



Thermal degradation of short kevlar fibre–thermoplastic polyurethane composite

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The thermal degradation of short kevlar fibre–thermoplastic polyurethane (TPU) composites has been studied by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). TGA showed that the thermal degradation of TPU takes place in two steps with peak maxima ($T_{1\max}$ and $T_{2\max}$) at 383°C and 448°C, respectively. In the presence of 10–40 phr of short kevlar fibres, $T_{1\max}$ and $T_{2\max}$ were shifted to lower temperatures. The temperature of onset of degradation was increased from 245 to 255°C at 40 parts per hundred rubber (phr) fibre loading. Kinetic studies showed that the degradation of TPU and kevlar–TPU composite follows first-order reaction kinetics. The DSC study showed that there is an improvement in thermal stability of TPU in the presence of 20 phr of short kevlar fibres.

INTRODUCTION

Short fibre–rubber composites combine the strength and stiffness of the fibres and the elastic behaviour of rubber. The mechanical properties have been the focus of earlier studies on these composites.^{1–5} O'Connor⁶ compared the mechanical properties of composites with five kinds of fibre and concluded that variables like fibre type, fibre content, fibre aspect ratio, fibre orientation, fibre dispersion and fibre–matrix adhesion had a profound influence on the ultimate mechanical properties. The effect of milling parameters on the fibre orientation and hence on the mechanical properties has been reported.^{7,8} Early work involved natural fibres like jute,⁹ silk¹⁰ and cellulose. Later, synthetic short fibres also found their place in rubber composites.¹¹ The matrices used varied from natural to synthetic and also thermoplastic elastomers.¹² The authors have already reported on the mechanical properties of

short kevlar fibre-filled millable polyurethane and thermoplastic polyurethane.^{13,14} Rheological and stress relaxation behaviour of short kevlar fibre–TPU have also been reported.^{15,16}

The degradation characteristics of TPU are important because of the instability of the urethane linkages at elevated temperature.^{17,18} It has been reported that the strength of short kevlar–TPU composite is reduced when subjected to a second round of mixing at 180°C for 6 min.¹⁴ Schollenberger *et al.*¹⁹ have reported that in the presence of high shear and stress and processing temperature, the urethane linkages may be broken and some scrambling of the segmented structure of the polymer may occur during polymer melt processing and thus affect properties. Yang *et al.*²⁰ studied the thermal degradation of urethanes based on 4,4'-diphenyl methane diisocyanate and 1,4-butane diol and concluded that the urethanes dissociated thermally to isocyanates and alcohols at elevated temperature. In this paper we report the results of our studies on the thermal degradation of

Table 1. Formulation of the mixes

Ingredient	Mix no.				
	TK ₀	TK ₁₀	TK ₂₀	TK ₃₀	TK ₄₀
TPU	100	100	100	100	100
Kevlar	—	10	20	30	40

short kevlar fibre-TPU composites with varying amounts of short fibre.

EXPERIMENTAL

The ether-based thermoplastic polyurethane (Estane 58311) used in this study was obtained from Urethane India Ltd (Madras, India) and Kevlar short fibres (T-970) of length approximately 6 mm and length-to-diameter ratio 500 was procured from Du Pont De Nemours and Co. (Wilmington, DE, USA).

Formulation of the mixes is given in Table 1. TPU and kevlar short fibres were dried in a hot air oven at 105°C for 2 h to remove moisture. Mixing was carried out in a cam-type Brabender plasticorder PLE 330 at 180°C for 6 min. The mixing sequence is shown in Table 2. At the end of 6 min, the mix was taken out and sheeted out

Table 2. Mixing sequence

Ingredient	Time (min)	RPM	Ram position
1/2 TPU	0	30	up
Fibre	1.5	30	up
1/2 TPU	3.0	60	down
—	9.0	—	dump

on a two-roll mill in tight nip. Sheets of 2 mm were moulded on a Labopress, provided with a cooling facility, at 180°C for 3 min and the sheets were cooled under pressure by passing water through the press platens. Thermogravimetric analysis and differential scanning calorimetric studies were carried out on a Du Pont 9000 thermal analyser, both at a heating rate of 10°C/min under nitrogen.

RESULTS AND DISCUSSION

Figure 1 shows the derivative TGA traces of mixes TK₀, TK₂₀, TK₄₀ and neat kevlar fibre. The peak maxima and the corresponding temperatures are given in Table 3. TPU in the neat form and as a composite with short kevlar fibres undergoes two-step thermal degradation as indicated by the two maxima at 383°C and 448°C

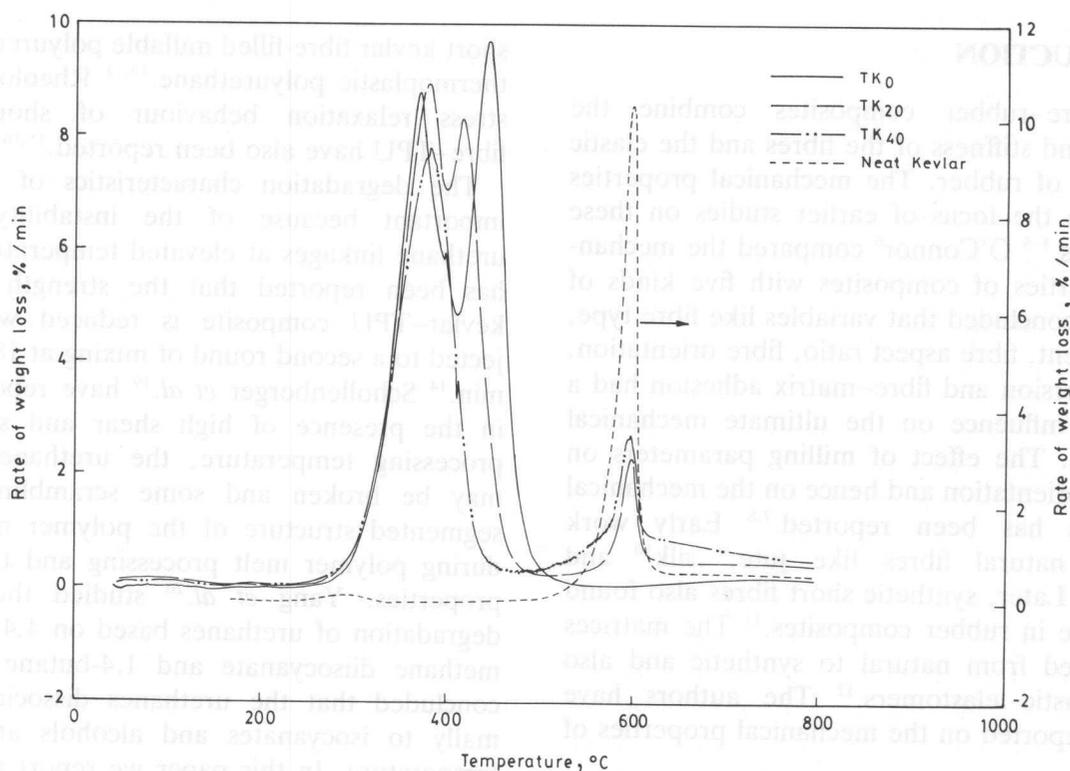


Fig. 1. TGA traces of mixes T₀, TK₂₀ TK₄₀.

Table 3. Degradation characteristics of TPU from TGA

Mix no.	Temperature of initiation (T_i) (°C)	First peak temperature ($T_{1_{max}}$) (°C)	First degradation rate ($R1_{max}$) ^a (%/min)	Second peak temperature ($T2_{max}$) (°C)	Second degradation rate ($R2_{max}$) ^a (%/min)	Third peak temperature ($T3_{max}$) (°C)	Third degradation rate ^b ($R3_{max}$) (%/min).
Kevlar	—	—	—	—	—	601.2	10.3
TK ₀	245	383.3	7.8	447.6	9.6	—	—
TK ₁₀	242	385.7	8.4	435.7	9.5	602.4	14.1
TK ₂₀	245	381.0	10.7	419.1	10.0	601.2	13.8
TK ₃₀	254	378.6	10.1	411.9	9.1	602.4	12.6
TK ₄₀	255	371.4	12.5	—	—	598.0	10.2

^a Corrected for % of TPU.

^b Corrected for % of kevlar.

(Fig. 1). The degradation starts at a temperature (T_i) of 245°C. The peak rates of degradation ($R1_{max}$ and $R2_{max}$) are 7.76 and 9.6%/min for the two steps, respectively. Degradation of TPU at two temperatures may arise from the multi-segment structure of TPU. Thermoplastic polyurethane comprises polyol soft segments and diisocyanate hard segments. The hard segments are joined to the soft segments through polyurethane links. Grassie and Mendoza, studying the thermal degradation of polyether urethane prepared from methylene bis(4-phenyl isocyanate) and high molecular weight poly(ethylene glycol), have reported that weight loss occurs in two stages.²¹ The first peak was around 300°C in both TGA and DSC analysis. Using very low molecular weight polyol, Grassie and Mendoza²² reported a single-step degradation around 300°C. Yang *et al.*²⁰ have reported that the primary degradation process in a urethane based on diphenyl methane 4,4'-diisocyanate/1,4-butanediol (MDI/BDO) is thermal dissociation into free isocyanates and alcohols. The second peak may be assigned to the subsequent degradation of the primary degradation products.

The degradation of neat kevlar fibre takes place in a single step and the derivative shows a maximum rate of 10.2%/min at 601°C.

It is evident from Table 3 that the degradation of TPU is affected by the presence of short kevlar fibres. The point of onset of degradation is shifted from 245 to 255°C at 40 phr fibre loading indicating improved thermal stability of the composite. However, $T1_{max}$ and $T2_{max}$ are reduced from 383.3 to 371°C and from 497.6 to 411.9°C for fibre loadings of 40 and 30 phr, respectively. At 40 phr the second peak is not distinguishable from the first. The change in peak degradation temperatures with increasing fibre content is shown in Fig. 2. The change of the first

degradation temperature to lower temperature more or less fits a straight line of gradient $-0.309^\circ\text{C}/\text{phr}$. The second degradation is shifted according to a straight line of gradient $-1.19^\circ\text{C}/\text{phr}$. This clearly establishes a definite dependence of the degradation characteristics of TPU on the amount of short kevlar fibres. The steeper gradient for the second degradation in Fig. 2 indicates that for every phr of short kevlar fibre incorporated, the reduction of the second degradation temperature is four times that of the first. The reduction of the degradation temperature of TPU in the presence of short fibres indicates improved diffusion of the primary degradation products. It is well known that the diffusion of the degradation products out of a degrading matrix plays an important role in TGA. This is confirmed by studying the degradation of a very thin film of TPU, keeping all other conditions the same. Comparison of TGA traces of the original sample of about 2 mm thickness and film of about 0.4 mm thickness (Fig. 3) shows that both $T1_{max}$ and $T2_{max}$ of the

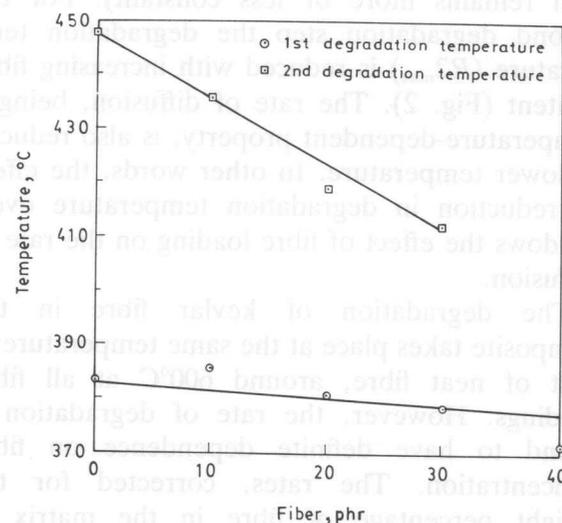


Fig. 2. Peak degradation temperature versus fibre loading.

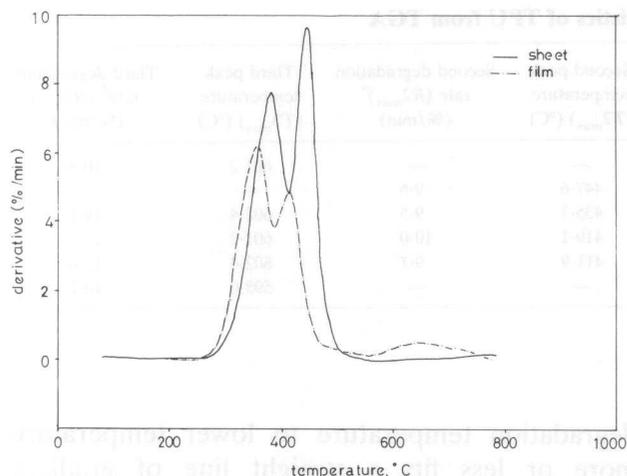


Fig. 3. TGA traces of TPU samples of different thicknesses. Sheet = 2 mm, thin film = 0.4 mm.

film occur at lower temperatures than those of the thicker sample. In a thin film, the diffusion of the degradation products takes place more easily. The comparatively lower rate of the second degradation step ($R2_{max}$) in the case of thin film is also in agreement with this view.

The rates of degradation of TPU at different fibre loadings are also shown in Table 3. The rate of weight loss in a thermal degradation reaction depends upon the ease of diffusion of the degradation products out of the matrix. The rate of the first degradation step is found to increase with increasing fibre loading, whereas the rate of the second step of TPU shows a marginal decrease. With increasing fibre loading, the diffusion rate of the degradation product increases and hence the rate of the first step ($R1_{max}$) increases (the temperature of degradation remains more or less constant). For the second degradation step the degradation temperature ($R2_{max}$) is reduced with increasing fibre content (Fig. 2). The rate of diffusion, being a temperature-dependent property, is also reduced at lower temperature. In other words, the effect of reduction in degradation temperature overshadows the effect of fibre loading on the rate of diffusion.

The degradation of kevlar fibre in the composite takes place at the same temperature as that of neat fibre, around 600°C at all fibre loadings. However, the rate of degradation is found to have definite dependence on fibre concentration. The rates, corrected for the weight percentage of fibre in the matrix at different fibre loadings, are given in Table 3. It is observed that the corrected rates of degradation

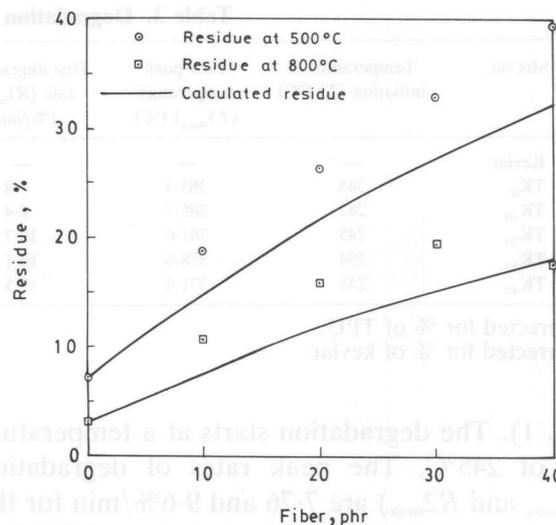


Fig. 4. Residue at 500 and 800°C versus fibre loading.

of kevlar fibres in the composite are slightly higher than that of the neat fibres, and the difference becomes negligible as the fibre content is increased.

The weights of the residues after degradation of urethane (500°C) and kevlar (800°C) in various mixes are shown in Fig. 4. The continuous lines represent the values calculated from the weights of residues of TPU and kevlar fibres at the corresponding temperatures when tested separately. The residue is 7.2% and 3.2% at 500 and 800°C, respectively, for TPU in the absence of short fibre, and for neat kevlar fibre the corresponding values are 94.8% and 55.8%. On incorporation of short fibre up to 40 phr, the residue is found to increase almost linearly at both temperatures. The observed values are consistently higher than the calculated values. The difference between the observed and calculated values at 500°C increases with increasing fibre content.

The order of the degradation reaction has been studied using the Freeman-Carroll method,²³ which uses the expression

$$\Delta \log \frac{dw}{dt} = n \cdot \Delta \log W_r - \left(\frac{\Delta E}{2.3R} \right) \Delta \left(\frac{1}{T} \right) \quad (1)$$

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

Dividing eqn (1) by $\Delta \log W_r$, we obtain

$$\left(\Delta \log \frac{dW}{dt} \right) / \Delta \log W_r = n - \left(\frac{\Delta E}{2.3R} \right) \Delta \left(\frac{1}{T} \right) / \Delta \log W_r \quad (2)$$

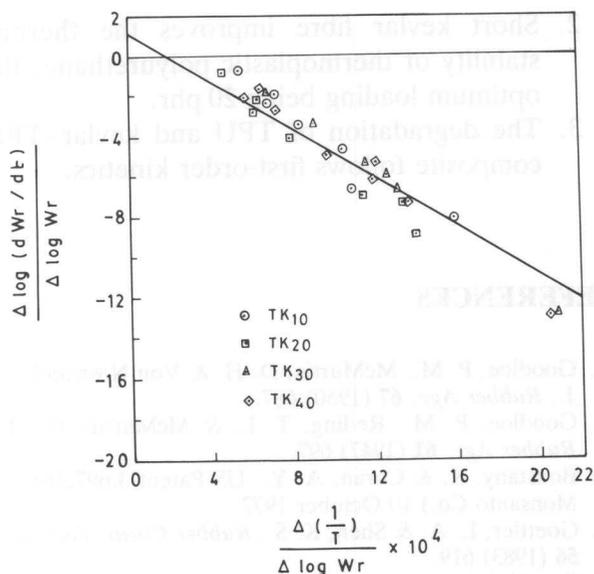


Fig. 5. Freeman-Carroll plot for the degradation of kevlar-TPU composites.

Thus the intercept and the gradient of the plot of the left-hand side of eqn (2) versus $\Delta(1/T)/\Delta \log W_r$, gives the order of the reaction and the activation energy, respectively.

Such plots for the degradation of the composite are given in Fig. 5. A first-order reaction is indicated by the intercept on the ordinate. This is in agreement with the studies

reported earlier.²⁰ That the points corresponding to different mixes may be represented by a single straight line with an intercept of unity on the ordinate, indicates the independence of the order of the reaction on fibre loading.

The degradation of short kevlar-TPU composite has been further studied by means of a differential scanning calorimeter (DSC) under nitrogen at the same heating rate as for TGA. The DSC traces of mixes TK₀, TK₂₀ and TK₃₀ are given in Fig. 6. The temperature of onset of degradation (T_i) and the temperature at which the degradation reaches a maximum (T_{max}) are given in Table 4. The DSC traces also reveal that the degradation of thermoplastic polyurethane takes place in two steps. The first step is indicated by a major endothermic peak in the region of 300–350°C which is followed by a minor peak which represents the second degradation step. This again indicates that the second stage of degradation of TPU may be the subsequent degradation of the primary degradation products.

Table 4 shows that the onset of degradation is at 277°C for the unfilled TPU and the reaction reaches a peak at 319°C. A comparison with Table 3 shows that the first degradation reaches a maximum at 383°C in TGA. Similarly the endothermic peak in DSC for the second step of

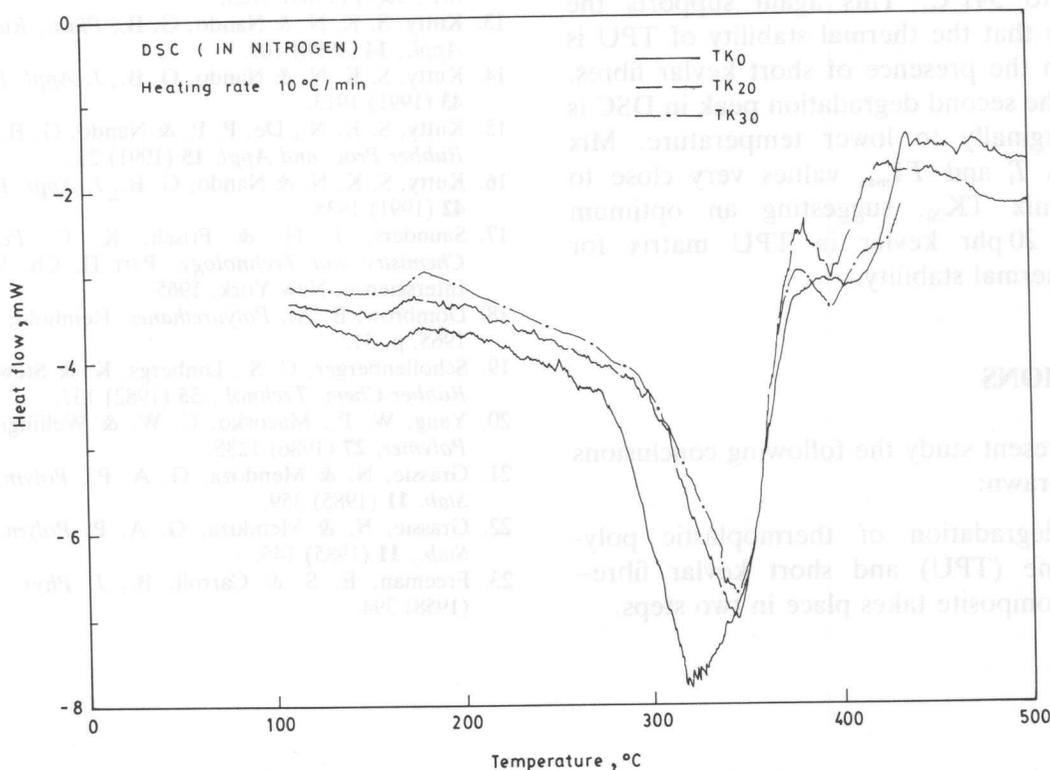


Fig. 6. DSC traces of mixes TK₀, TK₂₀ and TK₃₀.

Table 4. Degradation characteristics from DSC

Mix no.	Initiation temperature (T_i) (°C)	First peak temperature ($T_{1_{max}}$) (°C)	Second peak temperature ($T_{2_{max}}$) (°C)
TK ₀	277	319	402
TK ₂₀	296	341	395
TK ₃₀	291	346	397

degradation also occurs at a lower temperature than that in TGA. The consistently lower temperature of thermal degradation of TPU in DSC may be attributed to quicker detection of the degradation reaction. In DSC, the change in heat flow is monitored with respect to a reference sample and any change in sample temperature due to physical or chemical changes is detected instantaneously, whereas in TGA the weight loss of the sample is monitored. Since the diffusion of primary degradation products out of the sample is a time-dependent process, the weight loss due to the thermal degradation reaction occurs with a time lag and is hence detected at a higher temperature.

On incorporating 20 phr of kevlar fibre into TPU matrix (mix TK₂₀) both T_i and $T_{1_{max}}$ are shifted to higher temperature, indicating improved thermal stability of the composite. T_i is increased from 277 to 296°C and $T_{1_{max}}$ is shifted from 319 to 341°C. This again supports the earlier view that the thermal stability of TPU is increased in the presence of short kevlar fibres. However, the second degradation peak in DSC is shifted marginally to lower temperature. Mix TK₃₀ shows T_i and $T_{1_{max}}$ values very close to those of mix TK₂₀, suggesting an optimum loading of 20 phr kevlar in TPU matrix for improved thermal stability.

CONCLUSIONS

From the present study the following conclusions have been drawn:

1. The degradation of thermoplastic polyurethane (TPU) and short kevlar fibre-TPU composite takes place in two steps.

2. Short kevlar fibre improves the thermal stability of thermoplastic polyurethane, the optimum loading being 20 phr.
3. The degradation of TPU and kevlar-TPU composite follows first-order kinetics.

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