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Thermogravimetric analysis on thermal degradation of novoloid fiber/cotton fiber blend

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ABSTRACT

The flammability behavior of a blend fabric cannot be predicted from the flammability characteristics of its component fibers because of the physical or chemical interaction of the thermal degradation products of the blend during heating or combustion. In order to consider the design of flame retardant fabrics from blends of cotton as a flammable fiber and novoloid fiber as a nonflammable and heat-resistant fiber, the thermal degradation of each fiber and blend of fibers were studied using a conventional dynamic thermogravimetric technique in a flowing air atmosphere at several heating rates. Quantitative data are presented which pinpoint how the thermal degradation behavior of this blend differs from that of the components. Comparison of the thermogravimetric curves and calculated kinetic parameters indicates that interactions occur faintly between the novoloid and cotton components in the blends. The thermogravimetric analysis data show two degradation stages in air atmosphere.

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KEYWORDS

Nonflammable and
heat-resistant fiber;
Thermal degradation;
Thermal analysis;
Novoloid fiber.

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^[1,2]. 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. In this area of flammability and flame retardancy, thermal analysis techniques have been widely employed to obtain information regarding the thermal degradation processes and researchers have reported the thermal analytical behaviors of various blended fabrics with and without flame retardants^[3-6]. In all of these studies, the major interest has been to examine the thermal behavior of cottons made flame resistant by treatments with various retardant formulations and of cotton blended with a synthetic flame retardant fiber. However, little consideration has been given to any postulations regarding the

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degradation kinetics based upon the analysis of the magnitude of the temperature of the maximum rate of weight loss as a function of blend composition in flame retardant fiber/cotton blends.

In our previous papers^[7,8], a nonflammable and a flammable fiber blends were degraded and a mechanism was suggested for the interaction between blend fibers: The volatile products formed from a nonflammable fiber degradation at early degradation stages appear to play an important role in retarding the flammability of a flammable fiber. However, in the case of a heat-resistant fiber such as aromatic polyamide fiber, though interactions occurred faintly between cotton fiber and aromatic polyamide fiber, cotton fiber in this blend accelerated the thermal degradation for aromatic polyamide fiber.

In this work, I wish to report on further thermal analysis characterization conducted with a heat-resistant fiber blended with cotton fiber, having a lower degradation temperature than that of a heat-resistant fiber, in order to obtain a better understanding of combustion of these fiber blends and the nature of the interaction between the two components. This work concerns primarily two-component blends including novoloid fiber^[9] as an inherently nonflammable and heat-resistant fiber and cotton fiber as a flammable fiber component. The thermal behavior of these blends was 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^[11,12].

EXPERIMENTAL

Materials

The cotton fiber was absorbent cotton (bleached cotton) of the type delivered in the Japanese Pharmacopeia. In this work, we used Kynol fiber as novoloid fiber, which was produced from phenol-formaldehyde resin as a nonflammable and heat-resistant fiber in Nippon Kynol Inc., Japan^[9]. This fiber, having a limiting oxygen index (L.O.I) value of ca 36, was obtained from Kansai Iseikatsu Kenkyukai, Osaka. Various

blended samples used in thermal analyses were prepared as follows. The fiber samples were cut to less than 2mm long and then dried to a constant weight in a vacuum oven at 50°C. In order to prepare intimate novoloid fiber/cotton fiber blends, both fibers were fully dispersed in the required ratio in methanol, and after filtration the collected samples were dried in a vacuum oven at 50°C.

Limiting oxygen index measurement

The flammability of blended samples was evaluated using the limiting oxygen index (L.O.I) measured using a Suga Test Instruments ON-1. The blend samples for the measurement of L.O.I values were prepared by mixing well novoloid and cotton fibers (fiber length; ca 40mm) in the required weight ratios using hand carding. Conditioning of all samples for 24 h at 20°C and 65% RH was adopted as the standard condition prior to the measurement of L.O.I value.

Thermal analyses

Thermal analyses of premixed samples were performed in a flowing-air atmosphere. Thermogravimetric (TG) and differential thermogravimetric (DTG) experiments were carried out on a Shimadzu TGA-50 thermogravimetric analyzer and differential thermal analysis (DTA) was conducted using a Shimadzu DT-40 thermal analyzer attached to a DTA-40M module. Samples were approximately 8 and 4mg, respectively. The heating rate in the measurements of TG was varied between 2 and 50K/min and in the DTG and DTA measurements, it was 10K/min. The range sensitivity of 500 μ V in the DTA measurements was employed at temperature region of room temperature \sim 700°C. A calcined aluminum oxide as a thermally inert reference substance was used in this work. 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 moisture weight loss.

RESULTS AND DISCUSSION

L.O.I. values of novoloid fiber /cotton fiber blends

This study concerns primarily two-component

blends including an inherently nonflammable and a flammable fiber component. In our previous papers^[7,8], the mechanism of flame retardancy of fiber blends was reported by using L.O.I measurement and thermoanalytical techniques. The values of L.O.I. are used to provide a measurement of relative flame retarding efficiency of novoloid fiber/cotton fiber blends. In figure 1, the values of L.O.I. are plotted vs. the composition of novoloid fiber/cotton fiber blends. The average values of L.O.I. for the two-component blends measured are represented by the dashed line connecting the points for the two pure components (novoloid fiber and cotton fiber). In these blends, the experimental values of L.O.I. are lower than the average values. This negatively deviating effect from the expected values of L.O.I. suggests that the combustion of cotton fiber as a flammable material plays an important role in the combustion of these blends and a interaction between these fibers is difficult to take place. The amount of novoloid fiber required for value of L.O.I. of ca. 26 (assumed to be indicative of self-extinguishing behavior in the vertical test) is approximately 65% for blends with cotton fiber. From these observations, especially in blends with large amounts of cotton fiber, novoloid fiber apparently does not have any dramatic effect on the flammability of this blend. The burning behavior of blended fiber is considered to be complex and the question of the nature of possible component fiber interaction remains open.

Thermogravimetric analysis

The thermogravimetric weight loss (TG) and differential thermogravimetric (DTG) curves of novoloid fiber and cotton fiber are shown in figure 2, employing a 10 K/min heating rate in air atmosphere. Cotton fiber degraded into two stages, the first weight loss centered taking place at 300~370°C, where ca. 70% of weight was degraded, and the carbonized residue was gradually lost by 520°C at the second stage. On the other hand, the degradation temperature of novoloid fiber was very much higher than that of cotton fiber because of a heat-resistant fiber, and the TG curves in figure 2 shows that this degradation was gradually generated by the one step having a small shoulder peak observed in DTG curve. It can be seen that the degradation temperature of novoloid fiber was 350°C to 590°C, and the degra-

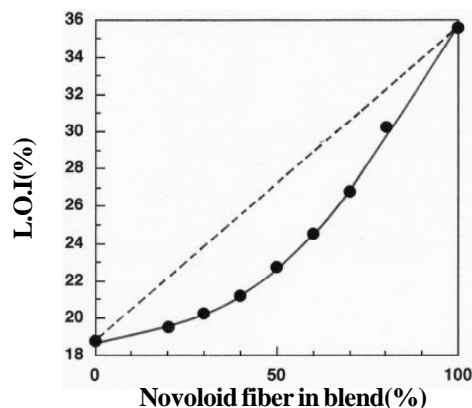


Figure 1 : L.O.I. values of novoloid fiber/cotton fiber blend as a function of novoloid fiber content

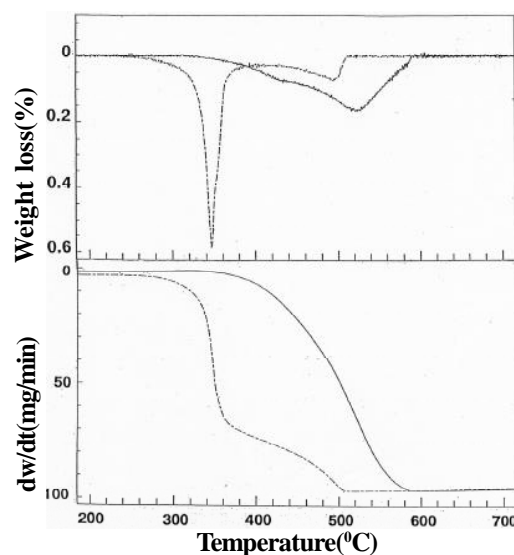


Figure 2 : Thermogravimetric and differential thermogravimetric curves for novoloid fiber (solid line) and cotton fiber (broken line) at a heating rate of 10 K/min in air atmosphere

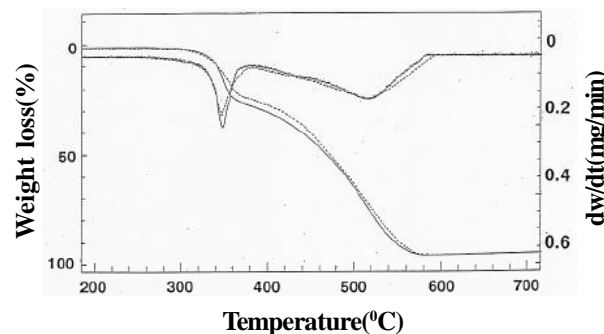


Figure 3 : Experimentally determined (solid line) and calculated (broken line) thermogravimetric and differential thermogravimetric curves for novoloid fiber/cotton fiber (70/30) blend determined at a heating rate of 10 K/min in air atmosphere

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gradation in this interval reached about 100% weight loss of its original weight.

Indication of interaction during thermal degradation at low heating rates can be obtained using conventional thermoanalytical techniques^[12,13]. Comparison of experimentally observed weight loss curves with its calculated curves is shown in figures 3-5, along with the differential thermogravimetric curves (DTG) of each of the three blends studied. These fiber blends are observed to degrade in two distinct stages though the thermal degradation process. The first weight loss centered around 340°C and the second weight loss occurring at 400~590°C correspond mainly to the thermal degradation of cotton and novoloid fiber, respectively. The calculated curves were calculated from individual TG and DTG data of novoloid fiber and cotton fiber by assuming no interaction between each component during thermal degradation. If no interaction was occurring between the novoloid fiber and cotton fiber in the blends, the experimental and calculated curves should coincide. The fact that differences are observed, as well as aromatic polyamide/cotton fiber blends reported in a previous paper^[8], suggests that some form of interaction must be taking place between the two blended fibers. Figures 3-5 reveal that these blended samples have two distinct stages through the thermal degradation process. Apparently, each temperature of the two degradation stages observed in these fiber blends does not shift significantly compared with that of novoloid fiber and cotton fiber. The first weight loss, centered around 340°C and dependent upon the amount of cotton fiber in the blend, mainly corresponds to thermal degradation of cotton fiber in blends. But it will be noted that the amount of weight loss in the thermal degradation process has increased from the calculated values, with the differences being largest for those blends having the largest cotton fiber content. This result suggests that the presence of cotton fiber in the blend influences the degradation of novoloid fiber component in the blend. This increased weight loss from the calculated values occurs because the degradation of novoloid fiber in the blend is accelerated by the heat rather than the volatile products generated with the degradation of cotton fiber. Thus, the difference between the experimental and calculated weight losses becomes gradually larger as the cotton component is raised in the blend. The second stage

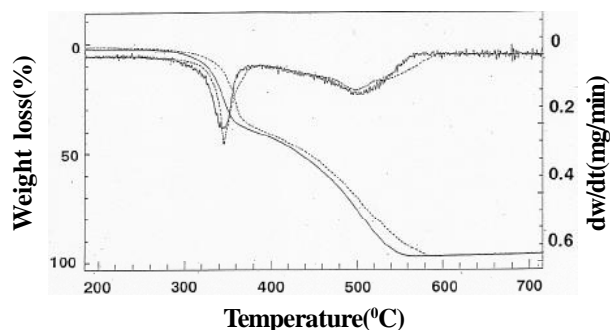


Figure 4. Experimentally determined (solid line) and calculated (broken line) thermogravimetric and differential thermogravimetric curves for novoloid fiber/cotton fiber (50/50) blend determined at a heating rate of 10 K/min in air atmosphere

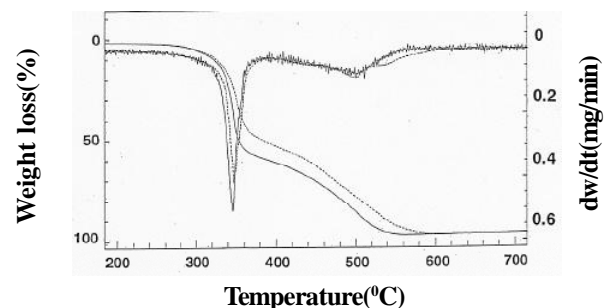


Figure 5 : Experimentally determined (solid line) and calculated (broken line) thermogravimetric and differential thermogravimetric curves for novoloid fiber/cotton fiber (30/70) blend determined at a heating rate of 10 K/min in air atmosphere

corresponds to the degradation of novoloid fiber which will remain till the thermal degradation temperature of its fiber as the interaction in this blend is smaller. However, detailed interpretation of the thermal analysis of the fiber blends is rather complicated because the thermal behaviour of these blend is more complex.

Differential thermal analysis

Indication of interactions during thermal degradation at low heating rates can often be obtained using conventional thermoanalytical techniques. Differential thermal analysis (DTA) was performed to investigate the behavior of fiber blends and particularly to ascertain the role of thermal resistance fiber. Figure 6 shows DTA curves for heating in air atmosphere from temperature to 600°C for novoloid fiber, cotton fiber, and novoloid fiber/cotton fiber blends. In the DTA measurements in an oxidizing atmosphere, the PR fiber exhibits a shoulder exothermic peak of oxidative reaction

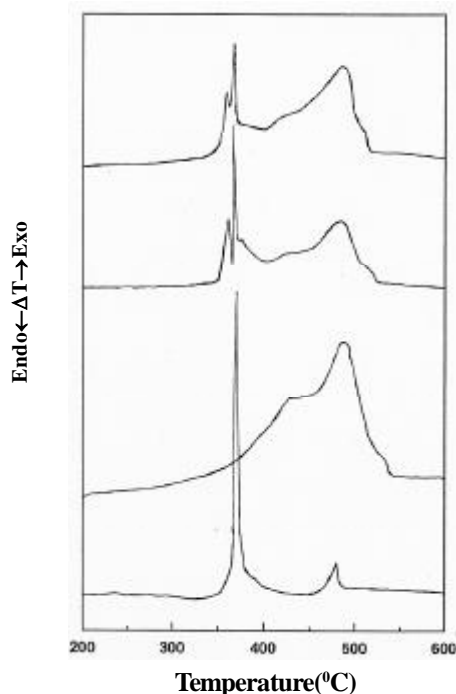


Figure 6 : DTA curves of novoloid fiber/cotton fiber blend determined at a heating rate of 10K/min in air atmosphere: (1) 0/100, (2) 100/0, (3) 30/70, (4) 50/50 novoloid fiber/cotton fiber blend from the DTA curve of the bottom

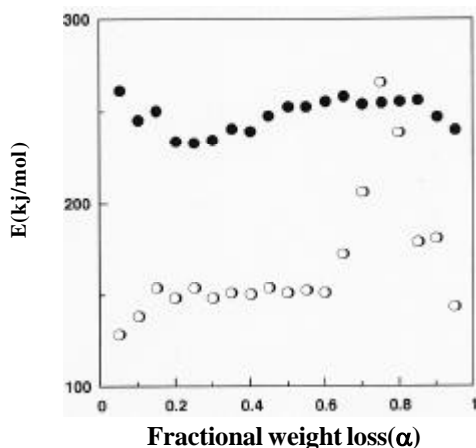


Figure 7. Activation energies as a function of fractional weight loss (α) for (λ) PR fiber and (μ) cotton fiber

at 430°C corresponding to a small shoulder peak as seen in DTG curve (Figure 2.) and afterwards a large exothermic peak centered at 490°C based on combustion of the residues. The DTA curve of cotton fiber is characterized by a large exothermic peak at about 360°C corresponding to combustion of the char generated by the thermal degradation of cotton fiber^[14]. It is well known that for heat-resistant fiber and cellulose,

generally, the DTA pattern is mostly the result of overlapping melting and degradation heat effects, as these polymers melt at a temperature higher than the temperature at which the thermal degradation begins^[15]. That is to say, the endothermic peak based on melting of these polymers does not appear on the DTA curve. The DTA curves for novoloid fiber/cotton fiber blends show the exothermic peak at about 360°C with very difference in the character of each component fiber degradation. At this temperature region, two peaks are observed in the presence of novoloid fiber and these peaks seem to change with the blend ratio. This result indicates that these DTA curves constitute evidence of any interaction between novoloid fiber and cotton fiber occurring in this fiber blend. Thus the increase of weight loss from calculated TG curves in experimentally determined TG curves of novoloid fiber/cotton fiber blends occurs because the combustion heat of cotton fiber at the first degradation stage is influencing the thermal degradation of novoloid fiber component in the blend. However, it should be noted that the DTA responses are not easy to interpret in detail. At high temperature, a large exotherm mainly corresponds to combustion of novoloid fiber component in the blend causing the weight loss in TG curves, and this exothermic peak becomes progressively greater as the ratio of novoloid fiber in blends is increased.

Evaluation of activation energy from TGA

The determination of kinetic parameters such as activation energy from thermogravimetric data has received considerable attention. The calculated apparent activation energies (E) for the various stages of thermal degradation of novoloid fiber and cotton fiber were determined from the TG curves using the method described by Flynn and Wall^[10]. This method was used because it yields activation energies without the necessity of assuming a possibly incorrect model for the reaction mechanism^[16,17]. All TG curves measured at various heating rates in a flowing-air atmosphere were therefore analyzed to determine the activation energies as a function of fractional weight loss. Plots of activation energy (E) versus fractional weight loss (α for PR and cotton fibers) are presented in figure 7. This figure shows that the activation energies associated with the weight loss of these fibers behave differently. The behavior of

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cotton fiber in this work is approximately the same as that in our previous paper. In the case of novoloid fiber, the E values vary between 90 and 140 kJ/mol ($\alpha=0.05\sim 0.25$) in the early stage of thermal degradation, where it appears as a shoulder on DTG curve of novoloid fiber in figure 2. The activation energy then becomes progressively greater as the value of α increase up to $\alpha=0.8$, after reaching a maximum value of about 160kJ/mol. Finally, the degradation of novoloid fiber residue can be identified above $\alpha=0.8$ as falling to around 140kJ/mol.

Although the kinetic data of individual materials as mentioned above are of interest, the object of this work is to determine whether the blending of novoloid and cotton fibers is responsible for any interaction between the two components or if the weight loss kinetics are simply an additive function of the individual materials. In this blend, the TG curves were displaced to higher temperatures due to the heat transfer lag with increased heating rate. In the 50/50 novoloid fiber/cotton fiber blend, all TG curves measured 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 E values with experimentally obtained E values at various fractional weight loss (α) are presented in figure 8. In all cases, differences are observed in the E for values obtained experimentally in comparison with calculated values, with the differences being dependent upon the composition of the blend and the fractional weight loss

(α) examination of this figure reveals two zones—one occurring at fractional weight loss (α) of 0–0.4 and the other for values greater than 0.4. In the first zone corresponding to the first weight loss at TG curves, the E values become progressively greater as the fractional weight loss (α) increases. After reaching a maximum value, the E value falls rapidly to 100kJ/mol at $\alpha=0.4$. But this sudden drop takes place at $\alpha=0.65$ in the calculated E values. In the second zone, the degradation of this blend residue above $\alpha=0.65$ has an E value rising about 140kJ/mol, corresponding primarily to the combustion of the carbonaceous char residue formed through the thermal degradation process, and the experimentally observed E values in the second zone are lower than the calculated E values. The magnitude of these differences clearly indicates that the presence of cotton fiber has significantly altered the kinetics of novoloid fiber degradation or vice versa. Since it appears that this difference of E values can be observed especially during the first stages of the weight loss (the first zone), it may be postulated that the cotton fiber component is producing the degradation heat responsible for the interaction. Further studies on the detailed mechanism of the degradation of this blend are now in progress, including the measurements of kinetic parameters and the kinetic compensation relationship.

CONCLUSIONS

The flammable measurement and the thermal analysis of the novoloid fiber/cotton fiber blend using a conventional dynamic thermogravimetric technique, are capable of providing valuable information on the kinetics of the thermal degradation processes. The experimentally L.O.I. values of these blends are significantly lower than the calculated values. This deviation from expected L.O.I. values is not so simple. The degradation data provide evidence for any chemical interactions during degradation, which may be the reason for anomalous degradation behavior. These blends cause changes in the weight loss curves associated with the thermal degradation of the individual components from those calculated by averaging. These changes have supplied evidence for any possible interactions occurring in novoloid fiber-cotton systems, which emphasize the difficulty in accounting for the thermal degradation of this blend. In

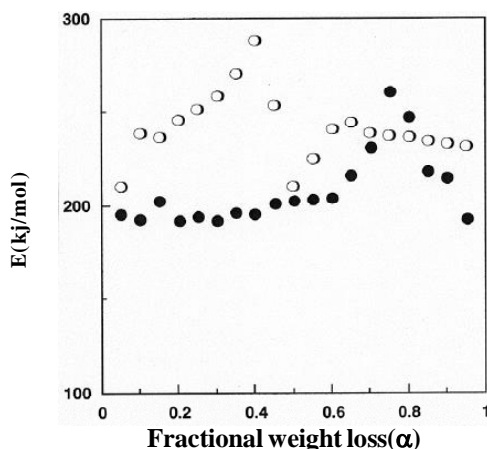


Figure 8. Activation energies as a function of fractional weight loss (α) for novoloid fiber/cotton fiber (50/50) blend: determined from (μ) experimental and (λ) calculated weight loss data

these blends, the cotton fiber starts to lose weight at a lower temperatures and accelerates the thermal degradation for the novoloid fiber. The cotton fiber appears to play an important role in the degradation of novoloid fiber in the blend, that is, the combustion heat of the cotton fiber at a low temperature accelerates the subsequent weight loss of the novoloid fiber occurring which appears at a lower temperature and with a higher activation energy than predicted based upon calculations assuming no interactions. On the other hand, the changes of activation energy according to the fractional weight loss suggest that the inherent degradation mechanism exists at each degradation temperature during the thermal degradation process. The blend shows a degradation behavior more complex than would be expected from the additive behaviors of the two components.

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