Thermal Decomposition of Cellulose/Synthetic Polymer Blends Containing Grafted Products. 1. Cellulose/Poly(methyl methacrylate) Blends

Noboru Nishioka,* Masayuki Yamaoka, Hiroki Haneda, Keizo Kawakami, and Masakuni Uno†

Faculty of Engineering and Junior College Division, Osaka Electro-Communication University, Neyagawa, Osaka 572, Japan

Received December 11, 1992; Revised Manuscript Received May 25, 1993

ABSTRACT: The homogeneous grafting of methyl methacrylate onto cellulose was carried out in a dimethyl sulfoxide (DMSO)/paraformaldehyde solvent system. The grafted products were added to cellulose/poly(methyl methacrylate) (PMMA) blends as compatibilizers. The thermal decomposition behavior of the blends was investigated. 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 values of accessibility for the former blends were larger than those of the latter and a cellulose sample cast from a DMSO solution. The microphase-separated structures of the former blends were finer than those of the latter. 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 the thermal decomposition measurement. The difference in thermal decomposition behavior was correlated to that in compatibility. Thermal decomposition measurements were effective for estimating the compatibility in cellulose/PMMA blends containing grafted products.

Introduction

In graft copolymerization, a graft copolymer and attendant homopolymer are synthesized simultaneously. There remains a fraction of main chain polymers not participating in grafting.[1-3] The as-grafted products thus are polymer blends containing graft copolymers as compatibilizers. The homogeneous grafting of vinyl monomers onto cellulose in a dimethyl sulfoxide/paraformaldehyde (DMSO/PF) solvent system was carried out under various conditions to synthesize grafted products with different compositions.[4-7] The thermal decomposition behavior of the grafted cellulose products was investigated.[8,9] The thermal stability of the grafted products with higher graft copolymer content decreased much more than that of the grafted products with lower graft copolymer content. The values of accessibility for the former products were larger than those of the latter products and a cellulose sample cast from a DMSO solution. The accessibility values are considered a measure of crystallinity of the cellulose fraction.[10] The thermal stability of cellulose mainly depends on its crystallinity.[11,12] It was considered that synthetic polymer chains hinder the crystallization of cellulose chains, leading to lower thermal stability of the former products. Moreover, the microphase-separated structures of the former products were finer than those of the latter products, implying good compatibility of cellulose with synthetic polymers in the former products. It was suggested that the thermal stability of the grafted cellulose products with good compatibility decreases remarkably.[8,9] In our work, the word "compatibility" does not refer to miscibility on a molecular scale.

The compatibility in polymer blends can be estimated from their glass transition temperatures (T_g).[13-15] However, cellulose does not undergo a clear glass transition. We have already reported that it is difficult to determine the T_g values for blends containing cellulose.[8,9] It is necessary to correlate the difference in thermal stability of blends containing cellulose to that in compatibility. Thermal decomposition behavior may become a novel measure for compatibility estimation. It is troublesome to synthesize the grafted products with different graft copolymer contents. The grafted products themselves thus were taken as compatibilizers. In this work, methyl methacrylate (MMA) grafted cellulose products were added to cellulose/poly(methyl methacrylate) (PMMA) blends to vary graft copolymer content widely. The difference in thermal decomposition behavior of the blends was correlated to that in compatibility.

Table I. Characterization of Grafted Products[a]

sample code	GE/%	PMMA content/wt % overall	graft polymer	homopolymer	$M_v \times 10^{-3}$ of graft[b]	no. of grafts
g-PMMA 4	73.4	33.7	24.8	8.9	56	0.98
g-PMMA 5	43.1	37.5	16.2	21.3	46	0.82

[a] The viscosity-average molecular weight (M_v) of backbone cellulose is 146×10^3. [b] M_v of the extracted homopolymer was used as that of the graft polymer.

Experimental Section

Grafting and Sample Preparation. The homogeneous grafting of MMA onto cellulose in a DMSO/PF solvent system and characterization of the grafted products were performed by the method described in our previous papers.[4-7] 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. The overall PMMA contents of both grafted products are about 35% but the graft polymer content of g-PMMA 4 is larger than that of g-PMMA 5. In homogeneous grafting, the molecular weight of the graft polymer is presumed to be equal to that of the attendant homopolymer.[1,3] We have already confirmed that both molecular weights are consistent with each other within experimental error.[5,7] The viscosity-average molecular weights (M_v) of cellulose and PMMA used for the blends were estimated to be 146×10^3 and 160×10^3 from the intrinsic viscosities obtained with cadoxen[16] at 20 °C and acetone[17] at 25 °C, respectively.

The crude reaction mixtures and the DMSO solutions of cellulose and PMMA were mixed to give proper blend ratios. The mixtures were cast onto glass plates at room temperature and dried at about 60 °C under reduced pressure for 24 h. After being immersed in water for several days, the samples were easily

† Junior College Division.

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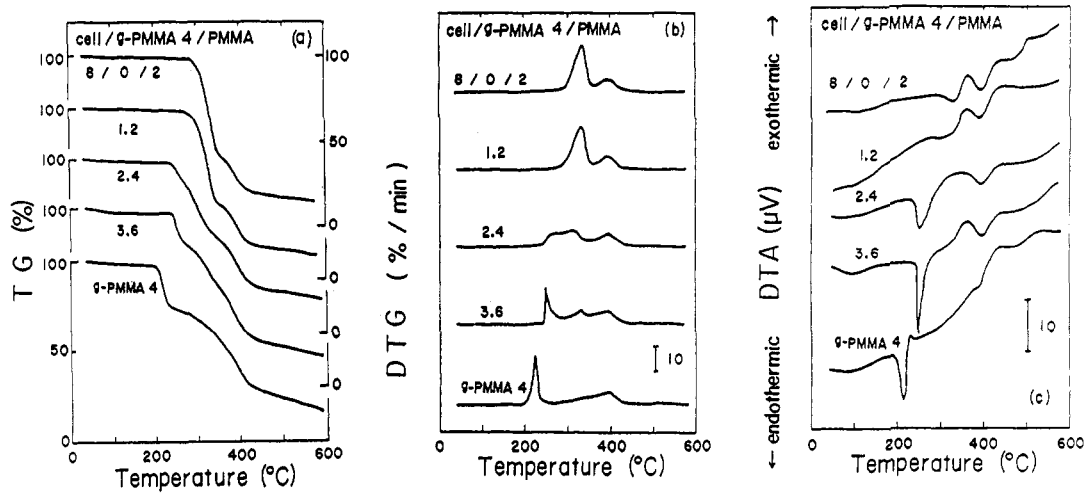

Figure 1. Thermograms of the grafted product (g-PMMA 4) and cellulose/PMMA(8/2) blends containing g-PMMA 4: (a) thermogravimetric (TG) curves; (b) derivative thermogravimetric (DTG) curves; (c) differential thermal analysis (DTA) curves.

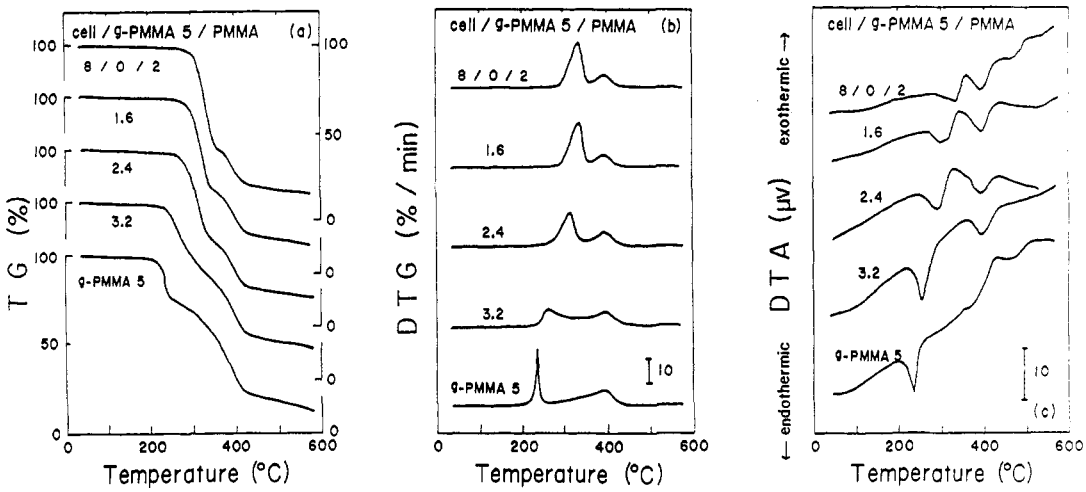

Figure 2. Thermograms of the grafted product (g-PMMA 5) and cellulose/PMMA(8/2) blends containing g-PMMA 5: (a) TG curves; (b) DTG curves; (c) DTA curves.

peeled off. The samples were air-dried on filter paper at room temperature and stored in a desiccator until use.

Measurements. A SEIKO SSC5000TA with a TG/DTA300 module was used for thermal analysis. The measurements were carried out from room temperature to 600 °C at a heating rate of 10 °C/min under a nitrogen atmosphere flowing at 50 mL/min. The samples (ca. 15 mg) were peheated 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. Since 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.

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 60 °C under reduced pressure for more than 24 h prior to measurements.

The samples (ca. 5 × 5 × 0.01 mm) for accessibility measurements 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. Accessibility (A) was calculated according to the equation[18]

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

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

A Hitachi HU-11A transmission electron microscope (TEM) 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 *n*-butyl methacrylate and MMA was used as an embedding medium. The embedded samples were cut into ultrathin sections of approximately 50-nm thickness.

Results and Discussion

Figure 1a indicates the thermogravimetric (TG) curves of the grafted product (g-PMMA 4) and cellulose/PMMA-(8/2 by weight) blends containing various amounts of g-PMMA 4. The weight of the blend (cellulose/g-PMMA 4/PMMA = 8/0/2) without g-PMMA 4 decreases sharply by about 60% at around 320 °C and about an additional 20% at around 400 °C followed by a gentle decrease. The residual weight percent at 600 °C is about 15%. On the other hand, a sharp weight loss for g-PMMA 4 amounting to about 25% is observed at around 220 °C followed by about 45% weight loss taking place over the temperature range 240–420 °C. The residual weight percent of this sample at 600 °C is also about 15%. The decomposition behavior of the blend (8/1.2/2) containing 1.2 parts of g-PMMA 4 is similar to that of the blend (8/0/2). However, the decomposition of the blend (8/2.4/2) starts gradually from around 250 °C. The sharp weight loss of the blend (8/3.6/2) occurs at around 250 °C. It is clear that the increase in g-PMMA 4 content makes the cellulose/PMMA blend thermally unstable.

The difference in thermal decomposition behavior of these samples can be seen more clearly from the derivative

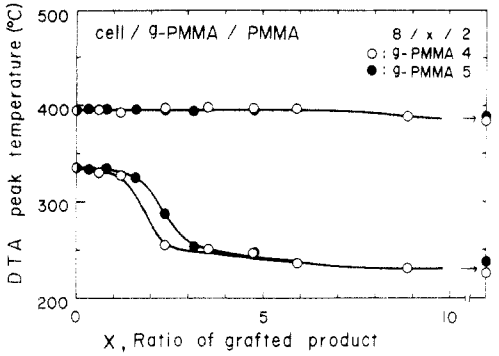

Figure 3. Dependence of the DTA peak temperatures for the cellulose/PMMA(8/2) blends containing different grafted products on the grafted product content.

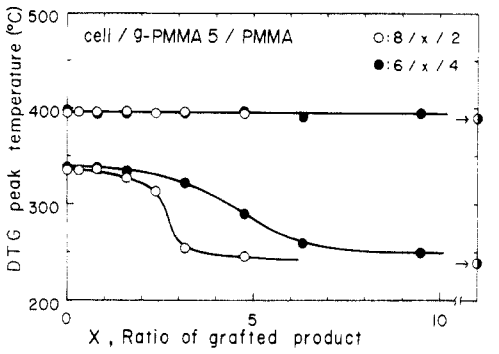

Figure 5. Dependence of the DTG peak temperatures for the cellulose/PMMA blends with different compositions on g-PMMA 5 content.

thermogravimetric (DTG) curves shown in Figure 1b. The decomposition rate of the blend (8/0/2) has two maxima at 335 and 395 °C, indicating the presence of two thermal decomposition processes. As indicated in our previous work,[8,9] the peaks at lower and higher temperatures result mainly from the decomposition of cellulose and PMMA fractions, respectively. We use these peak temperatures as a measure of thermal stability. The DTG curve of g-PMMA 4 shows a sharp peak at 226 °C and a broad peak at 392 °C. The thermal stability of g-PMMA 4, especially that of the cellulose fraction, is lower by about 110 °C than that of the blend (8/0/2). The peak temperatures of the blend (8/1.2/2) are almost equal to those of the blend (8/0/2). The peak at lower temperatures of the blend (8/2.4/2) is broad and shifts toward lower temperatures, but that at higher temperatures hardly shifts. The thermal stability of the blend (8/3.6/2) is lower than that of the blend (8/2.4/2).

Figure 1c illustrates the differential thermal analysis (DTA) curves of the same samples. Two endothermic peaks resulting from the decomposition of two components are recognized. The shift in DTA peak temperatures corresponds to that in DTG peak temperatures. These DTA peak temperatures are also used as a measure of thermal stability.

Figure 2 indicates the thermal decomposition behavior of the cellulose/PMMA(8/2) blends containing the other grafted product (g-PMMA 5). The DTG peak temperatures of g-PMMA 5 are 239 and 389 °C, implying similar thermal stability to g-PMMA 4. The thermal decomposition behavior of the blend (8/2.4/2) is almost equal to that of the blend (8/0/2), being different from the result shown in Figure 1.

The dependence of the DTA peak temperatures on the grafted product content is revealed in Figure 3. The higher peak temperature is almost independent of the amount and kind of grafted products, suggesting no influence on the thermal stability of the PMMA fraction. On the other hand, the lower peak temperature decreases at a certain amount of grafted product. The amount of grafted product required to reduce the thermal stability of the cellulose/PMMA(8/2) blend depends on the kind of grafted products. The addition of g-PMMA 4 is more effective than that of g-PMMA 5. As mentioned above, the graft copolymer content of g-PMMA 4 is larger than that of g-PMMA 5.

Figure 4 indicates the thermal decomposition behavior of the cellulose/PMMA(6/4) blends containing different amounts of g-PMMA 5. The weight loss of the blend (6/0/4) at lower temperatures amounting to about 45% is less than that obtained for the blend (8/0/2), supporting that the decomposition at lower temperatures results from that of the cellulose fraction. The DTG peak temperatures of the blend (6/0/4) are 338 and 398 °C, being similar to those of the blend (8/0/2). The shift in DTG peak at lower temperatures is hardly recognized for the blend (6/3.2/4), being different from the result shown in Figure 2.

The amount of g-PMMA 5 required to influence the thermal stability of the cellulose/PMMA blends with different compositions is compared in Figure 5. The higher peak temperature hardly depends on the amount of g-PMMA 5 and cellulose/PMMA composition, being consistent with the result shown in Figure 3. The lower peak temperature for the cellulose/PMMA(8/2) blends decreases sharply over the composition range 2–3 but that for the cellulose/PMMA(6/4) blends decreases gradually

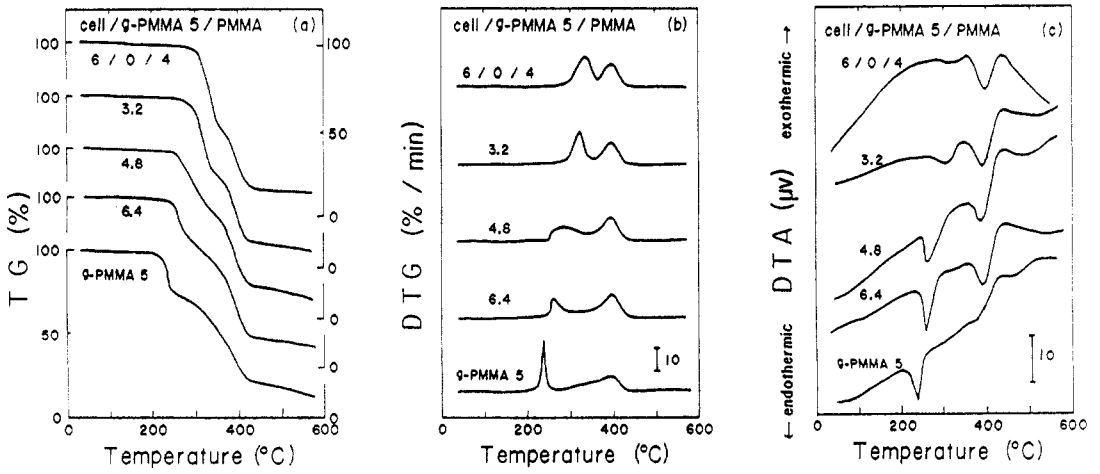

Figure 4. Thermograms of the grafted product (g-PMMA 5) and cellulose/PMMA(6/4) blends containing g-PMMA 5: (a) TG curves; (b) DTG curves; (c) DTA curves.

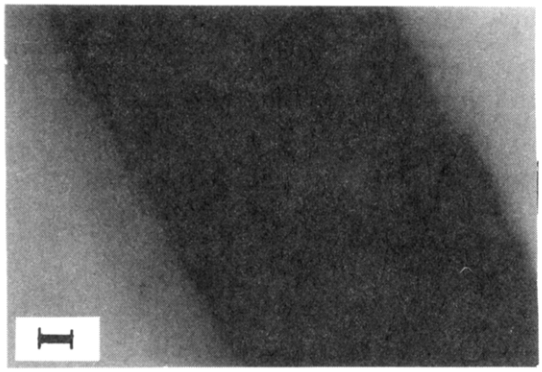

Figure 6. TEM micrograph of g-PMMA 5 stained with osmic acid. Scale bar represents 1 μm.

over the range 2–6. It is of interest to note that the amount of grafted product required to influence the thermal stability of cellulose/PMMA blends depends on the kind of grafted products and the cellulose/PMMA composition.

The values of accessibility determined by a deuteration method are summarized in Table II. The results obtained in the previous work[9,19] are also given in this table. In spite of the grafting of hydrophobic MMA, the values of the grafted products are larger than that of a cellulose sample cast from a DMSO solution. It is considered that the PMMA chains hinder the crystallization of cellulose chains, resulting in an increased fraction of free hydroxyl groups. The accessibility value slightly increases with the increase in grafted product content. A comparison of Table II with Figures 3 and 5 shows that the increase in accessibility corresponds to the decrease in thermal stability. As mentioned above, the thermal stability of cellulose mainly depends on its crystallinity.[11,12] Therefore, the decrease in thermal stability of the blends is attributable to that in crystallinity of the cellulose fraction.

Figure 6 shows the TEM micrograph of g-PMMA 5.

Table II. Accessibility Determined by a Deuteration Method for Cellulose and Grafted and Blended Samples

sample code	accessibility/%
cellulose	38.8
g-PMMA 4	49.3
g-PMMA 5	49.2
cellulose/PMMA	
8/2	26.3
6/4	29.1
cellulose/g-PMMA 4/PMMA	
8/1.2/2	33.5
8/2.4/2	41.3
8/3.6/2	44.1
cellulose/g-PMMA 5/PMMA	
8/1.6/2	27.3
8/2.4/2	35.7
8/3.2/2	44.5
8/4.8/2	45.1
6/1.6/4	27.4
6/3.2/4	40.3
6/4.8/4	41.4
6/6.4/4	45.7

The dark domains indicate the cellulose phases stained with osmic acid. The microphase-separated structure of g-PMMA 5 is very fine and the interfaces between cellulose and PMMA phases are not clear, indicating good compatibility of cellulose with PMMA. Figure 7 shows the TEM micrographs of the cellulose/PMMA(8/2) blends containing g-PMMA 5. In micrographs a and b of Figure 7, spherical white domains and ellipsoidal dark domains are dispersed in the gray matrix, respectively. The interfaces between both phases are clearer than those in Figure 6, indicating poor compatibility of cellulose with PMMA. The gray matrix may be miscible regions but the difference in microphase-separated structures is obvious. The microphase-separated structure of the blend (8/3.2/2) is fine and that of the blend (8/4.8/2) is finer. The microphase-separated structures of the cellulose/PMMA-(6/4) blends containing g-PMMA 5 are shown in Figure

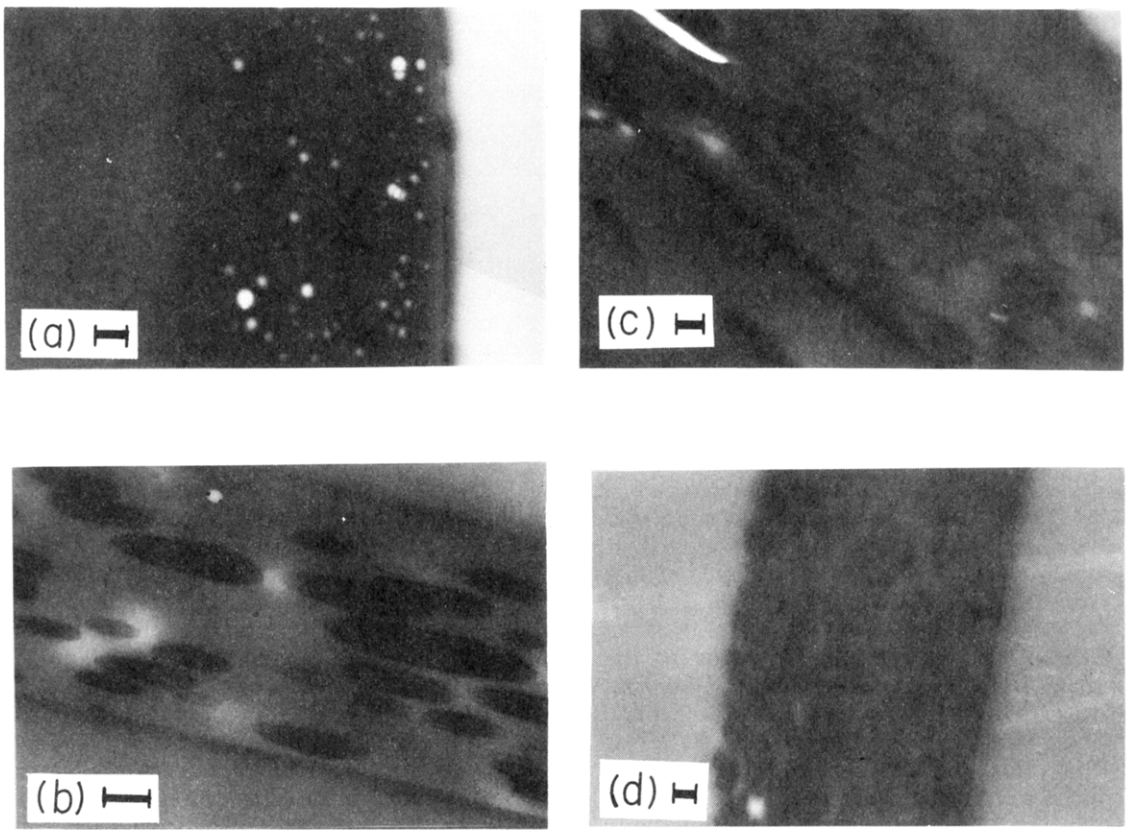

Figure 7. TEM micrographs of cellulose/PMMA(8/2) blends containing g-PMMA 5: (a) 8/0/2; (b) 8/2.4/2; (c) 8/3.2/2; (d) 8/4.8/2.

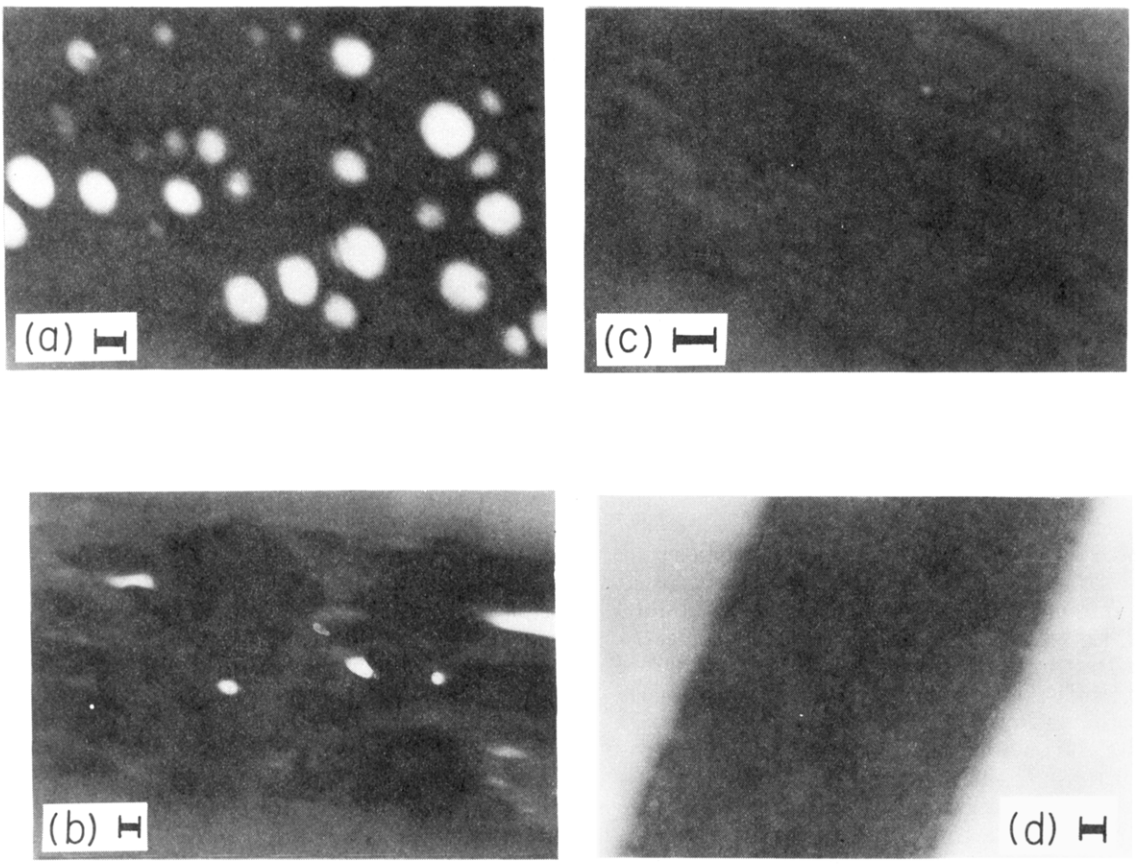

Figure 8. TEM micrographs of cellulose/PMMA(6/4) blends containing g-PMMA 5: (a) 6/0/4; (b) 6/1.6/4; (c) 6/3.2/4; (d) 6/4.8/4.

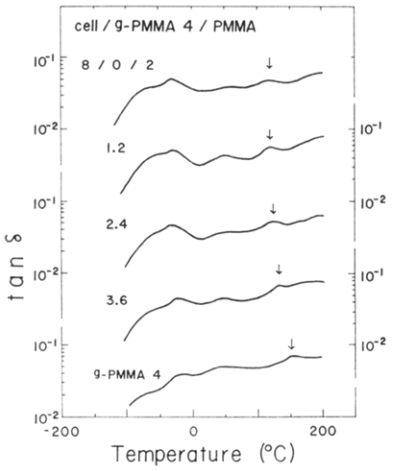

Figure 9. Temperature dependence of mechanical loss tangent for cellulose/PMMA(8/2) blends containing g-PMMA 4.

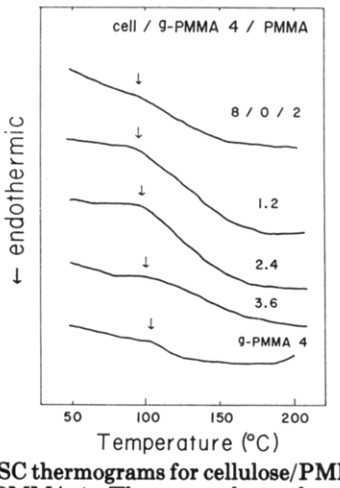

Figure 10. DSC thermograms for cellulose/PMMA(8/2) blends containing g-PMMA 4. The arrow shows the position of T_g.

8. The microphase-separated structures of the blends with lower g-PMMA 5 content are coarse but that of the blend (6/4.8/4) is fine. A comparison of TEM micrographs with thermal decomposition behavior indicates that the thermal stability of the blends with fine microphase-separated structures decreases remarkably.

Figure 9 shows the temperature dependence of mechanical loss tangent for the cellulose/PMMA(8/2) blends containing g-PMMA 4. The small relaxation peak of the blend (8/0/2) at around 110 °C corresponds to the relaxation of the PMMA fraction. The peak temperature shifts slightly toward higher temperatures with the increase in g-PMMA 4 content. The peak temperature of g-PMMA 4 is about 151 °C. This value is nearly equal to that estimated from the T_g values of PMMA[20] and cellulose[21] according to the equation proposed by Fox,[22] implying good compatibility of cellulose with PMMA in g-PMMA 4. The DSC curves for the same samples are depicted in Figure 10. The determination of T_g is less sensitive than dynamic mechanical measurements. A similar difficulty for determining T_g has also been reported for other cellulose/synthetic polymer blends.[21,23-25] The T_g value shifts slightly toward higher temperatures with the increase in g-PMMA 4 content. The shift in T_g values of the blends represents the change in compatibility. The fine microphase-separated structures of the blends imply good compatibility of cellulose with PMMA. The difference in thermal decomposition behavior of the cellulose/PMMA blends containing grafted products, therefore, can be correlated to that in compatibility.

The dependence of characteristic temperatures determined by three kinds of measurements on the g-PMMA 4 content is compared in Figure 11. The DTA peak temperature determined by thermal decomposition mea-

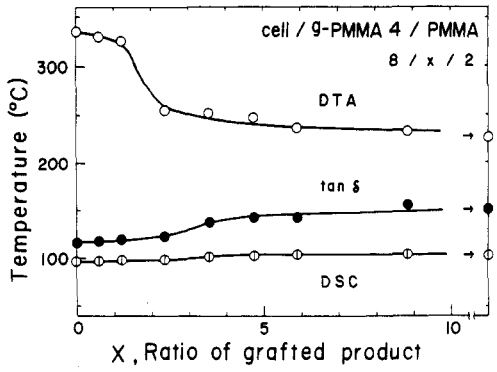

Figure 11. Comparison of characteristic temperatures determined by three kinds of measurements.

surements changes by more than 100 °C, whereas the loss tangent peak temperature determined by dynamic mechanical measurements varies by about 40 °C. The shift in T_g value determined by DSC is very small. It should be noted that the variation in characteristic temperature determined by thermal decomposition measurements is the largest among these three kinds of temperatures and its determination is not so difficult. Therefore, thermogravimetry will be effective for estimating compatibility in polymer blends.

It has been reported[8] that a difference in thermal stability is not found for the miscible polymer blend[13-15] of poly(vinyl acetate) (PVAc) with poly(methyl acrylate) (PMA). It is known that the thermal stability of polymers depends on crystallinity.[11,12,26] Both PVAc and PMA are amorphous polymers. 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 thermal decomposition behavior of vinyl monomer grafted cellulose has been investigated by many workers.[27-33] Grafting, however, was carried out in a heterogeneous reaction system and attendant homopolymers were extracted. No investigation has correlated the thermal stability of grafted products to the compatibility in their constituents. It has been reported[21,23-25,34-36] that cellulose is miscible with several synthetic polymers. The thermal decomposition behavior of these miscible cellulose/synthetic polymer blends is now under investigation.

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research (No. 03650735) from the Ministry of Education, Science, and Culture of Japan.

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