

Effect of Structure on Temperature Stability and Solubility of Polyester-Urethanes*

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INTRODUCTION

The reactions of isocyanates with amines,^{1,2} alcohols,³ carboxylic acids,³ and carbon-hydrogen linkages⁴ have been reported extensively in the literature.

It is well known⁵ that polyester-urethanes can be prepared from hydroxyl-terminated polyesters by reaction with diisocyanates. Crosslinked polyester-urethanes result when branched polyesters are utilized. Thus, when adipic acid is condensed with an excess of trimethylolpropane, a branched, hydroxyl-terminated polyester results which can be crosslinked to form a gelled structure by further reaction with 4,4'-diphenylmethane diisocyanate (DPMDI). The resulting products from these reactions are hard, infusible resins that exhibit reasonably good resistance to degradation at high temperatures and low solubility in organic solvents.

It is the objective of this laboratory study to correlate the effect of structure variations in crosslinked polyester-urethanes with temperature stability and solvent resistance. The degree of crosslinking in the polyester-urethanes described herein was altered while maintaining the concentration of urethane groups at a constant value by substituting a dihydric glycol (such as ethylene glycol) for a part of the trimethylolpropane. The ratio of ester to urethane groups in the final product was varied by changing the hydroxyl content of the polyester prior to crosslinking with the diisocyanate. Thus, a polyester with a low hydroxyl number required less diisocyanate to achieve stoichiometry in the urethane reaction than a polyester of a higher hydroxyl content.

Polyesters were prepared with various ratios of ethylene glycol to trimethylolpropane, at a constant hydroxyl number, and reacted with DPMDI to determine the effect of crosslinking density on the high temperature stability and solubility in organic solvents of the resultant polyester-urethanes.

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Polyesters were also synthesized from several ratios of trimethylolpropane to adipic acid and then crosslinked with an equivalence of DPMDI. The effect of the hydroxyl number of the polyester (or the concentration of urethane groups) on the physical properties was also determined.

EXPERIMENTAL

Materials

Adipic acid (reagent grade) obtained from the Eastman Organic Chemicals Department had a melting point of 151–152°C. and was used without further purification. Ethylene glycol (reagent grade) from the Eastman Organic Chemicals Department was used without further purification. Trimethylolpropane from the Celanese Corporation of America was recrystallized from ethyl acetate (m.p. 77–78°C.) and had a hydroxyl number of 1260 (Theo. 1258). 4,4' diphenylmethane diisocyanate was obtained from National Aniline Division, Allied Chemical Corporation; isocyanate equivalent = 125.5 (Theo. 125).

Preparation of Polyesters

The polymers from adipic acid and trimethylolpropane were prepared by melt polymerization in the following manner: Into a three-necked flask were weighed 175.2 g. (1.2 moles adipic acid, 249.2 g. (1.86 moles) trimethylolpropane, and 1.6976 g. (0.04%) PbO. The flask was fitted with a Dean-Stark trap connected to a condenser, a thermometer, and a nitrogen inlet tube. The initial esterification temperature was 125°C. with the temperature being allowed to rise slowly during the course of the reaction to a maximum of 200°C. The condensation was continued until an acid number less than two was obtained, requiring seven hours under these conditions. A total of 42 ml. of water was removed from the reaction through the Dean-Stark trap. Agitation and inert atmosphere were supplied by nitrogen bubbling at 0.5 l./min.

The same apparatus was used in the synthesis of polyesters from adipic acid, trimethylolpropane, and ethylene glycol. However, these polymerizations were carried out at lower temperatures (125–150°C.) than those described above in order to avoid the loss of ethylene glycol. These lower temperatures necessitated longer reaction times (20–60 hr.) before the reactions were complete.

Isocyanate Equivalent Determination

To a flask containing 0.3 g. of 4,4' diphenylmethane diisocyanate in 15 ml. of dry benzene, 15 ml. of 50% di-*n*-butylamine in benzene were pipetted. The sample was allowed to stand one hour at room temperature. One hundred milliliters of neutral ethyl alcohol were then added and the sample and blanks were titrated with 1.0*N* HCl in water, using bromphenol blue as indicator.

$$\text{NCO Equivalent} = \frac{\text{Sample Weight} \times 1000}{(\text{V blank} - \text{V sample}) \times N(\text{HCl})}$$

TABLE I
Polyester-urethanes Prepared from Adipic acid-
trimethylolpropane-4,4' diphenylmethane Diisocyanate

| Sample no. | Adipic acid (equiv.) | TMP ^a (equiv.) | DPMDI ^b (equiv.) |
|------------|----------------------|---------------------------|-----------------------------|
| 1 | 2.4 | 6.60 | 4.20 |
| 2 | 2.4 | 5.58 | 3.18 |
| 3 | 2.4 | 5.10 | 2.70 |
| 4 | 2.4 | 4.80 | 2.40 |

^a Trimethylolpropane.

^b 4,4' diphenylmethane diisocyanate.

Crosslinking of Polyesters

Into an Erlenmeyer flask were placed 12.7 g. (0.1 equiv.) of polyester #2 (Table I), 12.5 g. (0.1 equiv.) of 4,4'-diphenylmethane diisocyanate and 50 ml. of acetone. The solution was then heated to reflux, gelation taking place within two minutes. The crosslinking reaction was carried to completion at 200°C. for 40 min. The product was ground in a mortar and pestle and brought to constant weight in a vacuum over at 100°C. and 120 mm. Hg.

Heat Aging Tests

Into small test tubes were weighed 0.0950–0.1000 g. of the polyester-urethanes. The samples were placed in a large Erlenmeyer flask and heat aged in an oven at $175 \pm 1^\circ\text{C}$. Separate Erlenmeyer flasks were used for the samples aged in nitrogen and in air, and the atmospheres were controlled by passing nitrogen or air through the sample at 0.5 l./min. The samples were withdrawn periodically and the loss in weight determined.

Thermogravimetric Analysis

A sample of polyester-urethane in a platinum crucible was subjected to thermogravimetric analysis from 25–600°C. with the rate of temperature increase established at 5°C./min. The change in weight of the sample was detected on a Fisher thermobalance and charted on a sensitive recorder.

Solubility Tests

Into an extraction thimble (100 ml. Soxhlet capacity) were weighed 1.90–1.95 g. of polyester-urethane samples and extracted with toluene or methanol. The siphon rate was adjusted so that the extractor emptied every seven minutes and, in every case, extraction was completed in 24 hr. The amount of material extracted was determined by evaporating the solvent in a tared flask, then bringing to constant weight in a vacuum oven at 100°C. and 120 mm. Hg.

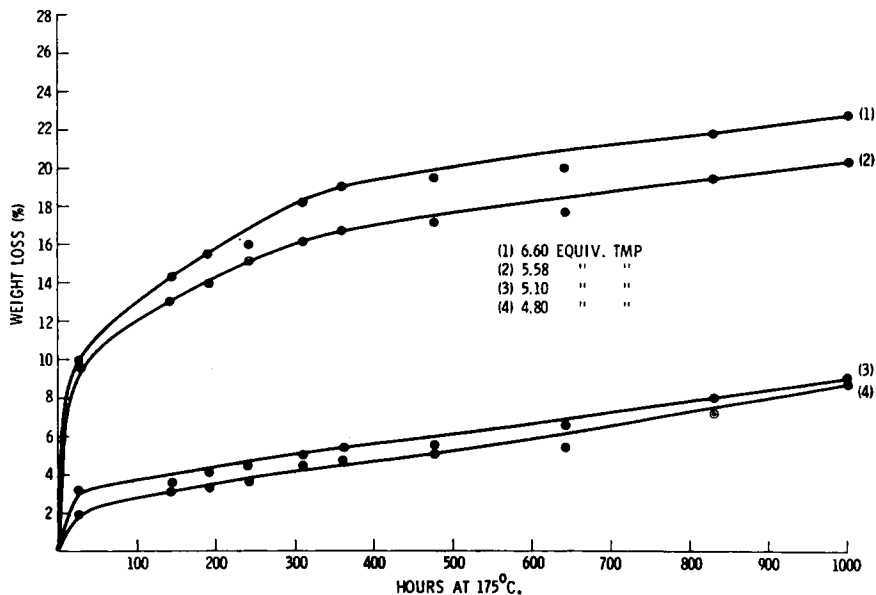


Fig. 1. Heat aging of polyester-urethanes from adipic acid and trimethylolpropane in air.

RESULTS AND DISCUSSION

Heat Aging

Although the degradation of polyamides⁶ and addition polymers such as polyvinyl chloride and polymethyl methacrylate⁷ have been extensively studied, degradation studies of polyurethanes have not been reported. The following data were obtained in order to provide information in this area.

The composition of the polyester-urethanes prepared by the condensation of adipic acid with trimethylolpropane, followed by crosslinking with DPMDI, are shown in Table I. The results of heat aging tests in air at 175°C. on these samples (Fig. 1) are given as plots of the weight loss versus time.

It is apparent that the resistance to heat aging decreases as the concentration of trihydric alcohol (trimethylolpropane) increases. An increase in trimethylolpropane content necessitates an equivalent increase in the amount of diisocyanate used to form the polyester-urethane and results in the formation of a larger concentration of urethane groups. This increase in the number of urethanes has resulted in the reduced resistance to heat aging. The urethane groups do not appear to be as resistant to decomposition at high temperatures as the ester groups.

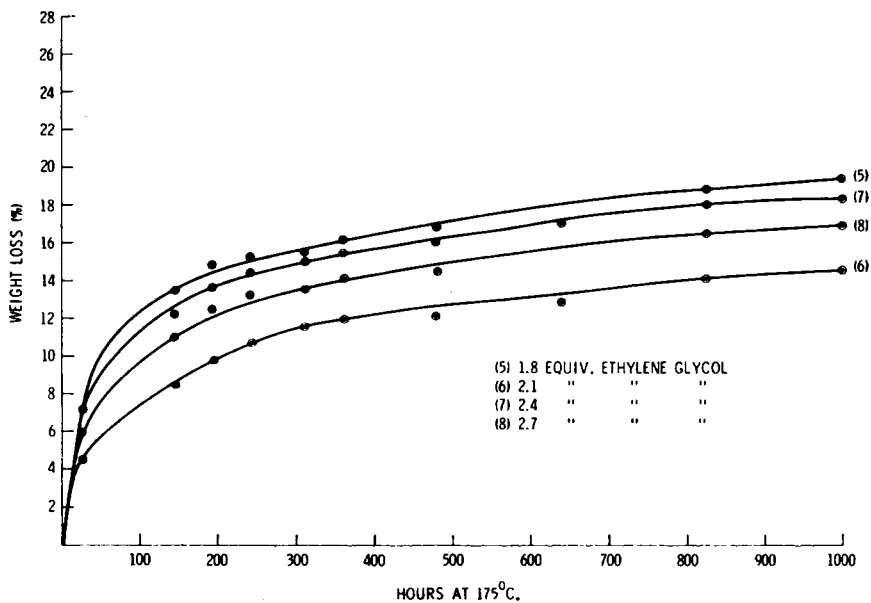


Fig. 2. Heat aging of polyester-urethanes from adipic acid, trimethylolpropane and ethylene glycol in air.

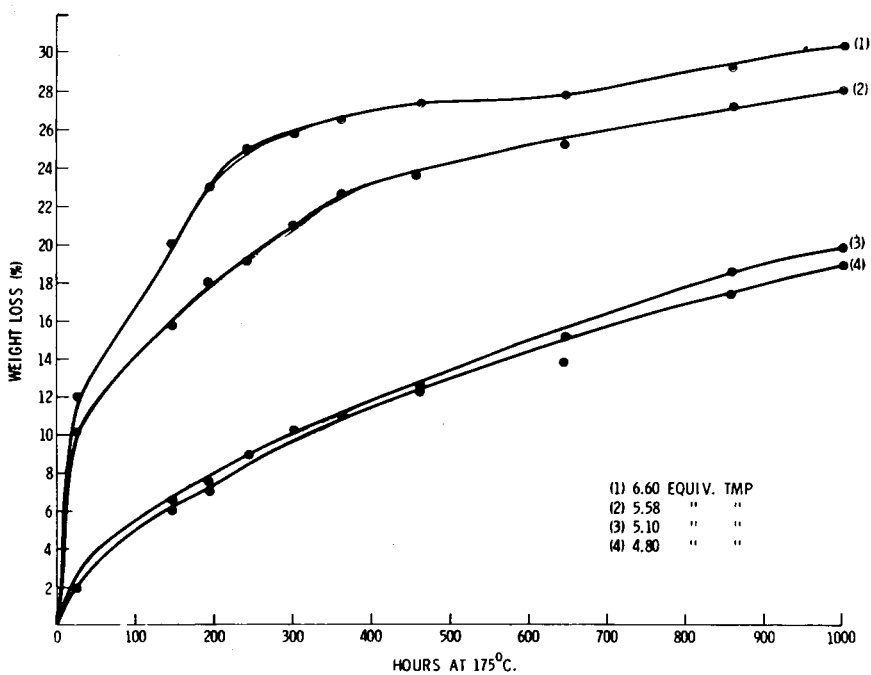


Fig. 3. Heat aging of polyester-urethanes from adipic acid and trimethylolpropane in nitrogen.

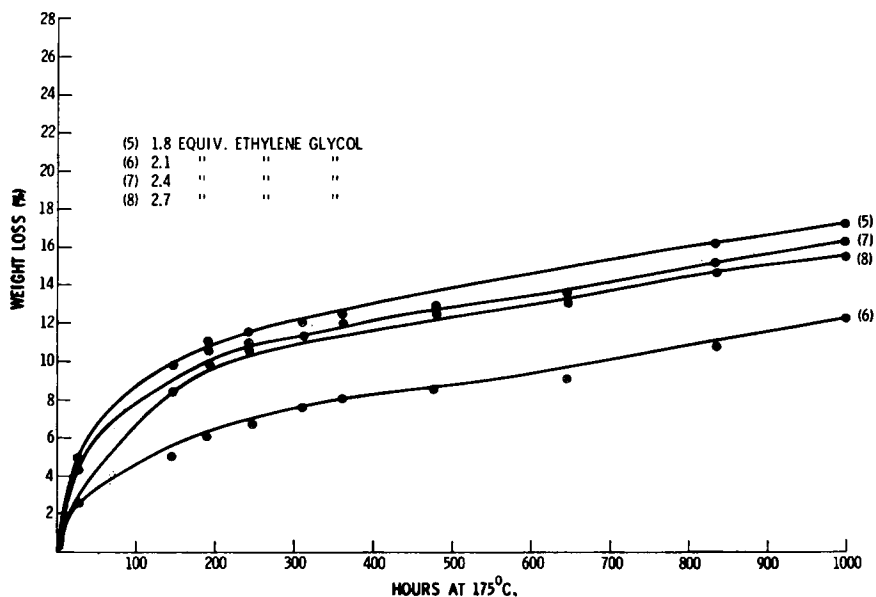


Fig. 4. Heat aging of polyester-urethane from adipic acid, trimethylolpropane and ethylene glycol in nitrogen.

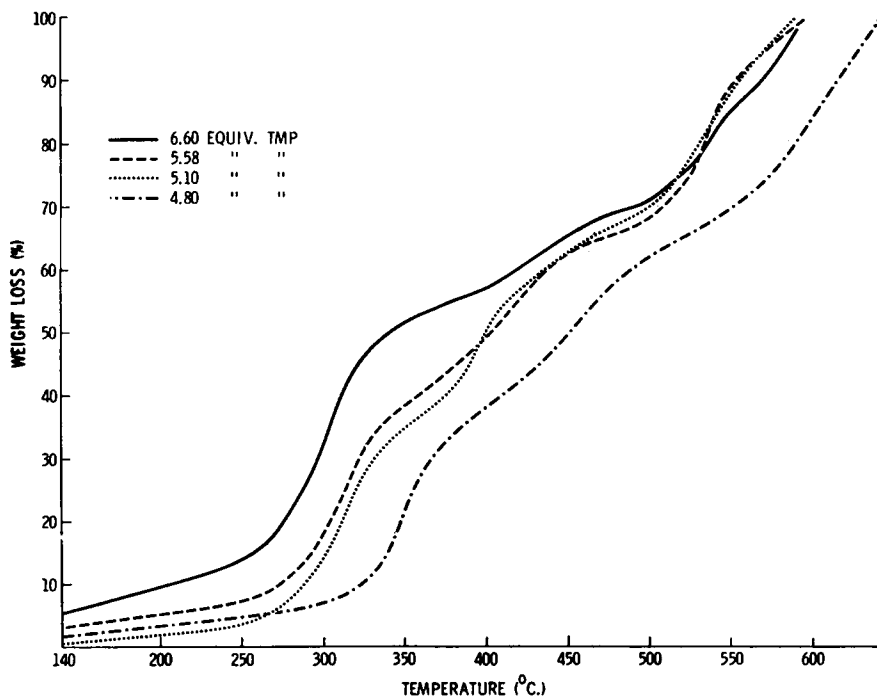


Fig. 5. Thermogravimetric analysis in air of polyester-urethanes from adipic acid and trimethylolpropane.

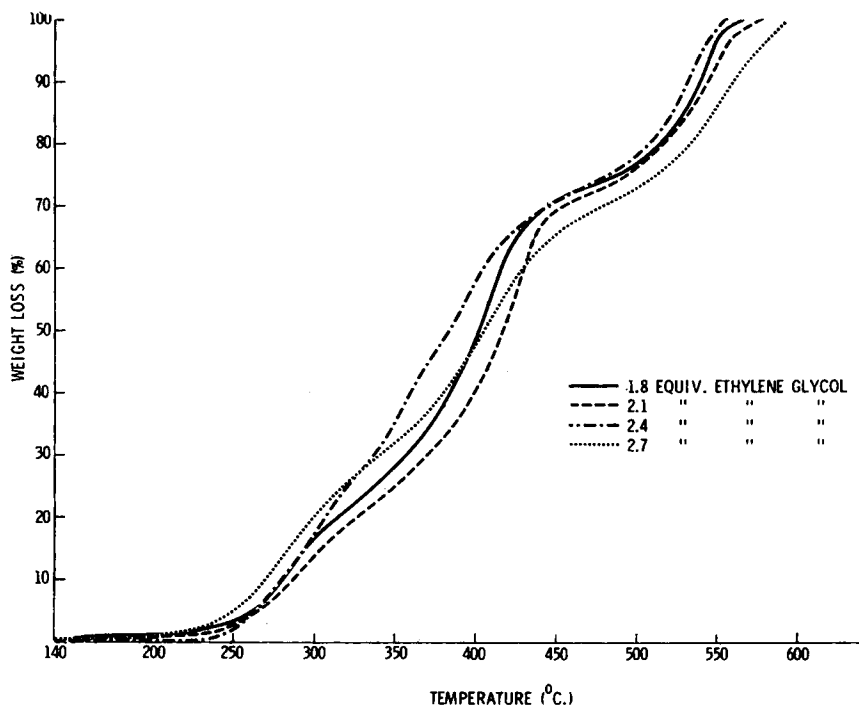


Fig. 6. Thermogravimetric analysis in air of polyester-urethanes from adipic acid, trimethylolpropane and ethylene glycol.

TABLE II

Polyester-urethanes prepared from Adipic acid-trimethylolpropane-ethylene glycol-4,4'-diphenylmethane diisocyanate

| Sample no. | Adipic acid (equiv.) | TMP ^a (equiv.) | Ethylene glycol (equiv.) | DPMDI ^b (equiv.) |
|------------|----------------------|---------------------------|--------------------------|-----------------------------|
| 5 | 2.4 | 1.2 | 1.8 | 0.6 |
| 6 | 2.4 | 0.9 | 2.1 | 0.6 |
| 7 | 2.4 | 0.6 | 2.4 | 0.6 |
| 8 | 2.4 | 0.3 | 2.7 | 0.6 |

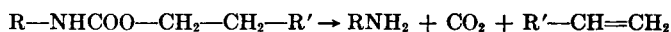
^a Trimethylolpropane.

^b 4,4'-diphenylmethane diisocyanate.

The polyester-urethanes prepared with the inclusion of ethylene glycol as one of the polyols are listed in Table II. It can be seen that the hydroxyl concentrations are the same for all these samples, but the ratio trimethylolpropane/ethylene glycol has been varied. Since the urethane/ester ratio remains constant in these polymers, data obtained from samples five to eight can be considered as an evaluation of the effect of crosslinking density. In Figure 2, the results of air heat aging at 175°C. on weight loss of samples five to eight have been plotted. The four samples give

similar curves and no connection can be seen between crosslinking density and weight loss on heat aging.

In Figures 3 and 4, the results of heat aging samples one through eight at 175°C. in a nitrogen atmosphere have been plotted. Again, the data indicate that decomposition increases with increasing urethane/ester ratio (Fig. 3) and that variations in crosslinking density do not affect the weight loss on heat aging when the urethane/ester ratio is held constant (Fig. 4). However, comparison of Figure 3 with Figure 1, which show the results of heat aging of samples one through four at 175°C. in nitrogen and air, respectively, indicates that each sample loses weight in nitrogen at a significantly higher rate than it does in air. This indicates that the degradation of polyester-urethanes proceeds mainly by a nonoxidative mechanism, which operates chiefly on the urethane linkage. Similar comparison of Figures 2 and 4 leads to the same conclusion. The fact that the rate of weight loss in all cases is higher in nitrogen than in air can possibly be accounted for by the formation of relatively oxidation-susceptible products of the initial decomposition of the urethane linkage. For example, Saunders⁸ has reported data indicating that the following reaction can take place at elevated temperature:



Either the amine or the olefin, or both, could oxidize at elevated temperatures, and the oxidation product might be expected to have a lower vapor pressure than the unoxidized decomposition product.

Thermogravimetric Analysis

The results of thermogravimetric analysis in air from 140–600°C. are plotted as percent weight loss vs. temperature in Figures 5 and 6. Procedural Decomposition Temperatures can be derived from the four curves in Figure 5 by drawing a straight line along the slope of the first steep ascent of each curve. When this line is extrapolated to 0% weight loss, the values listed in Table IV are obtained. The temperatures increase with decreasing urethane/ester ratio, indicating that the decomposition of the urethane linkage occurs more rapidly than the ester linkage. This is in agreement with the conclusions formed from the heat aging of these samples.

Thermogravimetric analysis data obtained similarly are plotted for samples five through eight in Figure 6. The four curves and the Procedural Decomposition Temperatures (Table III) are very nearly identical. Since samples five through eight vary only in crosslinking density, it appears that the latter property has no effect on degradation rate of these polymers. This conclusion is also in agreement with the conclusions derived from the heat aging data on samples five through eight.

When thermogravimetric analysis of a given sample was carried out in nitrogen (0.1 l./min.) the results of weight loss vs. temperature were nearly

TABLE III
Polyester-urethane Procedural Decomposition Temperatures

| Sample no. | Procedural decomposition temperature (°C.) | |
|------------|--|-------------|
| | In air | In nitrogen |
| 1 | 230 | 232 |
| 2 | 262 | 260 |
| 3 | 278 | 275 |
| 4 | 317 | 317 |
| 5 | 250 | 254 |
| 6 | 251 | 249 |
| 7 | 250 | 252 |
| 8 | 244 | 250 |

TABLE IV
Solubility of Polyester-urethanes in Toluene and Methanol

| Sample no. | Toluene (% polymer) | Methanol (% polymer) |
|------------|------------------------|-------------------------|
| 1 | 0.20 | 0.24 |
| 2 | 0.31 | 0.13 |
| 3 | 0.2 | 0.15 |
| 4 | 0.04 | 0.12 |
| 5 | 1.9 | 3.10 |
| 6 | 1.29 | 11.10 |
| 7 | 1.93 | 22.00 |
| 8 | 6.6 | 37.00 |

identical with the analysis in air. The Procedural Decomposition Temperatures were also in agreement. These data are shown in Table III and are in agreement with the data obtained from the isothermal heat aging of samples one through eight in inert atmosphere.

The conclusions from the heat aging and thermogravimetric analysis data indicate: (1) that polyester-urethanes of the greatest thermal stability can be obtained by keeping the urethane/ester ratio as low as possible; (2) that crosslinking density has no effect on thermal stability as long as the urethane/ester ratio is held constant; and (3) that the decomposition of the urethane linkage proceeds independently of the oxygen concentration in the atmosphere.

Solubilities

The solubilities of the polyester-urethanes in methanol and toluene are listed in Table III. Little difference can be detected from samples one to four, which contain only trimethylolpropane as the polyol component. Apparently, the degree of crosslinking in all these samples is sufficiently high to result in minimum solubility and the ratio of urethane/ester groups has no effect on solubility. The samples which contain ethylene glycol as one of the polyol components exhibit a significant decrease in resistance to

solubility. As the concentration of ethylene glycol increases, from samples five through eight, the solubility, especially in methanol, increases. The introduction of the diol into these polymers has reduced the crosslinking density to the point that noticeable differences in solubility can be detected. From the above data, it can be concluded that the optimum resistance to solubility can be obtained by maintaining the crosslinking density at a maximum value.

The data (Table V) report the effect of changes in composition of polyester-urethanes with low crosslinking density on the solubility in toluene and methanol. The samples were synthesized with equally low crosslinking densities (sample seven is included for comparison) but with variations in the urethane/ester ratio. The ratio increases from samples seven through eleven. The solubility data show virtually no effect of structure

TABLE V
Solubility of Polyester-urethanes in Toluene and Methanol

| Sample no. | Composition (equiv.) | Toluene (% polymer) | Methanol (% polymer) |
|------------|--|---------------------|----------------------|
| 7 | 2.4 Adipic acid 0.6 Trimethylolpropane 2.4 Ethylene glycol 0.6 DPMDI* | 1.93 | 22.0 |
| 9 | 2.0 Adipic acid 0.6 Trimethylolpropane 2.4 Ethylene glycol 1.0 DPMDI | 1.84 | 25.4 |
| 10 | 1.6 Adipic acid 0.6 Trimethylolpropane 2.4 Ethylene glycol 1.4 DPMDI | 1.46 | 28.7 |
| 11 | 1.2 Adipic acid 0.6 Trimethylolpropane 2.4 Ethylene glycol 1.8 DPMDI | 1.58 | 31.9 |

* 4,4'-diphenylmethane diisocyanate.

on solubility when toluene is used as the solvent. However, solubility in methanol increased slightly with increasing urethane/ester ratio. The lack of a solubility effect in samples one through four (Table IV) is probably due to the much higher crosslinking density.

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Synopsis

The composition of crosslinked polyester-urethanes has been varied by adjusting the ratio of ester to urethane groups. The crosslinking density of these materials has been varied by changes in the polyester functionality. The polyester-urethanes have been subjected to solvent extraction, wherein it was found that at high crosslinking densities, the solubility of the polymers is unaffected by the ester-urethane ratio. At low crosslinking densities, solubility increases slightly with increasing urethane concentration. The solubility was also found to increase with decreasing crosslinking density. Data obtained from isothermal heat aging and thermogravimetric analysis, both carried out in air and in inert atmosphere, indicate that thermal stability increases with increasing ester/urethane ratio and is independent of crosslinking density where the ester/urethane ratio is held constant. In addition, data obtained from heat aging and thermogravimetric analysis have indicated that decomposition of the samples occurs as rapidly in inert atmosphere as in air, indicating that the decomposition occurs chiefly by a nonoxidative mechanism.

Résumé

La composition de polyesters-uréthanes pontés a été considérée en faisant varier le rapport des groupes esters aux groupes uréthannes. On varie la densité de pontage de ces matériaux en changeant la fonctionnabilité du polyester. Les polyesters-uréthanes ont été soumis à l'extraction par solvant, ce qui a permis de trouver qu'à haute densité de pontage, la solubilité des polymères n'est pas affectée par le rapport ester-uréthane. À faible densité de pontage toutefois la solubilité augmente faiblement en fonction de l'augmentation de la concentration en uréthannes. On a aussi trouvé que la solubilité augmente en fonction de la diminution de la densité de pontage. Des données obtenues à partir du vieillissement isothermique et analyse thermogravimétrique sous atmosphère inerte montrent que la stabilité thermique croît en fonction de l'augmentation du rapport ester-uréthane et est indépendante de la densité de pontage, si le rapport ester-uréthane est maintenu constant. En outre des données de vieillissement thermique et d'analyses thermogravimétriques ont montré que la décomposition des échantillons se produit aussi rapidement en atmosphère inerte qu'à l'air, ce qui prouve que la décomposition se produit principalement par un mécanisme non-oxydant.

Zusammenfassung

Die Zusammensetzung von vernetzten Polyester-Urethanen wurde durch Wahl des Verhältnisses Ester- zu Urethangruppen variiert. Die Vernetzungsdichte dieser Stoffe wurde durch Änderung der Polyesterfunktionalität variiert. Die Polyester-Urethane wurden einer Lösungsmittelextraktion unterworfen, wobei festgestellt wurde, dass bei hoher Vernetzungsdichte die Löslichkeit der Polymeren nicht durch das Verhältnis von Ester zu Urethan beeinflusst wird. Bei niedriger Vernetzungsdichte nimmt die Löslichkeit mit steigender Urethankonzentration schwach zu. Die Löslichkeit zeigte auch eine Zunahme mit abnehmender Vernetzungsdichte. Ergebnisse bei der isothermen Hitzealterung und der thermogravimetrischen Analyse, beide unter Luft und in inerte Atmosphäre ausgeführt, zeigen, dass die thermische Stabilität mit steigendem Ester-Urethanverhältnis zunimmt und bei konstant gehaltenem Ester-Urethanverhältnis von der Vernetzungsdichte unabhängig ist. Ausserdem haben die Ergebnisse der Hitzealterung und der thermogravimetrischen Analyse gezeigt, dass die Zersetzung der Proben in inerte Atmosphäre gleich schnell wie in Luft vor sich geht, was beweist, dass die Zersetzung hauptsächlich über einen nicht-oxydativen Mechanismus verläuft.

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