Thermal Decomposition of Cellulose/Synthetic Polymer Blends Containing Graft Copolymers

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ABSTRACT: The homogeneous grafting of methyl acrylate, methyl methacrylate, or 2-hydroxyethyl methacrylate onto cellulose was carried out in a dimethyl sulfoxide/paraformaldehyde solvent system. The homopolymer fractions, ungrafted cellulose and attendant synthetic homopolymer, were not extracted from the grafted products. The grafted products are thus regarded as polymer blends containing graft copolymers. The thermal decomposition behavior of the grafted products, cellulose, synthetic polymers, and cellulose/synthetic polymer blends was investigated. The thermal stability of the grafted products with higher graft polymer content decreased much more than that of cellulose and synthetic polymers. The thermal stability of the grafted products with lower graft polymer content and blended samples was almost identical with that of the constituents. The microphase separated structures of the grafted products with higher graft polymer content were fine. The water accessibility of these grafted products was larger than that of cellulose. The difference in thermal decomposition behavior of the grafted and blended samples was correlated to that in compatibility.

KEY WORDS Thermal Decomposition / Cellulose / Grafted Product / Polymer Blend / Compatibility /

The thermal decomposition behavior of vinyl monomer grafted cellulose has been investigated by many workers.¹⁻⁶ Graft copolymerization, however, has been carried out in a heterogeneous reaction system. Grafting in such a system proceeds mainly in amorphous regions of cellulose.⁷⁻⁹ The homogeneous grafting of vinyl monomers onto cellulose in a dimethyl sulfoxide/paraformaldehyde (DMSO/PF) solvent system has been carried out under various conditions to characterize the grafted products.¹⁰⁻¹³ The thermal decomposition behavior of cellulose, polyacrylonitrile (PAN), acrylonitrile (AN) grafted cellulose products, and cellulose/PAN blends was investigated in our previous paper.¹⁴ The grafted products without extracting ungrafted cellulose and attendant PAN were regarded as polymer blends containing graft copolymers. The thermal stability of

the grafted products with higher PAN graft polymer content decreased much more than that of cellulose and PAN. It was suggested that thermal decomposition measurement is effective for estimating compatibility in polymer blends containing cellulose.

In this study, the thermal decomposition behavior of methyl acrylate (MA), methyl methacrylate (MMA), or 2-hydroxyethyl methacrylate (HEMA) grafted cellulose products with different amounts of the graft polymer and that of cellulose/synthetic polymer blends were investigated. The difference in thermal stability was correlated to that in compatibility.

EXPERIMENTAL

Grafting and Sample Preparation

The homogeneous grafting of MA, MMA,

Table I. Characterization of grafted and blended samples¹⁶⁻¹⁹

Sample code	GE	Synthetic polymer content/wt%			$\bar{M}_v \times 10^{-3}$ of graft ^a	Number of grafts
	%	Overall	Graft polymer	Homopolymer		
g-PMA 3	51.7	29.4	15.2	14.2	105	0.3
g-PMA 13	14.8	35.1	5.2	29.9	150	0.1
b-PMA 3 ^b	0	30.0	0	30.0		
g-PMMA 2	63.2	17.4	11.0	6.4	115	0.2
g-PMMA 15	24.7	17.0	4.2	12.8	49	0.4
b-PMMA 2 ^b	0	20.0	0	20.0		
g-PHEMA 1	71.8	26.0	18.7	7.3	150	0.3
g-PHEMA 13	37.5	27.2	10.2	17.0	260	0.1
b-PHEMA 3 ^b	0	30.0	0	30.0		

^a The viscosity-average molecular weight ($\bar{M}_v$) of the extracted homopolymer was used as that of the graft polymer.

^b The values of $\bar{M}_v$ for cellulose, PMA, PMMA, and PHEMA are 160×10^3 , 170×10^3 , 160×10^3 , and 220×10^3 , respectively.

or HEMA onto cellulose in a DMSO/PF solvent system and characterization of the grafted products were performed by the method in the previous papers.¹⁰⁻¹³ Crude reaction mixtures were cast at room temperature on glass plates and dried at about 60°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. The DMSO solutions of cellulose and synthetic polymers were mixed to give proper blended ratios. The blended and homopolymer samples were also prepared by the same method.

A graft copolymer and attendant homopolymer are produced simultaneously in grafting.^{7-9,15} Grafting efficiency (GE) is defined as the ratio of the amount of grafted monomer to that of polymerized monomer. Two kinds of radical initiators, ammonium persulfate and azobisisobutyronitrile, were used to obtain grafted products with different GE. There remains a fraction of cellulose not participated in grafting. The homopolymer fractions, ungrafted cellulose and attendant synthetic homopolymer, were not extracted

from the grafted products. The grafted products thus were taken as cellulose/synthetic polymer blends containing graft copolymers as a compatibilizer. In homogeneous grafting, the molecular weight of the graft polymer is similar to that of the attendant homopolymer.^{7,9,15} We reported that both molecular weights are consistent with each other within experimental error.¹¹ The samples are characterized in Table I. Some of the samples used in our previous studies¹⁶⁻¹⁹ were also used in this study.

Thermal Analysis

A SEIKO SSC5000TA with a TG/DTA300 module was used for thermal analysis carried out from room temperature to 600°C at a heating rate of 10°C min⁻¹ under nitrogen atmosphere flowing at 50 ml min⁻¹. All samples were preheated to 150°C under the conditions described above to evaporate water absorbed.

Accessibility

The samples were dried over P₂O₅ under reduced pressure for 24 h, immersed in D₂O for 4 h, and then dried again under reduced pressure for 24 h. Infrared spectra were

Figure 1. Thermograms of cellulose, g-PMA 3, g-PMA 13, b-PMA 3, and PMA: a) thermogravimetric (TG) curves; b) derivative thermogravimetric (DTG) curves; c) differential thermal analysis (DTA) curves.

measured by placing the samples between NaCl plates with hexachlorobutadiene. Accessibility (A) was calculated according to the equation²⁰:

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

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

RESULTS AND DISCUSSION

The thermogravimetric (TG) curves of cellulose, poly(methyl acrylate) (PMA), g-PMA 3, g-PMA 13, and b-PMA 3 are indicated in Figure 1a. The weight loss of cellulose amounting to about 60% of the total weight takes place over the temperature range 270 to 350°C followed by gentle weight loss. The residual weight percent at 600°C is about 22%, which is given in Table II. The decomposition of PMA occurs in the range of about 320 to 420°C . The residual weight percent at 450°C is almost equal to zero. The decomposition of the grafted and blended samples proceeds in two steps. The weight of g-PMA 3 decreases sharply about 20% at around 220°C and gradually about 40% at around 400°C . However, the decomposition of g-PMA 13 at lower temperatures takes place at

around 320°C and that at higher temperatures does at around 400°C . The decomposition behavior of b-PMA 3 is similar to that of g-PMA 13.

The difference in the thermal decomposition behavior of these samples can be seen more clearly from the derivative thermogravimetric (DTG) curves shown in Figure 1b. The decomposition rate of cellulose indicates the maximum value at 317°C . We use this peak temperature (T_{DTG}) as a measure of the thermal stability. The results are also summarized in Table II. The peak temperature of PMA is about 399°C , indicating higher thermal stability of PMA than that of cellulose. The DTG curves of the grafted and blended samples indicate two peaks for the two decomposition processes. The DTG curve of g-PMA 3 shows a sharp peak at 225°C and a broad peak at around 416°C , corresponding to rapid decomposition and gradual one, respectively. It can be seen that the thermal stability of g-PMA 3 is lower by about 90°C than that of cellulose. The peak temperatures of g-PMA 13 and b-PMA 3 are almost equal to each other, but peak shapes slightly differ from one another. Furthermore, the lower and higher peak temperatures of these samples

are almost equal to the peak temperatures of cellulose and PMA, respectively.

Figure 1c illustrates the differential thermal analysis (DTA) curves of the same samples. Peak temperatures (T_{DTA}) are also listed in Table II. The DTA curve of cellulose indicates a weak endothermic peak at around 280°C. A broad endothermic peak of PMA is recognized at around 400°C. The DTA curve of g-PMA 3 shows a sharp endothermic peak at 225°C and a small one at 411°C. The DTA

curves of g-PMA 13 and b-PMA 3 indicate two weak endothermic peaks. A comparison of peak temperatures for the grafted and blended samples with those for cellulose and PMA reveals that the decompositions of these samples at lower and higher temperatures correspond mainly to those of cellulose and PMA fractions, respectively. The decrease in the thermal stability of g-PMA 3 is attributed to that of cellulose fraction. The thermal stability of each component of g-PMA 13 and b-PMA 3 is hardly influenced. As can be seen from Table I, the overall PMA contents of the grafted and blended samples are about 30%, but their PMA graft polymer contents differ considerably. It is of interest to note that the thermal decomposition behavior of these samples depends on the graft polymer content.

The TG, DTG, and DTA curves of the MMA grafted products with different poly-(methyl methacrylate) (PMMA) graft polymer contents and of PMMA blended samples are depicted in Figure 2. The grafted and blended samples decompose at two steps. The decomposition of g-PMMA 2 at lower temperatures occurs at around 240°C but those of g-PMMA 15 and b-PMMA 2 do at around 320°C. It can also be seen that the thermal stability of g-PMMA 2 decreases considerably.

Table II. Peak temperatures of DTG and DTA curves and residual weight percent at 600°C

Sample code	Peak temperature/°C		Residual weight percent at 600°C
	T_{DTG}	T_{DTA}	
Cellulose	317	270	22.3
PMA	399	401	0.2
g-PMA 3	225/416	225/411	20.5
g-PMA 13	325/403	294/418	15.9
b-PMA 3	338/414	334/411	14.1
PMMA	374	271/372	0
g-PMMA 2	244/378	244/397	23.3
g-PMMA 15	325/401	303/407	19.1
b-PMMA 2	320/396	265/396	17.2
PHEMA	397	389	1.7
g-PHEMA 1	219/381	220	24.7
g-PHEMA 13	343/420	348	16.2
b-PHEMA 3	327/420	338	14.9

Figure 2. Thermograms of cellulose, g-PMMA 2, g-PMMA 15, b-PMMA 2, and PMMA: a) TG curves; b) DTG curves; c) DTA curves.

Figure 3. Thermograms of cellulose, g-PHEMA 1, g-PHEMA 13, b-PHEMA 3, and PHEMA: a) TG curves; b) DTG curves; c) DTA curves.

Figure 3 also displays the thermal decomposition behavior of the HEMA grafted products with different graft polymer contents and of poly(2-hydroxyethyl methacrylate) (PHEMA) blended samples. The thermal stability of g-PHEMA 1 decreases remarkably. As listed in Table I, overall PMMA and PHEMA contents are about 20 and 30%, respectively, but their graft polymer contents differ considerably. In any case, the thermal stability of the grafted products with higher graft polymer content decreases appreciably. We have already found a similar tendency for AN grafted cellulose products.¹⁴ Our results will be compared with those obtained for cellulose grafted with vinyl monomers in a heterogeneous reaction system.¹⁻⁶ The thermal stability of grafted cellulose changed depending on the monomer grafted but did not decrease appreciably. It is necessary to take into account the difference in grafting and sample preparation procedures.

In general, polymer blends indicate phase separated structures because of the incompatibility of constituent polymers.^{21,22} However, the addition of copolymers into the polymer blends of their components enhances the compatibility in such blends.^{21,22} As described

above, the grafted products were considered as cellulose/synthetic polymer blends containing graft copolymers as compatibilizers. We have already reported^{16-19,23-25} that the microphase separated structures of the grafted products with higher graft polymer content are very fine, while those with lower graft polymer content are rough. Moreover, the microphase separated structures of the blended samples were more rough than those of the latter. Therefore, it is clear that the samples with fine microphase separated structures showed remarkable change in decomposition behavior.

The values of accessibility determined by a deuteration method are summarized in Table III. The results obtained in the previous study²³ are also given in this table. In spite of the grafting of hydrophobic MA or MMA, the accessibility values of the grafted products with higher graft polymer content are larger than that of cellulose. It is considered that synthetic polymer chains hindered the crystallization of cellulose chains resulting in increased fraction of free hydroxyl groups. The difference in accessibility for the HEMA grafted and PHEMA blended samples is hardly discernible. This might be caused by

Table III. Accessibility determined by a deuteration method for cellulose, grafted, and blended samples

Sample code	Accessibility
	%
Cellulose	38.8
g-PMA 3	44.0
g-PMA 13	37.7
b-PMA 3	36.0
g-PMMA 2	40.9
g-PMMA 15	29.0
b-PMMA 2	26.3
g-PHEMA 1	40.7
g-PHEMA 13	39.5
b-PHEMA 3	39.6

the influence of hydroxyl groups on the PHEMA chains. The influence of fine structures of cellulose on its thermal decomposition has been investigated in detail.²⁶⁻³³ The thermal stability of cellulose was found to depend mainly on its crystallinity.^{27,33} The depression of decomposition temperature for the grafted products with higher graft polymer content thus is associated with increased fraction of amorphous regions in cellulose. In other words, the fine microphase separated structures and large accessibility values suggest good compatibility of cellulose with synthetic polymers in the grafted products with higher graft polymer content. Consequently, the difference in the thermal decomposition behavior of the grafted products is correlated to that in compatibility.

The compatibility in polymer blends is estimated from their glass transition temperatures determined by dynamic mechanical measurement, differential scanning calorimetry, and so on.^{21,22} However, cellulose does not undergo a clear glass transition. We have already reported¹⁴ that it is difficult to establish the glass transition behavior of polymer blends containing cellulose. In this work, the glass transition behavior of the grafted products was not observed clearly. As

shown in Figures 1, 2, and 3, the shift of T_{DTG} is remarkable. Therefore, thermogravimetry will be used as a new measure for estimating compatibility in polymer blends. It has been reported,¹⁴ however, that difference in the thermal stability is not found for the compatible polymer blend of poly(vinyl acetate) (PVAc) with PMA. It is known³⁴ that the thermal stability of polymer depends on crystallinity. Both PVAc and PMA are amorphous polymers. Any change in the thermal stability is not expected for blends composed of amorphous polymer pairs. The compatibility estimation by the thermal decomposition measurement may be a characteristic method for blends containing cellulose as one component. Many parameters such as molecular weights of graft and homopolymers, number of grafts, graft polymer content, and so on will influence compatibility, thermal stability, and crystallinity of the grafted products. First, the difference in the thermal stability of the grafted products was explained on the basis of that in their graft polymer contents. Different parameters must be also considered to clarify the relationship between the thermal stability of the grafted products and compatibility. The influence of the addition of grafted products on the thermal stability of cellulose/synthetic polymer blends is now under investigation.

In conclusion, the homogeneous grafting of MA, MMA, or HEMA onto cellulose was carried out in a DMSO/PF solvent system to obtain grafted products with different amounts of the graft polymer. The thermal stability of the grafted products with higher graft polymer content much more decreased than that of cellulose and synthetic polymers. The fine microphase separated structures and large accessibility of the grafted products imply good compatibility. The thermal decomposition measurement may be effective for estimating the compatibility in blends containing cellulose as one component.

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