Thermal Decomposition of Cellulose/Synthetic Polymer Blends Containing Grafted Products. II. Cellulose/Polyacrylonitrile Blends

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SYNOPSIS

The homogeneous grafting of acrylonitrile onto cellulose was carried out in a dimethyl sulfoxide/paraformaldehyde solvent system. The grafted products were added to cellulose/ polyacrylonitrile (PAN) blends as compatibilizers. The thermal decomposition behavior of the blends was investigated by thermogravimetry. The thermal stability of the blends with higher grafted product content was lower by more than 100°C than that of the blends without grafted product. The accessibility values of the former blends were larger than those of the latter. The microphase-separated structures of the grafted product blends were finer than those without the product. Dynamic mechanical measurements and differential scanning calorimetry were performed to estimate the glass transition temperatures, T_g, of the blends. The variation in T_g was smaller than that in characteristic temperatures determined by thermogravimetry. The difference in thermal decomposition behavior was correlated to that in compatibility. Thermogravimetry was found to be effective for estimating the compatibility in cellulose/PAN blends containing grafted products. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The homogeneous grafting of vinyl monomers onto cellulose in a dimethyl sulfoxide/paraformaldehyde (DMSO/PF) solvent system was carried out under various conditions to characterize the grafted products.[1-4] In grafting, a graft copolymer and attendant homopolymer are synthesized simultaneously. A fraction of cellulose not participating in grafting also remains.[5] The as-grafted products thus are polymer blends containing graft copolymers as compatibilizers. We have already reported the thermal decomposition behavior of the as-grafted cellulose products.[6,7] The thermal stability of the grafted products depended on their graft copolymer content. The difference in thermal stability of the grafted products was correlated to that in compatibility. The thermal

stability of vinyl monomer grafted cellulose has been investigated by many workers.[8-13] Grafting, however, was carried out in a heterogeneous reaction system and attendant homopolymers were extracted. No investigation has correlated the thermal stability of grafted cellulose to the compatibility in its constituents.

The compatibility in polymer blends can be estimated from their glass transition temperatures, T_g.[14] However, cellulose does not undergo a clear glass transition. The variation in thermal decomposition behavior of the blends containing cellulose must be correlated more precisely with that in compatibility. Thermal decomposition behavior then will become a novel measure for compatibility estimation. It is, however, troublesome to synthesize the grafted products with different graft copolymer contents. In a recent article,[15] the methyl methacrylate grafted cellulose products themselves thus were added to cellulose/poly(methyl methacrylate) blends as compatibilizers. In this work, acrylonitrile

(AN) grafted cellulose products were added to cellulose/polyacrylonitrile (PAN) blends to vary graft copolymer content widely.

EXPERIMENTAL

Grafting and Sample Preparation

The homogeneous grafting of AN onto cellulose in a DMSO/PF solvent system and characterization of the grafted products were performed by the method described in our previous works.[1-4] The grafted products are characterized in Table I. Grafting efficiency (GE) is defined as the ratio of the amount of grafted monomer to that of polymerized monomer. In homogeneous grafting, the molecular weight of the graft polymer is presumed to be equal to that of the attendant homopolymer.[5] We have already confirmed that both molecular weights are consistent with each other within experimental error.[2,4] The viscosity-average molecular weights, M_v, of the extracted PAN thus were used as those of the graft polymers. The values of M_v of cellulose and PAN used for the blends were estimated to be 146 $\times 10^3$ and 160 $\times 10^3$ from the intrinsic viscosities obtained with cadoxen[16] at 20°C and DMF[17] at 25°C, respectively.

The crude reaction mixtures and the DMSO solutions of cellulose and PAN were mixed to give proper blend ratios. The mixtures were cast onto glass plates at room temperature and dried at about 40°C under reduced pressure for 24 h. After being immersed in water for several days, the samples were easily peeled off. The samples were air dried on filter paper at room temperature and stored in a desiccator until use.

Thermal Analysis

A Seiko SSC5000TA with a TG/DTA300 module was used for thermal decomposition measurements. The measurements were carried out from room temperature to 600°C at a heating rate of 10°C/min under nitrogen atmosphere flowing at 100 mL/min. The samples (ca. 15 mg) were preheated to 150°C under the conditions described above to evaporate adsorbed water.

Differential scanning calorimetry (DSC) was performed with a Seiko SSC/560S DSC. The samples (ca. 20 mg) were heated from 20° to 200°C at a rate of 20°C/min. Because the first scan showed a broad endotherm due to the presence of adsorbed water, the measurements were repeated several times. The reported T_g values are the average values based on the second and subsequent scans.

Dynamic Mechanical Measurement

The dynamic mechanical measurements were conducted from −150° to 220°C at a frequency of 11 Hz with an Orientec Rheovibron DDV-II-C viscoelastometer. The samples (ca. 20 × 2 × 0.01 mm) were dried at about 40°C under reduced pressure for more than 24 h prior to measurements.

Accessibility

The samples (ca. 5 × 5 × 0.01 mm) were dried over P_2O_5 under reduced pressure for 24 h at room temperature, immersed in D_2O for 4 h, and then dried again under reduced pressure for 24 h. Infrared spectra were measured with a Hitachi EPI-G3 spectrophotometer by placing the samples between NaCl plates with hexachlorobutadiene.[18] Accessibility, A, was calculated according to the equation[19]:

Table I   Characterization of Grafted Products

| | | PAN Content (wt %) | | | | |
Sample Code	GE (%)	Overall	Graft Polymer	Homopolymer	$M_v \times 10^{-3}$ of Graft[a]	No. Grafts
g-PAN 6	77.4	35.5	27.5	8.0	27	2.3
g-PAN 7	90.1	20.1	18.1	2.0	12	2.8
g-PAN 8	95.5	26.4	25.2	1.2	13	4.0
g-PAN 9	97.8	30.5	29.8	0.7	22	2.0

The viscosity-average molecular weight, M_v, of backbone cellulose is 146 × 10³.
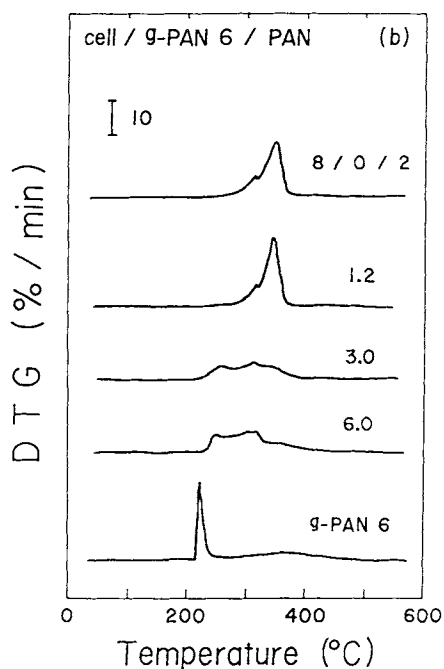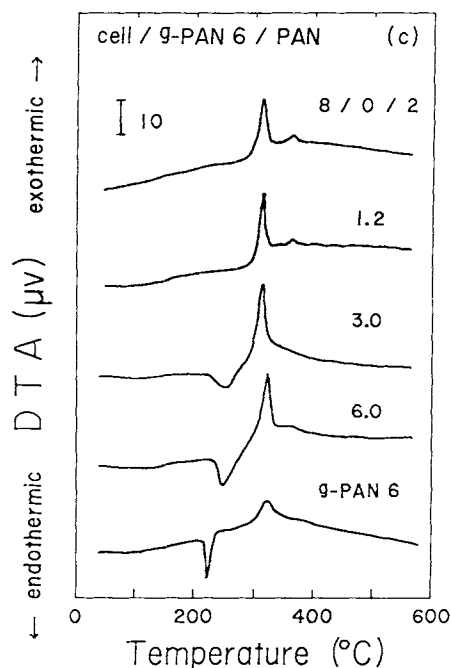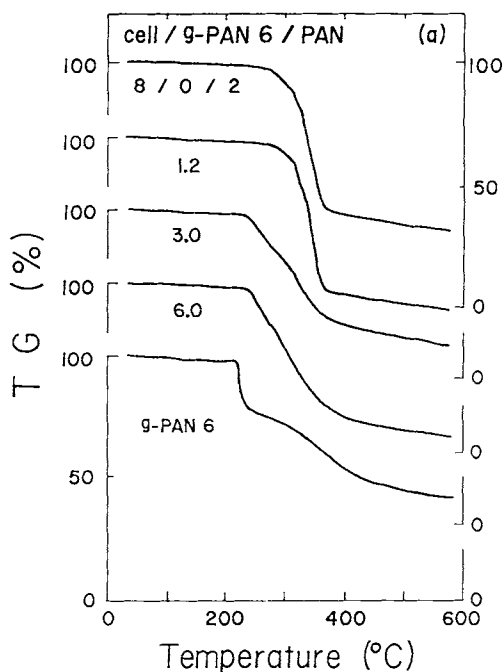[a] M_v of the extracted homopolymer was used as that of the graft polymer.

Figure 1 (*Continued*)

Transmission Electron Microscopy (TEM)

A Hitachi HU-11A transmission electron microscope was used to observe the microphase-separated structures of the samples. The samples were stained with osmic acid vapor for 24 h. The copolymer of

Figure 1 Thermograms of the grafted product (*g*-PAN 6) and 8/2 cellulose/PAN blends containing *g*-PAN 6: (a) thermogravimetric (TG) curves; (b) derivative thermogravimetric (DTG) curves; (c) differential thermal analysis (DTA) curves.

$$A = 100/\{1 + 1.11(A_{OH}/A_{OD})\}$$

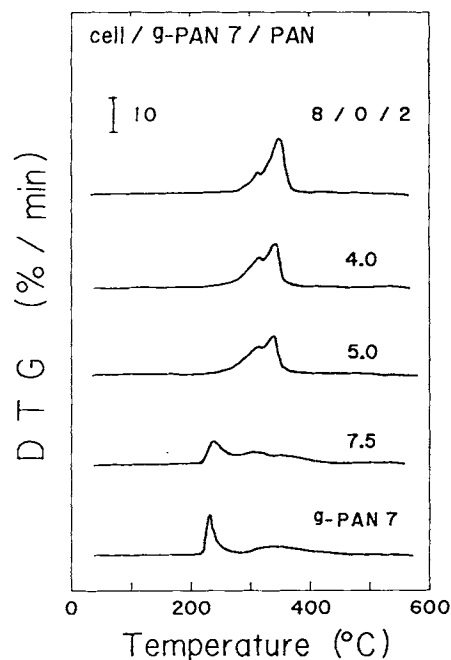where A_{OH} and A_{OD} are the absorbances at 3360 and 2530 cm^{-1}, respectively.

Figure 2 DTG curves of the grafted product (*g*-PAN 7) and 8/2 cellulose/PAN blends containing *g*-PAN 7.
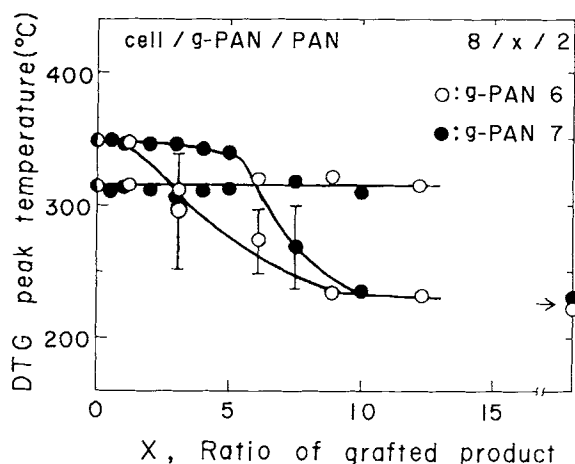
Figure 3 Dependence of the DTG peak temperatures for the 8/2 cellulose/PAN blends containing different grafted products on the grafted product content: (O) g-PAN 6; (●) g-PAN 7; (◐) 8/2 cellulose/PAN blend.

Figure 5 Dependence of the DTG peak temperatures for the cellulose/PAN blends with different compositions on g-PAN 7 content: (O) 8/×/2 cellulose/g-PAN 7/PAN blend; (●) 6/×/4 cellulose/g-PAN 7/PAN blend; (◐) g-PAN 7.

n-butyl methacrylate and methyl methacrylate was used as an embedding medium. The embedded samples were cut into ultrathin sections of approximately 50-nm thickness.

RESULTS AND DISCUSSION

Figure 1(a) shows the thermogravimetric (TG) curves of the grafted product (g-PAN 6) and cellulose/PAN (8/2 by weight) blends containing different amounts of g-PAN 6. The weight loss for the blend (cellulose/g-PAN 6/PAN = 8/0/2) without
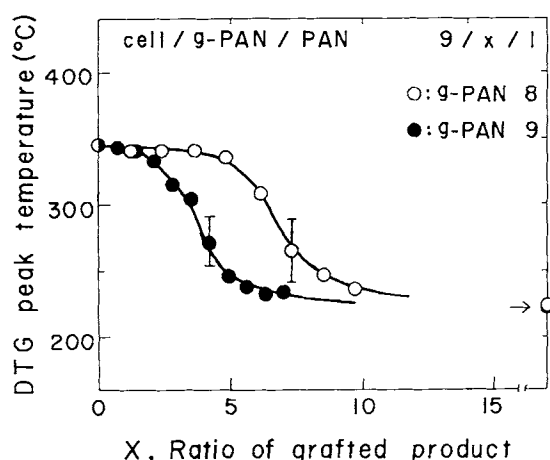
g-PAN 6, amounting to about 60%, is observed over the temperature range of 300°–360°C followed by a gentle weight loss. The residual weight percent at 600°C is about 30%. On the other hand, the weight of g-PAN 6 decreases sharply by about 20% at around 220°C followed by about 30% weight loss up to 400°C. The residual weight percent at 600°C is about 40%. The decomposition behavior of the blend (8/1.2/2) containing 1.2 parts of g-PAN 6 is almost similar to that of the blend (8/0/2). However, the decomposition of the blend (8/3.0/2) starts gradually from around 240°C.

Figure 4 Dependence of the DTG peak temperatures for the 9/1 cellulose/PAN blends containing different grafted products on the grafted product content: (O) g-PAN 8; (●) g-PAN 9; (◐) 9/1 cellulose/PAN blend.
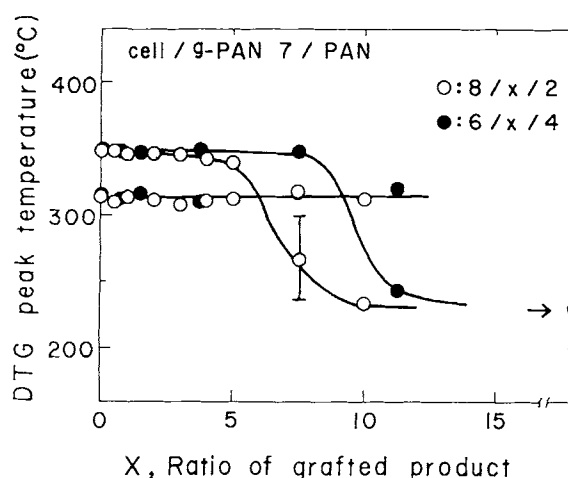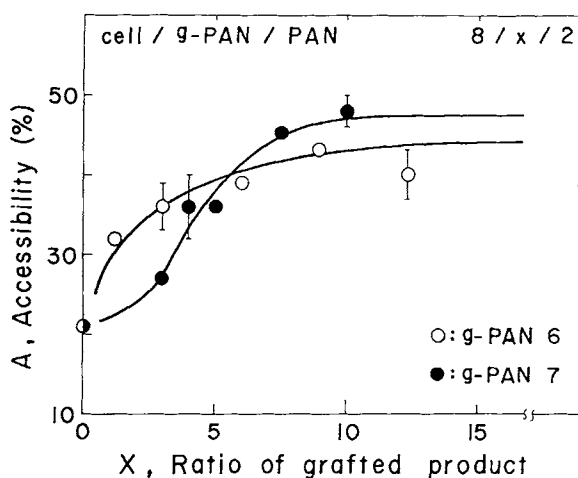

Figure 6 Dependence of accessibility for the 8/2 cellulose/PAN blends containing different grafted products on the grafted product content: (O) g-PAN 6; (●) g-PAN 7; (◐) cellulose; (◑) 8/2 cellulose/PAN blend.
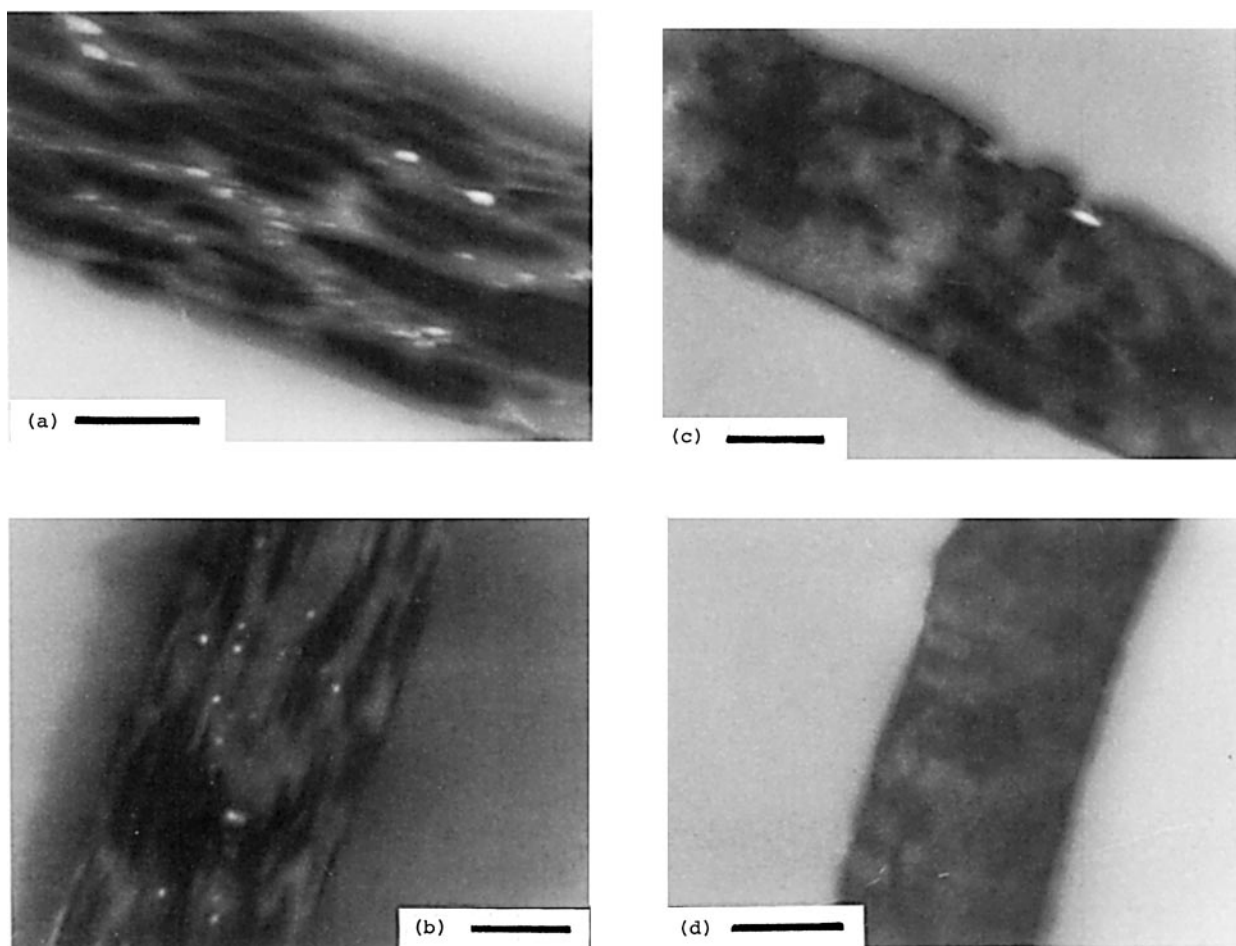
Figure 7 TEM micrographs of g-PAN 6 and 8/2 cellulose/PAN blends containing g-PAN 6: (a) 8/0/2; (b) 8/1.2/2; (c) 8/3.0/2; (d) 8/6.0/2; (e) 8/9.0/2; (f) g-PAN 6. Scale bar = 5 μm.

The difference in thermal decomposition behavior of these samples can be seen more clearly from the derivative thermogravimetric (DTG) curves shown in Figure 1(b). The decomposition rate of the 8/0/2 blend has two peaks at 314° and 348°C, indicating the presence of different thermal decomposition processes. As indicated in our previous work,[6] the peaks at lower and higher temperatures result mainly from the decomposition of PAN and cellulose fractions, respectively. We use these peak temperatures as a measure of thermal stability. The DTG curves of g-PAN 6 show a sharp peak at 222°C and a broad peak at around 360°C. The difference in thermal stability of these two samples is obvious. The peak temperatures of the 8/1.2/2 blend are almost equal to those of the 8/0/2 blend. The peak at around 350°C for the 8/3.0/2 blend becomes small and a new small peak appears at around 260°C, but the peak at around 314°C still exists. The peak at around 350°C for the 8/6.0/2 blend almost disappears.

Figure 1(c) illustrates the differential thermal analysis (DTA) curves of the same samples. The 8/0/2 blend has a sharp exothermic peak at 314°C associated with the conversion of the cyano group in PAN to the isocyano group.[20] The endothermic peak for the decomposition of cellulose fraction[6,21] is not observed by overlapping of a sharp exothermic peak. The endothermic peak of g-PAN 6 is recognized at 214°C. The DTA curve of the 8/1.2/2 blend is similar to that of the 8/0/2 blend. The 8/3.0/2 blend has a small endothermic peak at around 250°C. The endothermic peak of the 8/6.0/2 blend shifts toward lower temperatures. The exothermic peak at around 314°C is observed for all samples but hardly shifts. We also use these peak temperatures as a measure of thermal stability. It is clear that the increase in g-PAN 6 con-
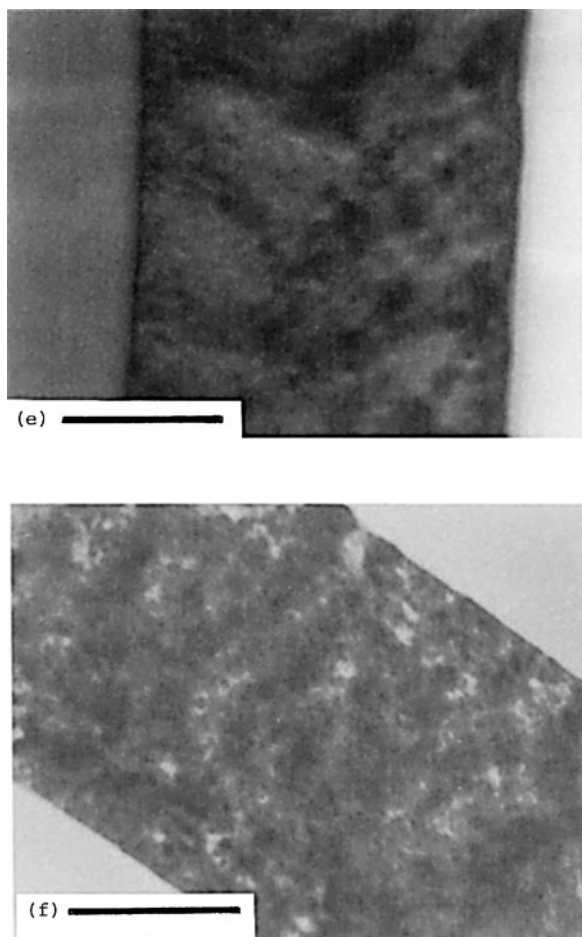
Figure 7 *(Continued from previous page)*

tent makes the cellulose/PAN blend thermally unstable.

Figure 2 also indicates the thermograms of the 8/2 cellulose/PAN blends containing another grafted product (g-PAN 7). The DTG peak temperature of g-PAN 7 is 314°C, implying similar thermal stability to g-PAN 6. The thermal decomposition behavior of the 8/5.0/2 blend is almost equal to that of the 8/0/2 blend, being different from the result shown in Figure 1.

The dependence of the DTG peak temperatures on the grafted product content is revealed in Figure 3. The peak temperature at around 320°C is almost independent of the amount and kind of grafted products, suggesting no influence on the thermal stability of the PAN fraction. On the other hand, the peak temperature for the cellulose fraction decreases at a certain amount of grafted product. The amount of grafted product required to reduce the thermal stability of the 8/2 cellulose/PAN blend depends on the kind of grafted products. The addition of g-PAN 6 is more effective than that of g-

PAN 7. As can be seen from Table I, the graft copolymer content of g-PAN 6 is larger than that of g-PAN 7.

Figure 4 also indicates the grafted product content dependence of DTG peak temperatures for the 9/1 cellulose/PAN blends containing g-PAN 8 or g-PAN 9. The DTG peak for the PAN fraction was scarcely recognized at around 320°C because of a small amount of PAN. The amount of grafted product required to reduce the thermal stability of the 9/1 cellulose/PAN blend also depends on the king of grafted products. The addition of g-PAN 9 is more effective than that of g-PAN 8. This result is also consistent with the data indicated in Table I.

The amount of g-PAN 7 required to influence the thermal stability of the cellulose/PAN blends with different compositions is compared in Figure 5. The peak temperature at around 320°C hardly depends on the amount of g-PAN 7 and cellulose/PAN composition, being similar to the result shown in Figure 3. The peak temperature for the cellulose fraction of the 8/2 cellulose/PAN blends decreases over the concentration range 5–7, but that of the 6/4 cellulose/PAN blends decreases over the range 7–11. The 8/2 cellulose/PAN blend is more sensitive to the addition of g-PAN 7. Comparison of Figures 3, 4, and 5 indicates that the amount of grafted product required to reduce the thermal stability of cellulose/PAN blends depends on both the kind of grafted products and cellulose/PAN composition. Moreover, it should be noted that the thermal stability of the cellulose fraction in the blends is mainly influenced.

In Figure 6 the value of accessibility determined by a deuteration method is plotted against the grafted product content. The value of a cellulose sample cast from a DMSO/PF solution is also indicated.[22] The accessibility is defined as the ratio of the number of hydroxyl groups reacted with a reagent to that of total hydroxyl groups. The accessibility value is a measure of crystallinity of the cellulose fraction: higher accessibility values correspond to lower crystallinity.[19,23,24] The values of the grafted products are larger than that of a cellulose sample, indicating that the PAN chains hinder the crystallization of cellulose chains to result in an increased fraction of free hydroxyl groups. The accessibility value increases with the increase in grafted product content and attains a constant value. Such an increase in accessibility value corresponds to the decrease in DTG peak temperature shown in Figure 3. The thermal stability of cellulose mainly depends on its crystallinity.[25,26] Therefore, the decrease in thermal stability of the blends is attributable to that in crystallinity of the cellulose fraction.

Figure 7 shows the TEM micrographs of g-PAN 6 and 8/2 cellulose/PAN blends containing various amounts of g-PAN 6. The dark domains indicate the cellulose phases stained with osmic acid. In micrographs (a) and (b), spherical white domains and ellipsoidal dark domains are dispersed in the gray matrix. The interfaces between both phases are clear, indicating poor compatibility of cellulose with PAN in these blend. The microphase-separated structure of g-PAN 6 is very fine and the interfaces between cellulose and PAN phases are not clear, indicating good compatibility of cellulose with PAN in this sample. The gray matrix may be miscible regions, but the change in microphase-separated structures with the addition of g-PAN 6 is obvious. A comparison of TEM micrographs with thermal decomposition behavior shown in Figure 1 indicates that the thermal stability of the blends with fine microphase-separated structures decreases remarkably. The fine microphase-separated structures and large accessibility values imply good compatibility of cellulose with PAN in the blends. Therefore, it is suggested that the thermal stability of the blends with good compatibility decreases remarkably. In
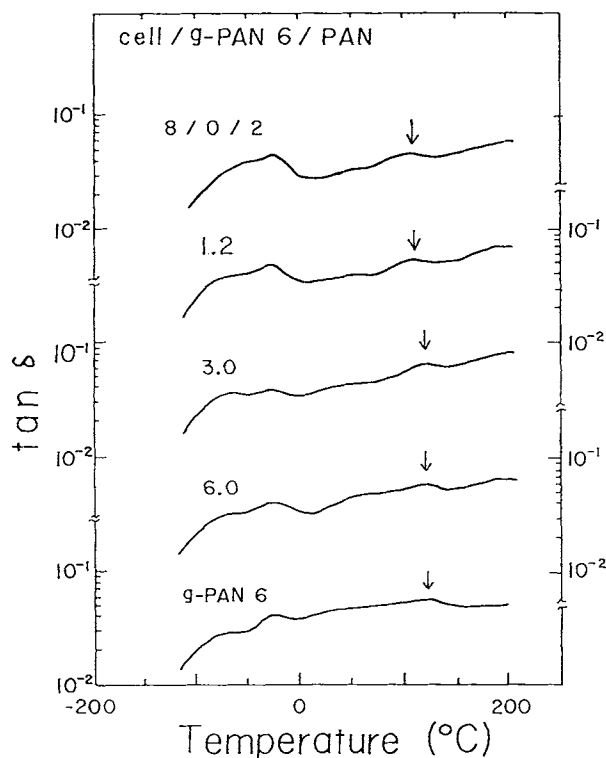

Figure 9 DSC thermograms for 8/2 cellulose/PAN blends containing g-PAN 6.

Figure 8 Temperature dependence of mechanical loss tangent for 8/2 cellulose/PAN blends containing g-PAN 6. The arrow shows the position of T_g.

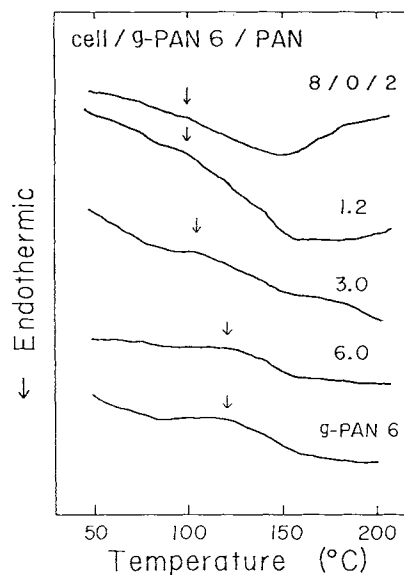our work, the word "compatibility" does not refer to miscibility on a molecular level.

As mentioned above, the compatibility in polymer blends is estimated from their glass transition temperatures.[14] However, cellulose does not undergo a clear glass transition. A difficulty in determining T_g for blends containing cellulose has been reported.[6,7,15,27-29] Figure 8 shows the temperature dependence of the mechanical loss tangent for the 8/2 cellulose/PAN blends containing g-PAN 6. The broad peak at around $-40°C$ is assigned to the relaxation caused by a motion of methylol groups in the glucose residues.[30-33] The small relaxation peak at around 110°C corresponds to the glass transition of the PAN fraction.[6,34] The peak temperature shifts slightly toward higher temperatures with the increase in g-PAN 6 content. However, the amount of temperature shift is at least 20°C, and the determination of peak temperature is not so easy. The DSC curves of the same samples are depicted in Figure 9. The determination of T_g is less sensitive than dynamic mechanical measurements. The T_g value shifts toward higher temperatures with the increase in grafted product content. The shift in T_g values of the blends represents the change in their compatibility by the addition of grafted product. The difference in thermal decomposition behavior of the cellulose/PAN blend containing grafted products thus can be correlated to that in compatibility. The partial compatibility in cellulose/PAN blends has been reported.[27,35,36] The reported T_g value for the
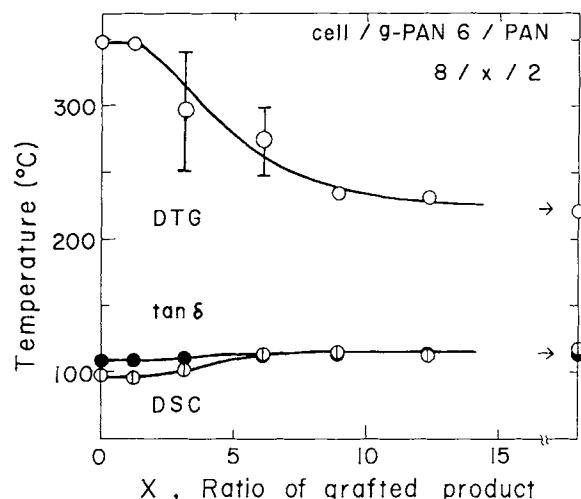
Figure 10 Comparison of characteristic temperatures determined by three kinds of measurements: (O) DTG peak; (●) loss tangent peak; (Φ) DSC.

8/2 cellulose/PAN blend prepared from a N,N-dimethylacetamide/lithium chloride solution system is higher than our result.[27] The difference in sample preparation method will be considered.

Figure 10 compares the characteristic temperatures determined by three kinds of measurements. The DTG peak temperature obtained by thermogravimetry changes by more than 100°C, whereas the glass transition temperatures determined by dynamic mechanical and DSC measurements change only by about 20°C. It should be noted that the variation in characteristic temperature determined by thermogravimetry is the largest among those in these three kinds of temperatures, and its determination is not so difficult. Therefore, thermogravimetry is found to be effective for estimating compatibility in cellulose/PAN blends.

As indicated in our previous study,[6] the depression of thermal stability was not found for the miscible polymer blend composed of the amorphous polymer pair, poly(vinyl acetate) and poly(methyl acrylate). It is known that the thermal stability of polymers depends mainly on their crystallinity.[25,26,37] Any change in thermal stability is not expected for blends composed of amorphous polymer pairs. The compatibility estimation by thermogravimetry may be a characteristic method for blends containing cellulose as one component. The miscibility in cellulose/synthetic polymer blends has been reported.[27-29,31,38,39] The thermal decomposition behavior of these miscible cellulose/synthetic polymer blends is now under investigation.[40] Some blends indicate a similar decrease in thermal stability, but

other blends do not. The difference in thermal decomposition behavior of the blends containing cellulose must be correlated thoroughly to that in compatibility. Moreover, the relationship between the compatibilizing effect of graft copolymers and their structures must be elucidated.

In conclusion, the AN grafted cellulose products were added to cellulose/PAN blends as compatibilizers. The thermal decomposition behavior, accessibility values, T_g values, and microphase-separated structures of the blends were investigated. The difference in thermal stability was correlated to that in compatibility. Thermogravimetry was found to be effective for estimating the compatibility in cellulose/PAN blends containing grafted products.

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