

Thermal Stability of Polyurethane Elastomers Before and After UV Irradiation

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ABSTRACT: In this work, we investigated the thermal degradation behavior of segmented polyurethane (PUR) elastomers before and after UV irradiation. The thermal degradation of PUR elastomers was studied over the temperature range of 25–600°C in an atmosphere of nitrogen using thermal gravimetric analysis (TGA). Four series of PUR elastomers derived from poly(oxytetramethylene)glycol (PTMO) of 1000 and 2000 molecular weight and poly(caprolactone glycol) (PCL) of 1250 molecular weight, 4,4'-diphenylmethane diisocyanate (MDI), and 4,4'-dicyclohexylmethane diisocyanate (H_{12} MDI) and 1,4-butanediol as a chain extender were synthesized by the prepolymer method. The derivative thermogravimetric (DTG) peaks observed in the experiments indicated that PUR elastomers degraded through two steps. We attributed the first step to degradation of the hard segment. The second degradation step could be ascribed to degradation of the soft segment. We found that the PUR elastomers based on poly(ester polyol) and aromatic diisocyanate exhibit better thermal stability than that of PUR elastomers based on the poly(ether polyol) soft segment in both steps of degradation. The thermal degradation is more prevalent in PUR elastomers based on cycloaliphatic diisocyanate. The higher values of the temperature of initial decomposition (T^i) indicate a higher thermal stability of UV-exposed elastomers on the beginning of degradation. This may be due to the formation of a crosslinking structure in the presence of UV irradiation. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 864–873, 2001

Key words: segmented polyurethane elastomers; thermal degradation; thermal gravimetric analysis; thermal stability

INTRODUCTION

The thermal degradation of polymeric materials has been the subject of many studies with the purpose to investigate the process that is responsible for the deterioration of the physical properties of materials. Most of these studies were concentrated on the investigation of the degradation process and stabilities. In general, polyurethanes (PURs) are not very thermally stable polymers.

From the literature,^{1–5} it is obvious that the thermal degradation of segmented PURs is a two-step process. The first step is ascribed to the thermal degradation of the hard segment, while the second step corresponds to the thermal degradation of the soft segment. The temperature of the initial decomposition of the urethane bond depends on the type of isocyanate and alcohol used.

Saunders and Frisch⁶ summarized the four types of reactions that may take place in the thermal degradation of urethanes. These are shown in Table I.

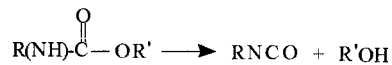
Because of the complex structure of PUR segmented elastomers, the degradation results in a complicated mixture of products that is often dif-

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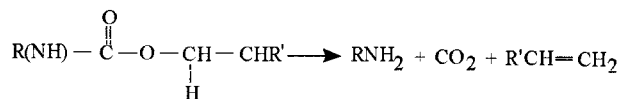
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Table I Degradation Mechanism of Urethane upon Heating

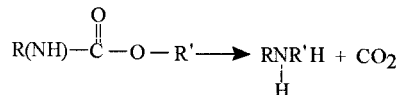
(1) Dissociation to isocyanate and alcohol



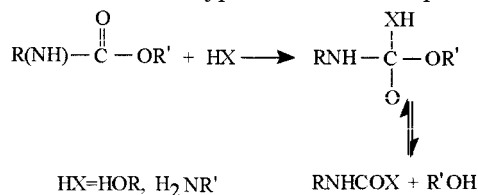
(2) Formation of primary amine and olefin



(3) Formation of secondary amine



(4) Transesterification type bimolecular displacement



difficult to relate precisely to the basic degradation mechanisms. The mechanism of the thermal degradation of PURs depends upon the type of the substituents on the N and O atoms in the urethane groups. It is well known that the principal mechanism of thermal degradation of PURs represents the reaction in which they are formed and thus yield diisocyanate and dialcohol or their secondary degradation products.⁷⁻¹⁴ A number of authors claimed that the thermal degradation is primarily a depolycondensation process (the first mechanism in Table I).¹⁵⁻²⁰

EXPERIMENTAL

Materials Used

Four series of PUR elastomers were synthesized by the prepolymer method. Before being used in the preparation of PUR elastomers, poly(oxytetramethylene)glycol (PTMO) with 1000 and 2000 molecular weights from the BASF Co. (Parsippany, NJ) and poly(caprolactone glycol) (PCL) of 1250 molecular weight from Union Carbide (Danbury, CT) were stirred continuously in a flask and degassed under a vacuum of 3 mmHg overnight at 80°C.

The isocyanates used were aromatic 4,4'-diphenylmethane diisocyanate (MDI) and cycloaliphatic 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI), both from Mobay Chemical (Pittsburgh, PA). 1,4-Butanediol (DuPont, Wilmington, DE) was stored over 4-Å molecular sieves prior to use. The materials used and their chemical structures are listed in Table II.

Synthesis of PUR Elastomers

The synthesis of PUR elastomers was carried out by a two-step method. The procedure for the synthesis of PUR elastomers by this method is as follows:

- Step I: Prepolymers were prepared by reacting the corresponding isocyanate and glycol at NCO/OH equivalent ratios of 2/1 and 4/1. The reaction was carried out under a stream of nitrogen at 80°C by the addition of glycol to the stirred diisocyanate in the absence of a catalyst.
- Step II: At 90°C, after the addition of 1,4-butanediol as the chain extender in the prepolymer, the reaction mixture was mechanically stirred for 1 min. The mixture was poured into an aluminum mold (covered with Teflon film for easy removal) and then heated to 100°C in a Carver hydraulic platens press for about 30 min. The elastomers were post-cured for 24 h at 105°C in an oven.

Procedures and Measurements

Irradiation of the PUR elastomers was carried out using a HANOVIA 679A quartz-mercury vapor lamp (400 W) at room temperature.

Thermal Gravimetric Analysis (TGA)

All the samples were investigated by using a DuPont 951 thermogravimetric analyzer in an atmosphere of nitrogen. The sample weight was 7–10 mg. The heating rate was 20°C/min and the temperature range was 25–600°C.

RESULTS AND DISCUSSION

Thermal Stability of PUR Elastomers Before UV Irradiation

The results of the TG and derivative thermogravimetric (DTG) analyses of all the investigated

Table II Chemical Structures and Composition of Materials Used in This Study

Sample Designation	Type of Polyol (Supplier)	Type of Diisocyanate (Supplier)	Soft-segment Molecular Weight	Hard-segment Content (wt %)	Prepolymer NCO/OH
	PTMO	MDI			
PUR-ET1-II	$\left[\text{-(CH}_2\text{)}_4\text{-O-} \right]_n$		1000	35	2/1
PUR-ET1-IV	(DuPont)	(Miles)		52	4/1
	PTMO	MDI			
PUR-ET2-II	$\left[\text{-(CH}_2\text{)}_4\text{-O-} \right]_n$		2000	35	2/1
PUR-ET2-IV	(DuPont)	(Miles)		53	4/1
	PCL	MDI			
PUR-ES-II	$\left[\text{-(CH}_2\text{)}_5\text{-C(=O)-O-} \right]_n$		1250	34	2/1
PUR-ES-IV	(Union Carbide)	(Miles)		51	4/1
	PCL	H ₁₂ MDI			
PUR-ES-W2	$\left[\text{-(CH}_2\text{)}_5\text{-C(=O)-O-} \right]_n$		1250	35	2/1
PUR-ES-W4	(Union Carbide)	(Miles)		53	4/1

PUR elastomers before UV irradiation are listed in Table III and shown in Figures 1–3. On the basis of the obtained qualitative results of the degradation process, it was evident that the thermal degradation occurs in two steps in PUR elastomers based on aromatic diisocyanate (MDI), whereas a one-step degradation was observed for the PUR elastomer based on cycloaliphatic

diisocyanate (H₁₂MDI) with a higher hard-segment content (PUR-ES-W4 elastomer). In the first and also second steps of degradation, we can see two characteristic temperatures: the temperature at which degradation started—the temperature of initial decomposition ($T_{1,2}^i$), and the temperature corresponding to the maximum rate of degradation ($T_{1,2}^{\max}$), that is, the

Table III Results of TGA for PUR Elastomers Before UV Irradiation

Sample Designation	T_1^i (°C)	T_1^{\max} (°C)	Δm_1 (%)	T_2^i (°C)	T_2^{\max} (°C)	Δm_2 (%)	Residue at 600°C (%)
PUR-ET1-II	282.0	352.3	31.2	385.0	433.0	62.4	6.4
PUR-ET1-IV	284.3	383.1	51.9	409.0	433.6	40.8	7.3
PUR-ET2-II	290.0	341.2	34.5	406.5	440.5	62.6	2.9
PUR-ET2-IV	298.6	343.5	49.5	388.0	435.9	39.8	10.7
PUR-ES-II	285.4	355.6	30.0	360.0	395.9	61.9	8.1
PUR-ES-IV	297.6	358.1	54.8	385.0	401.9	40.4	4.8
PUR-ES-W2	275.2	362.5	31.7	390.0	395.0	67.8	0.6
PUR-ES-W4	294.5	402.5	97.9	—	—	—	2.1

$T_{1,2}^i$, temperature of initial decomposition for the first and second steps of degradation from the TG curve; $T_{1,2}^{\max}$, temperature of maximum rate of decomposition for the first and second steps of degradation from the DTG curve. $\Delta m_{1,2}$, mass loss on the end of the first and second steps of degradation.

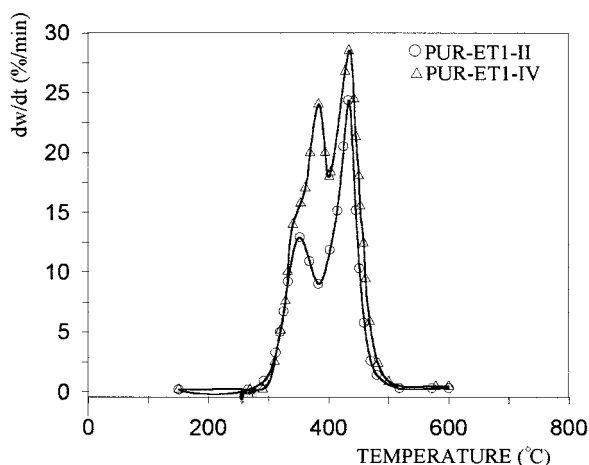
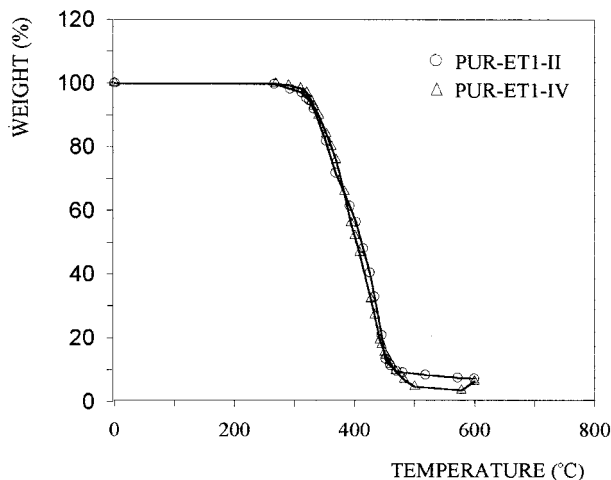


Figure 1 TG and DTG curves of unexposed PUR elastomers based on poly(ether polyol) of 1000 molecular weight, obtained at a heating rate of 20°C/min.

peak temperature in the DTG curve. These characteristic temperatures of degradation are presented in Table III.

The results in Table III show that the temperature of initial decomposition of the first step occurred in a range of temperature of 282.0–298.6°C; for the second step of degradation, the T^v 's are in the range of 360.0–409.0°C. The maximum rate of degradation in the first step (T_1^{\max}) is in the range of 341.2–402.5°C, and for the second step of degradation (T_2^{\max}), in the range of 395.0–440.5°C. From Table III, we can also see that the weight loss for all the investigated PUR elastomers in the first step of degradation (Δm_1) corresponds to the content of the hard segment (Table II). This also supports the suggestion that the hard segment degraded in the first degrada-

tion step, and the soft segment, in the second degradation step (Δm_2), meaning that degradation starts in the hard segment.

Effect of Type and Molecular Weight of Soft Segment on the Thermal Degradation of PUR Elastomers

The TG and DTG curves for PUR elastomers based on aromatic isocyanate (MDI) and poly(ether polyol) (PTMO) with different contents of the hard segment (NCO/OH ratios 2/1 and 4/1) and with different molecular weights of polyol (PTMO 1000 and PTMO 2000) before UV irradiation are shown in Figures 1 and 2. In each sample, a two-step of degradation results.

The TG and DTG curves for PUR elastomers based on 1000 molecular weight PTMO (PUR-

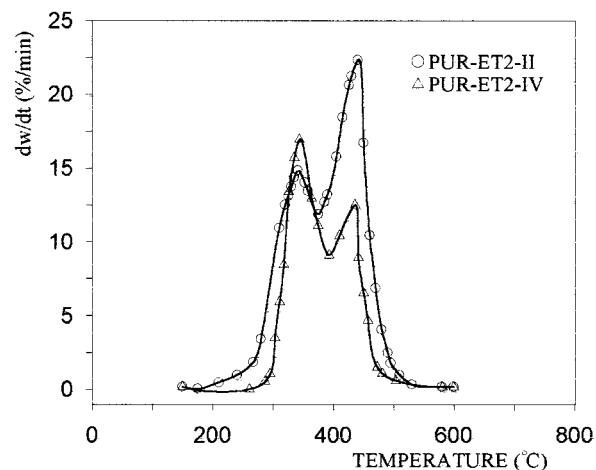
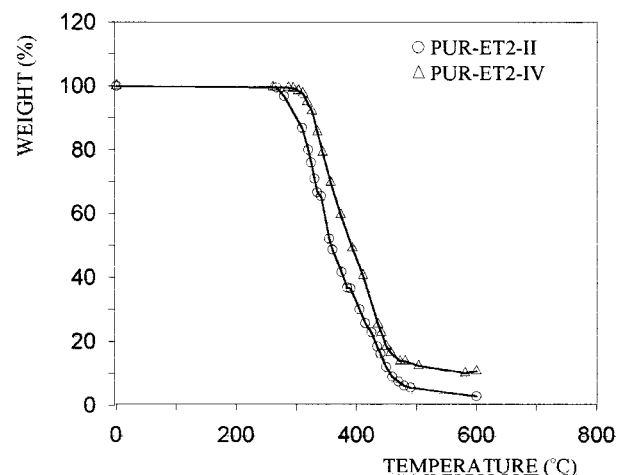


Figure 2 TG and DTG curves of unexposed PUR elastomers based on poly(ether polyol) of 2000 molecular weight, obtained at a heating rate of 20°C/min.

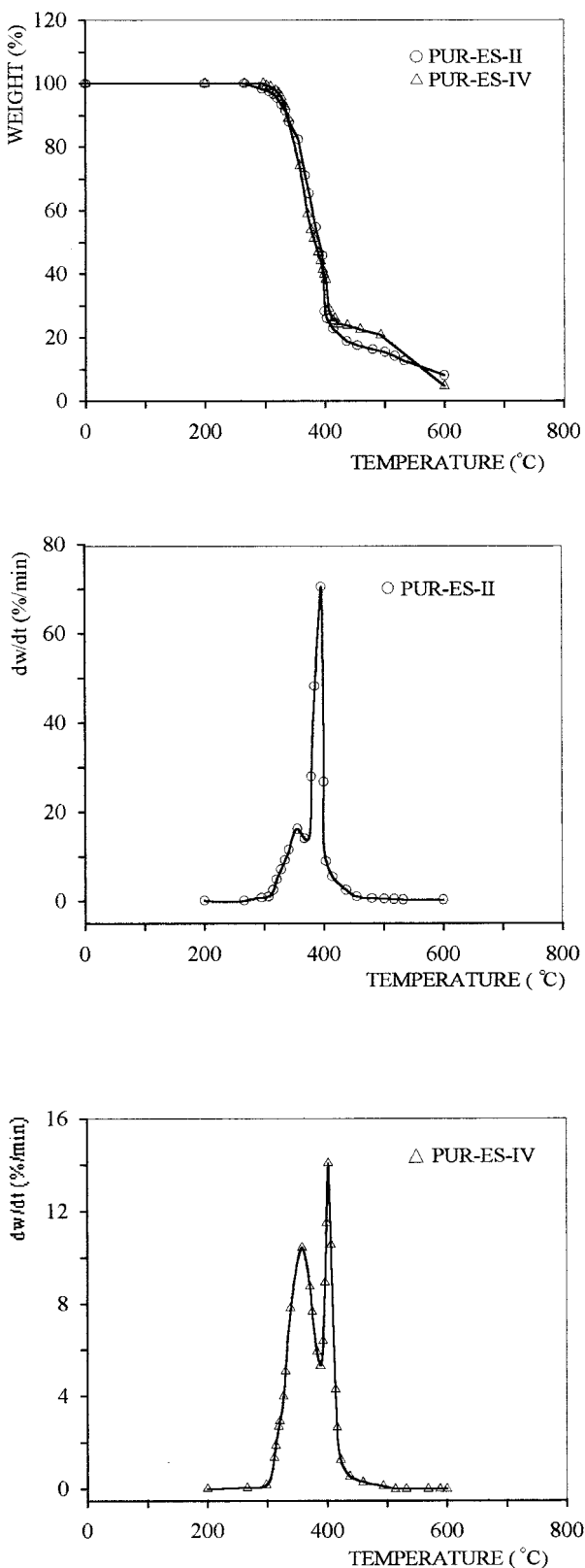


Figure 3 TG and DTG curves of unexposed PUR elastomers based on poly(ester polyol) and aromatic diisocyanate, obtained at a heating rate of 20°C/min.

ET1-II and PUR-ET1-IV elastomers) are shown in Figure 1. The temperature of the initial decomposition (T^i) of the first and second degradation steps is found to increase with increase of the hard-segment content.

T^{\max} , the temperature corresponding to the maximum rate of degradation, exhibits the same trend as that of T^i for the first and second steps of degradation, that is, $T_{1,2}^{\max}$ increases as the hard-segment content increases (Table III). The increase in the temperature of the initial decomposition in the PUR-ET1-IV elastomer indicates an increase in the thermal stability with increasing hard-segment content in this elastomer. The weight loss (Δm) increases in the first step of degradation, whereas Δm decreases in the second step of degradation with increase of the hard-segment content. As the hard-segment content increases, the amount of residue at 600°C increases.

The TG and DTG curves obtained for the PUR elastomers based on poly(ether polyol) with the higher molecular weight, PTMO 2000 (PUR-ET2-II and PUR-ET2-IV elastomers), before UV irradiation are presented in Figure 3 and reported in Table III. The temperature of the initial decomposition of the first step for elastomers based on PTMO 2000 are somewhat higher than are those based on PTMO 1000. This increase of temperature of the initial decomposition may be due to the better stability of the PUR elastomers with a higher molecular weight soft segment in the beginning of degradation. The results for degradation of the PUR elastomer based on PTMO 2000 with a higher hard-segment content (PUR-ET2-IV elastomer) show the same changes for T^i and T^{\max} as those of the PUR-ET1-IV elastomer, an elastomer with a lower molecular weight soft segment, in the first step of degradation, that is, the values of T^i and T^{\max} increase with increase of the hard-segment content (Table III).

The T^i and T^{\max} for the second step of degradation decrease with increase of the hard-segment content in the PUR elastomers with higher molecular weight, PTMO 2000. The weight loss also increases as the hard segment increases in the first degradation step, whereas it decreases in the second step of degradation. The weight of the residue remaining at 600°C shows that the residue is higher at higher hard-segment content. This behavior suggests that during thermal degradation higher hard-segment content may result in crosslinking structures, such as the carbodiimide structure.^{7-10,21-23}

The results in Table III show that with increase in the molecular weight of polyol (PUR-ET2-II and PUR-ET2-IV elastomers) the value of T^i of the first degradation step increases, while the temperature of the maximum rate of degradation decreases. In the second degradation step, T^i increases in the PUR elastomer with less hard-segment content (PUR-ET2-II elastomer). The elastomer with the higher hard-segment content (PUR-ET2-IV elastomer) exhibits a lower T^i . It was also observed that both elastomers based on PTMO 2000 show the highest values of T^{\max} for the second degradation step compared with the experimental values of PUR elastomers based on lower molecular weight soft segment.

Summarizing the results of the investigation of the thermal degradation for PUR elastomers based on different molecular weight soft segments, we found that the PUR elastomers based on PTMO 2000 are more thermally stable than are the PUR elastomers based on PTMO 1000. The results of thermal degradation for PUR elastomers based on a polyester type of polyol (PCL) and an aromatic diisocyanate (MDI) (PUR-ES-II and PUR-ES-IV elastomers) before UV irradiation are included in Table III and shown in Figure 3. Table II shows the composition of the investigated PUR-ES elastomers.

With increasing hard-segment content in the PUR-ES-IV elastomer, T^i as well as T^{\max} increased in both degradation steps, compared to the PUR-ES-II elastomer. The amount of weight loss increases in the first degradation step and decreases in the second degradation step as the hard-segment content increases. To compare the values of the temperature of the initial decomposition of PUR elastomers based on poly(ester polyol) (PUR-ES-II and PUR-ES-IV elastomers) with the T^i values obtained for the PUR elastomers based on poly(ether polyol) (PUR-ET1-II and PUR-ET1-IV elastomers), that is, elastomers with a similar molecular weight of the soft segment, it is clear that the thermal degradation of polyester elastomers begins at higher temperatures.

On the other hand, T^{\max} in the both degradation steps decreased in PUR elastomers based on poly(ester polyol). The values of weight loss for PCL PUR elastomers are less than those of PTMO 1000 PUR elastomers in the both steps of degradation.

All this evidence suggests that the thermal stability is higher in PUR elastomers based on poly(ester polyol) than those based on poly(ether

glycol). This may be because the strong cohesion energies of the H bonds between the C=O of the ester group and the N—H bond from the urethane group induced the higher thermal stability of polyester PURs.^{21–23}

Effect of Various Type of Diisocyanates on Thermal Degradation of PUR Elastomers

In this part of our work, we investigated the thermal degradation of PUR elastomers based on poly(ester polyol) (PCL) and aromatic diisocyanate (MDI) (PUR-ES-II and PUR-ES-IV elastomers) and poly(ester polyol) and cycloaliphatic diisocyanate (H₁₂MDI) (PUR-ES-W2 and PUR-ES-W4 elastomers) before UV irradiation. The results are presented in Table III and Figures 3 and 4.

Orlov et al.^{24–27} reported that the aromatic isocyanate-based PUR degraded primarily into amine and CO₂ while the aliphatic isocyanate-based PUR dissociated primarily into isocyanate and glycol. The results obtained for PUR elastomers based on poly(ester polyol) and aromatic diisocyanate were presented before in the last subsection.

Figure 4 shows the TG and DTG curves for PUR elastomers based on poly(ester polyol) and cycloaliphatic diisocyanate (PUR-ES-W2 and PUR-ES-W4 elastomers). As shown in Figure 4, the thermal degradation of the PUR-ES-W4 elastomer occurs in a single-step.

The results in Table III indicated that with higher content of the hard segment (PUR-ES-W4 elastomer) the value of T^i and T^{\max} increased. The weight loss and amount of residue after 600°C were higher in the PUR-ES-W4 elastomer.

Comparison of the thermal analysis results obtained for PUR elastomers based on poly(ester polyol) and aromatic diisocyanate (PUR-ES-II and PUR-ES-IV elastomers) with the results obtained for the PUR elastomers based on poly(ester polyol) and cycloaliphatic diisocyanate (PUR-ES-W2 and PUR-ES-W4 elastomers) indicates that the T^i of the first step in the PUR elastomer based on aromatic diisocyanate with less hard-segment content (PUR-ES-II elastomer) has a higher value than that of the PUR-ES-W2 elastomer based on cycloaliphatic diisocyanate. Also, the T^i value in the PUR-ES-IV elastomer is similar to that in the PUR-ES-W4 elastomer. Further, the weight-loss values are higher in the PUR elastomers based on cycloaliphatic diisocyanate than in the PUR elastomers based on aromatic diisocyanate. The resi-

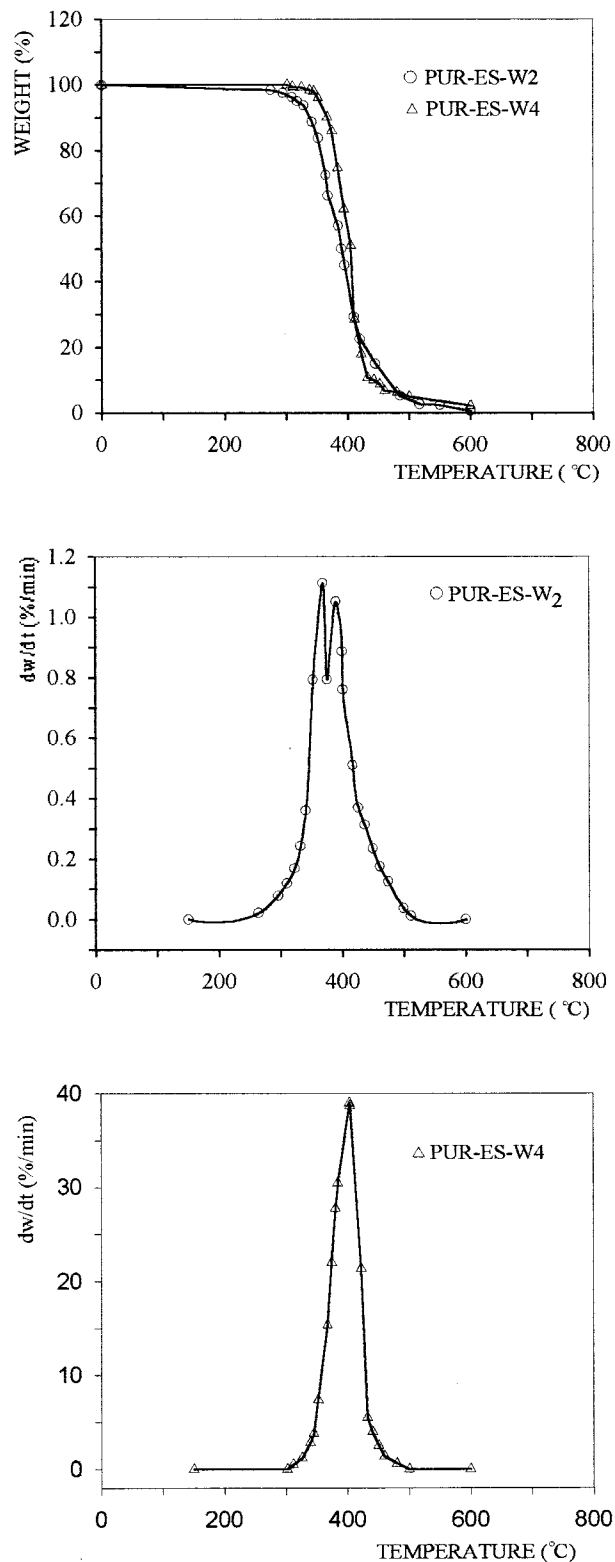


Figure 4 TG and DTG curves of unexposed PUR elastomers based on poly(ester polyol) and cycloaliphatic diisocyanate, obtained at a heating rate of 20°C/min.

due at 600°C was significantly lower than in the PUR elastomers based on cycloaliphatic diisocyanate. These results suggest that PUR elastomers based on aromatic diisocyanate are more thermally stable than are PUR elastomers based on cycloaliphatic diisocyanate.

Thermal Stability of UV-exposed PUR Elastomers

The thermal stability of PUR elastomers after UV irradiation was investigated. TG and DTG curves obtained for PUR elastomers based on poly(ether polyol) (PTMO, MW = 1000, PUR-ET1-II and PUR-ET1-IV elastomers; MW = 2000, PUR-ET2-II and PUR-ET2-IV elastomers), poly(ester polyol) and aromatic diisocyanate (PUR-ES-II and PUR-ES-IV elastomers), and poly(ester polyol) with cycloaliphatic diisocyanate (PUR-ES-W2 and PUR-ES-W4 elastomers) are shown in Figures 5–8. The thermal analysis data are presented in Table IV. As shown in Figures 5–8, the thermal degradation of the investigated elastomers, except the PUR-ES-W4 elastomer, occurs in a two-step degradation.

T_1^i , corresponding to the initial degradation temperature of the hard segment in the first degradation step, occurs in the range of temperature of 274.6–311.8°C, and for the second degradation step (T_2^i), that is, the initiation of degradation for the soft segment, in the range of 378.0–432.0°C (Table IV). The maximum degradation rate for the first degradation step (T_1^{\max}) occurs in the range of temperature of 366.4–400.9°C, and for the the second degradation step (T_2^{\max}), in a range of temperature 390.0–456.4°C (Table IV). Comparing the results of thermal analysis obtained for PUR elastomers after UV irradiation with the same results of unexposed PUR elastomers suggests the following conclusions: The effect of various types of polyols and diisocyanates, different molecular weights of the soft segments, and different content of hard segments in PURs on the onset temperature and T^{\max} , the temperature of degradation, has the same trend in unexposed and UV-exposed elastomers, meaning that PUR elastomers based on poly(ester polyol) have higher thermal stability than that of PUR elastomers based on poly(ether polyol) soft segments, as well as higher thermal stability of the PUR elastomers based on aromatic diisocyanate than those based on cycloaliphatic diisocyanate.

Comparison of the data in Tables III and IV indicates clearly that all UV-exposed PUR elastomers, except PUR elastomers based on poly(es-

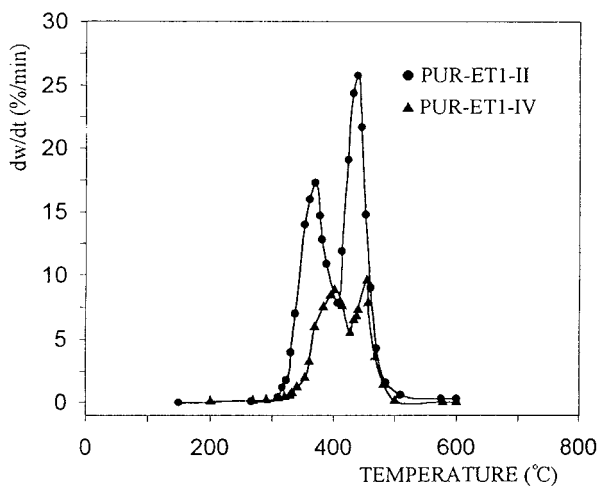
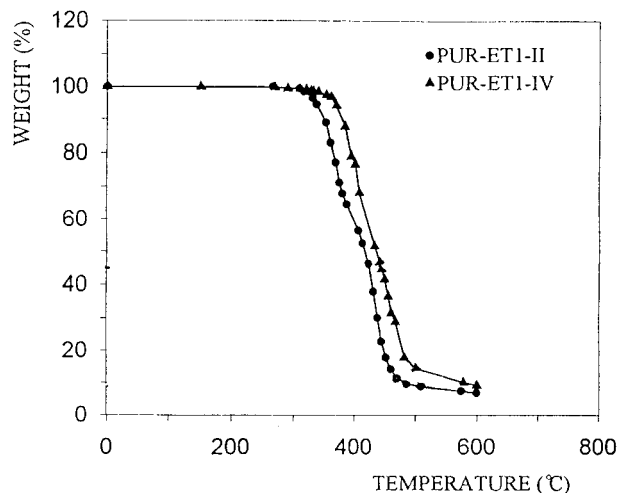


Figure 5 TG and DTG curves of UV-exposed PUR elastomers based on poly(ether polyol) of 1000 molecular weight, obtained at a heating rate of 20°C/min.

ter polyol) and cycloaliphatic diisocyanate, show a higher T^i and T^{max} temperature in both steps of degradation. Also, the weight loss increased in UV-exposed PUR elastomers in both steps.

The higher values of T^i and T^{max} indicate a higher stability of UV-exposed PUR elastomers at the beginning of the thermal degradation. However, UV-exposed PUR elastomers more easily degraded than did unexposed elastomers. This agrees with the higher weight loss of UV-exposed elastomers in the first degradation step.

We concluded that higher values of T^i of UV-exposed PUR elastomers may be due to the formation of a crosslinking structure in the presence of UV irradiation. Evidence for a crosslinking structure is the higher amount of residue after UV irradiation.

CONCLUSIONS

The thermal degradation of the all examined PUR elastomers occurs in two steps of degradation, while the PUR elastomer based on cycloaliphatic diisocyanate and poly(ester polyol) with higher hard-segment content (PUR-ES-W4 elastomer) shows a one-step thermal degradation. The first step is connected with the thermal degradation of the hard segment, while the second step corresponds to the degradation of the soft segment. The good correlation between the weight loss and hard- and soft-segment contents was established in all PUR elastomers.

The obtained results show that the PUR elastomers based on poly(ester polyol) and aromatic diisocyanate exhibit better thermal stability com-

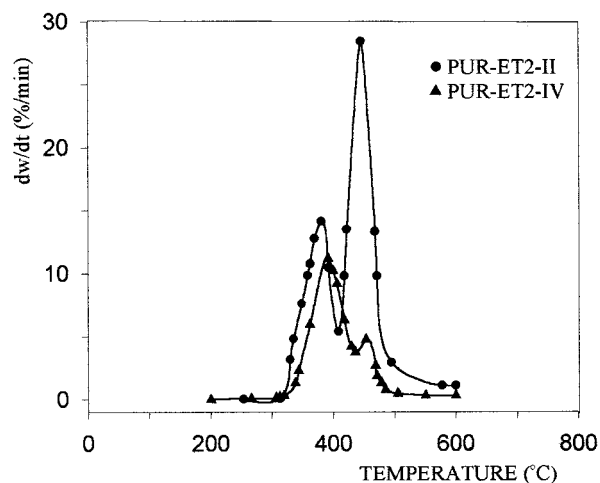
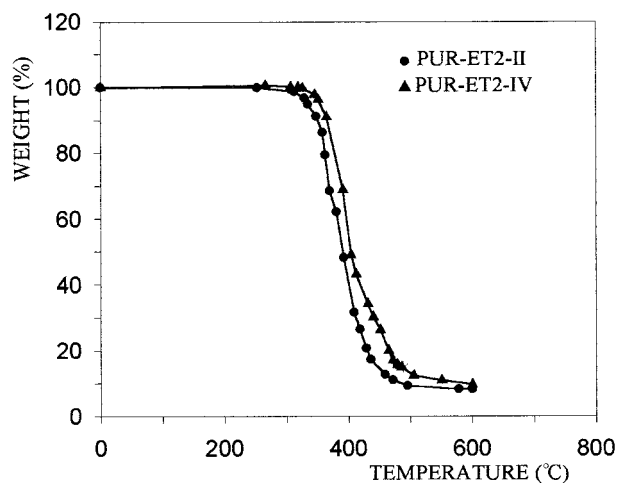


Figure 6 TG and DTG curves of UV-exposed PUR elastomers based on poly(ether polyol) of 2000 molecular weight, obtained at a heating rate of 20°C/min.

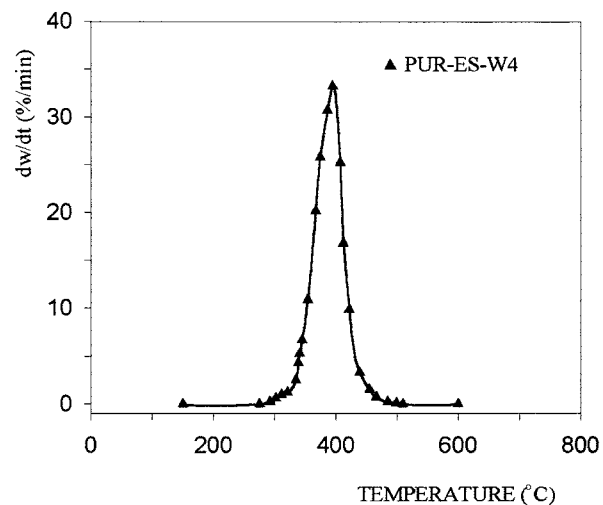
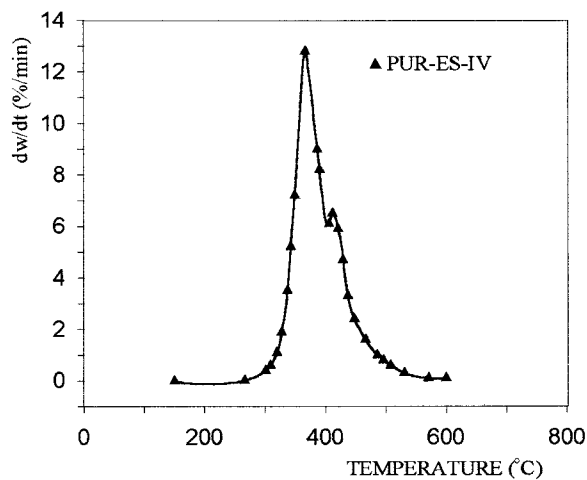
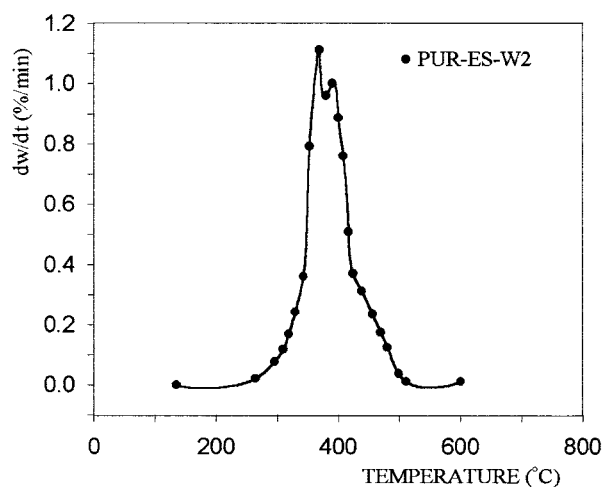
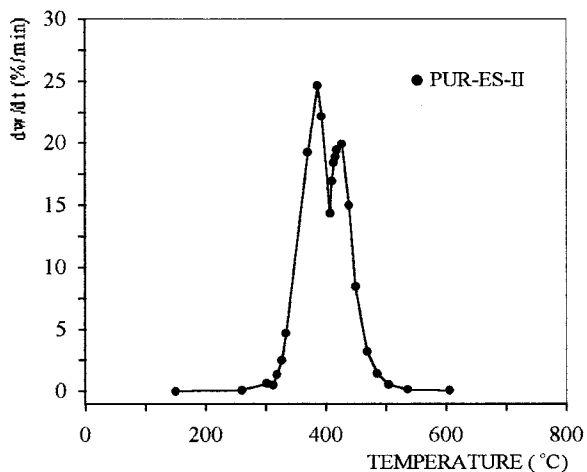
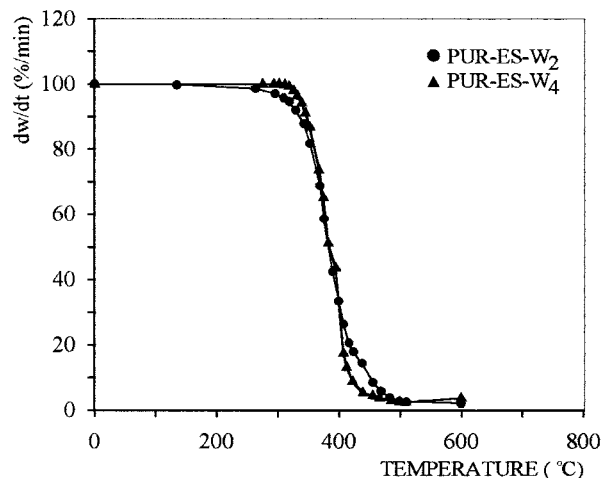
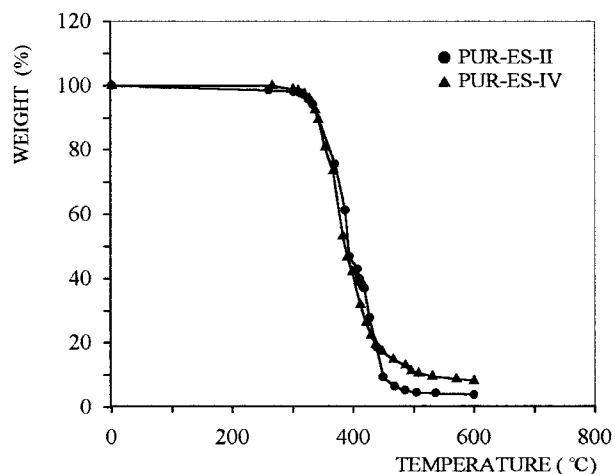


Figure 7 TG and DTG curves of UV-exposed PUR elastomers based on poly(ester polyol) and aromatic diisocyanate, obtained at a heating rate of 20°C/min.

Figure 8 TG and DTG curves of UV-exposed PUR elastomers based on poly(ester polyol) and cycloaliphatic diisocyanate, obtained at a heating rate of 20°C/min.

Table IV Results of Thermal Gravimetric Analysis for PUR Elastomers After UV Irradiation

Sample Designation	T_1^i (°C)	T_1^{\max} (°C)	Δm_1 (%)	T_2^i (°C)	T_2^{\max} (°C)	Δm_2 (%)	Residue at 600°C (%)
PUR-ET1-II	295.4	369.5	48.0	405.0	438.5	45.2	6.8
PUR-ET1-IV	305.1	400.9	53.6	430.0	456.4	37.3	9.1
PUR-ET2-II	302.5	380.7	56.6	418.4	446.0	35.3	8.2
PUR-ET2-IV	310.0	391.9	64.5	432.0	453.5	25.9	9.6
PUR-ES-II	305.5	386.3	55.4	405.0	426.7	40.7	3.9
PUR-ES-IV	311.8	366.4	58.8	395.0	406.1	32.9	8.3
PUR-ES-W2	274.6	368.8	69.5	378.0	390.0	28.5	2.0
PUR-ES-W4	290.4	394.6	96.2	—	—	—	3.8

See footnote to Table III for definitions.

pared with that of the PUR elastomers based on a poly(ether polyol) soft segment of 1000 molecular weight in both steps of degradation. Polyurethane elastomers based on a higher molecular weight of poly(ether polyol) show better thermal stability than that of PUR elastomers based on PTMO 1000 in the first degradation step. Finally, thermal stability is the least in PUR elastomers based on cycloaliphatic diisocyanate with lower hard-segment content in the first degradation step.

In comparing the results of T^i before UV irradiation with the same results after UV irradiation, it appears that the T^i 's of all UV-exposed PUR elastomers, except the PUR elastomers based on H₁₂MDI, were shifted to higher temperature in both degradation steps. The same behavior was observed for weight loss in the first degradation step, that is, values of Δm_1 after UV irradiation. The higher values of T^i indicate a higher thermal stability of UV-exposed elastomers on the beginning of degradation, which may be due to the formation of the crosslinking structure on which to designate higher residue.

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