



Thermal degradation of short polyester fiber–polyurethane elastomer composite

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The thermal degradation of short polyester fiber reinforced polyurethane composites with and without different bonding agents has been studied by thermogravimetric analysis. It was found that degradation of the polyurethane takes place in two steps and that of the composites takes place in three steps. With the incorporation of 30 phr of fiber in the matrix, the onset of degradation was shifted from 230 to 238°C. The presence of bonding agents in the virgin elastomer and the composite gave an improved thermal stability. Results of kinetic studies showed that the degradation of polyurethane and the reinforced composites with and without bonding agents follows first-order reaction kinetics. © 1998 Published by Elsevier Science Limited. All rights reserved

1 INTRODUCTION

The reinforcement of elastomers with short fibers results in good strength and stiffness for both the soft and tough elastomer matrices.^{1–3} Short fiber reinforced elastomer composites have attracted much attention due to their better mechanical properties and economic feasibility.^{4–8} Elaborate studies on the various aspects of these reinforced composites have been done earlier.^{9–17} In our earlier communications, we have reported the cure characteristics, mechanical properties and rheological properties of a short polyester fiber reinforced polyurethane elastomer composite.^{18–20} Thermal degradation of polyurethanes has also been investigated extensively. The thermal degradation of urethanes based on 4,4'-diphenylmethanediisocyanate and 1,4-butane diol was studied by Yang *et al.*²¹ who showed that the urethane undergoes degradation at elevated temperature giving rise to isocyanates and alcohol. Schollenberger *et al.*²² have also reported that the urethane linkages may

be broken due to the high shear and stress at the elevated processing temperature. The influence of short fibers on the thermal resistance of the matrix, T_g and kinetic parameters of the degradation reaction of a thermoplastic polyurethane was studied by Ronald *et al.*²³ Nando and co-workers²⁴ studied the degradation characteristics of short Kevlar fiber reinforced thermoplastic polyurethane. The present work explores the thermal degradation of short polyester fiber reinforced polyurethane elastomer composites.

2 EXPERIMENTAL

The ether based polyurethane (Adiprene CM) used in this study was obtained from Uniroyal, USA and the polyester short fiber (PET) of length approximately 14 mm and 21 μ m diameter was supplied by Madura Coats, India. All the other ingredients were of commercial grade.

The formulation of the mixes is given in Table 1. Mixes A1–A3 and mixes C1–C3 contain 5 phr of bonding agents (MD resins) based on polypropyleneglycol (PPG) and glycerol (GL) with 4,4'-diphenylmethanediisocyanate (MDI). These mixes were prepared on a laboratory two roll mill as per

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Table 1. Formulation of mixes

Ingredients	Mix no.									
	A	B	C	D	A1	A2	A3	C1	C2	C3
PET Fiber	—	10	20	30	—	—	—	20	20	20
PPG	—	—	—	—	4.44	—	2.22	4.44	—	2.22
GL	—	—	—	—	—	0.90	0.07	—	0.90	0.07
MDI	—	—	—	—	0.56	4.10	0.56	0.56	4.10	0.56

Adiprene 100, caytur-4 0.35 phr, dibenzothiazylsulphide (MBTS) 4 phr, 2-mercaptobenzothiazole (MBT) 1 phr, sulphur 0.75 phr and zinc stearate 0.5 phr are common to all mixes.

ASTM D 3182 (1984). Sheets of 2 mm thickness were molded on a hydraulic press at 150°C. Thermogravimetric analysis was carried out under nitrogen atmosphere at a heating rate of 10°C/min.

3 RESULTS AND DISCUSSION

The derivative TGA curves of mixes A–D are shown in Fig. 1. The peak degradation rates and the corresponding temperatures (T_{1max} , T_{2max} and T_{mmax}) are given in Table 2. It is clear from the figure that the degradation of the virgin polyurethane occurs in two steps as indicated by the two maxima at 257 and 401°C. The onset of degradation is at 230°C. The peak rates of degradation at the two maxima are 3.01 and 10.92%/min, respectively. The second degradation, occurring at around 400°C, is due to the decomposition of the primary degradation products. The plots also show that the fiber-containing samples (mixes B–D) undergo a three-step degradation. The major

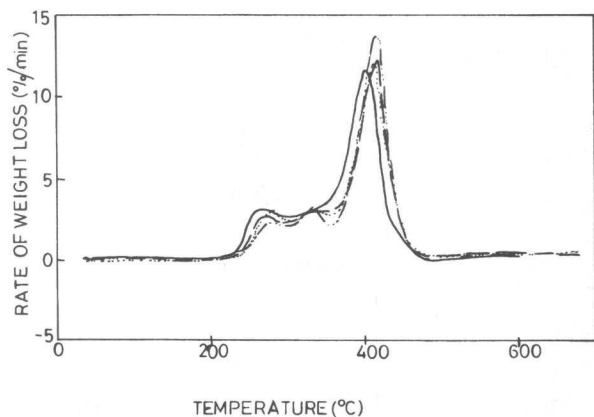


Fig. 1. TGA traces of mixes A–D. — mix A, --- mix B, ... mix C, -.- mix D.

degradation occurs at around 400°C, similar to that of the gum vulcanisate. The peak degradation rate at around 330°C is more prominent at higher fiber loadings. This indicates that the incorporation of polyester fiber affects the degradation stages of the matrix. The onset of degradation is shifted from 230 to 238°C with the addition of 30 phr of fiber, indicating improved thermal stability of the composite. Similar results are reported earlier.²⁴ The degradation temperatures T_{1max} and T_{mmax} are increased from 257 to 274°C and 401 to 417°C, respectively, for the fiber loading of 30 phr. The variation of temperatures at which two degradation rate maxima occur (T_{1max} and T_{mmax}) with fiber loading is shown in Fig. 2. The initial degradation temperature (T_{1max}) increases linearly up to 20 phr of fiber loading and then levels to a constant value, and the major degradation temperature (T_{mmax}) increases with the increase of fiber content. The increase of the two temperature maxima indicates a lower rate of diffusion of the degraded products out of the matrix as indicated by the lower peak degradation rates exhibited at these temperatures (Table 2). Thus, it is evident that fiber incorporation restricts the diffusion of the degradation products from the matrix. The second peak degradation rate and the corresponding temperature (T_{2max}) are not changed considerably by the increase of fiber content.

The weights of residues above 600°C in various mixes (mixes A–D) are given in Table 2. The weights of residue increase with the increase of fiber content.

The order of degradation was calculated from the Freeman–Carroll method using the equation:

$$(\Delta \log dW/dt) = n \cdot \Delta \log W_r - (\Delta E/2.3R)\Delta(1/T) \quad (1)$$

where dW/dt is the rate of reaction, n is the order of reaction, R is the gas constant, T is the absolute temperature and W_r is proportional to the amount of reactant remaining.

The above equation can be rearranged to

$$\begin{aligned} (\Delta \log dW/dt)/\Delta \log W_r \\ = n - (\Delta E/2.3R)\Delta(1/T)/\Delta(\log W_r) \end{aligned} \quad (2)$$

The order and activation energies can be obtained from the intercept and gradient of the plot of the left hand side of eqn (1) versus $\Delta(1/T)/\Delta \log W_r$

Table 2. Degradation characteristics of mixes A-D

Mix no.	T_i (°C)	T_{1max} (°C)	R_{1max} (%/min)	T_{2max} (°C)	R_{2max} (%/min)	$T_{m\ max}$ (°C)	$R_{m\ max}$ (%/min)	Weights of residue after 600°C (%)
A	230.1	257.5	3.01	—	—	401.4	10.92	3.88
B	238.1	266.7	2.65	328.6	2.98	414.3	11.45	5.56
C	239.3	275.0	2.98	333.3	3.00	411.9	11.98	5.87
D	238.3	274.0	2.37	330.1	2.75	417.8	13.48	4.88

T_i = Initiation temperature of degradation.

R_{1max} , R_{2max} and $R_{m\ max}$ are the peak degradation rates, and T_{1max} , T_{2max} and $T_{m\ max}$ are the corresponding temperatures.

and such plots are given in Fig. 3. The intercept shows that the degradation follows a first order reaction mechanism which is in accordance with the earlier reports.^{21,24}

The degradation of virgin elastomer and composites with different bonding agents were also

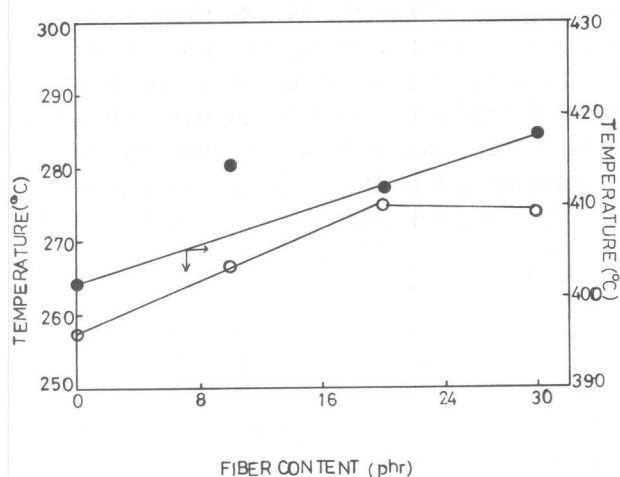


Fig. 2. Variation of degradation temperature with fiber loading. ○ first degradation temperature, ● major degradation temperature.

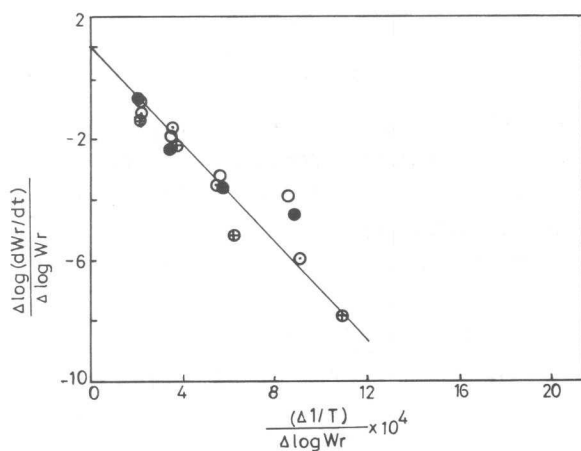


Fig. 3. Freeman-Carroll plot of mixes A-D. ○ mix A, ● mix B, ⊙ mix C, ⊕ mix D.

studied. Figure 4 shows the degradation curves of the mixes A, A1, A2 and A3, and shows that the mixes containing bonding agents also show a two-step degradation similar to that of mix A. The temperature of onset of degradation is higher for the mixes containing bonding agents and is highest for the mixes containing the glycerol-based bonding agent (mix A2). This indicates that the bonding agents improve thermal stability.

The peak degradation rates and the corresponding temperatures (T_{1max} and $T_{m\ max}$) are given in Table 3. T_{1max} is higher for the mix containing bonding agent based on glycerol with MDI. The degradation rates are more or less the same for the gum compound with and without bonding agents. The major degradation occurs at around 400°C and is higher for the mixes containing bonding agents. The major degradation temperature of mixes A1-A3 remains more or less the same, and the degradation rates are marginally higher than the gum without bonding agents. The weights of residues remaining after 600°C of the mixes A-A3 are given in Table 3. The plot of the Freeman-Carroll method also shows that all the mixes show first order degradation kinetics (Fig. 5).

Figure 6 shows the derivative TGA traces of mixes C, C1, C2 and C3. All these composites

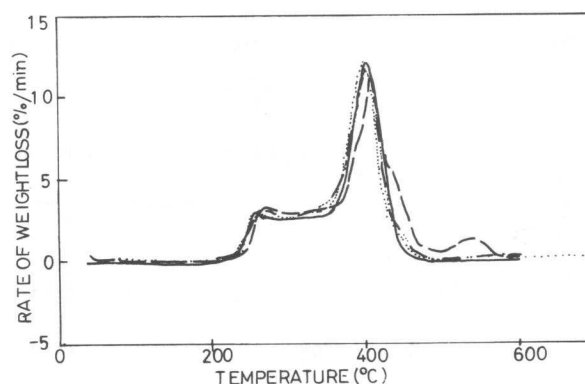


Fig. 4. TGA traces of mixes A, A1, A2 and A3. --- mix A, — mix A1, ··· mix A2, ···· mix A3.

Table 3. Degradation characteristics of mixes A, A1, A2 and A3

Mix no.	T_i (°C)	T_{1max} (°C)	R_{1max} (%/min)	T_{2max} (°C)	R_{2max} (%/min)	$T_{m\ max}$ (°C)	$R_{m\ max}$ (%/min)	Weights of residue after 600°C (%)
A	230.1	257.4	3.01	—	—	401.4	10.9	3.88
A1	233.1	257.1	3.10	—	—	407.1	11.9	4.56
A2	239.3	263.1	3.31	—	—	407.1	11.0	—
A3	235.6	257.5	3.02	—	—	405.5	12.1	3.55

T_i = Initiation temperature of degradation.

R_{1max} , R_{2max} and $R_{m\ max}$ are the first, second and major peak degradation rates, and T_{1max} , T_{2max} and $T_{m\ max}$ are the corresponding temperatures.

show a three-step thermal degradation with maxima at around 270, 330 and 410°C. The peak degradation rates and the corresponding temperatures for the composites are given in Table 4. For the composites with bonding agents, initiation of degradation occurs at higher temperatures than that of composites without bonding agents. The enhanced thermal stability may be due to the formation of the more constrained matrix in the presence of bonding agents. The initial degradation temperature is lower for mixes C1 and C3, while it is higher for mix C2 when compared to mix C. The T_{2max} and the corresponding peak degradation

rates are not considerably influenced by the presence of bonding agents. The major degradation temperature is higher for composites with bonding agents and the rate of degradation is marginally higher than that of the composites without bonding agents. The same behavior is observed in the case of gum vulcanisates with bonding agents. The weight of residue remaining after 600°C of these composites (Table 4) shows that the residue is higher for mixes C2 and C3. The Freeman–Carroll plots of the mixes (Fig. 7) show that the presence of bonding agents does not alter the degradation kinetics of the composite.

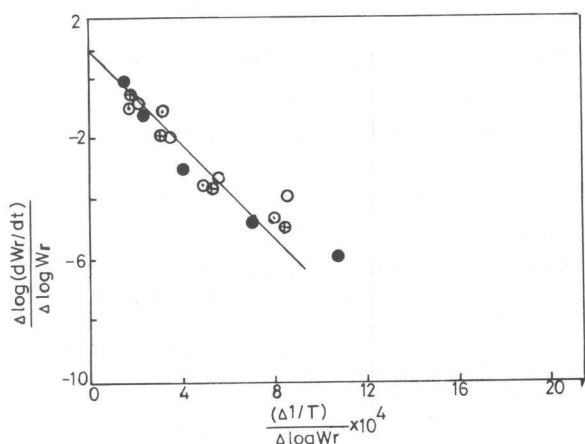


Fig. 5. Freeman–Carroll plot of mixes A, A1, A2 and A3.
○ mix A, ● mix A2, ⊕ mix A3.

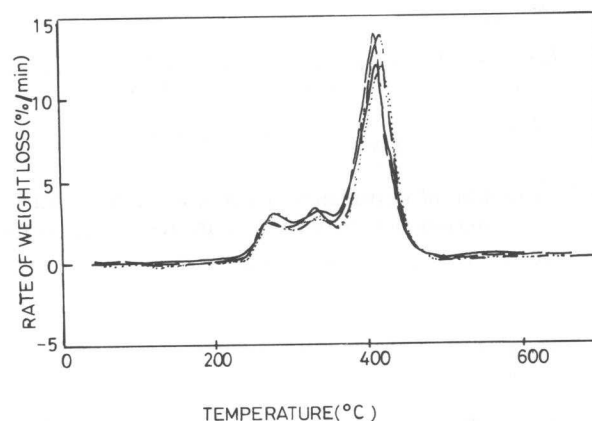


Fig. 6. TGA traces of mixes C, C1, C2, and C3. — mix C, --- mix C1, ... mix C2, -·-· mix C3.

Table 4. Degradation characteristics of mixes C, C1, C2 and C3

Mix no.	T_i (°C)	T_{1max} (°C)	R_{1max} (%/min)	T_{2max} (°C)	R_{2max} (%/min)	$T_{m\ max}$ (°C)	$R_{m\ max}$ (%/min)	Weights of residue after 600°C (%)
C	239.3	275.0	2.98	333.3	3.00	411.9	11.98	5.87
C1	239.3	266.7	2.36	330.9	3.29	414.3	13.27	4.14
C2	245.4	279.4	3.01	335.9	2.65	419.2	11.86	9.58
C3	242.5	269.9	2.49	335.6	2.87	420.5	13.80	6.17

T_i = Initiation temperature of degradation.

R_{1max} , R_{2max} and $R_{m\ max}$ are the first, second and major peak degradation rates, and T_{1max} , T_{2max} and $T_{m\ max}$ are the corresponding temperatures.

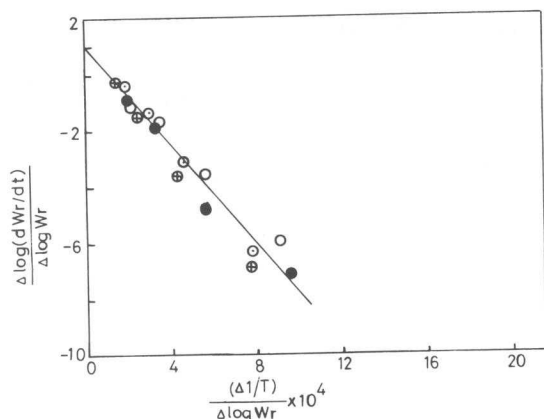


Fig. 7. Freeman-Carroll plot of mixes C, C1, C2 and C3.
 ○ mix C, ● mix C1, ○ mix C2, ⊕ mix C3.

4 CONCLUSIONS

The following conclusions can be drawn from the present study:

1. Polyurethane elastomer shows a two-step thermal degradation, while the short polyester fiber reinforced composite shows a three-step thermal degradation.
2. Polyester fiber increases the thermal stability of polyurethane, the optimum being at 20 phr fiber loading.
3. The presence of bonding agents also improves the thermal stability of the composite and the maximum improvement is shown by the bonding agent based on glycerol with 4,4'-diphenylmethanediisocyanate.
4. The reaction kinetics of the elastomer and the composites with and without bonding agents follow a first-order reaction.

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