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A KINETIC STUDY OF THE THERMAL DEGRADATION OF POLYESTER/COTTON BLENDS BY THERMOGRAVIMETRY *

J.D. COONEY, M. DAY and D.M. WILES

Division of Chemistry, National Research Council of Canada, Ottawa,
Ontario K1A OR9 (Canada)

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ABSTRACT

The weight loss curves obtained from a series of polyester/cotton blends heated in air at heating rates of 0.1–5°C min^{-1} have been determined and compared with those calculated from the individual components. Comparison of the thermogravimetric curves and calculated kinetic parameters indicates that interactions occur between the polyester and cotton components in the blends. Although these interactions may be primarily physical in nature, they are sufficiently large to cause changes in the degradation kinetics of the weight loss processes responsible for gaseous product formation.

INTRODUCTION

The North American apparel fabric market utilises large amounts of polyester/cotton blends because of their unique physical properties. For example, polyester provides durability, strength and easy care properties, while cotton contributes good moisture absorption and thermal properties associated with comfort. Unfortunately, blend fabrics have burning characteristics that are not predictable from the burning behaviour of the individual fibres. Because of these problems and the requirements for textiles with reduced flammability, research has been undertaken in many countries to develop a better understanding of the combustion process and design flame retardant systems for these blends [1,2]. In this area of flammability and flame retardancy, thermal analysis techniques have been widely employed to obtain information regarding the thermal degradation processes [3] and several researchers have published thermogravimetric curves for polyester/cotton blends in both nitrogen [4–6] and air [5–8] environments. However, in all of these studies, the major interest has been to

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study the thermograms or their first derivative in order to speculate on the role of flame retardants in the thermal degradation processes or char formation. Only one study [3] makes any speculations regarding the decomposition kinetics based upon the position of the temperature of the maximum rate of weight loss as a function of blend composition. However, although this research suggested that the cotton degradation was not influenced by the presence of polyester in the blend, the polyester degradation kinetics appeared to be altered slightly due to the presence of cotton char residues. The exact nature of this interaction, was, however, not clarified, although other studies have proposed both physical [9] and chemical [4] interactions. Recent studies [10] in our laboratories on the combustibility of the gaseous pyrolysates have indicated that both physical and chemical interactions are taking place in the blends.

In order to obtain a better understanding of the combustion of polyester/cotton blends and the nature of the interaction between the two components, it was decided to undertake a more detailed study of the kinetics of the thermal degradation of a series of such materials. The technique employed was the non-isothermal thermogravimetry (TG) approach used previously in our laboratories to study the degradation kinetics of untreated [11] and flame retarded polyesters [12]. The thermogravimetric curves obtained in air for a series of heating rate experiments were then analysed according to the procedure developed by Ozawa [13] and Flynn and Wall [14].

EXPERIMENTAL

The woven cotton and polyester fabrics used in this study were obtained from Testfabrics Inc., Middlesex, NJ. The cotton was 100% bleached sheeting (style 405), while the polyester was 100% spun Dacron Type 54 (style 767). These fabrics were initially passed through a Wiley Mill (Model 4276) fitted with a 20 mesh screen at 3500 rpm to produce a fine fluff. Intimate polyester/cotton blends were then produced by mixing the polyester and cotton fluffs together in the required weight ratios using a ball mill followed by a pass through the Wiley Mill. In addition to the 100% polyester and cotton samples, blends of 2/1, 1/1 and 1/2 polyester/cotton were also produced.

The thermogravimetry (TG) experiments were performed on a DuPont 951 Thermogravimetric Analyzer coupled to a 1090 Thermal Analyser in a similar manner to that described in detail in an earlier paper [11]. Because of the potential sensitivity of non-isothermal thermogravimetry to sample size [15], experiments were performed on specimens weighing 9.06 ± 0.12 mg while heating rates of 0.1, 0.3, 1, 2 and 5°C min^{-1} were employed. To simulate actual combustion conditions, air was employed as a purge gas at a controlled flow rate of 50 ml min^{-1}. Although all samples were stored in a conditioning room at 65% RH and 20°C prior to testing, the recorded thermograms obtained were normalised to zero moisture content prior to data reduction and kinetic calculations with an Apple II + computer.

RESULTS AND DISCUSSION

The thermogravimetric weight loss curves for the 100% cotton and the 100% polyester materials are shown in Fig. 1 employing a 1°C min^{-1} heating rate. Also shown in this figure are the calculated weight loss curves obtained using the DuPont File Modification Utility Software program. These curves were calculated from the individual weight loss data of each component. Comparison of these calculated curves with experimentally observed weight loss curves is presented in Fig. 2 along with the differential thermogravimetric curves. If no interaction was occurring between the polyester and the cotton in the blends, the calculated and experimental curves should coincide. The fact that differences are observed indicates that some form of interaction must be occurring. Essentially, the blended samples are observed to degrade in three distinct stages. The first weight loss centered around 300°C corresponds to the thermal degradation of cotton. The second weight loss occurring between 350–400°C corresponds to degradation of the polyester. The final weight loss above 400°C is assumed to be due to oxidative degradation of the cellulosic char and further degradation of the polyester residue. Comparison of the calculated and experimental curves presented in Fig. 2 indicates that the blending together of the two components influences all three weight loss stages to some extent. In the case of cellulose degradation, although no changes were observed in the peak temperature of decomposition between the predicted (303°C) and experimentally observed values (303°C), the actual rates of degradation were

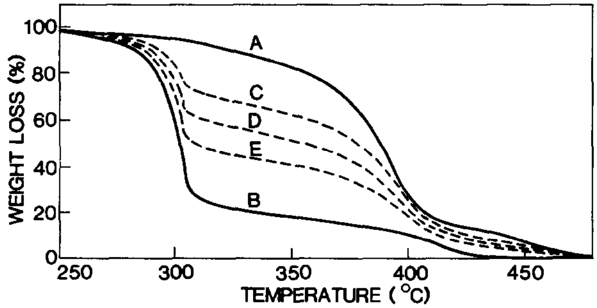

Fig. 1. Experimentally determined weight loss curves for polyester (A) and cotton (B) obtained at a heating rate of 1°C min^{-1} in air and calculated weight loss curves for 2/1 (C), 1/1 (D) and 1/2 (E) polyester/cotton blends determined from curves A and B.

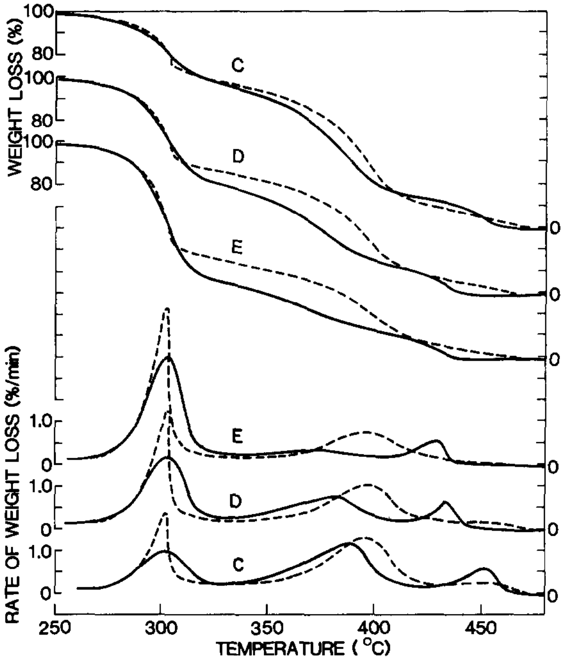

Fig. 2. Experimentally determined (———) and calculated (— — —) thermogravimetric and differential thermogravimetric curves for 2/1 (C), 1/1 (D) and 1/2 (E) polyester/cotton blends determined at 1°C min^{-1} in air.

significantly different, as were the temperature ranges associated with the cellulosic weight loss. Although the onset of cellulosic weight losses was similar in the experimental and calculated curves, the actual peak temperature rates of weight loss were greatly different, with the observed experimental maximum rate of weight loss decreasing as the amount of polyester in the blend increases. This observation is still noted when corrections are made for actual blend compositions. Because of these lower rates of peak temperature weight loss, the actual weight loss associated with the degradation of cellulose occurs over a wider temperature range with the result that appreciable weight loss is occurring up to 320°C (a higher temperature than would be expected based upon the calculated weight loss curves). This decrease in the rate of weight loss of the cellulose and its broadening to higher temperatures suggests that the polyester is inhibiting the cellulosic weight loss process. One way this may be occurring can be attributed to the melting of the polyester (T_m = 260°C) which is responsible for the formation of a liquid membrane which acts to restrict the escape of the gaseous cellulosic products from the sample pan.

The weight loss associated with polyester (see Fig. 1) commences early (below 300°C) and gradually increases in rate to reach a maximum rate of weight loss at about 395°C, a value that would be predicted from the calculated curves if no interactions were occurring in the blends. Examination of Fig. 2 reveals that the presence of cotton in the blend is influencing the degradation and weight loss of the polyester component in the blend. First, it will be noted that the rate of weight loss of the polyester has been advanced in that more degradation products are being produced at lower temperatures than those predicted. Because of this advancement in the degradation at lower temperatures, the actual peak temperatures corresponding to the maximum rates of weight loss now occur at lower temperatures with the decrease from the calculated values increasing as the proportion of cotton in the blend increases. It will also be noted that the maximum rates of weight loss have decreased from the calculated values with, once again, the differences being largest for those blends having the largest cotton content.

In addition to the weight losses associated with the degradation of the cotton and polyester, both components exhibit a high temperature weight loss zone above 400°C. In the case of cotton, this has been attributed to the oxidation of the carbonaceous char residue, while in the case of the polyester, it has been attributed to the degradation of pyrolysis residues. Comparison of the calculated and experimentally observed weight loss curves associated with this process (Fig. 2) reveals that they appear to occur at lower temperatures and faster rates than predicted. Increasing the polyester content in the blend, however, appears to cause the peak temperature to move to higher values indicative of the higher thermal stability of the polyester residue.

In the case of the burning of polyester/cotton blends, the enhanced combustion of these systems has been attributed to the cotton acting as a "scaffold" for the molten polyester assisting its burning in a similar manner to that of paraffin wax at the wick of a candle. This supporting role of cotton on the combustion of polyester may also be responsible for influencing the polyester's weight loss as noted above in the blended experiments. Since it is known that the degradation of cellulose leaves a carbonaceous residue, it was speculated that this residue is capable of influencing the thermal or chemical characteristics of the polyester's weight loss. In order to elucidate the possible nature of this interaction, it was decided to perform experiments on polyester blended with glass fibres to act as an inert non-combustible support in much the same way as the cellulosic char may be acting in the blend. The results obtained at the 1°C min^{-1} heating rate are presented in Fig. 3 for polyester and a 1/1 polyester/glass fibre blend. In order to correct for the weight of the non-volatile glass fibre in the 1/1 blend, the curve has been "normalised" using the DuPont File Modification Utility program. The comparisons between these curves show a great deal of similarity to the behaviour of the polyester portions of the curves in Fig. 2. For example, in the presence of the glass fibre, the polyester initially commences to lose weight more rapidly, reaching a peak rate of weight loss

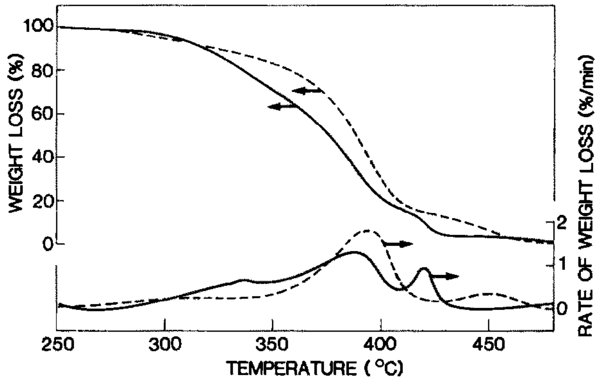

Fig. 3. Thermogravimetric and differential thermogravimetric curves for polyester (— — —) and the polyester portion of a 1/1 polyester/glass fibre blend (———) determined at 1°C min^{-1} in air.

at a lower temperature than in the absence of glass fibre. The actual maximum rate of weight loss for the polyester is also reduced in the presence of the glass fibre in a similar manner to that observed with the polyester/cotton blends. The residual weight loss at 420°C also closely resembles that observed in the polyester/cotton systems occurring at a temperature approximately 30°C below that found in the polyester alone. In view of this observed effect of the glass fibre and its close resemblance to that observed in the polyester/cotton blends, it seems likely that physical heat transfer effects associated with the cellulosic char (inert support in the case of the glass fibre) are influencing the degradation and weight loss of the polyester in the blends.

The calculated apparent Arrhenius activation energies (E) plotted as a function of fractional weight loss (α) for the individual polyester and cotton materials are presented in Fig. 4. These values, as were all kinetic data presented in this paper, were determined using the isoconversional method reviewed by Flynn [16]. This method was chosen because of its capability of yielding values for E without assumptions being required for n, the order of reaction. Examination of Fig. 4 reveals that the activation energies associated with the weight loss of cotton and polyester behave differently. In the case of cotton, the activation energies are relatively constant up to about 0.65 fraction weight loss with values between 149 and 169 kJ mol^{-1}. At fractional weight loss values around 0.80, there is some uncertainty in the data due to the deviation of the linear heating rates associated with the exothermic oxidation of the cellulosic carbon in the carbonaceous residue. Meanwhile, the oxidative degradation of the char above $\alpha = 0.85$ has an E value of 181–194 kJ mol^{-1}. These values are in reasonable agreement with the majority of published values recently reviewed by Davies et al. [17] who reported an activation energy of pyrolysis of 146 kJ mol^{-1}.

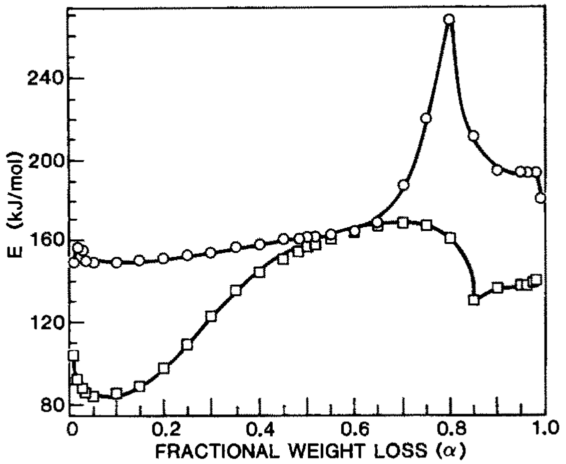

Fig. 4. Activation energies as a function of fractional weight loss for cotton (○) and polyester (□).

Meanwhile, the activation energy for the polyester material shows a range of values dependent upon fractional weight loss. In the early stages of weight loss, the E values vary between 83 and 103 kJ mol^{-1} ($\alpha = 0.01$–0.2). The activation energy then increases as the value of α increases up to a maximum value of 168 kJ mol^{-1} at $\alpha = 0.7$. Finally, the degradation of polyester residue can be identified above $\alpha = 0.85$ as having an E value between 130–140 kJ mol^{-1}. These values, while not identical to those reported earlier [11,12] are very similar, and any differences observed may be attributable to the differences in sample preparations and the improved data reduction techniques employed in this present study.

Although the above kinetic data are of interest, the main concern of this study was to determine whether the blending of the polyester and cotton was responsible for any interaction between the two components or if the weight loss kinetics are simply an additive function of the individual species. All weight loss curves at all heating rates were therefore analysed and the activation energies determined as a function of fractional weight loss. These curves are given in Figs. 5–7 for the 1/2, 1/1 and 2/1 polyester/cotton blends, respectively. In all cases, differences are observed in the E values obtained experimentally in comparison with calculated values, with the differences being dependent upon the composition of the blend and the fractional weight loss. Figure 5 which provides data for the 1/2 polyester/cotton blend can be seen to be composed of two main zones. The first zone, up to an α value of about 0.6, corresponds primarily to kinetics associated with the cellulosic weight loss. The second zone, above $\alpha = 0.6$ meanwhile, corresponds to the weight loss associated with the polyester. Examination of the activation energies for the weight loss of the cellulosic material indicates that the experimentally determined E values are in very

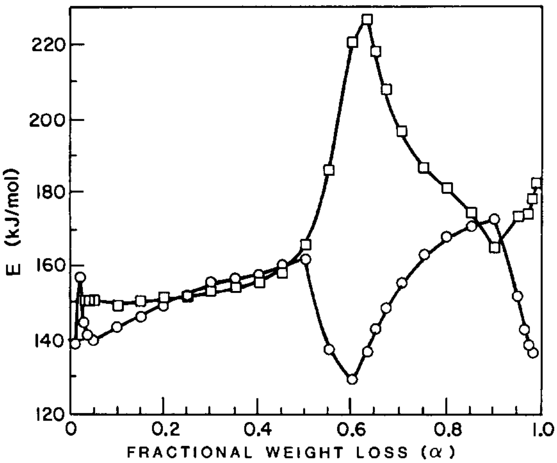

Fig. 5. Activation energies as a function of fractional weight loss for 1/2 polyester/cotton blend; determined from experimental (□) and calculated (○) weight loss data.

close agreement with the values predicted based upon an additive combination of the weight loss curves for the cotton and polyester. Thus, kinetically, the blending of the polyester with the cotton has little influence on the degradation of the cellulose. The experimentally observed activation energies obtained for the polyester weight loss zone, however, are greatly different from the calculated values. The magnitude of these differences clearly indicates that the presence of the cotton has significantly altered the kinetics of the polyester degradation.

The results obtained with the 1/1 blend are shown in Fig. 6. Once again there is evidence of differences between the experimentally determined

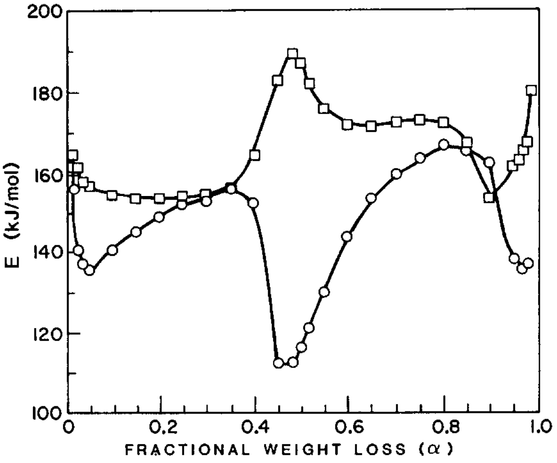

Fig. 6. Activation energies as a function of fractional weight loss for 1/1 polyester/cotton blend; determined from experimental (□) and calculated (○) weight loss data.

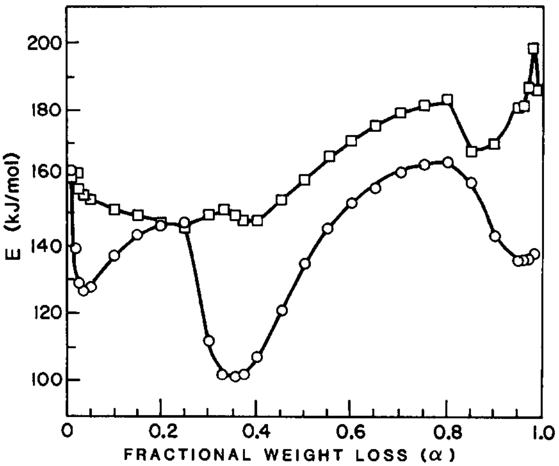

Fig. 7. Activation energies as a function of fractional weight loss for 2/1 polyester/cotton blend; determined from experimental (□) and calculated (○) weight loss data.

values and those calculated for the polyester weight loss region. However, in view of the smaller proportion of cotton in the blend, there will be a corresponding reduction in cellulosic char residue present when the polyester degrades, consequently the differences are less. Although no significant changes were detected in the cellulosic *E* values with the 1/2 polyester/cotton blend, it now appears that differences between the experimental and calculated *E* values can be observed especially during the initial weight loss. Thus, it appears that the polyester (presumably in the molten form) is influencing the kinetics of the cellulosic weight loss. The fact that higher initial activation energies are observed than those predicted based upon no interaction, it may be speculated that the molten polymer is actually acting as an inhibitor to gaseous degradation products' volatilization.

Examination of the 2/1 polyester/cotton data (Fig. 7) reveals the same type of differences as was noted previously, except that the magnitude of the changes in the cellulosic zone have increased, whilst those in the polyester zone have decreased. Thus, it is evident that there are differences in the *E* values between the experimental and calculated weight losses for both the cotton and polyester degradation processes. It also appears evident that the magnitude of these differences is dependent upon the amount of each component in the blend. While it can be speculated that the increased activation energies for the cellulosic weight loss can be attributed to the molten polyester restricting gaseous mobility to the atmosphere, the increases in the values for the polyester needs further investigation.

The weight loss data obtained with the 1/1 polyester/glass fibre blend (see Fig. 3) were therefore subjected to the same kinetic analysis and the resulting *E* values obtained as a function of α are plotted in Fig. 8. From

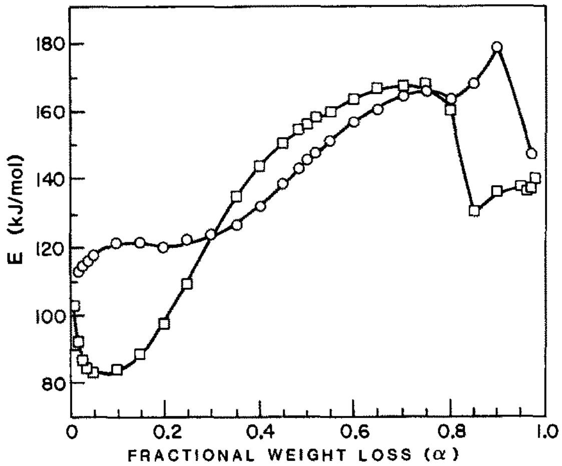

Fig. 8. Activation energies as a function of fractional weight loss for polyester (□) and 1/1 polyester/glass fibre blend (○).

this data it can be seen that it is only in the initial stages of polyester degradation and weight loss that the inert glass fibre plays a significant role in causing an increase in the activation energy for the weight loss process. Comparing Fig. 8 with the polyester portion of Fig. 6 ($\alpha = 0.5$–1.0) a similarity in behaviour can be observed between the glass fibre-containing sample and that containing the residual cellulosic char. Thus, it may be speculated that in the polyester/cotton blends, the cellulosic char residue is capable of acting as an inert heat sink causing changes in the polyester kinetics which result in an increase in the apparent activation energy.

In the analysis of kinetic data, it has been suggested [18] that the existence of a kinetic compensation effect (CE) should be investigated since it is capable of providing some instructive information on the system being evaluated. The CE, which can be observed in many cases of heterogeneous reactions, is the existence of a linear relationship between the logarithm of the pre-exponential factor and the activation energy. Because our study involves first, the calculation of E, and then log A from this value of E, care must be taken in ensuring that CE is not an artefact of the method of calculation [19]. In addition, since CEs can undoubtedly arise due to experimental errors, it was decided to limit our study to a comparison of the CEs obtained in calculated and experimentally determined kinetic data. In this way any differences in the CE plots would be indicative of interactions between the two components of the blend during the thermal degradation process. The basic equation for the CE takes the form

$$\log A = ME + C$$

The values for M and C determined from the slopes and intercepts for all systems studied are given in Table 1. From an examination of these data it

TABLE 1

Regression coefficients from the compensation effect plots

		Data from experimental curves		Data from calculated curves	
System	Zone[a]	Slope *M*	Intercept *C*	Slope *M*	Intercept *C*
Cotton	1st	−0.1129 ± 0.0015	−2.2605 ± 0.2403	–	–
	3rd	−0.1075 ± 0.0020	−4.2534 ± 0.4122	–	–
P/C[b] 1/2	1st	−0.0951 ± 0.0021	0.3489 ± 0.3265	−0.1058 ± 0.0013	−1.2678 ± 0.1910
	2nd	−0.1121 ± 0.0010	−4.1373 ± 0.1955	−0.0681 ± 0.0004	3.2648 ± 0.0644
	3rd	−0.0689 ± 0.0035	2.8749 ± 0.6034	−0.0867 ± 0.0008	−0.1537 ± 0.1173
P/C 1/1	1st	−0.0905 ± 0.0045	1.0036 ± 0.7109	−0.1026 ± 0.0010	−0.8357 ± 0.1453
	2nd	−0.1240 ± 0.0022	−5.6332 ± 0.3927	−0.0725 ± 0.0031	2.4326 ± 0.0441
	3rd	−0.0742 ± 0.0028	1.8576 ± 0.4591	−0.0910 ± 0.0016	−0.7773 ± 0.2371
P/C 2/1	1st	−0.0955 ± 0.0032	0.0085 ± 0.4890	−0.0987 ± 0.0009	−0.3572 ± 0.1237
	2nd	−0.0681 ± 0.0007	3.4004 ± 0.1226	−0.0754 ± 0.0002	1.9112 ± 0.0288
	3rd	−0.0725 ± 0.0023	1.8842 ± 0.4233	−0.0955 ± 0.0014	−1.4126 ± 0.2051
PET[c] only		−0.0808 ± 0.0002	0.9450 ± 0.0296	–	–
PET/glass fibre 1/1		−0.0742 ± 0.0007	2.1020 ± 0.1049	–	–

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[a] 1st designated weight loss associated with cotton. 2nd designated weight loss associated with polyester. 3rd designated weight loss associated with residues.

[b] P/C designates polyester/cotton blends.

[c] PET designates polyester.

can be seen that for the degradation of cotton in the blends, only small differences occur between the experimental and calculated values. When the data for the polyester in the blends are considered, however, large differences are noted between the experimental and calculated values with the 1/2 and 1/1 polyester/cotton blends, but not with the 2/1 polyester/cotton system. Meanwhile, the residual weight loss values seem to show consistent differences between the experimental and calculated values, especially in the value of *C*. These data suggest that mechanistically the polyester has little influence on the degradative weight loss associated with the cellulose in the polyester/cotton blends, although physical (thermal) interactions may be occurring. Meanwhile, the cellulose, when present in polyester/cotton blends of high cotton content, appears to be responsible for changes in the degradation reaction mechanisms of polyester in addition to changes due to physical effects. To illustrate this point, consider the CE data for the 1/1 polyester/cotton and the 1/1 polyester/glass fibre. It will be noted that while the *M* and *C* values for the 1/1 polyester/glass fibre (-0.0742 and 2.102) are characteristically different from those obtained from experimental blends (-0.1240 and -5.6332) they do show close agreement with those determined from the calculated curves (-0.0725 and 2.4326). From these data, it can be concluded that the degradation kinetics of the polyester in this blend have been modified by the cotton component in the blend. If heat transfer effects alone had been responsible, the CE values for the experimental 1/1 polyester/cotton blend would have been similar to those obtained from the 1/1 polyester/glass fibre.

CONCLUSIONS

Based upon the data presented, it has been shown that the blending of polyester and cotton causes changes in the weight loss curves associated with the thermal decomposition of the individual components. In the case of the cellulosic degradation weight loss, the presence of the polyester in the blend appears to be responsible for a more diffuse weight loss occurring at a slower rate and with a higher activation energy than predicted based upon calculations assuming no interactions. This effect appears to arise due to the polyester melting during the cellulosic degradation process inhibiting the escape of the gaseous pyrolysates.

The polyester degradation, on the other hand, occurs at a slower rate and higher activation energies than would be predicted based upon calculations; but the onset of decomposition is also moved to lower temperatures indicating a lower thermal stability. Comparison of the polyester weight loss data obtained from the polyester/cotton blends with data generated from a polyester/glass fibre mixture suggests that although some physical heat transfer effects are occurring, the degradation kinetics of the polyester are being modified by the presence of the cellulosic material in the blends.

REFERENCES

1 C.W. Jarvis and R.H. Barker, Flame Retardant Polym. Mater., 2 (1978) 133.
2 R.H. Barker, G.L. Drake, J.E. Hendrix and J.E. Bostic, Flame Retardancy Polym. Mater., 5 (1979) 67.
3 E.M. Pearce, Y.P. Khanna and D. Raucher, in E.A. Turi (Ed.), Thermal Characterisation of Polymeric Materials. Academic Press, New York, 1981, Chap. 8, p. 793.
4 B. Miller, J.R. Martin, C.H. Meiser and M. Gorguillo, Text. Res. J., 46 (7) (1976) 530.
5 J.P. Neumeyer, J.I. Wadsworth, N.B. Knoepfler and C.H. Mack, Thermochim. Acta, 16 (2) (1976) 133.
6 R.M. Perkins, J.P. Neumeyer, J.I. Wadsworth and N.B. Knoepfler, Thermochim. Acta, 20 (3) (1977) 263.
7 I.P. Pensa and S.B. Sello, J. Fire Flammability, 5 (1974) 227.
8 N. Inagaki, T. Shintani, H. Kunisada and K. Katsuura, J. Appl. Polym. Sci., 24 (1) (1979) 1.
9 E.M. Pintauro and D.R. Buchanan, Text. Res. J., 49 (6) (1979) 326.
10 M. Day, T. Suprunchuk and D.M. Wiles, Proc. 1st Symp. Fire Safety Science, 1985, in press.
11 J.D. Cooney, M. Day and D.M. Wiles, J. Appl. Polym. Sci., 28 (1983) 2887.
12 J.D. Cooney, M. Day and D.M. Wiles, J. Appl. Polym. Sci., 29 (1984) 911.
13 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
14 J.H. Flynn and L.A. Wall, Polym. Lett., 4 (1966) 323.
15 A.K. Lahiri and H.S. Ray, Thermochim. Acta, 55 (1982) 97.
16 J.H. Flynn, J. Thermal Anal., 27 (1983) 95.
17 D. Davies, A.R. Horrocks and M. Greenhalgh, Thermochim. Acta, 63 (1983) 351.
18 Z. Adonyi and G. Korosi, Thermochim. Acta, 60 (1983) 23.
19 J.M. Criado and M. Gonzalez, Thermochim. Acta, 46 (1981) 201.