

Thermal Stability of Polyurethanes Based on Vegetable Oils

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ABSTRACT: A series of polyurethanes from polyols derived from soybean, corn, safflower, sunflower, peanut, olive, canola, and castor oil were prepared, and their thermal stability in air and nitrogen assessed by thermogravimetric analysis, FTIR, and GC/MS. Oil-based polyurethanes generally had better initial thermal stability (below 10% weight loss) in air than the polypropylene oxide-based polyurethane, while the latter was more stable in nitrogen at the initial stage of degradation. If weight loss at a higher conversion is taken as the criterion of stability, then oil polyurethanes have better thermal stability both in air and in nitrogen. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1723–1734, 2000

Key words: vegetable oil; polyurethane; thermal degradation

INTRODUCTION

Vegetable oils have a number of excellent properties, which could be utilized in producing valuable polymeric materials such as polyurethanes. Polyurethanes (PU) are a class of polymers with an extremely versatile range of properties and applications.^{1,2} Their structure can be tailored to suit specific requirements by selecting the type of polyols and isocyanates. However, these materials have relatively low thermal stability, primarily due to the presence of urethane bonds. The onset of urethane bond dissociation is somewhere between 150 and 220°C, depending on the type of substituents on the isocyanate and polyol side.^{3–5} Saturated hydrocarbons are known to possess relatively good thermal and thermo-oxidative resistance compared to polyether and polyester polyols. The objective of this study was to compare relative thermal resistance of vegetable oil-based polyurethanes to that of the most frequently used polyol, based on polyoxypropylene (PPO). Vegetable oils are triglycerides of fatty acids. The com-

position of fatty acids vary from oil to oil, and it determines the degree of unsaturation of the oils. Polyols are formed by introducing hydroxyl groups at the position of double bonds. Thus, oils with higher unsaturation should give polyols with higher functionality. Table I shows the composition of the oils used in this work.^{6,7}

To convert oils into polyols they were first epoxidized using the standard epoxidation procedure.^{8,9} Epoxy groups were then converted into hydroxyl groups to give structures analogous to those of the soybean polyol, shown in Figure 1, where Me designates the methyl group. As Figure 1 shows, the idealized structure of polyols has a saturated hydrocarbon structure with one OH and one methoxy group per double bond. However, due to the incomplete epoxidation and hydroxylation, the hydroxyl number of the polyols used in this work was lower than theoretical, as shown in Table II.

Thermal stability of polyurethanes based on these polyols will depend on the functionality of the polyol, i.e., on the number of urethane groups per unit volume, as well as structural differences. In this work we have converted seven oils into polyols, which were then reacted with modified diphenylmethane diisocyanate—Isonate 143 L—to give

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Table I Major Fatty Acids in Oils Used in This Work

No.	Oil	16 : 0	18 : 0	18 : 1	18 : 2	18 : 3	Iodine Value Range	
1	Olive	9.0		80.3	6.3		76–88	
2	Peanut	11.1		46.7	32		84–100	
3	Canola			60.9	21	8.8	100–115	
4	Corn	10.9		25.4	59.6		118–128	
5	Soybean	10.6	4	23.3	53.7	7.6	123–139	
6	Sunflower	4	4.5	24	64		125–140	
7	Safflower	6.8		12	77.7		140–150	
8	Castor	90% ricinoleic, hydroxyl value 164 mg KOH/g						86

polyurethane. The glass transition of these polymers, irrespective of their chemical structure, was almost linearly dependent of the polyols OH number, and thus, crosslinking density of polyurethanes. Castor oil, a natural polyol containing 2.6 double bonds per molecule, which are not present in other polyols, was included as well. The molecular weight of the polyols is typically about 1000. A poly(oxypropylene) triol of approximately the same molecular weight was used for comparison.

Degradation kinetics of polymers was studied using a thermogravimetric analyzer. Experimental data were processed using the Flynn method, which includes three isothermal and one dynamic TGA curve.¹⁰ Our simulation studies have shown that in the case of simple kinetics, all differential and integral methods gave correct results.¹¹ However, because the kinetics of degradation is never simple, the results from different methods applied to the real materials are different.¹² Using several isothermal curves and combining them with a dynamic curve assures better reliability of the results. The method used in this work allows determination of the activation energy, E , from the slope of the time vs. conversion curve and crosschecking of E from the conversion vs. time curves. The rate of weight loss, dC/dt in isothermal conditions is related to the temperature of

degradation, T_A , and the extent of reaction (conversion), $C = 1 - (w - w_\infty)/(w_0 - w_\infty)$:

$$\frac{dC}{dt} = f(C)k(T_A) \quad (1)$$

$$F(C) = \int \frac{dC}{f(C)} = \int k(T_A) dt = k(T_A)t \quad (2)$$

where w_0 , w , and w_∞ are initial weight of the sample, weight at time t , and final weight of the given degradation step, respectively. For isothermal condition where $k(T) = A \exp(-E/RT)$, eq. (2) becomes:

$$\log F(C) = \log A + \log t - \frac{E}{RT_1} \quad (3)$$

The same equation can be written for other isothermal temperatures, T_2 , T_3 , ... invoking the Flynn-Wall equation:¹³

$$\log F(C) \cong \log \frac{AE}{R} - \log \beta - 2.315 - 0.457 \frac{E}{RT_1} \quad (4)$$

and combining it with eq. (3), one obtains:

$$\log t_a - \log t_b = 0.457 \frac{E}{R} \left(\frac{1}{T_{\beta b}} - \frac{1}{T_{\beta a}} \right) \quad (5)$$

Here, β is the heating rate, and a and b refer to two isothermal points (conversions). The plan of the experiment involves running a single dynamic TGA at a selected heating rate, β , selecting the region of conversions for which E will be determined, selecting conversions, C_a , C_b , C_c , etc.,

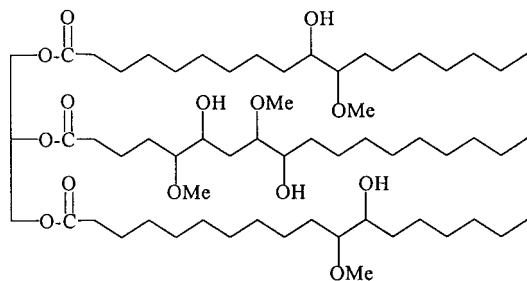
**Figure 1** Idealized structure of soya polyol.

Table II Properties of Polyols Obtained from Different Vegetable Oils

Polyol	Theoretical OH Number, mg KOH/g	Actual OH Number, mg KOH/g	Viscosity at 30°C mPa · s	Calculated Polyol mol wt	GPC M_w/M_n
Olive	165	138	840	996	1.2
Peanut	173	111	1200	977	1.4
Canola	212	144	1000	1006	1.3
Corn	229	140	1900	992	1.5
Soybean	228	213	3700	1069	1.3
Safflower	236	180	4200	1035	2.0
Sunflower	238	161	4800	1017	2.0
Castor	164	164	840	928	1.0

and their corresponding absolute temperatures $T_{\beta a}$, $T_{\beta b}$, $T_{\beta c}$.

The next step involves selecting several isothermal temperatures, T_1 , T_2 , T_3 (which are lower than $T_{\beta a}$), and running isothermal TGA experiments. From the first isothermal curve select the same conversions as in the dynamic TGA curve, C_a , C_b , C_c , etc., and corresponding (iso) times, t_{1a} , t_{1b} , t_{1c} , etc. Repeat the procedure with the second and third isothermal curve to obtain times t_{2a} , t_{2b} , t_{2c} , and t_{3a} , t_{3b} , t_{3c} . With the data obtained, construct the diagram as in Figure 2, plotting $\log t_{\text{iso}}$ vs. temperatures T_β from dynamic TGA corresponding to different conversions. If a relatively simple degradation process is taking place, a grid of straight lines should be obtained. The slope of the isothermal straight lines (T_1 , T_2 , T_3) is $(-0.457 E/R)$. Activation energies can be also determined from the distance between iso-conversional lines. For example, from the distance between times at a given conversion, i , at isothermals T_2 and T_1 , one can determine E :

$$\log t_{i2} - \log t_{i1} = \frac{E}{2.3R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (6)$$

This method allows checking the change of activation energy with conversion as well as with temperature. Generally, kinetic parameters are meaningful if they refer to a particular chemical reaction. Unfortunately, polymer degradation is always a complex process consisting of a number of parallel and consecutive reactions. Activation energy in such cases refers to the compounded degradation reactions, and better insight into the process is obtained from the study of the mechanism of degradation. Degradation of polyurethanes is a complex multistage process, but the most important is the onset of degradation. We have studied the initial stage of degradation using FTIR and GC/MS. IR spectra of isothermally degraded samples in nitrogen were recorded after different exposure times and the gaseous component were analyzed by GC/MS.

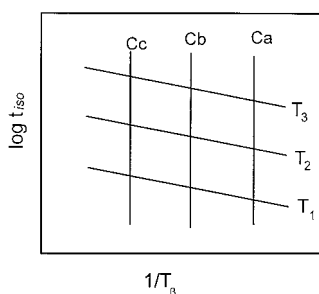


Figure 2 Schematic representation of the plot of isothermal reaction times vs. reciprocal temperature for selected conversions from dynamic TGA. T_1 , T_2 , T_3 , are isothermal temperatures and C_a , C_b , C_c are selected conversions.

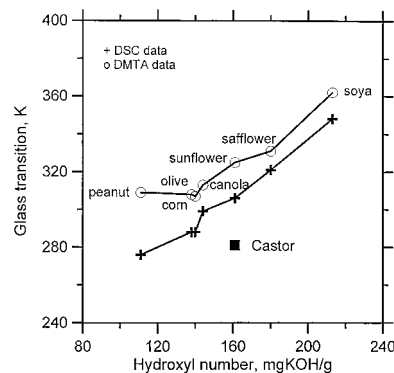


Figure 3 Effect of OH number of vegetable polyols on the glass transition of polyurethanes.

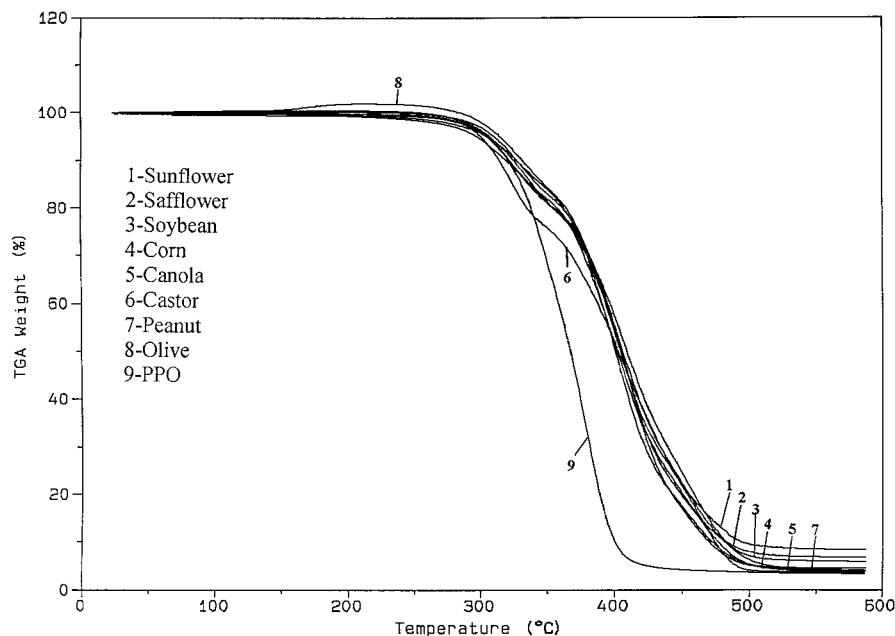


Figure 4 Dynamic TGA curves in nitrogen of all polyurethanes used in this study.

EXPERIMENTAL

Materials

Safflower oil was purchased from Aldrich. Castor oil (DB) was generously supplied by CasChem, New Jersey. All other oils were purchased from a local store. Isonate 143 L was obtained from Dow

Chemical Co. The oils were epoxidized using the procedure described in literature^{8,9} and then hydroxylated using the proprietary method to obtain polyols. Properties of the polyols given in Table II show that the degree of conversion of double bonds to hydroxyl groups varied from oil to oil.

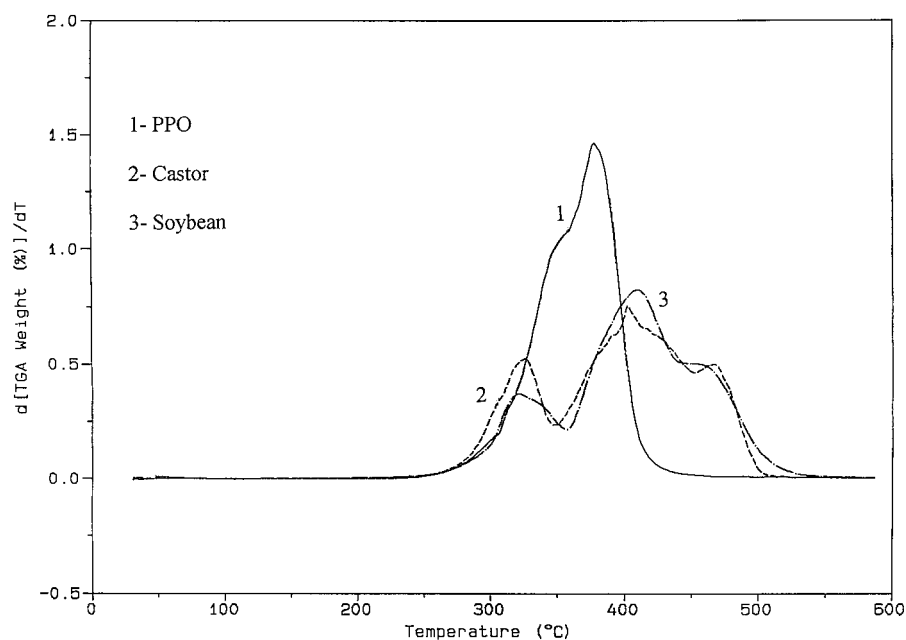


Figure 5 Derivative TGA curves of PPO-based PU, castor PU, and soybean-based PU in nitrogen.

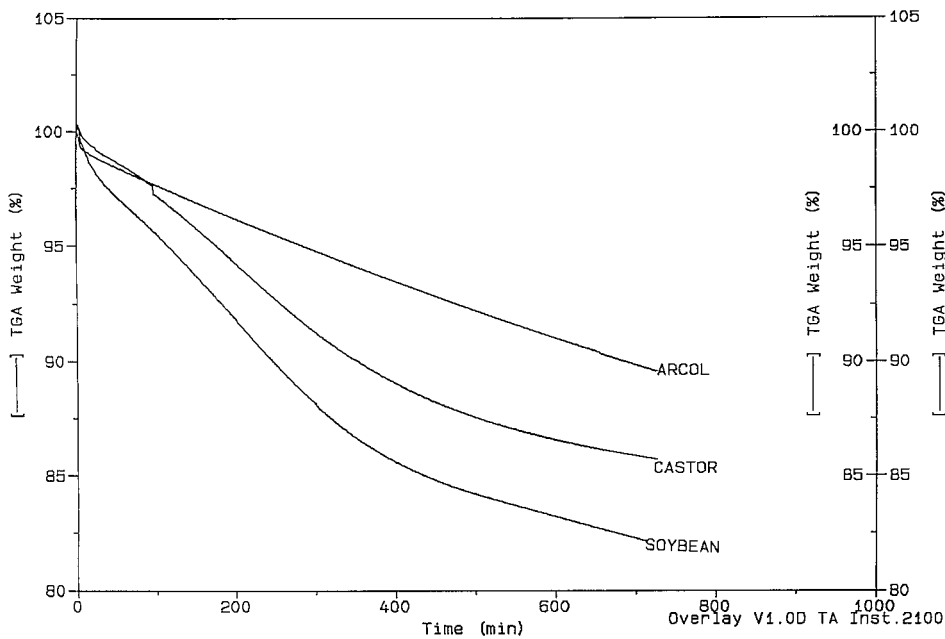


Figure 6 Isothermal TGA curve at 230°C of three polyurethanes in nitrogen.

Arcol LG-168, having an OH number of 168 mg KOH/g, was supplied by ARCO Chemical. It is a 1000 molecular weight polyoxypropylene triol that was used for comparison with vegetable oil-based polyols.

Polyurethane samples were prepared by mixing stoichiometric amounts of the polyol and the isocyanate component and casting to a mold to

obtain a 3 mm-thick sheet. The samples were heated at 100°C for 24 h to complete curing.

Methods

A thermal analyst system from TA Instruments, consisting of a Controller 3100 with a DSC 2910

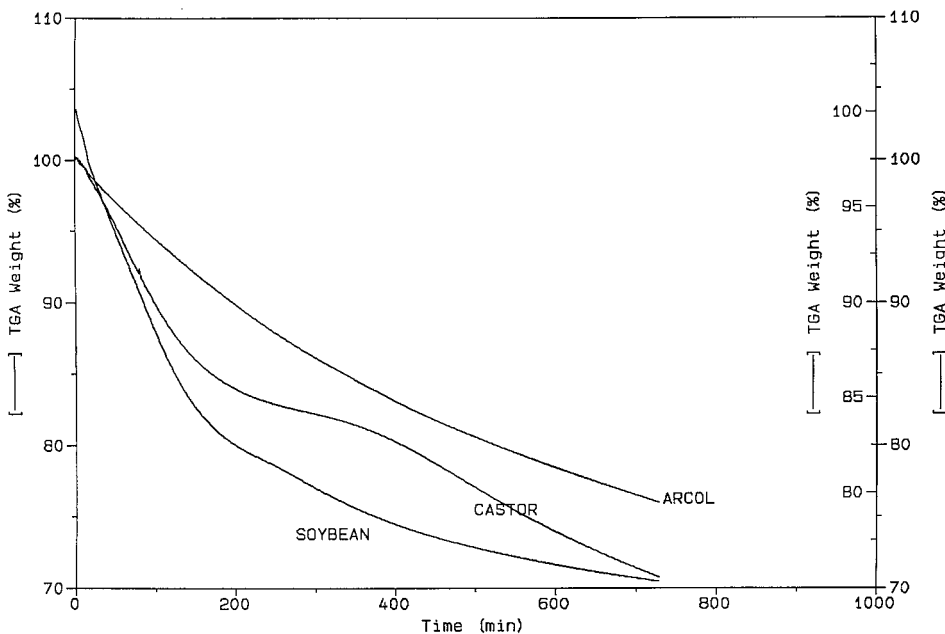


Figure 7 Isothermal TGA curve at 240°C of three polyurethanes in nitrogen.

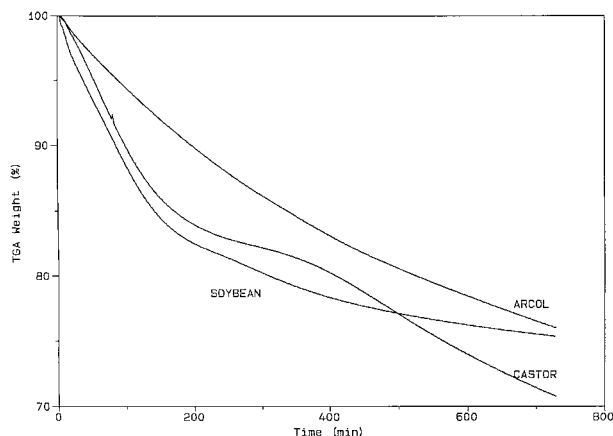


Figure 8 Isothermal TGA curve at 250°C of three polyurethanes in nitrogen.

module and TGA 2050 module was used to determine the glass transition of polymers and measure the kinetics of degradation. The heating rate in the TGA dynamic mode was 10°C/min. Isothermal measurements were carried out at 230, 240, and 250°C. Dynamic mechanical tests were carried out on a Rheometric DMTA, model Mark III, at 5°C/min and 10 Hz. A Shimadzu GC-17A Gas Chromatograph/QP5000 Mass Spectrometer was used to analyze gaseous degradation products.

RESULTS AND DISCUSSION

Vegetable polyol functionality varied from about 4 to about 2, resulting in a different crosslinking density of the polyurethane networks, and different glass transitions. Figure 3 shows that glass transitions of the oil-based polyurethanes in-

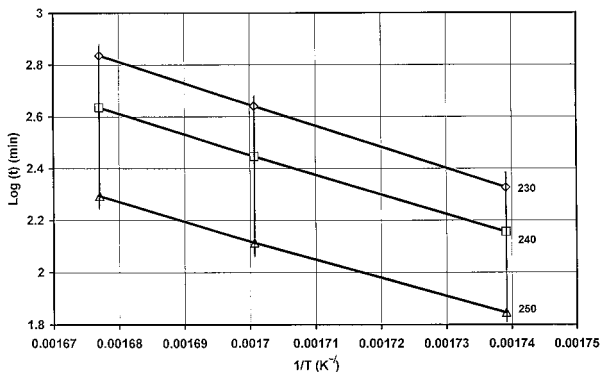


Figure 9 Dependence of degradation times in nitrogen on conversion at three temperatures (isothermal and isoconversional lines) for PPO-PU.

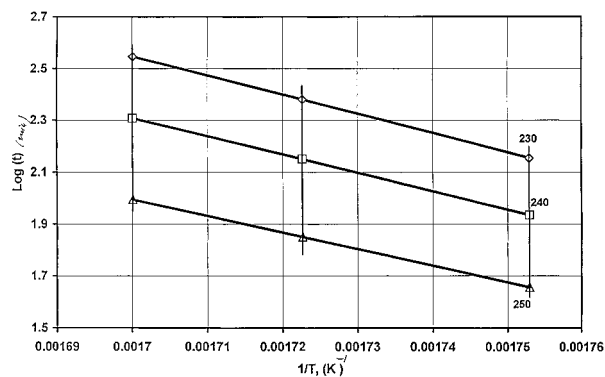


Figure 10 Dependence of degradation times in nitrogen on conversion at three temperatures (isothermal and isoconversional lines) for castor-PU.

creases almost linearly with increasing the OH number. These polyurethanes were transparent, amorphous, single-phase polymers.

Dynamic TGA curves in nitrogen of all oil-based polyurethanes are shown in Figure 4. Whereas PPO-based polyurethane degrades in a single step, oil-based polyurethanes show two-step degradation. Derivative TGA curves of the same polymers reveal actually two and three main degradation processes, (Fig. 5). The first step is associated with the first 20% of the weight loss, and the second with the remaining 80%.

The shapes of the weight loss curves of all polyurethanes are almost identical, and overall differences in thermal stability appear to be small. If measured by 20% weight loss temperature, PPO-based polyurethane showed the lowest thermal stability polyurethane and then castor oil-based polyurethane. However, initial weight loss is similar in all polymers, suggesting that

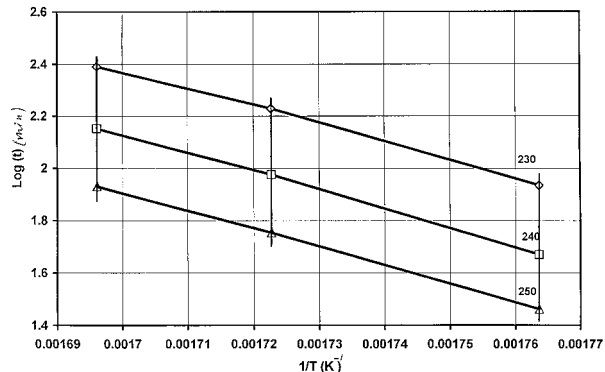


Figure 11 Dependence of degradation times in nitrogen on conversion at three temperatures (isothermal and isoconversional lines) for soy-PU.

Table III Activation Energy of the Initial Step of Degradation (Below 10%) in Nitrogen of Three Selected Polyurethanes

Sample	<i>E</i> from Isothermals, kJ/mol			<i>E</i> from Isoconversionals, kJ/mol		
	230°C	240°C	250°C	4%	7%	10%
PPO-PU	156.8	147.7	137.8	121.0	132.2	136.1
Castor-PU	141.8	134.5	122.7	138.8	133.0	125.5
Soy-PU	128.8	136.1	132.5	119.4	119.5	115.7

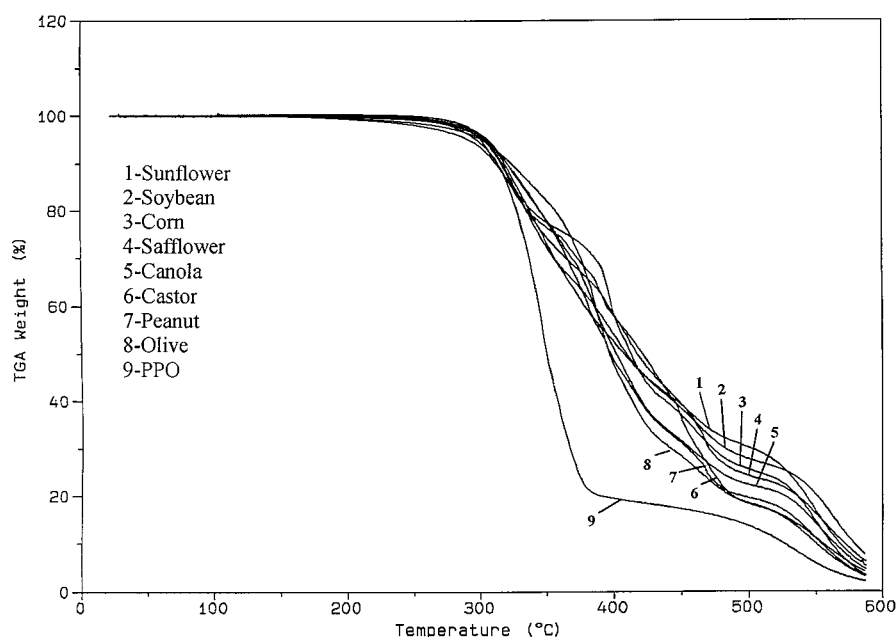
degradation starts at the urethane bond. Urethanes were known to be relatively thermally unstable materials.¹⁴⁻²⁰ Decomposition of the urethane bond starts at about 150–200°C. Three mechanisms of decomposition of urethane bonds were proposed:¹⁴

- (1) Dissociation to isocyanate and alcohol
 $\text{RHNCOOR}' \rightleftharpoons \text{RNCO} + \text{HOR}'$
- (2) Formation of primary amine and olefin
 $\text{RHNCOOCH}_2\text{CH}_2\text{R}' \rightarrow \text{RNH}_2 + \text{CO}_2 + \text{R}'\text{CH}=\text{CH}_2$
- (3) Formation of secondary amine
 $\text{RHNCOOR}' \rightarrow \text{RHNHR}' + \text{CO}_2$

All three reactions may proceed simultaneously. To extract kinetic parameters, three polyurethanes were selected for isothermal study: PPO-based PU (designated as Arcol), castor oil-

based PU, and soybean-based PU. Castor oil differs from other polyols in that it contains three double bonds. Figures 6, 7, and 8 display the rate of weight loss in nitrogen for the three selected polyurethanes at 230, 240, and 250°C. The curves show that initial rate loss is the lowest in the PPO-based polyurethanes and has somewhat better stability in the castor oil-based PU vs. soybean-based PU. The difference between the last two can be explained by the difference in urethane content in these polymers—soybean-based PU having about 30% more unstable urethane groups. PPO-based PU had about the same urethane content as castor oil-based PU. The isothermal curve for castor PU shows a more complex degradation mechanism than the other two.

The temperatures (from dynamic TGA curves) and times (from isothermal TGA curves) corresponding to 4, 7, and 10% weight loss were mea-

**Figure 12** Dynamic TGA curves in air of all polyurethanes used in this study.

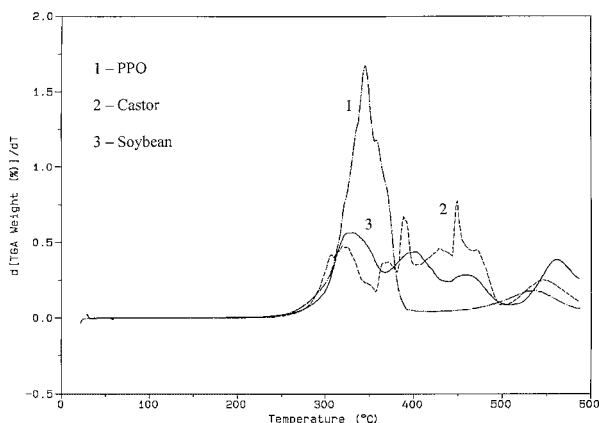


Figure 13 Derivative TGA curves of PPO-based PU, castor PU, and soybean-based PU in air.

sured. Figure 9, 10, and 11 show dependence of degradation times in nitrogen upon conversion at three temperatures for castor PU, soybean-based PU, and PPO-based PU, respectively. Activation energy calculated from the slope of isothermal curves and distance between isoconversionals are given in Table III.

As Figures 9, 10, and 11 show, the isothermals are fairly parallel, indicating that activation energy does not appreciably change with temperature. The average activation energies for the three temperatures are 147.4 kJ/mol for PPO-PU, 133.0 kJ/mol for castor-PU, and 132.5 kJ/mol for soy-PU. Average activation energy for the three sample over the three conversions (from 4 to 10%) are 130.0 kJ/mol for PPO-PU, 132.4 kJ/mol for castor-PU, and 118.2 kJ/mol for soy-PU. The variation in activation energy of about 10 kJ/mol, ascribed to the experimental error, demonstrates the complexity of the process. First, urethane bonds in PPO-PU are stabilized with electron donating methyl groups, which are not present in the other two polyurethanes. Second, although the early stage is dominated by urethane bond decomposition, the polyol component may contribute to a weight loss at higher conversions. This is particularly true in the case of PPO-PU, where activation energy increased from 121 kJ/mol at 4% conversion loss to 136 kJ/mol at 10% conversion. The values of the activation energy of degradation are of the same order of magnitude as in segmented polyurethanes at 10% conversion.²¹

Degradation in air under dynamic heating is displayed in Figures 12 and 13. Figure 12 shows that initial degradation up to 10% weight loss is

almost independent of the type of polyurethane, but the differences are exhibited immediately at higher conversions. It is believed that the mechanism of urethane decomposition is the same both in nitrogen and air, but further oxidation of the products in air introduces the differences. As Figure 13, shows at least four derivative peaks are shown in polyurethanes and two in PPO-based PUs. The residue at 500°C appears to correlate with the amount of isocyanate in the polymer except for PPO-based PU, which displayed the fastest rate of weight loss of all polymers and the lowest residue. Comparison of the TGA curves in air and nitrogen (Fig. 14) shows that PPO-PU is very sensitive to oxidative degradation, while polyurethanes displayed higher stability in air than in nitrogen, at least at higher conversions (above 20–30%). This could be explained by crosslinking in the former, rather than depolymerization, which takes place in the latter.

Isothermal weight loss–time curves for the three selected polyurethanes, at 230, 240, and 250°C, are shown in Figures 15, 16, and 17.

The simple inspection of the curves indicates low thermo-oxidative stability of PPO-PU, better stability of soy-PU, and the highest stability of castor-PU. At higher temperatures (240 and 250°C) the last two curves are getting closer. Isothermal-isoconversional diagrams for the three polymers are shown in Figures 18, 19, and 20.

Figures 18 and 20 illustrate irregular spacing between isothermals for PPO-PU and soy-PU. Activation energies of degradation in air for the three polymers are presented in Table IV. Average activation energies for the temperature region of 230–250°C were 112.9 kJ/mol for PPO-PU,

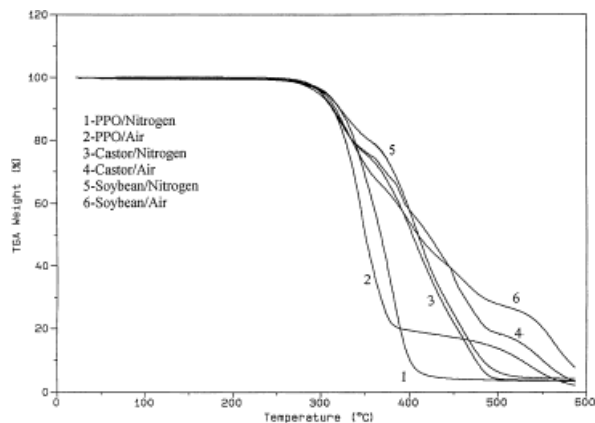


Figure 14 Dynamic TGA curves of three polyurethanes in air and nitrogen.

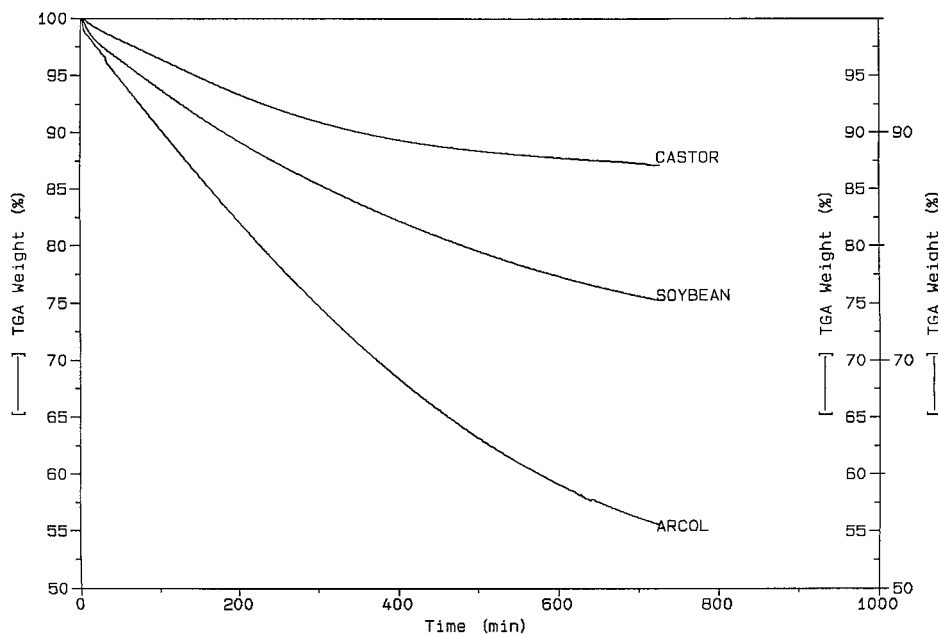


Figure 15 Isothermal TGA curve at 230°C of three polyurethanes in air.

180.7 kJ/mol for castor-PU, and 171.5 kJ/mol for the soy-PU. Average activation energies for the conversion region below 10% were 67.3 kJ/mol for PPO-PU, 138.1 kJ/mol for castor-PU, and 80.4 kJ/mol for soy-PU. Activation energy for the isothermal degradation of polypropyleneglycol was reported to be about 100 kJ/mol.²² Much lower

values for PPO-PU and soy-PU from isoconversionals reflected the complex nature of the degradation, which resulted in nonparallel isothermals in Figures 18 and 20. The comparison of activation energies of degradation in nitrogen and air points to the higher stability of the oil-based polyurethanes in air than in nitrogen, and the oppo-

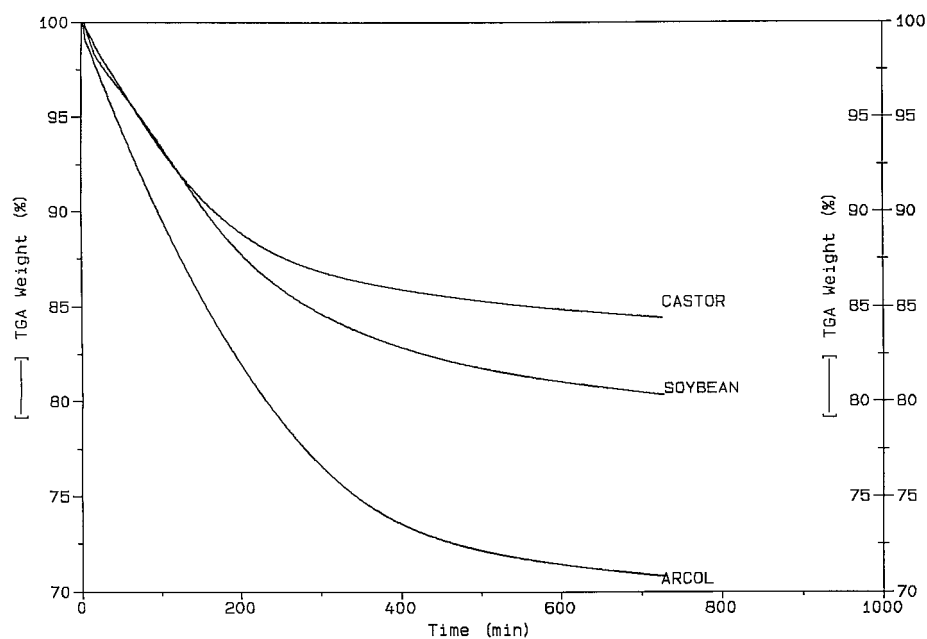


Figure 16 Isothermal TGA curve at 240°C of three polyurethanes in air.

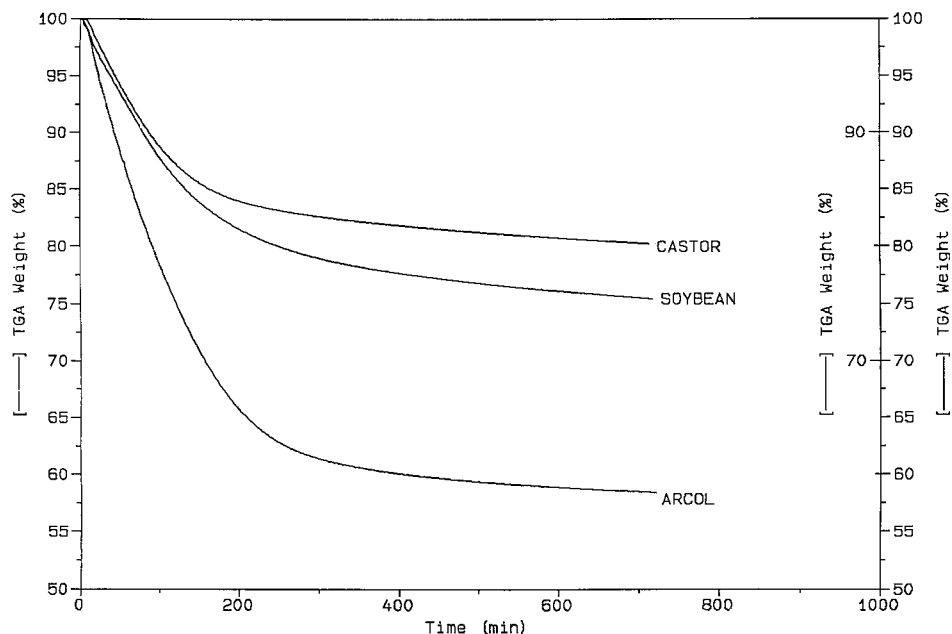


Figure 17 Isothermal TGA curve at 250°C of three polyurethanes in air.

site for PPO-PU. Castor-PU appears to be the most thermally stable of all three polymers.

MECHANISM OF THE DEGRADATION AT THE INITIAL STAGE

This study was concerned primarily with kinetics of degradation, but a limited number of experiments were carried out to identify main processes at the initial stage of degradation in air and nitrogen. Three selected polyurethane samples—PPO-PU, castor-PU and soy-PU—were placed in sealed glass vials under nitrogen, and heated at

250°C for various times, but little change was observed in the FTIR spectra at times shorter than 60 min. TGA showed that the samples lost about 5–10% of their weight after 60 min. The isocyanate peak at 2240 cm^{-1} was not observed in any of the samples after heating (Fig. 21). All samples before heating display the carbodiimide twin peak at about 2140 cm^{-1} , originating from Isonate 143 L. This peak disappeared after heating for 60 min. The urethane NH band at 3300 cm^{-1} widened and possibly split into two peaks, indicating the presence of amines. A carbonyl band from urethane amide I, at 1727 cm^{-1} , also changed, indicating the presence of ketones. A

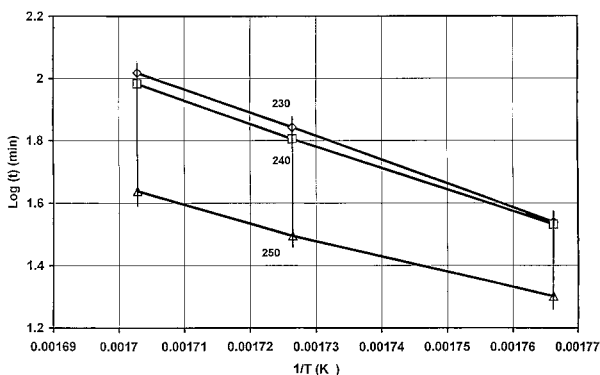


Figure 18 Dependence of degradation times in air on conversion at three temperatures (isothermal and iso-conversional lines) for PPO-PU.

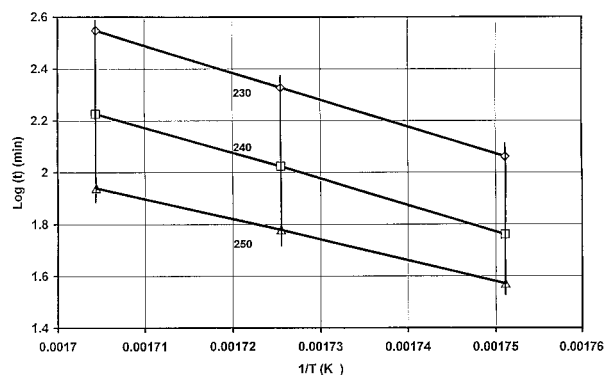


Figure 19 Dependence of degradation times in air on conversion at three temperatures (isothermal and iso-conversional lines) for castor-PU.

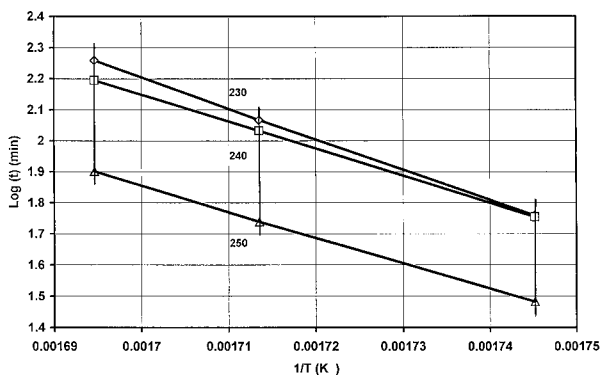


Figure 20 Dependence of degradation times in air on conversion at three temperatures (isothermal and iso-conversional lines) for soy-PU.

doublet at about 2350 cm^{-1} was caused by CO_2 from air.

GC/MS of the gaseous products after 60 min degradation in nitrogen showed the presence of

air (nitrogen and oxygen) and the mass of 44 in all three cases. That peak was assigned to carbon dioxide. It appears that carbon dioxide was a single product of the initial stage of degradation. CO_2 could come only from the urethane bond. Chain scission in aliphatic chains in oils or PPO chains would rather generate higher molecular weight products that may not be volatile at this temperature but was observed in FTIR. In summary, it appears that degradation resulting in weight loss starts at the urethane bond, which is split by the second or and third mechanism but not by dissociation into isocyanate and polyol.

CONCLUSIONS

Thermal degradation of oil-based and PPO-based polyurethanes was studied using TGA. The early stage of weight loss in nitrogen is determined by the concentration of urethane groups, the main

Table IV Activation Energy of the Initial Step of Degradation (Below 10% Weight Loss) in Air of Three Selected Polyurethanes

Sample	<i>E</i> from Isothermals, kJ/mol			<i>E</i> from Isoconversionals, kJ/mol		
	230°C	240°C	250°C	4%	7%	10%
PPO-PU	102.4	135.3	101.0	59.5	87.0	55.3
Castor-PU	200.0	190.4	151.7	123.5	138.0	152.9
Soy-PU	189.1	167.1	158.2	69.1	82.3	89.7

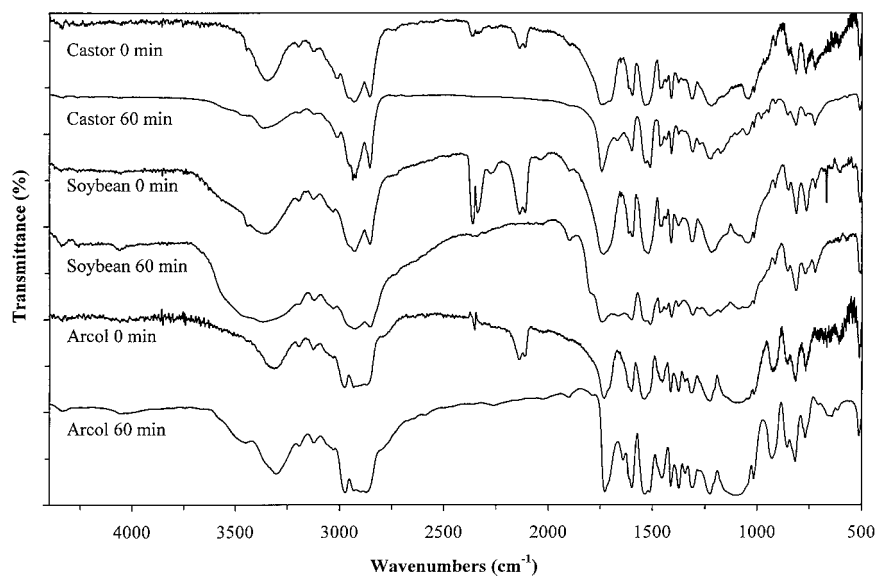


Figure 21 FTIR spectra of original and degraded polyurethane samples for 60 min in nitrogen at 250°C .

degradation product being carbon dioxide. This was considered to be the origin of higher stability of castor oil-based polyurethanes over those based on soybean oil. PPO-based PU shows lower initial weight loss in nitrogen than oil-based polyurethanes, but the situation is reversed in air. If a higher weight loss (50%) is taken as the criterion of thermal stability, then oil-based polyurethanes appear to be more thermally stable materials.

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