Thermal Decomposition Behavior of Miscible Cellulose/Synthetic Polymer Blends

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ABSTRACT: The thermal decomposition behavior of the miscible cellulosic blends cellulose(Cell)/poly(*N*-vinyl-2-pyrrolidone)(PVP), Cell/poly(ethylene glycol)(PEG), and Cell/poly(vinyl alcohol)(PVA) was investigated by thermogravimetry. The thermal stability of Cell in the Cell/PVP blends decreased but that of Cell in the Cell/PEG and Cell/PVA blends was hardly influenced. The thermal stability of synthetic polymers in the blends was little affected. The difference in thermal decomposition behavior was correlated to the difference in miscibility. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2133–2137, 1998

Key words: thermal decomposition behavior; thermogravimetry; cellulosic blend; compatibility

INTRODUCTION

In our previous work,[1,2] the thermal decomposition behavior of vinyl monomer grafted cellulose (Cell) products was investigated by thermogravimetry. The grafted products are considered to be polymer blends consisting of Cell, synthetic attendant homopolymers, and graft copolymers as compatibilizers. The thermal stability of the grafted products, especially the Cell fraction, depended on their graft copolymer content. In addition, it was found that the grafted products with higher graft copolymer content indicated fine microphase separated structures and low crystallinity. It was suggested that the thermal stability of the grafted products with good compatibility decreased remarkably. To more precisely correlate the thermal stability of the cellulosic blends with their compatibility, grafted products with different graft copolymer contents are necessary. In a series of our subsequent work,[3-5] the grafted products were added to Cell/synthetic polymer blends as compatibilizers to widely vary graft copolymer content. The change in thermal decomposition behavior was correlated with in compatibility. We suggested that thermogravimetry was effective for compatibility estimation in cellulosic blends containing grafted products.

In this study the thermal decomposition behavior of miscible cellulosic blends [Cell/poly(*N*-vinyl-2-pyrrolidone) (PVP),[6] Cell/poly(ethylene glycol) (PEG),[7] and Cell/poly(vinyl alcohol) (PVA),[8]] was investigated by thermogravimetry. The effectiveness of thermogravimetry for miscibility estimation was discussed.

EXPERIMENTAL

Sample Preparation

Bleached softwood pulp supplied by ITT Rayonier Inc. was used as the cellulosic material. Synthetic polymers were purchased from Wako Pure Chemical Industries, Ltd. The viscosity-average molecular weights (M_v) of the polymers were estimated from their intrinsic viscosities. The M_v values were as follows: Cell[9] $= 146 \times 10^3$, PVP[10] $= 360$
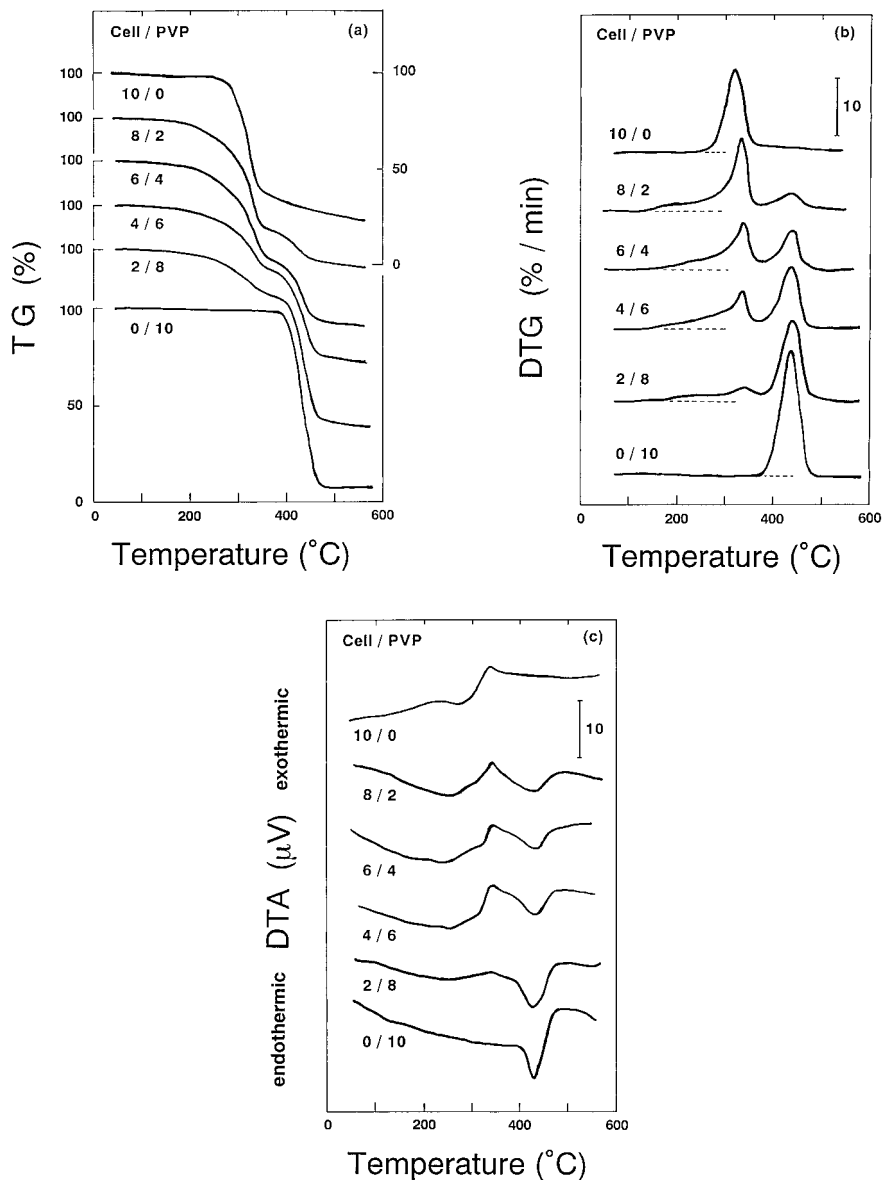
Figure 1 Thermograms of Cell, PVP, and Cell/PVP blends with various compositions: (a) thermogravimetric (TG) curves, (b) derivative thermogravimetric (DTG) curves, and (c) differential thermal analysis (DTA) curves.

$\times 10^3$, $PEG^{11} = 31 \times 10^3$, and $PVA^{12} = 140 \times 10^3$. Reagent grade dimethyl sulfoxide (DMSO) and paraformaldehyde (PF) were used without further purification.

Thoroughly dried Cell was dissolved in DMSO containing PF by a method described previously.[13] Synthetic polymers were also dissolved in DMSO. The separately prepared solutions were mixed in appropriate amounts to give blends of various compositions. After the blend solutions were stirred for 24 h at room temperature, the solutions were cast onto polypropylene (PP) or glass sheets

at room temperature and dried at about 40°C under reduced pressure for 24 h. The Cell/PVP blends cast on PP sheets were easily peeled off without an immersion in solvent. The Cell/PEG and Cell/PVA blends cast on glass sheets were immersed in methyl alcohol and acetone, respectively. After immersion for several days, the films were easily peeled off.

Thermal Analysis

A Seiko SSC5000TA with a TG/DTA300 module was used for thermal decomposition measure-
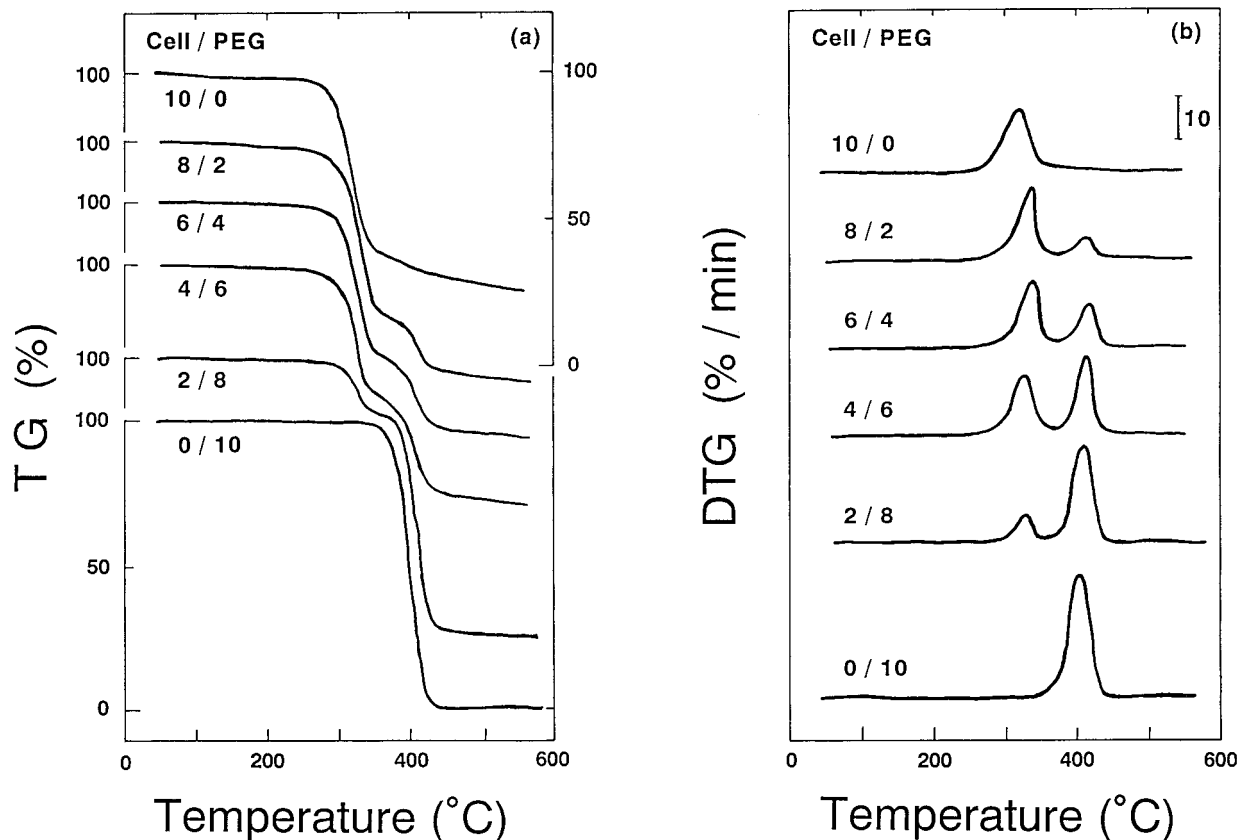
Figure 2 Thermograms of Cell, PEG, and Cell/PEG blends with various compositions: (a) TG curves and (b) DTG curves.

ments. The samples (ca. 15 mg) were preheated to 150°C at a heating rate of 10°C/min under nitrogen flow at 100 mL/min to evaporate adsorbed water. The measurements were carried out from room temperature to 600°C under the conditions described above.

RESULTS AND DISCUSSION

Figure 1(a) shows the thermogravimetric (TG) curves of Cell, PVP, and Cell/PVP blends with different compositions. The weight of Cell decreases by about 60% over the temperature range of 260–360°C and is followed by a gentle decrease. The residual weight percent at 600°C is about 20%. The weight of PVP decreases sharply by about 95% over the temperature range of 400–460°C. The weight of the Cell/PVP (8/2 by weight) blend decreases gradually from around 150°C and the secondary decrease occurs at around 400°C, indicating the presence of different thermal decomposition processes. The other

blends with different compositions also indicate similar thermal decomposition behavior. The weight loss at lower temperatures decreases with the decrease in Cell content but that at higher temperatures increases with the increase in PVP content. This suggests that the decompositions at lower and higher temperatures correspond mainly to that of Cell and PVP fractions, respectively.

The difference in thermal decomposition behavior of these samples can be seen more clearly from the derivative TG (DTG) curves in Figure 1(b). The DTG peak of Cell is present at around 320°C and that of PVP at around 420°C. We use these peak temperatures as a measure of thermal stability. The DTG curves of the blends indicate two peaks. Although the peak at lower temperatures of the (8/2) blend shifts slightly to higher temperatures, the deviation from the baseline occurs at around 150°C. On the other hand, the peak at higher temperatures is observed at around 420°C. As the Cell content decreases, the peak at lower temperatures becomes weak but that at
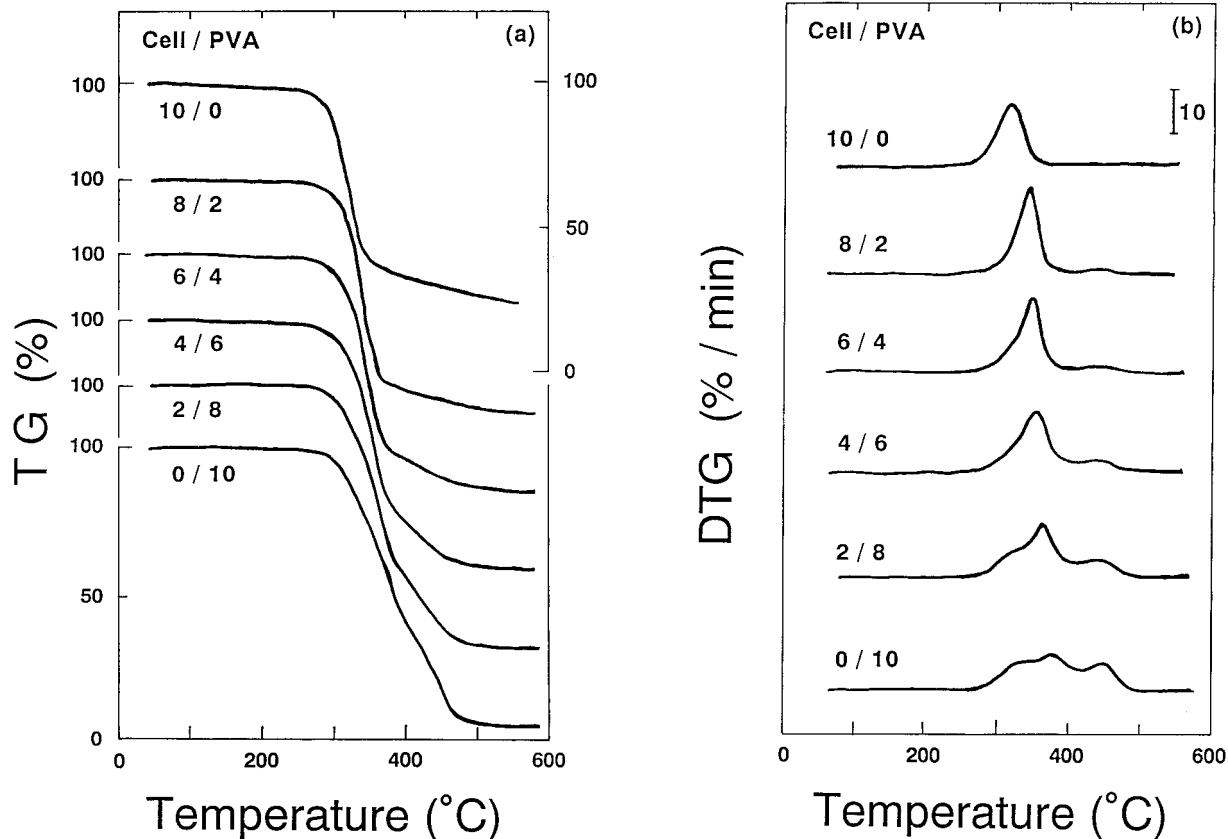
Figure 3 Thermograms of Cell, PVA, and Cell/PVA blends with various compositions: (a) TG curves and (b) DTG curves.

higher temperatures becomes predominant. The deviation from the baseline occurs at around 150°C, but the shift of both peak temperatures is hardly recognized. The beginning of deviation from the baseline corresponds to that of thermal decomposition. Thus, as a measure of thermal stability, we take into account not only the DTG peak temperature but also the beginning temperature of decomposition.

Figure 1(c) illustrates the differential thermal analysis (DTA) curves of the same samples. Broad endothermic peaks of the blends observed at around 250°C become obscure with the decrease in Cell content. With the increase in PVP content, the endothermic peaks at around 420°C become clear but hardly shift. These results in Figure 1 indicate that the thermal stability of the Cell fraction decreases but that of the PVP fraction is little affected. As indicated in our previous articles,[1-5] the DTG peak temperature for the Cell fraction in the grafted products was lowered by more than 100°C. It is of interest that the thermal

stability of the Cell fraction in the Cell/PVP blends is influenced, but weakly.

Figure 2 indicates the TG and DTG curves for the Cell/PEG blends. The thermal decomposition behavior of PEG is similar to that of PVP; but the DTG peak temperature of PEG is around 400°C, indicating that the thermal stability of PEG is lower than that of PVP. The DTG curves of the blends indicate two peaks. Their peak temperatures are independent of their blend compositions. Moreover, the deviation from the baseline at lower temperatures is not detected. The thermal decomposition of one polymer is independent of the presence of the other polymer. For these miscible blends, the decrease in thermal stability of the Cell and PEG fractions is scarcely recognized.

Figure 3 shows the TG and DTG curves for the Cell/PVA blends. The weight of PVA does not decrease as sharply as that of PVP and PEG. The DTG curve of PVA indicates several broad peaks. The DTG curves of the blends also do not clearly indicate two peaks. The peak temperatures are

independent of their blend compositions. Moreover, the deviation from the baseline at lower temperatures is also not recognized. The decrease in thermal stability of the Cell and PVA fractions is hardly found for these miscible blends.

The thermal stability of Cell mainly depends on its crystallinity.[14,15] The grafted Cell products included the synthetic polymers that are essentially incompatible with Cell. Compatibilization was induced by the presence of the graft copolymers. The coexisting synthetic polymer chains were considered to hinder the crystallization of the Cell chains in influencing the thermal stability of Cell.[1-5] For polymers to be miscible, specific intermolecular interactions are necessary.[16] Cell containing hydroxyl groups has the potential of being miscible with synthetic polymers containing functional groups that can interact with hydroxyl groups. The presence of such an interaction based on hydrogen bonding has been reported for miscible cellulosic blends used.[6-8] In this study, the decrease in thermal stability of the Cell fraction was not recognized in the Cell/PEG and Cell/PVA blends. This was because of the presence of such an intermolecular interaction. It is of interest that only the Cell/PVP blends indicate the decrease in thermal stability. This implies that the interaction strength (i.e., the extent of miscibility) depends on the cellulosic blends. Kondo et al.[17] reported that the hydrogen bonding sites in Cell/PVA blends differ from those in Cell/PEG blends. The difference in thermal stability of the Cell fraction is associated with that in hydrogen bonding sites.

As indicated previously,[1] the depression of thermal stability was not found for the miscible amorphous polymer blend of poly(vinyl acetate) with poly(methyl acrylate). The thermal stability of polymers mainly depends on their crystallinity.[14,15,18] It is difficult to expect a change in thermal stability for blends of amorphous polymer pairs. Moreover, as indicated above, the thermal stability of the miscible cellulosic blends was hardly influenced. The compatibility estimation by thermogravimetry thus may be a characteristic method for cellulosic blends containing compatibilizers.

REFERENCES

1. N. Nishioka, H. Ono, and M. Karasuno, *Polym. J.,* **24,** 301 (1992).
2. N. Nishioka and N. Yoshida, *Polym. J.,* **24,** 1009 (1992).
3. N. Nishioka, M. Yamaoka, H. Haneda, K. Kawakami, and M. Uno, *Macromolecules,* **26,** 4694 (1993).
4. N. Nishioka, Y. Nakano, T. Hirota, N. Fujiwara, and M. Uno, *J. Appl. Polym. Sci.,* **59,** 1203 (1996).
5. N. Nishioka, M. Tabata, M. Saito, N. Kishigami, M. Iwamoto, and M. Uno, *Polym. J.,* **29,** 508 (1997).
6. J.-F. Masson and R. St. J. Manley, *Macromolecules,* **24,** 5914 (1991).
7. Y. Nishio, N. Hirose, and T. Takahashi, *Polym. J.,* **21,** 347 (1989).
8. Y. Nishio and R. St. J. Manley, *Macromolecules,* **21,** 1270 (1988).
9. G. Jayme and P. Kleppe, *Papier,* **15,** 492 (1961).
10. G. B. Levy and H. P. Frank, *J. Polym. Sci.,* **17,** 247 (1955).
11. G. Allen, C. Booth, S. J. Hurst, M. N. Hones, and C. Price, *Polymer,* **8,** 391 (1967).
12. M. Matsumoto and Y. Ohyanagi, *Kobunshi Kagaku (Tokyo),* **17,** 191 (1960).
13. N. Nishioka and K. Kosai, *Polym. J.,* **13,** 1125 (1981).
14. A. Basch and M. Lewin, *J. Polym. Sci., Polym. Chem. Ed.,* **11,** 3071 (1973).
15. M. E. Calahorra, M. Cortázar, J. I. Eguiazábal, and G. M. Guzmán, *J. Appl. Polym. Sci.,* **37,** 3305 (1989).
16. D. R. Paul and S. Newman, Eds., *Polymer Blends,* Academic Press, New York, 1978.
17. T. Kondo, C. Sawatari, R. St. J. Manley, and D. G. Gray, *Macromolecules,* **27,** 210 (1994).
18. L. Reich and S. S. Stivala, *Elements of Polymer Degradation,* McGraw–Hill, New York, 1971.