Technology Section

POLYMERIZATION AND CHARACTERIZATION OF SEGMENTED POLYURETHANES

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A number of linear polyurethanes were prepared by using a variety of hydroxyl ended low molecular weight polymers, diisocynates and diols. Dimethyl formamide was found to be the best solvent in the two shot solution polymerization technique. The NCO/OH ratio was kept at1:1 in all the preparations and the polymers were precipitated from water.

After preliminary characterization for melting points, viscosities etc, the polymers were solution cast into thin films and were used for the measurement of tensile properties. The polymers from aliphatic diisocynates gave a better set of tensile properties, as compared to those derived from aromatic diisocynates. The nature of diol also plays an important role in determining the properties of polyether based polyurethanes. It has been observed that as the number of CH_2 units increases in diol there is considerable decrease in modulus and other tensile properties.

INTRODUCTION

Linear polyurethanes are block copolymers, consisting of flexible chains of low glass transition temperature (soft segment) and highly polar and rigid blocks of hard segments. The molecular weight and structure of polyols used in their preparation influences their properties [1,2], polyesters generally give polyurethanes with inferior properties [3]. When a diamine is employed as chain extender a high level of physical properties is observed as compared to the diol extender [4,5]. As the ratio of the diisocynate and chain extender to soft block increases in polyurethanes the hardness, modules and flow temperature of the polymer increases, while elongation at break decreases [6]. This is associated with the hydrogen bond interactions which results in domains containing covalent linkages [7]. The internal structure of polyurethanes have been elaborated by x-ray diffraction techniques [8]. A systematic approach in assessing the property-structure relationship in linear polyurethanes has been described in present communication.

EXPERIMENTAL

Polyols. Hydroxy terminated polyols like polyoxyethylene glycol, (PEG-1000), polyoxytetramethylene glycol (PTHF-1000), polypropylene glycol (PPG-2025) and polyethylene/tetramethylene adipate (PETA-2000) were used in the preparation of polyurethanes. Their respective abbreviations and molecular weights are given in brackets.

All these polyols were dried before they could be used in polymerization. The required amount of polyol was taken in a conical flask and was left under vacuum at 50° for 24 hours. The flask was stoppered with a rubber bung and polyol was dissolved in dimethyl formamide (DMF) and transferred in the reaction vessel.

Diisocynates. The three diisocynates which were used are 4.4 diphenyl methane diisocynate (MDI), toluene diisocynate (TDI) and hexamethylene diisocynate (HDI). Each diisocynate was distilled under reduced pressure before it can be used. A great care was taken to avoid any moisture getting in. The redistilled samples were stored in a vacuum desiccator over P_2O_5. Before their

use. each diisocynate was dried under vacuum at 30° and then a solution of diisocynate was made in DMF. The solution was transferred to reaction vessel by means of a syringe. A steady stream of nitrogen was maintained over the diisocynate solution.

Diols. A series of diols including ethane 1.2 diol, propane 1.3 diol, butane 1.4 diol, pentane 1.5 diol, hexane 1.6 diol, and decane 1.10 diol were used. These diols were redistilled under vacuum, and the same drying and transferring procedure was adopted as it was done with polyols and diisocynates.

Polymerization. A number of methods were tried until successful results were obtained:

1. *Melt Polymerization*: The dried polyol was transferred tor reaction vessel, which was kept at 70° under a stream of nitrogen. After about 45 min, lumps of polymeric material appeared in the reaction vessel and were present even after the addition of diol. These lumps seemed to be cross linked polymer insoluble in solvents like DMF, nitrobenzene and tetrahydrofuran.

2. *Solution Polymerization:* Solution polymerization was carried out in two ways:

a) *One Shot Technique:-* The reagents were dried under vacuum. The polyol was poured into the reaction vessel which was maintained at 70° under nitrogen. When the polyol was melted 400 cm^3 of the solvent was added, followed by the addition of diisocynate and diol. After sometime it was observed that similar lumps were formed as they were formed in the melt polymerization.

b) *Two Shot Technique:-* In this technique a prepolymer of diisocynate and polyol was made and then extended with a diol. The reagents were rigorously purified and dried. Instead of putting the reagents into the reaction vessel in solid form, their solution was made in the solvent. The polyol and diisocynate were transferred to the reaction vessel with a syringe. The solution was stirred and nitrogen was allowed to pass continuously. The reaction vessel was kept at room temperature for one hour and then the temperature was raised to 70° gradually. The reaction was continued for further two hours. After the completion of this first stage of reaction the amount of NCO groups left unreacted was determined by titration and the diol was added in the required amount. The reaction was continued for further three hours and then stopped. The solution was in the form of a viscous mass which was cooled to room temperature and the polymer was dried under vacuum at 70° for two days and stored until characterization. The results from this technique were encouraging and a series of polyurethanes (Table 1)

Table 1. Physical characteristics of polymerized polyurethanes.

S. No.	Polyol	Diisocynate	Chain extender	m.p. °C	Intrinsic viscosity (L.V.N.)	General appearance
1.	PEG	MDI	1,4 Butane diol	129−131	0.21	Light yellow powdry
2.	PTHF	MDI	1,4 Butane diol	160−165	0.36	White−strong
3.	PTHF	MDI	1,6 Hexane diol	168−174	0.29	White−Strong
4.	PTHF	MDI	1,2 Ethane diol	150−154	0.21	Yellow-powdery
5.	PTHF	MDI	1,3 Propane diol	156−160	0.85	White-tough
6.	PTHF	MDI	1,10 Decane diol	135−140	0.19	White-soft
7.	PTHF	TDI	1,4 Butane diol		0.154	Yellow-sticky
8.	PTHF	TDI	1,10, Decane diol		0.27	Brown-sticky
9.	PTHF	HDI	1,4 Butane diol	126−127	0.30	White-strong
10.	PTHF	HDI	1,10 Decane diol	116−119	0.35	White-strong
11.	PETA	HDI	1,4 Butane diol	115−117	0.31	White-strong
12.	PETA	MDI	1,5 Pentane diol	87−89	0.34	White-strong
13.	PPG	MDI	1,3 Propane diol	122−125	0.44	Light brown sticky
14.	PETA	MDI	PTHF	80−86	0.31	Light brown sticky

were polymerized by this technique.

Characterization: The polymers were characterized by physical properties such as melting point, solution viscosity, infrared spectra, X-ray diffraction and mechanical properties.

Melting points were obtained on an optical microscope, solution viscosities were determined on a PCL suspended level solution viscometer at 25°, IR spectra of the polymer films were obtained in the region of 4000 to 650 cm^{-1} on a Perkin-Elmer spectrophotometer, and wide angle X-ray pictures were taken to study the morphology of polyurethanes. Tests for mechanical properties were performed on INSTRON tensile tester, model TM.SH.

RESULT AND DISCUSSION

Having tried various techniques of polymerization, it was found that two shot polymerization method is suitable for obtaining linear polyurethanes. The formation of cross linked polymer is melt and one shot polymerization technique may be due to the fact that isocynate has already dimerized. This dimer then hindered the polymerization of high molecular weight linear polymer either by offsetting the reactants balance or by introducing potential branching or cross linking sites into the polymer chain. The same thing can happen if the diisocynates terimerizes. It can be avoided by using pure and dried diisocynates. DMF was used as a solvent, although it has been reported (9) that DMF can react with diisocynate under certain conditions, however, no such reaction was observed under the experimental conditions used in our investigations. The difference in reactant balance can affect the molecular weight of the polymer. In this case NCO/OH ratio was maintained at 1:1 for all the polymers.

An excess of diisocynate is usually essential to have very low cross links for the better mechanical properties. It was thought that 70° may be causing crosslinking of the polymer in the first stage of polymerization, so this stage of polymerization was carried out at room temperature and hence crosslinking was avoided. In cases of polymer 4 (Table 1) the temperature was raised beyond 100° after the completion of the reaction. It was noticed that polymer has changed its colour from white to yellow, decrease in viscosity was also observed. This was obviously due to the degradation of the polymer at this temperature.

The general physical properties of all the polymerized polyurethanes is shown in Table 1. Polymer 9 was quite strong, while polymers obtained from TDI were slightly yellow in colour and sticky in nature with low melting points. It is probably due to the fact that polymers from TDI have not attained reasonable molecular weights, although the conditions of polymerization were same. Polymer 13 was obtained from PPG and was brown in colour. In case of polymer 14, the chain was extended with polyether instead of diol, with the result that this polyether instead had a brown colour and was sticky in nature. It was not suitable for film formation. Table 1 also shows that the polyurethanes obtained from MDI had higher melting points compared to those obtained from HDI. The main factor which increases the melting points are internal molecular cohesion energy, the shape of the chain and chain flexibility. The polymers containing phenylene groups will have considerably higher melting points than those obtained from aliphatic series. The low melting points of TDI may be due to the fact that those polymers had low molecular weight.

The intrinsic viscosities of all the polyurethanes are also shown in Table 1. Polymer 5 shows a very high value of intrinsic viscosity as compared to the other polymers, the high molecular weight of the polymer is exhibited by its better tensile properties. Polymer 14 with high viscosity did not form film either from solution or from melt. This probably could be due to the extension of the polymer with polyether which might have resulted in poor hard segment.

The infrared spectra of polyether based polyurethanes revealed the major NH absorption band at 3320 cm^{-1}, the small shoulder on the side of this peak was attributed to nonbonded NH groups. The carbonyl absorption was split distinctly into two peaks one at 1735 cm^{-1} and other at 1703 cm^{-1}, these two peaks were attributed to free and bonded carbonyl groups.

In polyester based polyurethanes the appearance of NH absorption was similar to those of polyether based urethanes. The absorbance at 2940 cm^{-1} was ascribed as antisymmetric vibration of CH_2. Symmetric stretching vibration of CH_2 from (CH_2-0) group appeared at 2795 cm^{-1}. The bands appearing at 1733 and 1710 cm^{-1} were associated with free and associated C=0 group, respectively. The bands at 3340 cm^{-1} were associated with NH group, while one appearing at 2960 cm^{-1} was due to CH_2. The one which ranged between 1700 to 1750 cm^{-1} was ascribed to C=O of urethane and ester,

X-ray diffraction pictures for polymer 2 both in stretched and unstretched form were taken. The diffused halo in unstretched film picture indicated an amorphous material with no sign of crystallinity of either hard segment or the soft segment. The picture of the same polymer on 500% stretching showed strong equitorial reflections of the polyether, indicating the stress induced crystallization of

the soft segment. There was still no sign of hard segment crystallisation. This was also supported by the presence of an amorphous halo in the stretched polymer film.

The tensile properties of the polyurethanes are shown in Table 2. The structure-properties relationship are discussed in terms of soft and hard segment.

strength as compared to those prepared from aromatic diisocynates. This can be seen in Table 2 by comparing polymers 9 and 10 with the polymers 2, 3, 5 and 6, where polymers form HDI have superior properties than polymers from MDI.

The effect of diol was observed on polyether (PTHF)

Table 2. Mechanical properties of polymerized polyurethanes.

Polymer No.	Young modulus Kg/cm2	Yield stress Kg/cm^2	Yield strain %	Tensile strength Kg/cm^2	% Elongation
2	122.3	11.9	68	87.6	1274
3	82.3	16.3	73	29.3	522
5	43.6	17.4	40	395.3	814
6	21.7	2.1	38	3.7	374
9	200.7	14.5	17	26.1	118
10	211.7	31.3	48	185.0	1167
11	172.7	23.0	47	40.0	451
12	248.8	37.2	45	59.2	248

Soft Block: When a polyether with a molecular weight of 1000 was used as a soft block the tensile properties were found to be poor, even the polymers were not suitable for making the films. On changing the polyether with a molecular weight of 2000, the tensile properties of the polyurethanes improved to a fairly good extent. This was consistent with the previous findings (10,11), which suggested an optimum molecular weight of polyethers for better set of properties.

The polyester based elastomers show a large increase in the activation energy of bonding as compared to the polyethers based elastomers (12). This is in agreement with the greater crystallization of polyesters upon extension and supports that the elastomers derived from PPG have lower modulus than corresponding polyester based materials. Polymers obtained from PTHF (2−10) have lower modulus values as compared to PETA based polymers. This is probably due to the increased crystallinity in polyester, which results in close packing of the polymer chains and retarding their flexibility.

Hard Block: The properties of hard block determine the interchain interactions and network structure. It is influenced by the nature of diisocynate and diols.

The polymers obtained from TDI did not form films and were of low melting points with sticky nature. This is attributed to the reduced symmetry of TDI and in the cause of poor tensile properties. The polyurethanes obtained from aliphatic diisocynate have high modulus and tensile
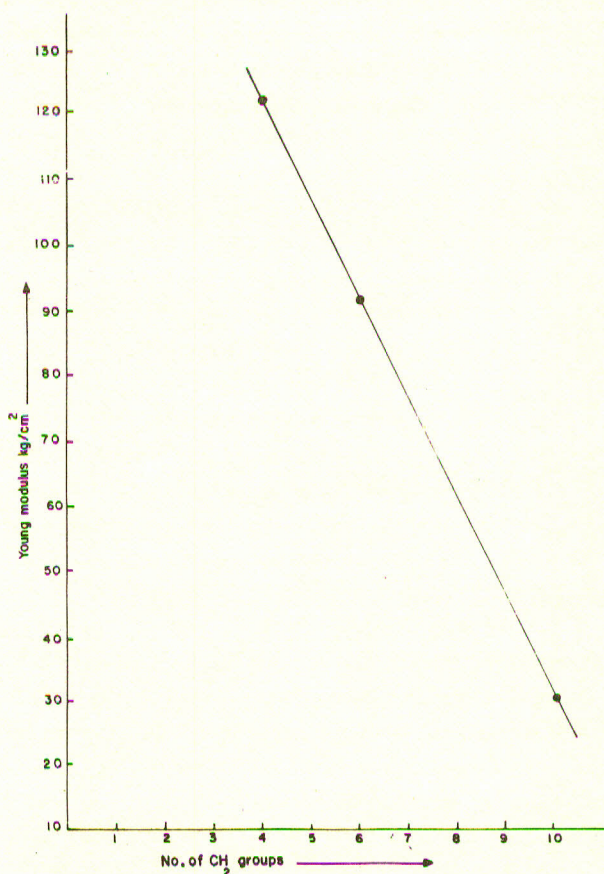

Fig. 1. MDI/P the polymers

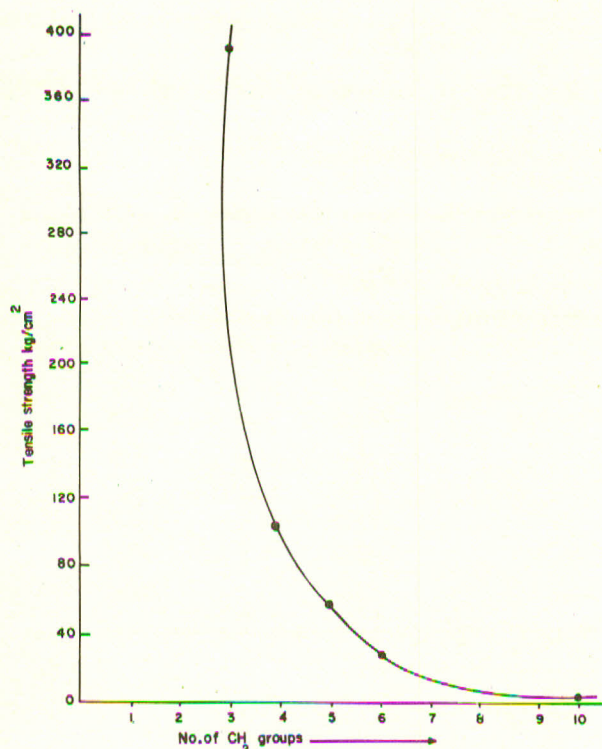based polymers. The tensile properties were found to decrease as the number of CH$_2$ groups increases in the

diols. There is a linear relationship between the Young modulus of the polyurethane and the number of CH$_2$ groups in the polymer (Fig. 1). Similar effect has been observed elsewhere (13) for polyester and ethylene glycol based polymers. This may be due to the increased flexibility provided by CH$_2$ groups in the hard segment and lowering
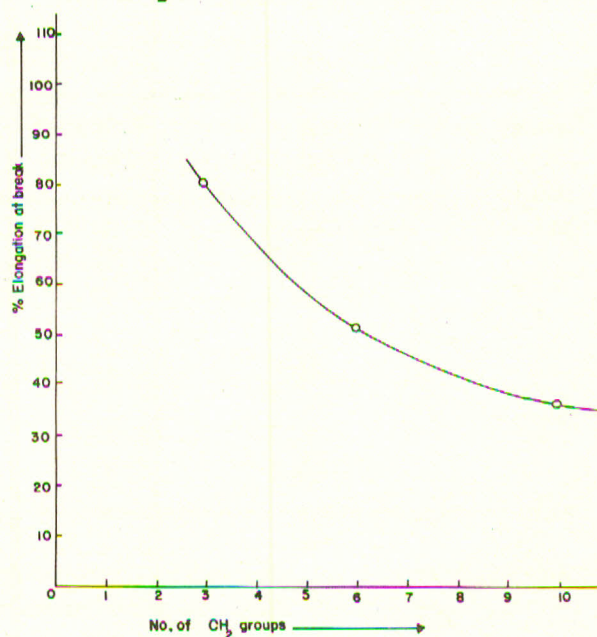
Fig. 2. PTHF/MDI polymers.
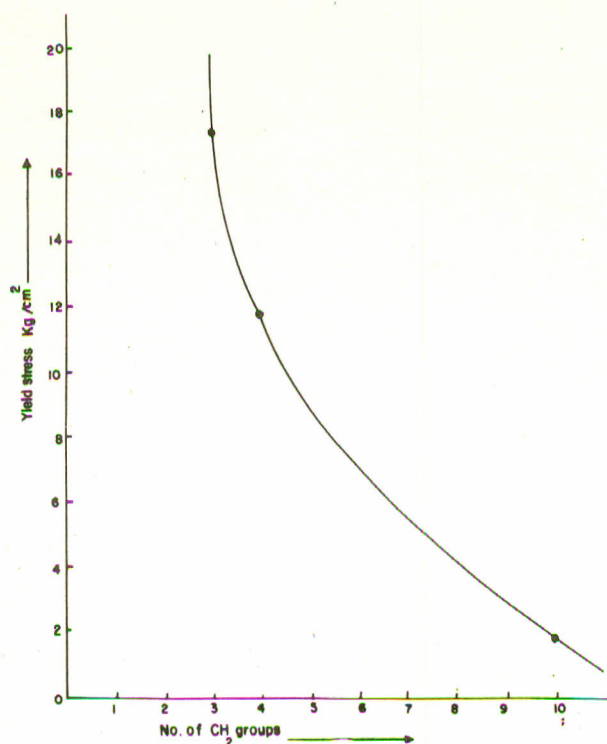
Fig. 4. MDI/PTHF polymers.
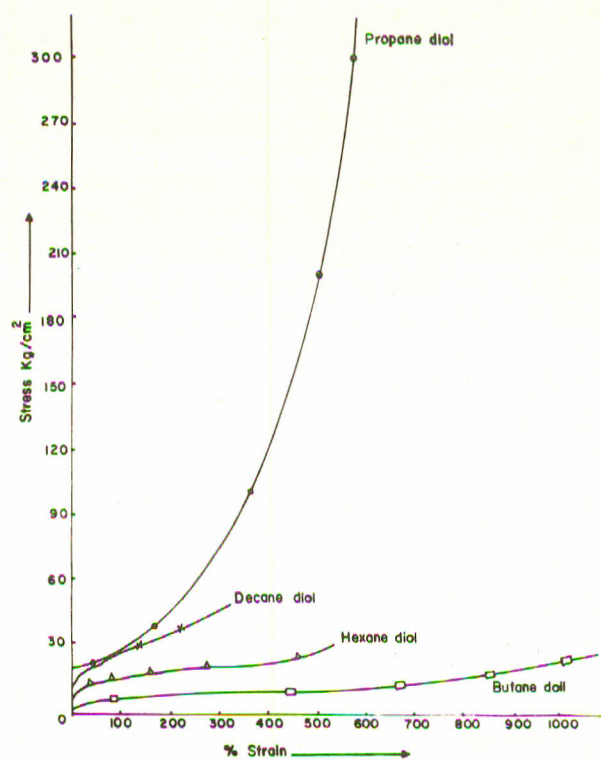
Fig. 3. MDI/PTHF ploymers.

Fig. 5. PTHF/MDI polymers.

down the overall useful properties of the polymer. The polyurethanes extended with 1, 3 propane diol have higher tensile strength and that extended with 1, 10 decane diol has the less as shown in (Fig. 2). The yield stress and elongation at break are shown in Figs. 3 and 4. The stress strain curves given in (Fig. 5) shows the changes which take place by changing the diol.

REFERENCES

1. L. Morbitzer and R. Bonart, Kolloid-Z 232, 764 (1969)
2. K.A. Piggot, B.F. Frye, J.Chem. Eng. Data., 5, 391 (1960).
3. J.H. Saunder. J.Inst. Rubber. Ind., 2,21 (1968)
4. A.J. Sampson, C.F. Blaich. Rubber Age, 89, 263 (1961).
5. L. Charkasove, Y.A. Sinorvich, Polym. Sci. USSR, 14, 82 (1972).
6. H. Rinke. Chimia, 22, 164 (1968).
7. S.B. Clough, N.S. Schoreider, J. Marcomol. Sci. Phys. B.2,553 (1968).
8. D.S. Trifan, J.F. Terenzi, J.Polym. Sci., 28, 443 (1958).
9. B.F. Malchank, Polym. Sci. USSR., 9, 2975 (1967)
10. B.F. Goodrich Co. U.S.2, 871,218, 1.12.55.
11. Eastman Kodak Co. Brit. 1, 118, 731, 296.64 (U.S.A.)
12. L.B. Weisfeld, J. Polym. Sci., 56,455 (1962).
13. L.A. Cherkasova, Polym. Sci. USSR. 14,4,1817 (1972)