smaller number of imide groups. The IR spectra showed the absorptions due to the imide carbonyl group at 1780 cm^{-1} apart from the peaks due to other groups like NH (3310 cm⁻¹), urethane carbonyl (1740 cm⁻¹), and urea carbonyl (1640 cm⁻¹). Because urea groups are generated on end-capping with the diamines, these PU-imides are actually PU-urea-imides.

PEG-Based PUI

Mechanical and Thermal Properties

The films of the samples of polyurethane-ureaimides prepared from PEG-600 and PEG-1000 as the base polyols were analyzed for mechanical and some thermophysical properties. The mechanical properties of the polyurethane-imides are compiled in Table V, along with those of the reference polymers. It is seen that the incorporation of the imide moieties helps enhance the tensile strength and modulus, because imidization makes the chain more rigid. The effect of the nature of the diamine (used for end-capping) on the mechanical property of the PUimide can also be seen. It is observed that the DDS-modified PU-imide has a higher tensile strength and lower elongation than the corresponding ether diamine (DDE)-modified PUI. This is due to the higher polarity of the sulfone group, which imparts higher cohesive strength. The glass transition temperatures are also comparatively lower for this system. The rigidity

Polymer Type	Tensile Strength ^a	Elongn. (%)	Modulus at 100% Elongn.ª	$\eta_{\mathrm{inh}}{}^{\mathrm{b}}_{\mathrm{(dL/g)}}$	$\begin{array}{c} T_g \\ (^{\circ}\mathrm{C}) \end{array}$
P-600/DDS-(PU-Urea)	8.5	275	4.1	0.58	-20
P-600/DDE-(PUI)	12.5	225	5.8	0.81	
P-600/DDS-(PUI)	18.5	200	8.7	0.85	-18
P-1000/DDS-(PU-Urea)	7.5	285	3.9	0.63	-25
P-1000/DDE-(PUI)	10.5	210	4.9	0.91	-20

Table V Mechanical and Physical Properties of PU-imides and PU-Urea

^a MPa.

^b In DMAc, at 30°C.

Polymer Type	Starting Polyol	IDT (°C)	PDT (°C)	Residual Wt (%) at 400°C	Residual Wt (%) at 600°C
PU (TMP-cured)	PEG-600	225	380	10	0
PU-Urea/DDS	PEG-600	250	390	25	5
PU-Imide/DDS	PEG-600	290	425	65	25
PU-Imide/DDS	PEG-1000	290	418	62	28
PU-Imide/DDE	PEG-600	275	410	55	22

Table VI Thermal Decomposition Characteristics of Various Polyurethanes

and the enhanced intermolecular dipolar interaction caused by the imide groups are responsible for the enhancement in the inherent viscosity of the polymer.

The thermal stability of the polymers was evaluated by thermogravimetric analysis (TGA) in nitrogen at a heating rate 10°C/min. The mass loss at different temperatures and the initial and peak decomposition temperatures (IDT and PDT, respectively) were evaluated from the thermograms, and the results for the DDS-based system are given in Table VI. The rate of thermal erosion was found to decrease with increase in concentration of the hard segments in the polyurethaneimide. The typical thermograms of the unmodified polyurethane and the PU-Is are presented in Figure 1. Of the two polyurethane-imides investigated, the superior thermal stability of the sulphone-containing imide is evident from the thermogram.

It can be observed from the table and thermograms that the temperature of onset of decompo-



Figure 1 Thermograms of PEG-600 based PU: (—) unmodified PU; (– –) PU-I (DDE based); (—o—) PU-I (DDS based); N₂ atmosphere; heating rate, 10°C/min.

sition has increased from 225°C for the neat polyurethane resin, to a maximum of 290°C for the polyurethane-imide when diamino diphenyl sulphone is used for polyurethane-diamine synthesis. The proportional increase in the anaerobic char yield also sustantiates the thermal stabilization effect of the imide as well as the sulfone groups. It may also be observed from the table that incorporation of the imide causes an increase in glass transition temperature consequent to the agglomeration of hard urea and imide segments. This behavior is expected because these groups render the chains more rigid. It may further be noted that the increase in glass transition temperature is still in affordable limits, as the modified PUs exhibits glass transition well below room temperature. It is remarkable that these modifications, aimed at enhancing the thermal stability, do not significantly impair the flexibility and toughness of the PU system.

Isothermal Aging

The effect of imide on the thermomechanical profile of the polyurethane was examined by isothermal aging studies. The mechanical properties and mass loss were monitored as a function of time at various temperatures for a typical PEG-based PUI, along with the result for a reference PU from the same polyol obtained in conventional way. The percentage retention of tensile strength for various cases is shown in Figure 2. It is remarkable that the property is retained for over 20 h at 170°C for the PU-I. The loss in property is not significant at higher temperatures as well. The effect of imide is evidenced from a better retention of the properties in PU-Imide vis-à-vis the base PU in their thermomechanical profiles at 210°C given in same figure. The mass loss shown in the same figure is also proportionately less for the imide-polyurethane under identical conditions.



Figure 2 Effect of isothermal aging in N₂ on tensile strength and mass loss of PUI (P-600/DDS), at (\blacksquare) 170°C; (\blacktriangle) 190°C; (\bigcirc) 210°C; (\blacktriangledown) unmodified PU at 210°C.

Effect of Varying Imide Content

In one set of study the imide content was varied in the PU-I based on a typical PEG-600. This was done by partial chain extension of the isocyanate prepolymer using diamine by adjusting the molar ratio of isocyanate to amine during amine endcapping. The details of the polyurethane-ureadiamine thus synthesized can be found in Table VII. The chain-extended polyurethanes from PEG-600 was converted to the corresponding imide as usual to study the effect of the hard-segment content (sum of urethane and imide groups) on the polymer properties. The results obtained from the evaluation of thermal and mechanical properties have been summarized in the same table.



Figure 3 Dependency of tensile strength and char yield on hard-segment content for PU-I (PEG-600/DDS).

It may be observed from the table that, as the isocyanate content is increased in the chainextended prepolymer, there is a corresponding decrease in the urea and an increase in imide content, on transformation to the polyurethane-urea-imide. Consequently, the thermal stability is improved. Both IDT and char yield at high temperatures are increased. The thermograms in Figure 3 illustrates this. The tensile strength is found to increase, followed by a decrease in elongation progressively as the hard-segment content is increased. The relative improvement in mechanical properties and the anaerobic char yield at 600°C depicted in Figure 4 show that these properties are a direct function of the hard-segment content. This set of studies could help in fixing proportion of urethane and imide groups in polyurethane-imide

Table VII Characteristics of Chain-Extended Prepolymers and the Corresponding PUI with Varying Hard Segment Content (Isocyanate-Terminated Polyurethane, Derived from the System PEG-600/IPDI)

OUNCO	NCO	Mn.	Amine (P	e Value ^b U-A)	A - 1 X7 - 1 b	Hard	Ш ана 1 а	El	IDA
Ratio	(wt %)	(VPO) isoPU	Exp.	Theor.	of PU-AA	(%)	Strength ^a	(%)	(°C)
1:1.4	2.4	3700	25.2	26.5	24.6	20.1	5.5	385	265
1:1.5	3.1	2725	33.1	34.3	32.5	25.5	8.1	365	265
1:1.8	4.4	1885	46.2	47.8	42.9	33.1	10.5	324	275
1:2.0	7.8	1080	71.8	72.9	63.9	46.3	18.5	300	290

^a MPa.

^b mg KOH/g.



Figure 4 Thermograms of PU-I with varying hardsegment content (PEG-600/DDS system): $(-\times)$ 20.1%; $(-\bullet)$ 25.5%; (--) 33.1%; (-) 46.3%.

for optimizing the mechanical and thermal properties.

HTPB-Based Polyurethane-imides

The polyurethane-imide, based on HTPB, was synthesized the same way as the PEG-based system. Both DDE and DDS were employed as the end-capping amines. The properties of amine- terminated polyurethane precursor and corresponding amic acids are included in Table III. The mechanical property and thermal stability were evaluated, and the data are presented in Table VIII. For comparison, the properties of PU, derived from HTPB using IPDI and TMP combination and IPDI-DDE or DDS (i.e., PU-Urea) combination, are also given. In the latter cases the structure contains more urea than urethane groups. The superiority of the imide-modified PU over the urea-modified (reaction with diamine) and the TMP-crosslinked PU is evident both in mechanical and thermal properties. DDS improves the mechanical properties better than does DDE as in the case of PEG system. Initial decomposition temperature and anaerobic char yield at high temperatures are enhanced in this case also, as the system incorporates more of the imide segment. However, unlike in the case of PEG, thermograms did not differentiate between DDE and DDS.

CONCLUSION

Polyurethanes, encompassing polyimide groups in the backbone were realized by the diamineamic acid route. Use of the aliphatic and, consequently, less reactive IPDI at the place of TDI for end-capping, the polyol was helpful in deriving the isocyanate-terminated precursor without causing significant chain-extension reactions. It appears that other aliphatic diisocyanates like hexamethylene diisocyanate could also serve for the synthesis of isocyanate precursor. But IPDI has obvious superiority over other primary aliphatic diisocyanate because its reaction with the polyol principally leads to the secondary isocyanate terminals. These secondary isocyanate groups, due to their still reduced reactivity, does not cause crosslinking or significant chain extension on reacting with the diamine for amine endcapping. The mechanical and thermal properties of polyurethanes could be improved considerably by the incorporation of urea and imide (or both together) groups in the backbone. The improvements in mechanical properties are direct functions of the hard-segment content in the backbone, and is also dependent on the nature of the

 Table VIII Mechanical and Thermal Properties of HTPB-Based Polyurethane,

 Polyurethane-Urea, and Polyurethane-Urea-imide

Polymer Type	Composition	Tensile Strength (MPa)	Elongn. (%)	T_{g} (°C)	IDT (°C)	PDT (°C)	Resid. Wt (%) at 600°C
PU^{a}	TMP-crosslink	1.5	450	-60	260	475	0
PU-Urea	DDS-cured	3.5	325		275	482	25
PU-Urea	DDE-cured	3.1	345		280	478	25
PU-I	DDS-Imide	6.0	275	-30	300	488	35
PU-I	DDE-Imide	5.0	315	-35	300	485	35

^a Unmodified polyurethane.

diamine used for end-capping the isocyanate precursor. Incorporation of the imide group, evem though it does not significantly improve the onset of decomposition of the resultant PU, is conducive in reducing the rate of thermal erosion and in enhancing the thermomechanical profile. The two-step method of urethane-urea-imide synthesis permits tailoring of the properties of the polyurethane-imide through proper selection of the chain extender, the aromatic diamine, and the anhydride.

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