Kinetic and Thermogravimetric Analysis of Thermal Degradation of Polychlal Fiber/Polyester Fiber Blend

KAZUHIKO FUKATSU

Faculty of Living Science, Kumamoto Women's University, Kumamoto 862, Japan

SYNOPSIS

The flammability behavior of a series of polychlal fiber/polyester fiber blends has been investigated in terms of the oxygen index and the thermal degradation characteristics. The thermal degradation behavior of these fiber blends has been studied by a conventional dynamic thermogravimetric technique in a flowing air atmosphere at several heating rates. Quantitative data are presented that pinpoint how the flammability behavior of the blends differs from that of the components. These results indicate that interactions occur between the polychlal and polyester fibers in the blends. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Flame retardants for blends of a nonflammable and a flammable fiber are of particular importance, since these fabrics are used to produce a wide range of textiles.[1] However, textile combustion is a complex phenomenon involving heating, degradation leading to gasification, ignition, and propagation. The flammability of these blends is not defined simply in terms of the additive behavior of component fibers, which have completely different individual burning characteristics. In fact, the flammability behavior cannot be predicted, since reactions occurring during the thermal degradation and combustion of one component are inevitably affected by the presence of the other component. Therefore, the exact nature of the interactions of the nonflammable and the flammable fibers in the blend is both complex and not well understood. 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.[2-4] The flammability properties of blends have become of major research interest with a view to producing materials in which the burning process is retarded.[5,6]

In our previous investigation,[7] polychlal fiber/cotton blend has been degraded and a mechanism was suggested for the interaction between polychlal fiber and cotton: The volatile products formed from polychlal fiber degradation at early degradation stages appear to play an important role in retarding the flammability of cotton.

In this paper, we wish to report on further thermal analysis characterization conducted with polychlal fiber/polyester fiber blends. As in our previous work on polychlal fiber/cotton blends,[1] the thermal behavior of these blends has been investigated in this study using thermogravimetry (TG), derivative thermogravimetry (DTG), and differential thermal analysis (DTA). The thermogravimetric curves recorded in air atmosphere for a series of heating rate experiments were then analyzed according to the procedure developed by Flynn and Wall.[8]

EXPERIMENTAL

Materials

The polychlal fiber (type FBCH, 5 denier staple) used in this study was obtained from Kohjin Co., Kumamoto, Japan, whereas the polyester fiber was a commercially available plain fabric with 100% polyester filament (warp: 50 denier, 25 multifilament, no twist; weft: 75 denier, 38 multifilament, no twist) was obtained from Iseikatsu Kenkyukai,

Tokyo. Various blended samples used in thermal analyses were prepared as follows: The fiber samples were cut to less than 2 mm long and then dried to a constant weight in a vacuum oven at 50°C. To prepare intimate polychlal fiber/polyester fiber blends, both fibers were fully dispersed in the required ratio in CH_3OH, and after filtration, the collected samples were air-dried at room temperature.

Instrumental Measurements

The flammability of blended samples was evaluated using the oxygen index (O.I.) measured using a Suga Test Instruments ON-1. The blend samples for the measurement of O.I. values were prepared by mixing well polychlal and polyester fibers (fiber length; 51 mm) in the required weight ratios using hand carding. Thermal analyses of premixed samples were performed in a flowing-air atmosphere using a Shimadzu Thermal Analyzer. The TGA-40M and DTA-40M modules were employed and samples were approximately 8 and 4 mg, respectively. The heating rate in the measurements of TG was varied between 2 and 50 K/min, in the measurements of DTG and DTA, it was 10 K/min. The range sensitivities of 50 and 500 μV in the measurements of DTA were employed at temperature regions of 100–300°C and above 300°C, respectively. Although all samples were stored in a conditioning room at 65% RH and 20°C prior to testing, the recorded thermograms were normalized to zero moisture content prior to data reduction and kinetic calculations to avoid the influence of the weight loss of moisture.

RESULTS AND DISCUSSION

O.I. Values of Polychlal Fiber/Polyester Fiber Blends

This study concerns primarily two-component blends including an inherently nonflammable and a flammable fiber component. Blends containing varying amounts of polychlal fiber have been studied extensively. The polychlal fiber, which is composed of poly(vinyl alcohol) and poly(vinyl chloride) and contains about 2% of stannic acid as a flame retardant, is well known as a synthetic flame-retardant fiber having a value of O.I. of 32.[9] In our previous study,[10] the mechanism of flame retardancy of this fiber was examined by using thermoanalytical techniques. The values of O.I. are used to provide a measurement of relative flame-retarding efficiency of polychlal fiber/polyester fiber blends.
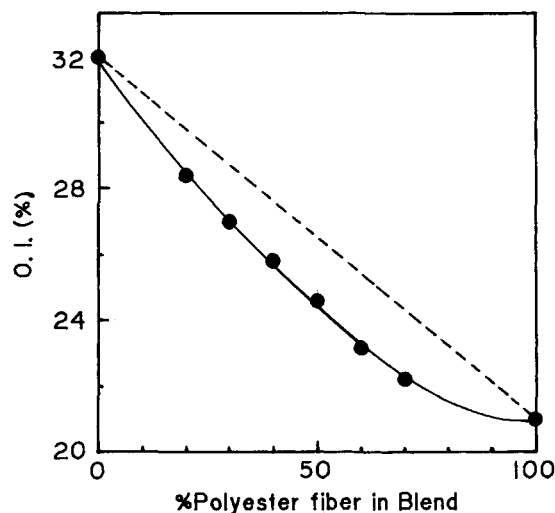

Figure 1 O.I. values of polychlal fiber/polyester fiber blend as a function of polyester fiber content.

In Figure 1, the values of O.I. are plotted vs. the composition of polychlal fiber/polyester fiber blends. The average values of O.I. for the two-component blends studied are represented by the dashed line connecting the points for the two pure components (polychlal and polyester fibers). The experimental values of O.I. for specific blends examined are lower than the average values. In polychlal fiber/polyester fiber blends, this negatively deviating effect from the expected values of O.I. suggests that the combustion of polyester fiber as a flammable material plays an important role in the combustion of these blends. The lower-than-expected values of O.I. for these blends show that, in addition to the scaffolding effect,[11] interaction may occur between the different fiber types during burning. Obviously, the values of O.I. for the blends cannot be accurately predicted from the values of O.I. for the pure components and must be determined experimentally. The amount of polychlal fiber required for values of O.I. of ca. 26 (assumed to be indicative of self-extinguishing behavior in the vertical test) is approximately 60% for blends with polyester fiber. From these observations, especially in blends with large amounts of polyester fiber, polychlal fiber apparently does not have any dramatic effect on the flammability of these blends. The burning behavior of this blend is considered to be complex and the question of the nature of possible component fiber interactions remains open.

Thermogravimetric Studies

The thermogravimetric weight loss curves (TGA) of the 100% polychlal and the 100% polyester fibers

are shown in Figure 2, employing a 10 K/min heating rate in air atmosphere. Also, the calculated weight loss curves are shown in this figure. These curves were calculated from individual weight loss data of polychlal and polyester fibers by assuming no interaction between each component during thermal degradation. The calculated curves of these blends suggests that the blend should undergo three distinct stages of degradation. The first weight loss centered about 275°C corresponds to the thermal degradation of the polychlal fiber portion in the blend. The second weight loss occurs at about 425°C, which is characteristic of the degradation of the polyester fiber portion and the second stage of the degradation of the polychlal fiber portion, and final weight loss occurs at about 500°C, which is assumed to be due to oxidative degradation of the char residue or the combustion.

Comparison of these calculated curves with experimentally observed weight loss curves is presented in Figures 3, 4, and 5, along with the differential thermogravimetric curves (DTG) for each of the three blends studied. If no interaction was occurring between the polychlal and the polyester fibers in the blends, the calculated and experimental curves should coincide. The fact that differences are observed suggests that some form of interaction must be occurring. Apparently, these blends have three distinct stages through the thermal degradation process. The first weight loss centered around
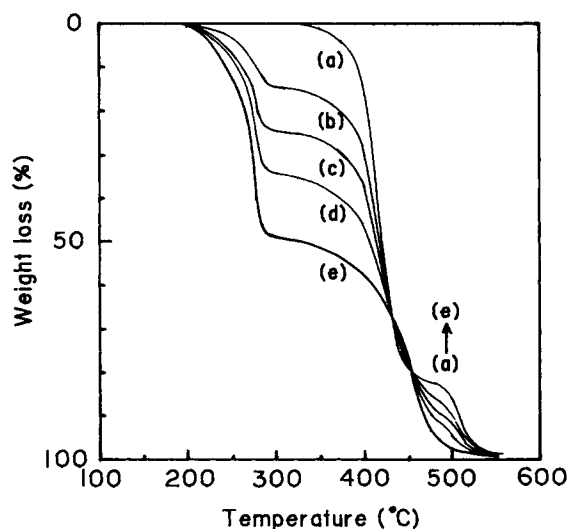

Figure 3   Experimentally determined (———) and calculated (-----) thermogravimetric and differential thermogravimetric curves for polychlal fiber/polyester fiber (30/70) blend determined at a heating rate of 10 K/min in air atmosphere.

285°C and independent of the amount of polychlal fiber in the blend, corresponds to thermal degradative interaction between the two components in the blends. This degradation was found to occur at a temperature higher than that of the calculated curves by about 10°C. In a way, this can be attributed to the molten polyester that is responsible for the formation of a liquid membrane that acts to reduce the escape of the gaseous products from the polychlal fiber. It will also be noted that the amount of weight loss during 300–380°C has increased from the calculated values, with the differences being largest for those blends having the largest polychlal fiber content. This result suggests that the presence of polychlal fiber in the blend in influencing the degradation of the polyester fiber component in the blend. This observed weight loss is because the degradation of polyester fiber is accelerated by the volatile products generated by the degradation of polychlal fiber, but since this interaction is smaller, a large portion of the polyester fiber will remain in the molten state. The second weight loss stage, at 380–450°C, is primarily due to degradation of the polyester fiber. The weight loss associated with polyester fiber com-

Figure 2   Experimentally determined weight loss curves for (a) polyester fiber and (e) polychlal fiber obtained at a heating rate of 10 K/min in air atmosphere and calculated weight loss curves for (b) 30/70, (c) 50/50, and (d) 70/30 polychlal fiber/polyester fiber blends determined from curves (a) and (e).
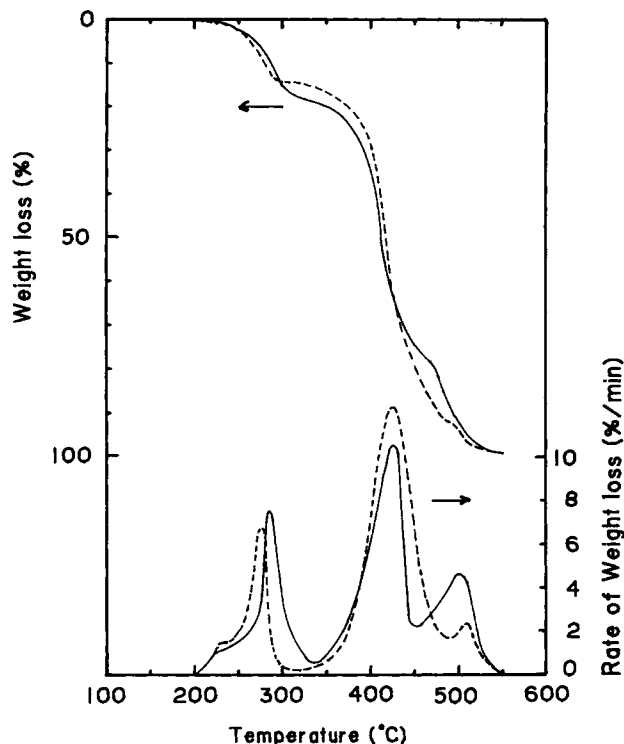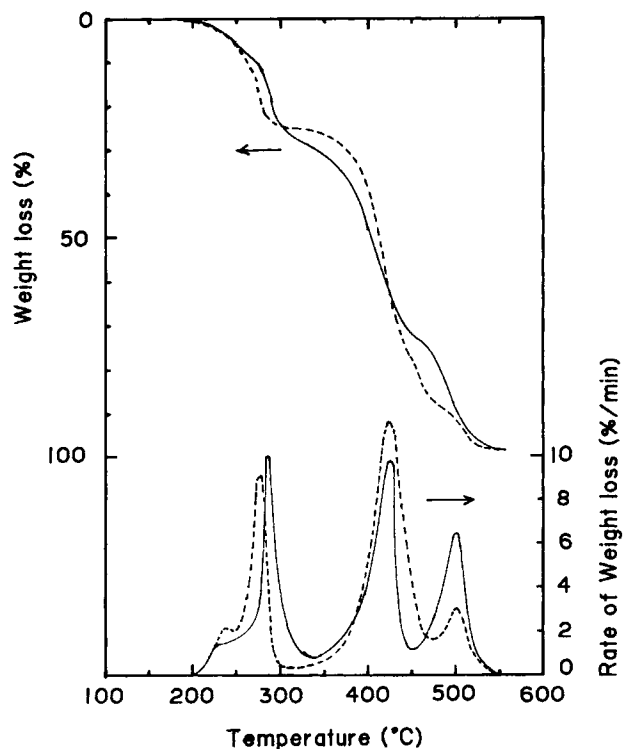
Figure 4 Experimentally determined (———) and calculated (- - - -) thermogravimetric and differential thermogravimetric curves for polychlal fiber/polyester fiber (50/50) blend determined at a heating rate of 10 K/min in air atmosphere.

menced early (below 380°C) and gradually increased in rate to reach a maximum rate of weight loss at about 425°C, a value that would be predicted from the calculated curves if no interactions were occurring in the blends. However, 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 polychlal fiber content.

These degradation curves show a greater residual char than would be predicted from the behavior of the uncombined components. The degradation of the polyester fiber has clearly been modified by the presence of the polychlal fiber; this effect may be due to the transfer of the derived species, HCl and Sn derivatives, from polychlal fiber to polyester fiber. The final weight loss stage is seen at a temperature of about 500°C and accounts for about 20% weight loss, which is probably due to char oxidation. Detailed interpretation of the thermal analysis of these blends is rather complicated, but at the early and later degradations, a gradual decrease and increase in the amount of the residue, respectively, were noted as the amount of the polychlal fiber was in-

creased. This may be attributed to the interaction between two components through the degradation process.

Differential Thermal Analytical Studies

Indication of interactions during thermal degradation at low heating rates can often be obtained using conventional thermoanalytical techniques. One must, of course, be careful in attempting to relate data obtained at these low heating rates to a flaming situation where the rates are much higher. Nevertheless, these studies might be valuable in helping to detect and identify potential preignition interactions. Figure 6 shows differential analysis (DTA) curves for heating in air atmosphere from room temperature to 600°C for polyester fiber, polychlal fiber, and polychlal fiber/polyester fiber blends. In the case of the polyester fiber, the endotherm at 260°C represents polymer melting, and around 505°C, a large exotherm appears in the thermogram due to oxidative decomposition of polymer and combustion of the char residue. The polychlal fiber
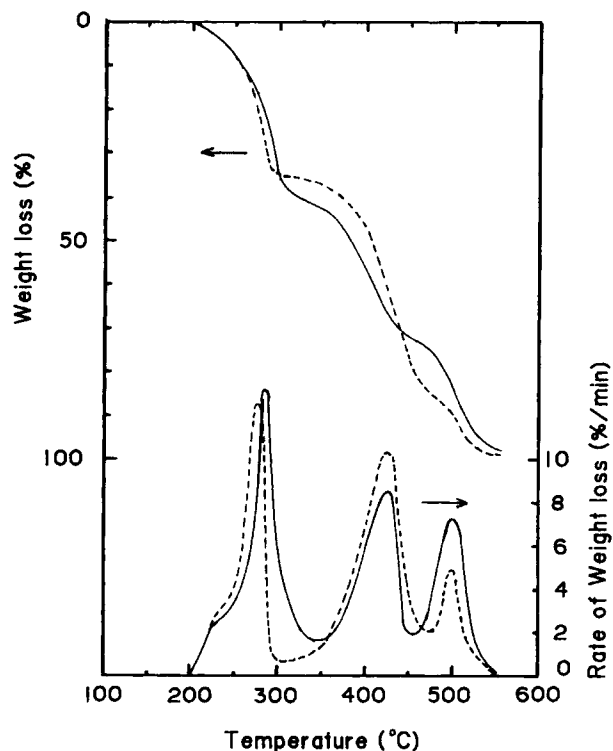

Figure 5 Experimentally determined (———) and calculated (- - - -) thermogravimetric and differential thermogravimetric curves for polychlal fiber/polyester fiber (70/30) blend determined at a heating rate of 10 K/min in air atmosphere.
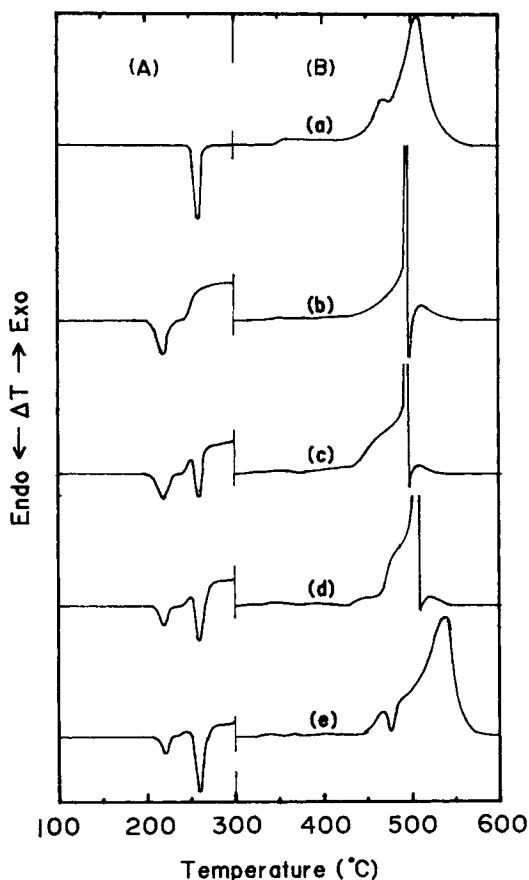
Figure 6 DTA curves of polychlal fiber/polyester fiber blend determined at a heating rate of 10 K/min in air atmosphere: (a) polyester fiber; (b) polychlal fiber; (c) polychlal fiber/polyester fiber = 70/30; (d) 50/50; (e) 30/70. Range sensitivity: (A) 50 μV; (B) 500 μV.

appears to play an important role in the formation of structure features to retard the flammability, by reactions such as dehydration and cross-linking.

Evaluation of Activation Energy from TGA

The calculated apparent activation energies (E) plotted as a function of fractional weight loss (α) for the individual polychlal fiber and polyester fiber are shown in Figure 7. Several methods are available for assessing the constancy of the activation energies (E) during the course of pyrolysis.[8,12,13] These reported values were determined using the isoconventional method reviewed by Flynn.[14] This method was used because it yields activation energies without the necessity of assuming a possibly incorrect model for the reaction mechanism.

Figure 7 shows that the activation energies associated with the weight loss of polychlal fiber and polyester fiber behave differently. In the case of polyester fiber, the E values vary between 90 and 110 kJ/mol ($\alpha = 0.05 - 0.2$) in the early stages of thermal degradation. The activation energy then becomes progressively greater as the value of α increases up to $\alpha = 0.7$, after reaching a maximum value of about 175 kJ/mol. Finally, the degradation of polyester residue can be identified above $\alpha = 0.85$ as having an E value between 130 and 140 kJ/mol. The values obtained in this study are in reasonable agreement with the values reported by Cooney et al.[15] Meanwhile, the activation energy for polychlal fiber shows a range of values dependent upon the
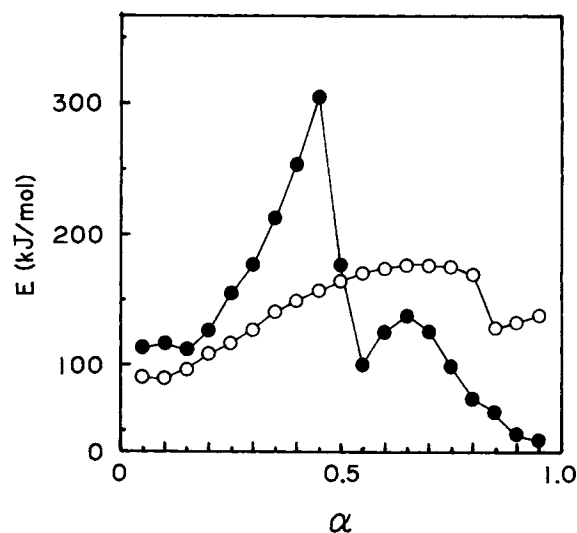
exhibits a melting endotherm at 220°C and a sharp exotherm at 495°C corresponding to combustion of the char. In addition, after the melting endotherm, a small continuous exotherm is observed due to an oxidative reaction of the small amount of the residue that is formed during the first degradation corresponding to dehydrochlorination and dehydration.

At high temperature, DTA curves in an oxidizing atmosphere result in poorly defined curves due to many overlapping reactions. However, polychlal fiber/polyester fiber blends show all the parent endotherms and exotherms with only a slight perturbation in the character of each component fiber degradation. Especially, the exotherm corresponding to combustion of the char residue seems to change with the blend ratio. Exothermic activity in blends occurs following melting, followed by a rise in the curve at about 400°C to a prominent peak at about 500°C. This exotherm, which is nonoxidative in character,

Figure 7 Activation energies as a function of fractional weight loss (α) for ($\bullet$) polychlal fiber and ($\circ$) polyester fiber.

fractional weight loss. Figure 7 shows two stages at α values of 0–0.55 and 0.6–1.0. In the first stage, the E values increase as the value of α increases up to a maximum value of about 260 kJ/mol at $\alpha = 0.45$, then fall rapidly to 100 kJ/mol or so. In the second stage, the degradation of polychlal fiber residue above $\alpha = 0.6$ has an E value rising to 135 kJ/mol and then falling to 40 kJ/mol. These values indicate that the degradation of this fiber is a complex phenomenon.

Although the kinetic data of individual fibers as mentioned above are of interest, the main concern of this study is to determine whether the blending of the polychlal and polyester fibers is responsible for any interaction between the two components or if the weight loss kinetics are simply an additive function of the individual fibers. In the case of the 50/50 polychlal fiber/polyester fiber blend, all TGA curves observed at various heating rates in air atmosphere were, therefore, analyzed to determine the activation energies as a function of fractional weight loss.

Comparison of these calculated curves with experimentally obtained curves is shown in Figure 8 for the 50/50 polychlal fiber/polyester fiber blend. The shape of the experimentally obtained curve is similar to that of the calculated curve, compared with the polychlal fiber/cotton blend in the previous study.[7] However, there is evidence of differences between the experimentally obtained values and those calculated. This figure can be seen to be composed
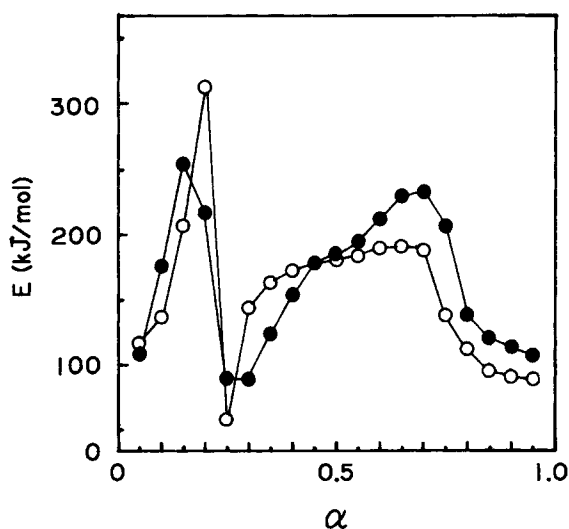
of three main zones: The first zone, up to an α value of 0.3, corresponds primarily to degradation associated with the polychlal fiber weight loss. The second zone, a range of $\alpha = 0.3$–0.7, corresponds to the weight loss associated with the polyester and the degradation residue formed in the first degradation process. The final zone, above 0.7, corresponds to the combustion of the carbonaceous char residue formed through the thermal degradation process.

Thus, kinetically, the blending of the polychlal fiber with the polyester fiber has a slight influence on the degradation of the polyester fiber. The magnitude of these differences in the E values clearly indicates that the presence of the polychlal fiber has significantly altered the kinetics of the polyester degradation or vice versa. This difference of E values is smaller than that observed at polychlal fiber/cotton blend.[7] This phenomenon can be attributed to the weakness of the vapor–solid phase interaction that leads to polyester fiber degradation by volatile products from the polychlal fiber component.

CONCLUSIONS

The flammability measurement and the thermogravimetric analysis of the polychlal fiber/polyester fiber blend using measurements of O.I. values and a conventional dynamic thermogravimetric technique, respectively, are capable of providing valuable information on the flammability behavior of this blend and the kinetics of the thermal degradation processes. The experimentally O.I. values of these blends are significantly lower than the calculated values. This deviation from expected O.I. values is not so simple. These blends show degradation behavior more complex than would be expected from the additive behaviors of the two components. The degradation data provide evidence for chemical interactions during degradation, which may be the reason for the anomalous degradation behavior. In the first degradation stage, the temperature range where this process starts to shift toward the higher temperature side. This effect appears to be due to the polyester melting during the degradation, corresponding to thermal degradation of polychlal fiber, inhibiting the escape of the gaseous pyrolysates. In the case of the polyester fiber degradation, the presence of the polychlal fiber in the blend appears to be responsible for increasing the residue weight occurring at the second degradation stage with a higher activation energy than predicted based upon calculations assuming no interactions.

Figure 8 Activation energies as a function of fractional weight loss (α) for polychlal fiber/polyester fiber (50/50) blend; determined from (●) experimental and (○) calculated weight loss data.

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