Thermochimica Acta, 23 (1978) 371–385

INTERACTIONS OBSERVED DURING THE PYROLYSIS OF BINARY MIXTURES OF TEXTILE POLYMERS

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(Received 20 May 1977)

ABSTRACT

The techniques of differential thermal analysis (DTA), thermogravimetry (TG), large scale pyrolysis (LSP) and hot-stage microscopy (HSM) have been used to determine the pyrolysis behaviour of three binary polymer systems: wool/Terylene, wool/Courtelle and Terylene/Courtelle. Pyrolysis was carried out in a flowing nitrogen atmosphere at a heating rate of approximately 10 °C min^{-1}.

Evidence from DTA and TG indicates that the thermal stability of the polyester fibre Terylene is reduced when pyrolysed in the presence of either wool or Courtelle. It is considered that this reduction in thermal stability is the result of chemical interactions between Terylene and degradation products arising from the breakdown of the second polymer present. Unexpectedly high residual yields (at 1213 K) have been observed from LSP experiments on the wool/Courtelle and Terylene/Courtelle systems.

HSM observations for these two systems indicate the formation of a coating of the fusing polymer around the non-fusing polymer during pyrolysis. TG studies indicate that this coating of fused polymer may be effective in retaining volatile degradation products from the non-fusing polymer within the solid residue. The eventual chemical bonding of these degradation products into the solid residue thus accounts for the unexpectedly high yields of solid residue observed by LSP.

INTRODUCTION

Tarim and Cates[1] have examined the pyrolysis behaviour of various binary mixtures of textile polymers using the techniques of DTA and TG. They reported that the thermal stability of a polyester fibre (Dacron) was reduced when this fibre was pyrolysed in the presence of either wool or bleached cotton. They explain this phenomenon in terms of physical interaction involving heat transfer, i.e., exothermic reactions in one fibre raise the temperature of the second fibre sufficiently for it to undergo reactions which it would normally undergo later after the whole DTA block had reached a particular temperature.

Tarim and Cates[1] also observed some unexpectedly high yields of solid residue at the final heat treatment temperature. They suggest this yield behaviour may also result from physical interaction involving the retention of volatile degradation products within a coating of fused polymer. In addition to physical interaction, the occurrence of chemical interaction during the pyrolysis of binary polymer mixtures has been reported by several workers[1-4]. The aim of this study is to use the techniques of DTA, TG, LSP and HSM to examine more systematically than has been attempted before, the pyrolysis behaviour of three binary polymer systems: wool/Terylene, wool/Courtelle and Terylene/Courtelle. Hence, a more detailed assessment can be made of the extent and cause of any interactions detected in relation to the chemical and physical changes taking place in the polymers during pyrolysis. This work forms part of an extended study to determine if any relationship exists between the pyrolysis behaviour of a binary mixture of textile polymers and the surface properties of the carbonaceous products of pyrolysis (as measured by the porosity accessible to the adsorbate carbon dioxide at 195 K). It is fairly well accepted that for single polymers the initial polymer structure and its subsequent behaviour, particularly in the temperature range 298–773 K, determines to a significant extent the surface properties of the final carbon product and also those of any "activated" carbon derived from this product[5].

EXPERIMENTAL

Details of the textile fibres used are listed in Table 1. All fibres were cut to a length of 7.5×10^{-4} m and soxhlet-extracted with petroleum ether (boiling point range 313–333 K) for a period of 4 h to remove grease and commercial finishes. The wool was further extracted with methanol over an additional 4-h period to remove soaps and animal sweat. The fibres were then warm-air-dried for 4 h and then left for 12 h in the atmosphere to regain their normal moisture content. Homogeneity of a fibre mixture was achieved by double passage through a B.S. 12-mesh sieve. A particular fibre mixture is therefore denoted by the two component fibres and their relative proportions expressed as a mass percent, e.g., W75/C25. Experimental details are listed in Table 2. It was decided to study in detail only those peaks in the DTA curves of the single fibre which had peak temperatures reproducible to ± 5°C. Each peak temperature is the mean of five experiments and is followed by the maximum observed variation for that peak temperature.

TABLE 1

Fibre type	*Fibre diameter*[a]	*Source*
Merino Top 64 wool	23.1×10^{-6} m	WIRA, Leeds
Courtelle filament yarn	20.5×10^{-6} m	Courtaulds, Spondon
Terylene staple	18.3×10^{-6} m	ICI Fibres, Harrogate

[a] Determined by IWTO method[8] at WIRA, Leeds.

TABLE 2

DETAILS OF EXPERIMENTAL TECHNIQUES EMPLOYED IN THIS STUDY

Technique	*Apparatus*	*Temperature range*	*Heating rate*	*Sample size/ presentation*	*Sample container*	*Atmosphere, flow-rate*
DTA	Stanton Redcroft 67 fitted with IB module	ambient – 773 K	10 deg min^{-1}	3×10^{-3} g – 4×10^{-3} g, loose packed. Reference material alumina (BDH)	Aluminium dishes fitted with lids	Nitrogen, 1×10^{-2} dm^3 min^{-1}
TG	Modified[a] Stanton Instruments Thermo-balance, type TRO2	ambient – 1213 K	9 deg min^{-1}	0.1 g, loose packed	Silica crucible	Nitrogen, 1.58 dm^3 min^{-1} (entry) 1.53 dm^3 min^{-1} (exit)
LSP	Amalgams type HT2 furnace fitted with mullite furnace tube (internal diameter 4.0×10^{-2} m, length 0.9 m)	ambient – 1213 K	10 deg min^{-1}	0.5 g – 0.8 g, compressed into pellets	Nickel crucible	Nitrogen, 1.05 dm^3 min^{-1}
HSM	Reichert hot-stage microscope type MEF fitted with Vacutherm microfurnace	ambient – 773 K	Manually controlled variable transformer	0.01 g, loose packed	Sample held between glass microscope slides	Nitrogen, 1.2 dm^3 min^{-1}

[a] Thermobalance modification described by McEnaney and Rowan[7].

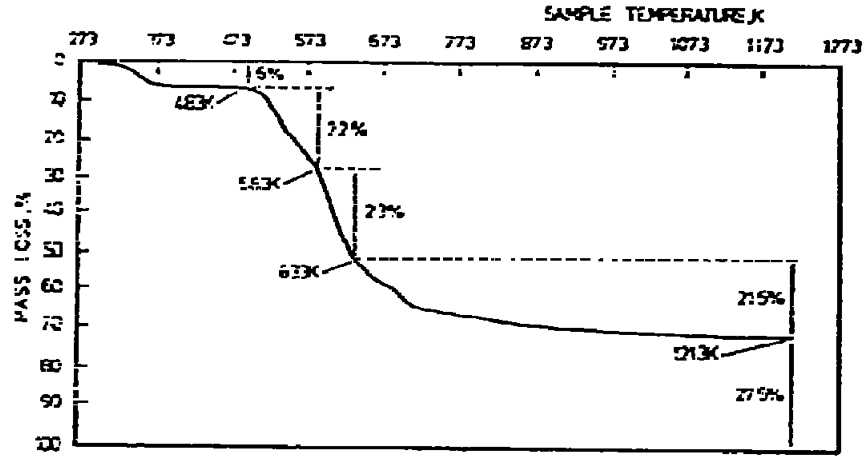

Fig. 1. TG curve for Merino Top 64 wool.

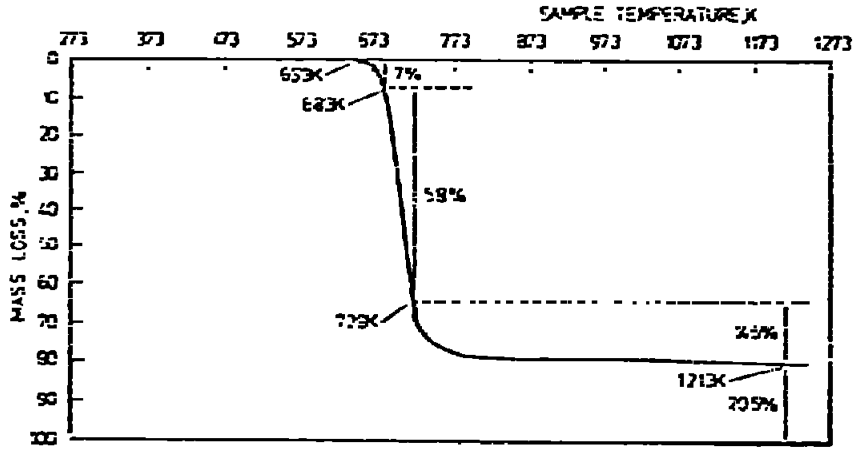

Fig. 2. TG curve for Terylene.

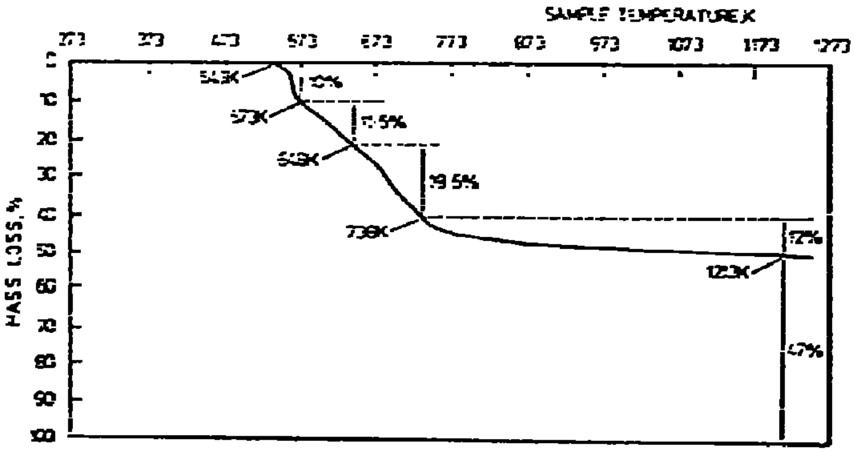

Fig. 3. TG curve for Courtelle.

TABLE 3

Position of:

(a) Terylene endotherm 710 K (702–712 K) *(b) Terylene exotherm 745 K (741–746 K)* *In the DTA curves of wool/Terylene mixtures.*			*(c) Terylene endotherm 710 K (702–712 K)* *(d) Terylene exotherm 745 K (741–746 K)* *In the DTA curves of Terylene/Courtelle mixtures.*			*(e) Terylene endotherm 710 K (702–712 K)* *(f) Terylene exotherm 745 K (741–746 K)* *In the DTA curves of Terylene/kieselguhr mixtures.*		
	Mixture (mass %)	*Peak temperature*		*Mixture (mass %)*	*Peak temperature*		*Mixture (mass %)*	*Peak temperature*
(a)	Wool (W)	—	(c)	Courtelle (C)	—	(e)	Kieselguhr (K)	—
	W75/T25	653 K (647–656 K)		C75/T25	669 K (666–697 K)		K75/T25	711 K (706–716 K)
	W50/T50	676 K (673–679 K)		C50/T50	695 K (682–706 K)		K50/T50	712 K (707–713 K)
	W25/T75	693 K (687–699 K)		C25/T75	701 K (697–706 K)		K25/T75	714 K (711–716 K)
	Terylene (T)	710 K (702–712 K)		Terylene (T)	710 K (702–712 K)		Terylene (T)	710 K (702–712 K)
(b)	Wool (W)	—	(d)	Courtelle (C)	—	(f)	Kieselguhr (K)	—
	W75/T25	Not resolved		C75/T25	706 K (701–711 K)		K75/T25	738 K (734–741 K)
	W50/T50	713 K (711–716 K)		C50/T50	724 K (720–725 K)		K50/T50	741 K (737–748 K)
	W25/T75	730 K (725–737 K)		C25/T75	734 K (730–741 K)		K25/T75	741 K (740–741 K)
	Terylene (T)	745 K (741–746 K)		Terylene (T)	745 K (741–746 K)		Terylene (T)	745 K (741–746 K)

The buoyancy effect (TG) was found to be a linear function of temperature and for an empty crucible amounted to 4 × 10^{-3} g at 1213 K. Since similar buoyancy effects were operative for successive TG experiments, it is considered that these effects cancel when mass loss data over similar temperature ranges are compared. On this basis, no buoyancy correction has been applied to the TG curves reported in this study (Figs. 1-3).

In the LSP experiments the maximum heat-treatment temperature (1213 K) was maintained for 1 h prior to natural cooling. Gravimetric yields reported are the arithmetic mean of at least 6 experiments.

RESULTS

It is clear from an examination of Table 3 (parts a, b, c, d) that the endotherm [710 K (702-712 K)] and exotherm [745 K (741-746 K)] occurring in the DTA curve of Terylene (Fig. 6) are observed at lower temperatures in the DTA curves of both wool/Terylene and Terylene/Courtelle mixtures (Figs. 4 and 5). The amount of peak movement is approximately a linear function of fibre mixture composition.

The TG curves for wool/Terylene and Courtelle/Terylene mixtures (Figs. 7 and 9) indicate that the rapid mass loss associated with the Terylene component of the mixture is occurring at lower temperatures. In addition, a reduction in the initial mass loss from the Courtelle component in wool/Courtelle and Terylene/Courtelle mixtures is apparent from an examination of Figs. 8 and 9.

Both the TG and LSP data indicate unexpectedly high yields of pyrolysis residue at the final heat-treatment temperature (1213 K). A summary of the visual changes taking place during pyrolysis of the individual fibres is recorded in Table 4.

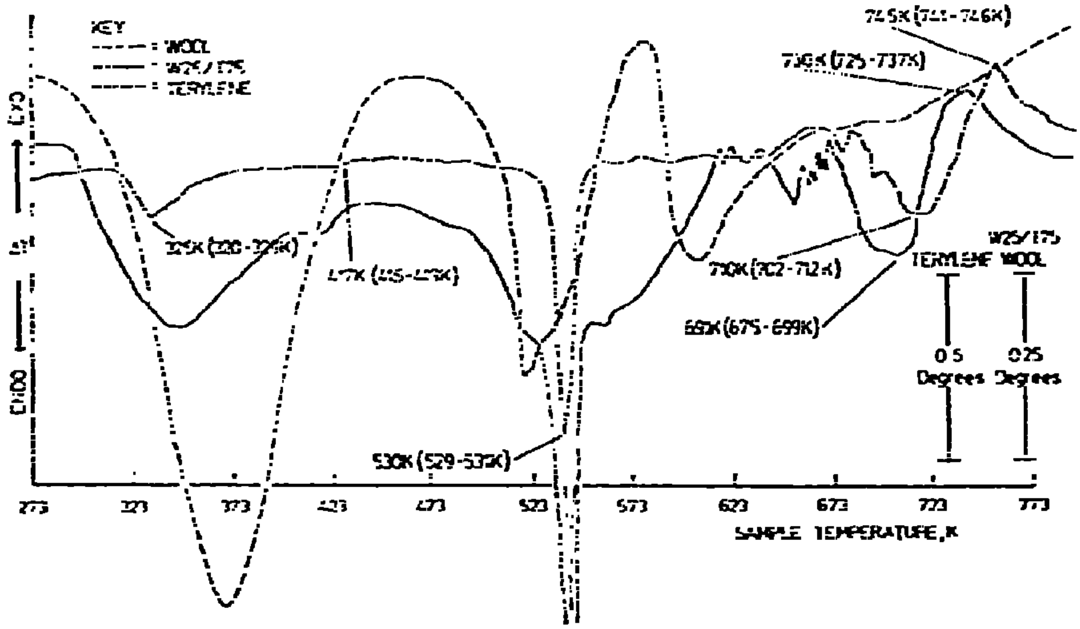

Fig. 4. DTA curves for wool, W25/T75 and Terylene.

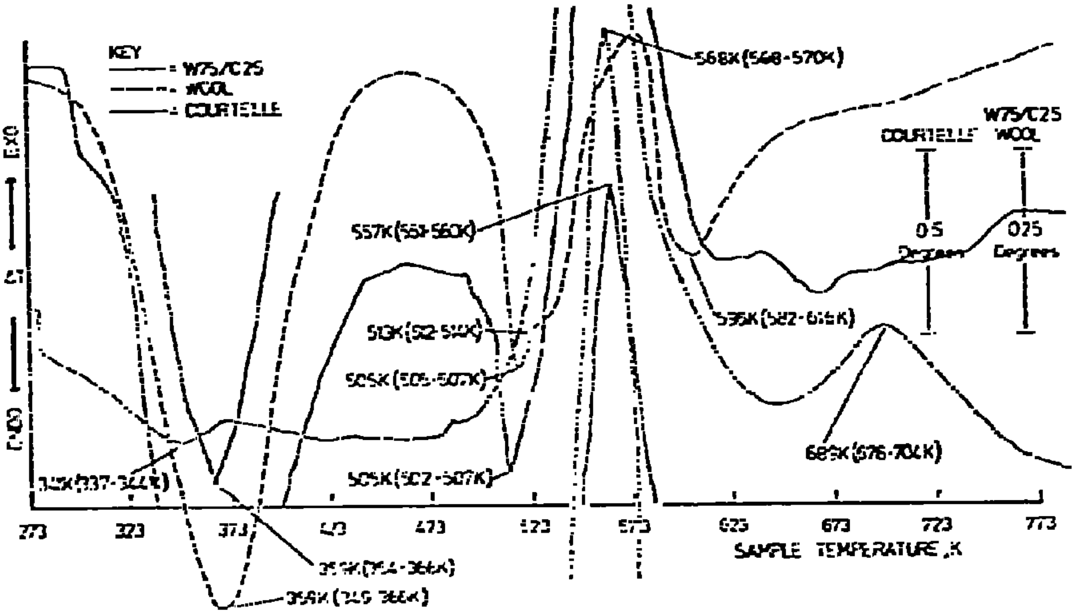

Fig. 5. DTA curves for wool, W75/C25 and Courtelle.

FIGURE 6

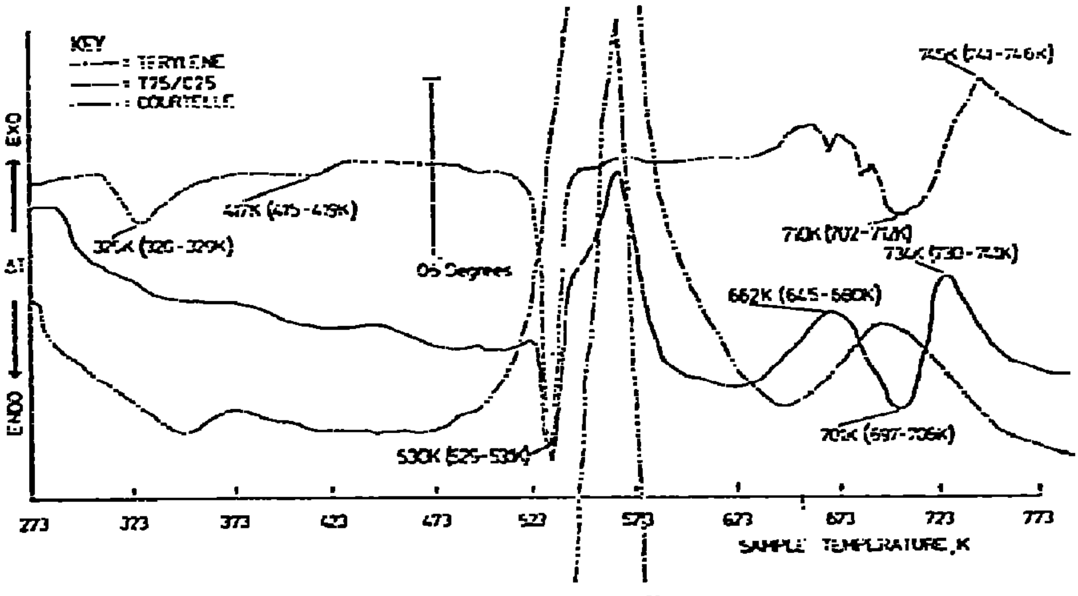

Fig. 6. DTA curves for Terylene, T75/C25 and Courtelle.

The progressive coating of Courtelle fibres by fused Terylene following Terylene fusion at 530 K is illustrated in the HSM photographs (Figs. 10–12).

DISCUSSION

It is generally agreed that the endothermic peaks observed at 325 K (320–329 K) and 530 K (529–531 K) in the DTA curve of Terylene reflect the occurrence of water loss and sample fusion, respectively.

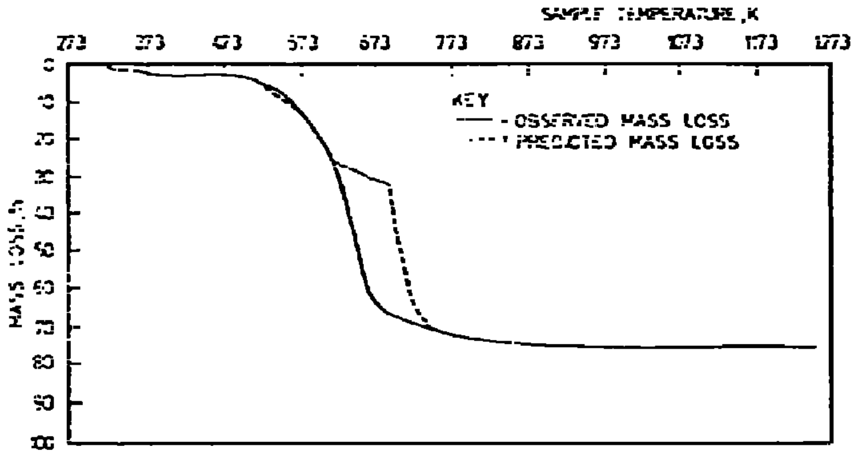

Fig. 7. TG curve for W50/T50.

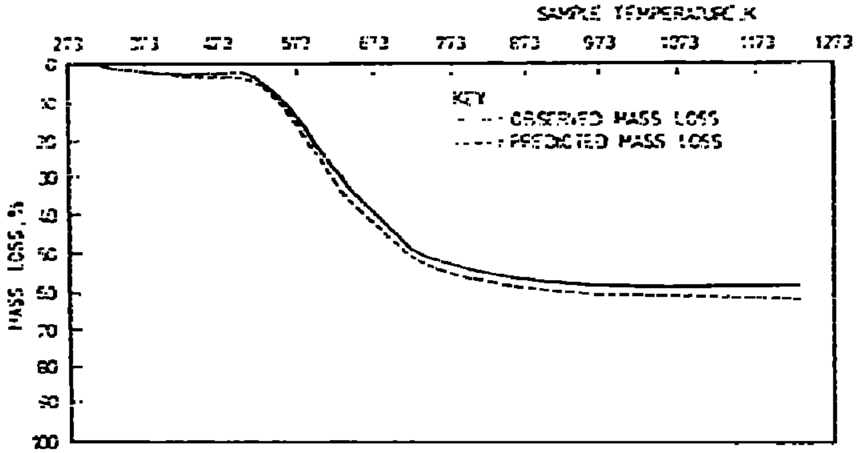

Fig. 8. TG curve for W50/C50.

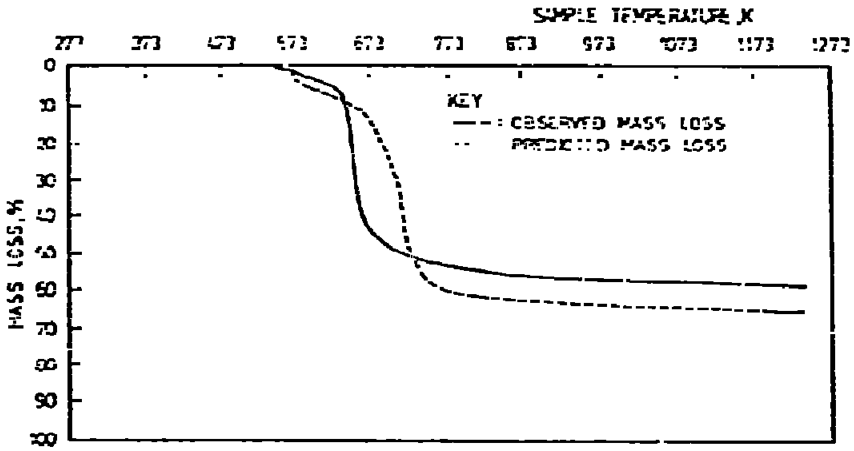

Fig. 9. TG curve for C50/T50.

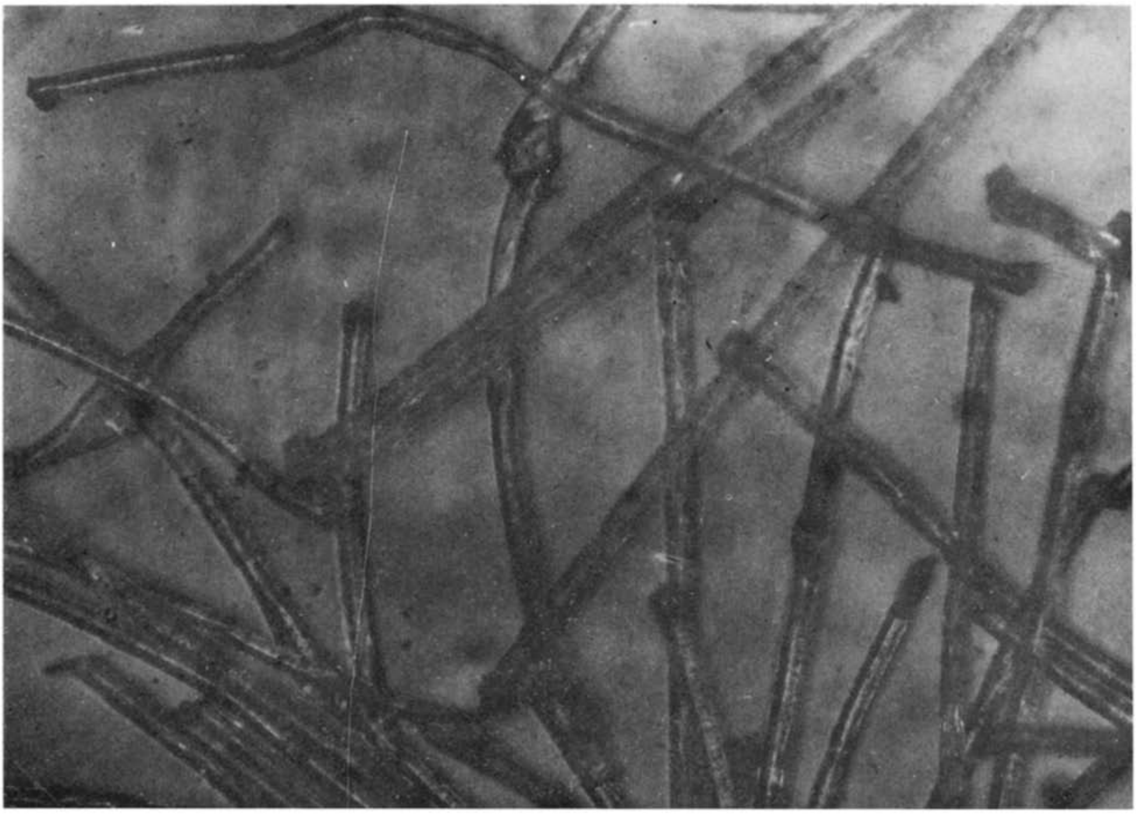

Fig. 10. Terylene/Courtelle fibre mixture at room temperature.

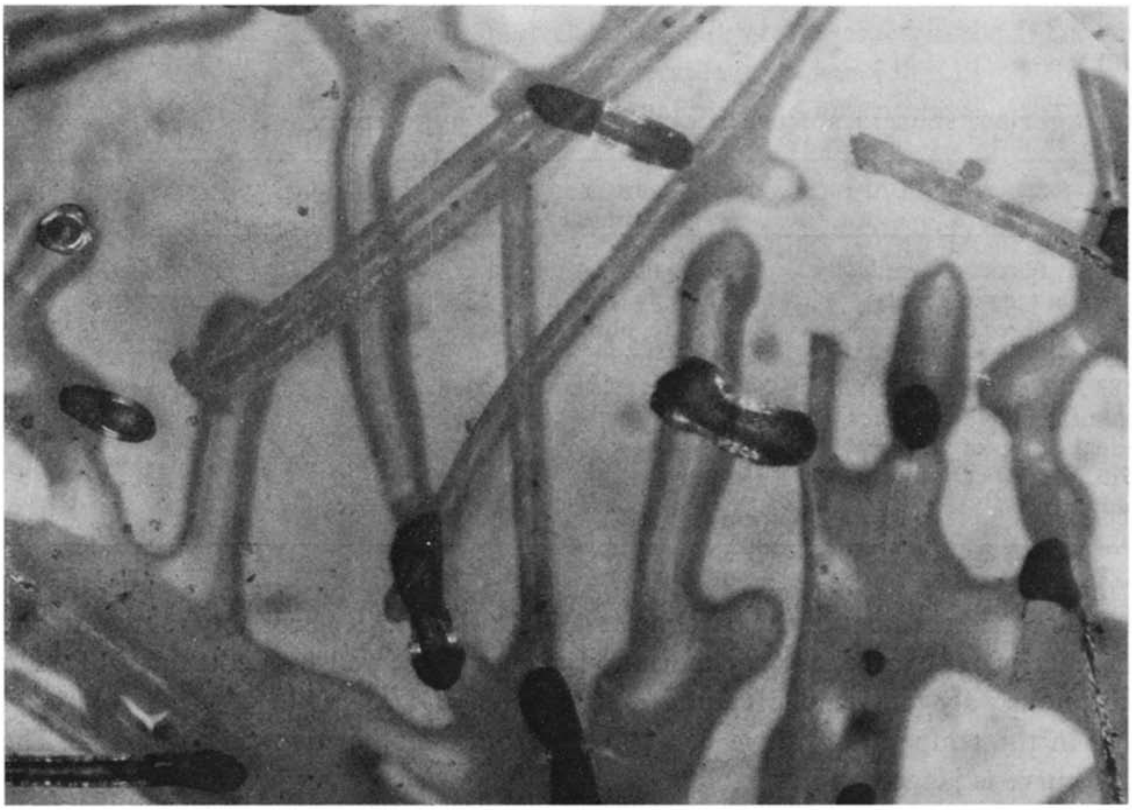

Fig. 11. Terylene/Courtelle fibre mixture at 529 K.

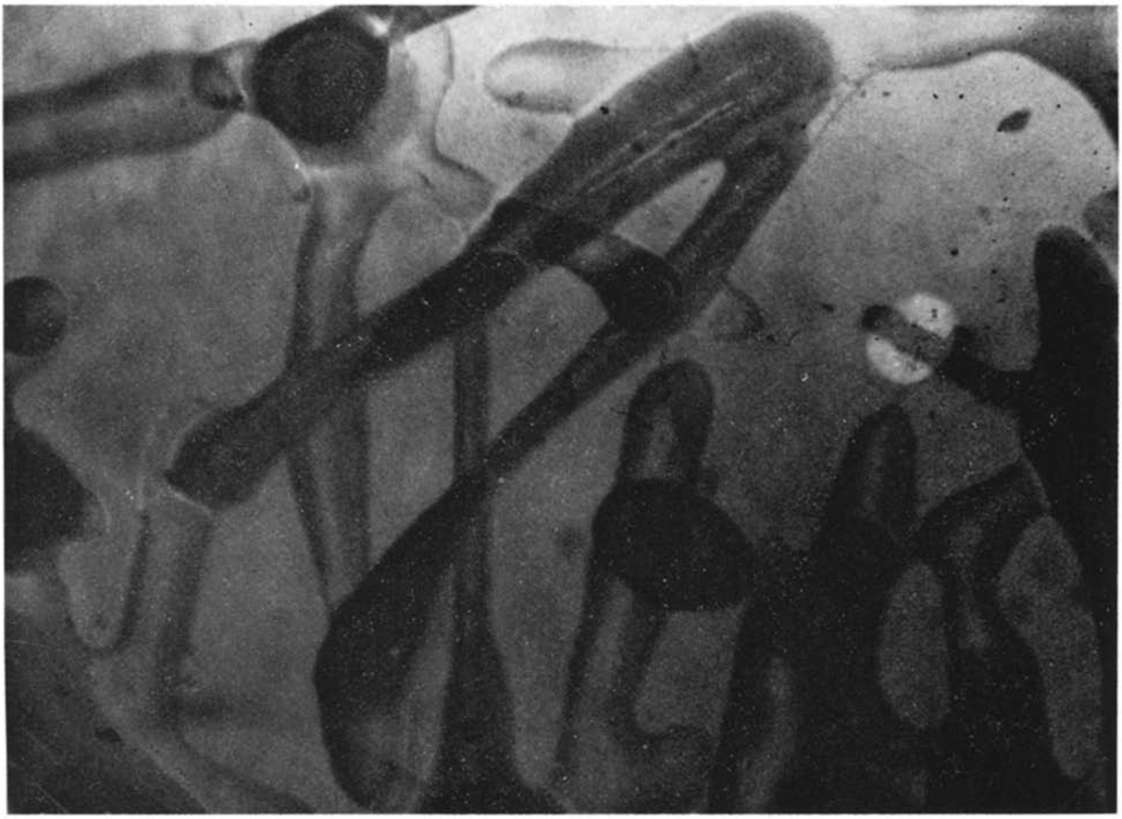

Fig. 12. Terylene Courtelle fibre mixture at 623 K.

TABLE 4

SUMMARY OF HOT STAGE MICROSCOPE OBSERVATIONS FOR THE SINGLE FIBRES

Wool	*Terylene*	*Courtelle*
> 508 K, fibres curl gradually forming a tangled mass. > 513 K, fibres begin to darken ~ 583 K, formation of bubbles within the individual fibres, gradual fusion of fibres. > 613 K, sodification of fused mass.	530 K, fibres observed to fuse. ~ 673 K, bubble formation observed within fused Terylene.	Gradual darkening of the Courtelle fibres over the temperature range 298–773 K.

The displacement of the baseline at 417 K (415–419 K) probably represents the remnants of an exothermic crystallisation process observed by Scott[8] at 413 K in amorphous poly-(ethylene terephthate), (PET).

In the temperature range 653–683 K, exothermic behaviour is observed. The DTA curve is jagged and variable in shape, presumably reflecting the occurrence of bubbling within the sample as observed by HSM at approximately 673 K. Whilst unresolved in this study, an exothermic peak has been recorded in the DTA curve of drawn Dacron fibre (nitrogen atmosphere) at 653 K[9] and 662 K[10].

The TG curve for Terylene (Fig. 2) indicates that significant mass loss commences at 653 K. The exothermic activity in the DTA curve (temperature range 653–683 K) therefore represents the initiation of Terylene degradation reactions.

The mechanism of the pyrolytic breakdown of PET has been reviewed by Buxbaum[11]. He considers that degradation is initiated by main-chain breakdown at the ester linkages. Various cross-linking reactions involving breakdown products are then considered to occur. Further, it is considered that the 2-hydroxy-ethyl end group may break down to form acetaldehyde or alternatively react with the products of main-chain breakdown. In view of the reaction between 2-hydroxyethyl end groups and the products of main-chain breakdown Buxbaum[11] considers that there is no significant decrease in molecular weight until all the 2-hydroxyethyl end groups have been consumed. The occurrence of the recombination reactions involving 2-hydroxyethyl end groups is consistent with the exothermic activity observed in the DTA curve of Terylene in the temperature range 653–683 K. The small associated mass loss of 7% presumably reflects evolution of acetaldehyde which may thus account for the sample bubbling observed by HSM at approximately 673 K. If Buxbaum's[11] postulates are correct, then, once all the 2-hydroxyethyl end groups have been consumed, the occurrence of endothermic chain scission reactions should result in an effective decrease in molecular weight. The more volatile fragments formed during these reactions escaping from the pyrolysis residue. Again, this reaction scheme is consistent with the DTA and TG data for an endothermic peak are observed in the DTA curve at 710 K (702–712 K) accompanied by considerable mass loss (58%).

Gillham and Schwenker[9] using Torsional Braid Analysis have detected the formation of a highly cross-linked residue at 773 K from the pyrolysis of PET (nitrogen atmosphere). The occurrence of these exothermic cross-linking reactions may account for the exothermic peak observed in the DTA curve of Terylene at 745 K (741–746 K). It is clear from this analysis that the displacement of the peaks observed in the Terylene DTA curve [endotherm 710 K (702 712 K), exotherm 745 K (741–746 K)] to lower temperatures in the DTA curves of wool/Terylene and Terylene/Courtelle mixtures indicates a decrease in the thermal stability of Terylene.

It is significant that the DTA curve obtained by Tarim and Cates[1] for wool is different from that reported in this and other work[4, 12]. This difference cannot be explained in terms of the type of gas atmosphere employed. It is generally found that the wool DTA curve consists of a series of endothermic peaks followed by a general movement of the curve in the exothermic direction at temperatures above ca. 773 K. Tarim and Cates[1] report similar peaks but describe the series below 773 K as exothermic. It is possible that this assignment may be the result of extensive baseline drift. Therefore, it is doubtful that the occurrence of Dacron degradative peaks at lower temperatures in wool/Dacron DTA curves is caused by exothermic behaviour on the part of the wool component as originally proposed[1].

However, it is reasonable to consider heat transfer as a possible cause of the observed reduction in the thermal stability of Dacron and Terylene when pyrolysed in the presence of bleached cotton[1] and Courtelle, respectively (Table 3, parts c, d). For, in both these binary systems, the second fibre present (bleached cotton, Courtelle) exhibits exothermic behaviour prior to the onset of degradation reactions in the respective polyester fibre present.

In this discussion, i. is relevant to consider the design of the DTA apparatus employed. The apparatus employed by Tarim and Cates[1] consisted of an aluminium block incorporating three symmetrically placed compartments. The differential temperature (ΔT) was measured between the sample compartment and a reference material compartment whilst the temperature (T) was measured in the third compartment which also contained reference material.

The basis of the heat transfer effect as proposed by Tarim and Cates[1] is that exothermic changes in the second fibre raise the temperature of the polyester fibre sufficiently for it to undergo degradation reactions which it would normally undergo later after the whole block including the temperature-sensing thermocouple had reached a particular temperature. The DTA curves reported by Tarim and Cates[1] record peak positions in terms of the temperature of the reference material. Therefore, any displacement of peaks to lower temperatures as a result of heat transfer reflect only an *apparent* reduction in peak temperature since this localised heating in the sample compartment goes undetected.

If such localised heating occurs, then the magnitude of the differential temperature (ΔT) should be comparable in magnitude with the degree of displacement to lower temperature observed for the peaks representing the polyester degradation reactions. It is not, however, possible to apply such a test to Tarim and Cates' data[1] for no differential temperatures (ΔT) are recorded.

In the present study the maximum peak displacement was observed for the Terylene exotherm [745 K (741–746 K)] which occurred in the DTA curve of the mixture C75/T25 at 706 K (701–711 K) [Table 3, d], i.e., a displacement of 39 °C. Since the maximum differential temperature observed was of the order of 4 °C, it would seem that the reduction in the thermal stability of Terylene cannot be explained by heat transfer and must be considered to be a real rather than an *apparent* effect. The DTA data for kieselguhr/Terylene mixtures are presented in Table 3, parts e, f. In these mixtures, kieselguhr is considered to act as a chemically and thermally inert support material. It is clear from these data that there is little evidence for peak displacement in the DTA curves of kieselguhr/Terylene mixtures. It is therefore considered that the second fibre present acting as an inert support material to facilitate Terylene degradation reactions cannot account for the observed reduction in the thermal stability of Terylene.

There is evidence to suggest, however, that chemical interactions occur during the pyrolysis of binary polymer mixtures. Both Schwenker[4] and Tarim[1] have observed additional peaks in the DTA curves of binary polymer mixtures which they consider to arise as a result of the chemical interaction of degradation products. Further, Crighton[16] reported that the Nylon-6 degradation endotherm normally observed at

733 K appeared in the DTA curve of a Nylon 6/viscose rayon mixture at 673 K.

No new peaks were observed in the DTA curves of the binary mixtures employed in this study, however, whilst only indirect evidence is available, the results of Crighton[16] and those reported here may be interpreted in terms of the occurrence of chemical interaction. Indeed, the DTA and TG data for wool/Terylene, Terylene/Courtelle and Dacron/bleached cotton systems indicate that significant degradation of the second polymer present (wool, Courtelle, bleached cotton, respectively) occurs prior to the onset of degradation reactions in the respective polyester fibres. It is therefore postulated that the thermal stability of the polyester fibre is reduced through chemical interaction with degradation products arising from the second fibre present.

It is interesting to note that ammonia has been detected in significant quantities as a degradation product from the pyrolysis of both wool[13] and acrylic fibres including Courtelle[14, 15]. Further, it has been reported[11] that the thermal stability of PET is reduced in the presence of amines. It is therefore possible that ammonia can reduce the thermal stability of PET through attack by a mechanism similar to that of amine attack.

The second area for discussion concerns the TG behaviour and LSP yields observed for the wool/Courtelle and Terylene/Courtelle systems. The TG data for both systems suggest that initial mass loss from the Courtelle component is reduced (Figs. 7, 9). Further, for the majority of wool/Courtelle mixtures and for all the Terylene/Courtelle mixtures significantly higher than predicted yields are observed at 1213 K from LSP (Figs. 14, 15). It is clear from the HSM data (Table 4) that both these systems comprise of a fusing and a non-fusing polymer. HSM observations of the Terylene/Courtelle system indicate that, following fusion at 530 K, the molten Terylene coats Courtelle fibres. Wool fusion is observed by HSM at 583 K. In wool/

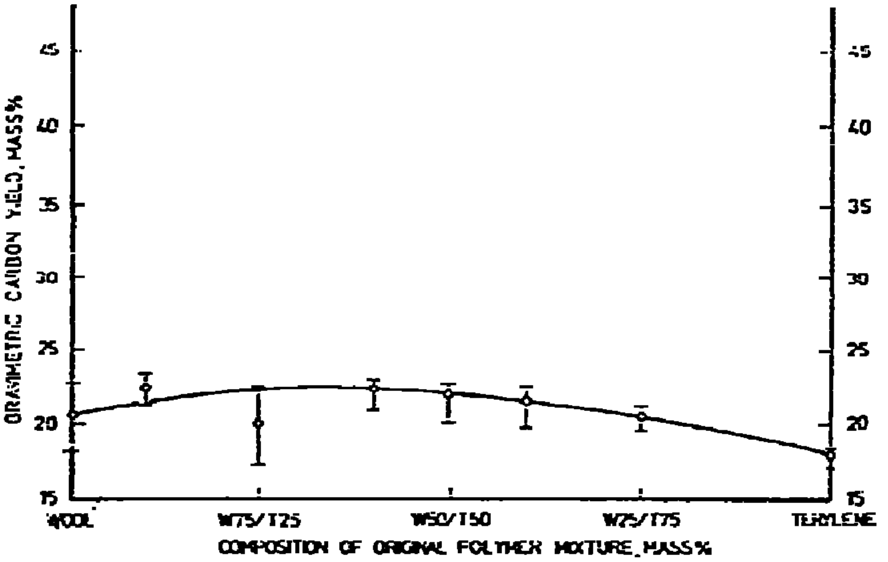

Fig. 13. Variation of the gravimetric carbon yield obtained at 1213 K from LSP with original mixture composition for the wool/Terylene system.

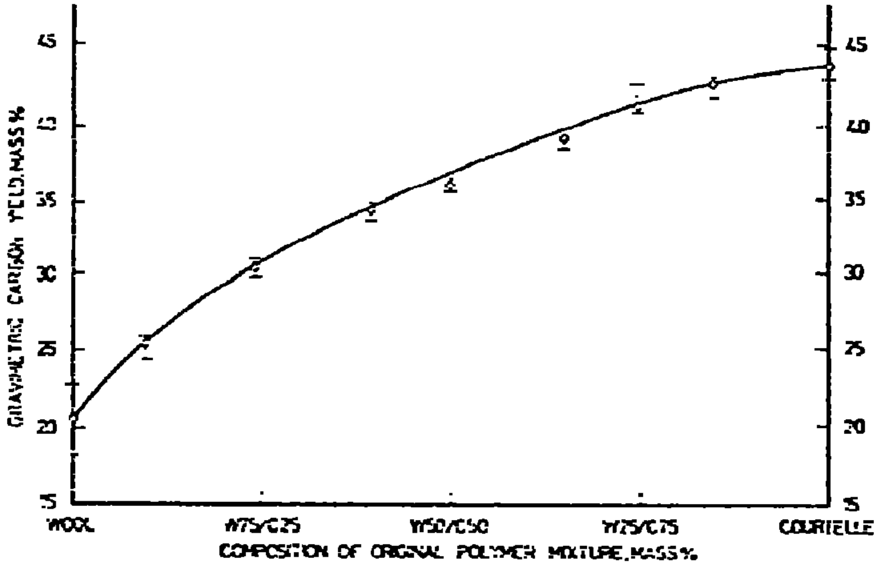

Fig. 14. Variation of the gravimetric carbon yield obtained at 1213 K from LSP with original mixture composition for the wool/Courtelle system.

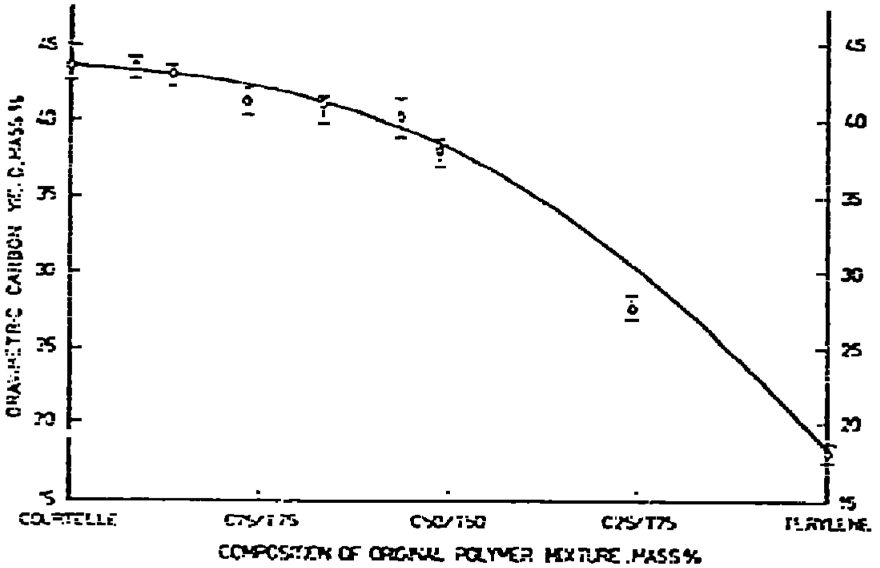

Fig. 15. Variation of the gravimetric carbon yield obtained at 1213 K from LSP with original mixture composition for the Courtelle/Terylene system.

Courtelle mixtures, wool fusion was observed to occur to a more limited extent. Once fused, the wool did not flow as extensively as fused Terylene.

It is considered that the "high" yields obtained from LSP and the apparent reduction in mass loss from Courtelle for the wool/Courtelle and Terylene/Courtelle systems may be explained in terms of the coating of the non-fusing polymer by the fusing polymer during pyrolysis. This coating effect was observed previously for the Orlon/polystyrene system[1].

In the Terylene/Courtelle system, coating is observed by HSM to take place shortly after Terylene fusion at 530 K and prior to the initiation of Courtelle mass loss at 543 K. Since no degradation reactions are observed in the DTA curve of Terylene until the exothermic activity in the temperature range 653–683 K, the Terylene coating presumably forms a continuous and therefore effective barrier, trapping volatile Courtelle degradation products. The permanent incorporation of these degradation products within the Courtelle pyrolysis residue explains the "high" yields at 1213 K from LSP. Whilst "high" yields from LSP and a reduction in initial Courtelle mass loss were observed for both Terylene/Courtelle and wool/Courtelle systems, the effects were less marked for the wool/Courtelle mixtures. TG data for the wool/Courtelle system indicate that a Courtelle mass loss of 12% occurs prior to wool fusion at 583 K. Further, a major wool degradation reaction represented by the endotherm in the wool DTA curve at 596 K (582–616 K) follows shortly after fusion. This degradation reaction may reduce the effectiveness of the fused wool in retaining Courtelle degradation products, thus accounting for the less marked behaviour of the wool/Courtelle system.

In binary polymer systems containing Terylene, the effect of the decreased thermal stability of the Terylene component on the magnitude of the residual yield at 1213 K is difficult to assess. However, if the decomposition of Terylene at lower temperatures leads to a reduction in the amount of carbon derived from Terylene in the residue at 1213 K, then the magnitude of yield increases observed at 1213 K and attributed to degradation product retention may be greater than those actually observed.

ACKNOWLEDGEMENTS

The authors thank the Wool Industries Research Association, Leeds, for sponsoring this research.

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