SHORT COMMUNICATIONS

Thermal Analysis of Cellulose/Poly(ethylene oxide) Blends

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A variety of new nonaqueous solvents for dissolution of unmodified cellulose has been described in the past several years[1-5] and the study of cellulose blends with synthetic polymers is now a subject of increasing interest and importance,[6-11] in relation to practical applications as new polymeric materials with wider ranging physical properties. In the preceding papers[9,10] of this series, it was demonstrated that blend films of cellulose with a few conventional polymers can be easily prepared over the whole composition range using the solvent N,N-dimethylacetamide (DMAc)–lithium chloride (LiCl). The present study is concerned with the thermal characterization of binary blends of cellulose (CELL) and a highly crystalline polyether, poly(ethylene oxide) (PEO), the blends being obtained by a solution–coagulation method similar to that described previously.[9,10] A few results of the measurements carried out on the blends by differential scanning calorimetry (DSC) are reported here.

EXPERIMENTAL

Sample Preparation

A wood pulp with a degree of polymerization of 935 was used as the cellulose sample, which was treated by a solvent-exchange technique with water, methanol, and dimethylacet-amide (DMAc) before dissolution in DMAc containing 4.5 wt% lithium chloride (LiCl).[9] The other polymer, poly(ethylene oxide) (PEO), was PEG #20,000 of Nakarai Chemicals, Ltd.; the manufacturer's literature claims a molecular weight of *ca.* 15,000, and a reference[12] also reports $\bar{M}_v = 16,000$ as the viscosity-average molecular weight of this PEO product.

Solutions of cellulose (CELL) and PEO in DMAc–LiCl and pure DMAc, respectively, were prepared separately and then mixed with each other in the desired proportions. The relative composition of the two polymers in the mixed solutions (polym. conc., ~2 wt%) ranged from 10/90 to 90/10 in a ratio of weight percent, the first numeral referring to CELL content throughout this work.

Binary blends of CELL and PEO were prepared from mixed polymer solutions according to a coagulation method described in previous papers[9,10]; but here methyl ethyl ketone was used at 10°C as the coagulant and washing of the precipitated films was carried out with acetone at 15°C. The blend films, dried once at ambient temperature, were further dried at 35°C overnight under high vacuum.

Measurements

Differential scanning calorimetry (DSC) was

conducted with a Seiko DSC 200 apparatus equipped with a thermal analysis station SSC-4000. The measurements were made on 6—10 mg samples at a scanning rate of 10°C min^{-1}, unless otherwise indicated. The temperature readings were calibrated with an indium standard.

The thermal properties of CELL/PEO blends were examined in three scans, *i.e.*, the first heating, second heating, and cooling scans. Each sample inserted in the DSC cell at *ca.* 20°C was first heated to 100°C, this being the first heating scan. The second heating scan was carried out in the temperature range of −100 to 95°C, after quick cooling (∼100°C min^{-1}) following the first heating. The cooling scan was done after the sample was kept at the terminal temperature in the second heating process for 5 min in the DSC pan. The melting temperature, T_{m}, and the apparent enthalpy of fusion, ΔH_{f}, of each sample were determined from the maximum and area of the melting peak, respectively. In a similar manner, the crystallization temperature T_{c} was also evaluated from the peak of the exothermic curve in the cooling scan. The glass transition temperature T_{g}, estimated in the second heating scan, was taken as the onset of change of slope in DSC heat flow.

Another DSC experiment was performed on CELL/PEO samples with compositions of 0/100—50/50 in the following way: Film specimens introduced into aluminium sample pans were heated to 95°C and maintained at this temperature for 7 min to eliminate PEO crystalline residues. The samples were then quenched to the desired crystallization and heat-treating temperature T_{ic} and still held at T_{ic} for at least 1 h to be allowed to crystallize completely. In a subsequent cooling run to 20°C, it was ascertained that the samples showed no evidence of secondary crystallization. For each sample thus isothermally crystallized, the melting point T'_{m} was measured in the heating process. Any peaks other than a single endothermic peak, *e.g.*, those due to reorganization of already formed crystals during heating, were not perceived.

RESULTS AND DISCUSSION

Figure 1 shows several examples of the DSC thermograms obtained in the second heating scan carried out on a series of CELL/PEO
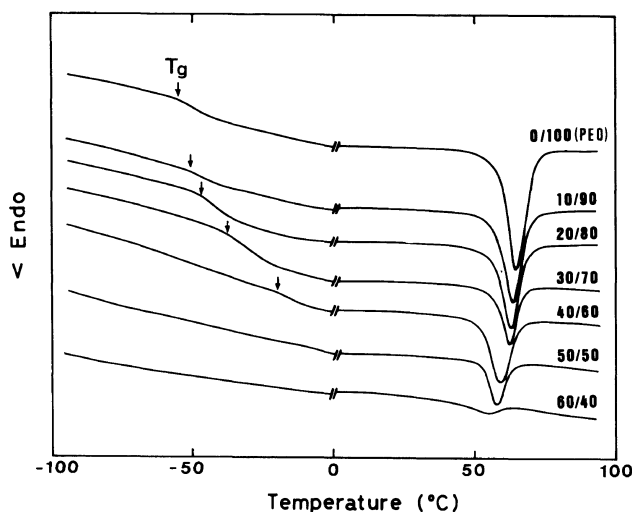
Figure 1. DSC thermograms in the second heating scan for CELL/PEO samples. The curves are depicted on an enlarged scale of heat flow in the temperature region below 0°C.

samples. The plain PEO sample exhibits a sharp melting endotherm with a peak maximum at 64°C and a clear base-line gap caused by passing through the glass transition of the polymer. From the onset point of the discontinuity in heat flow, the glass transition temperature T_g of the PEO sample was estimated to be -55°C. As the CELL is blended with PEO up to 40 wt%, the T_g of PEO shifts explicitly to the higher temperature region, sensitively depending on the blend composition. When the CELL content reached 50 wt%, however, precise estimation of the T_g value became difficult within the permissible limits of the sensitivity of the DSC scan, in spite of slight indication of change in the slope of the DSC base-line at around -5°C. At compositions containing 60 wt% and more CELL, it was no longer possible to detect a discontinuity reflecting T_g in the DSC curves. A depression phenomenon of the melting point of PEO is also evident in Figure 1 as another striking effect due to adding CELL to PEO. Similar depression effects were noted not only in the melting behavior in the first heating scan but also in the crystallization behavior in the cooling scan for the blends (see Figure 2). In all the scans, there was no indication of development of PEO crystallinity in blends containing 70 wt% and more CELL. The rapid decrease in crystallinity of PEO with increase in CELL content was also ascertained by wide-angle X-ray diffraction measurements. The other component CELL showed a very low degree of crystallinity, even in the homo-polymer film prepared by the present coagulation method.

To make clearer the thermal transition behavior of CELL/PEO blends, the DSC data obtained in the three scans are presented in Figure 2; here the composition dependence of the values of T_m, T_c, T_g, and ΔH_f (heat of fusion per gram sample) is depicted by plotting them against CELL content in the blends. The regenerated CELL films showed no definite thermal transition before the polymer began
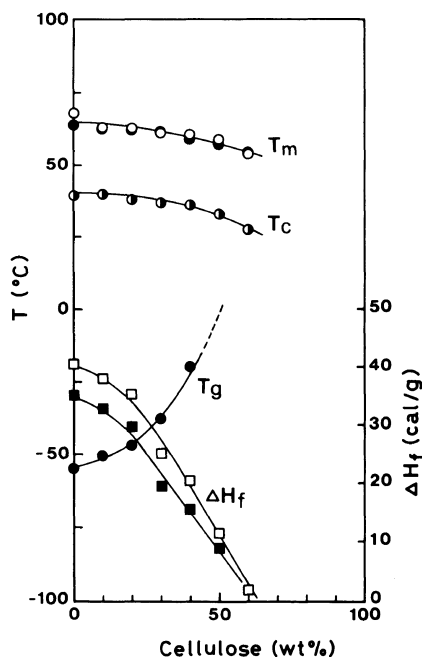

Figure 2. Composition dependence of thermal transitions, determined by DSC for CELL/PEO blends. ○ and □, data in the first heating scan; ● and ■, data in the second heating scans; ◐, data in the cooling scan.

to undergo thermal decomposition above *ca.* 240°C. In the previous estimates,[9,10] however, the cellulose T_g was predicted to lie in the neighbourhood of 240°C, based on measurements of the dynamic mechanical properties of a few, cellulose-based blends.

Observations of thermal transition behavior for the present system, *i.e.*, the composition-dependent shift in the T_g of PEO and the depressions in the melting and crystallization temperatures of PEO, may allow us to assume the polymer pair to be miscible at least in the amorphous fraction of the mixture. The good state of miscibility is presumably due to the capability of the two polymers to interact mutually, *e.g.*, through hydrogen bonding between hydroxyl and ether groups. The occurrence of such a specific intermolecular interaction is supported by a result of analysis of the equilibrium melting-point depression data obtained in a control DSC experiment using
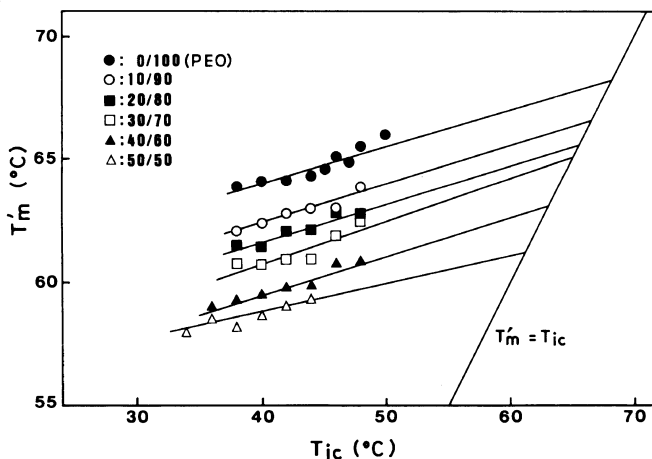
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Figure 3. Hoffman–Weeks plots for isothermally crystallized PEO and CELL/PEO blends.

isothermally crystallized blends, as demonstrated below.

Figure 3 shows the so-called Hoffman–Weeks plots[13] for isothermally crystallized PEO and CELL/PEO beldnds. The variation of the observed melting temperature T'_m of the samples with the crystallization temperature T_{ic} is depicted in this figure. The experimental data may be fitted by the equation[13,14]

$$T'_m = \phi T_{ic} + (1-\phi)T_m^{eq} \qquad (1)$$

where T_m^{eq} is the equilibrium melting point, and ϕ is a stability parameter[14] which is usually related to morphological factors concerning perfectness and size of the crystal. As shown in Figure 3, values of T_m^{eq} for PEO and its blends with CELL can be obtained by extrapolation with a least-squares fit of the data by eq 1 to the intersection with $T'_m = T_{ic}$. A value of $T_m^{eq} = 68.2°C$ was obtained for unblended PEO (0/100), and the following melting-point depressions were observed for blends containing 10—50 wt% CELL: $\Delta T_m = 1.7°C$ (10/90), 2.7°C (20/80), 3.1°C (30/70), 5.1°C (40/60), and 6.8°C (50/50). Values of the parameter ϕ, determined from the slope of each straight line, were as follows: $\phi = 0.150$ (0/100), 0.157 (10/90), 0.152 (20/80), 0.172 (30/70), 0.154 (40/60), and 0.128 (50/50). The relatively small

values for ϕ, ranging ca. 0.13—0.17, suggest that the crystals formed isothermally are considerably stable.

The equilibrium melting point depression observed above may be primarily ascribed to the diluent effect of amorphous CELL molecules and can be treated using a thermodynamic approach based on polymer–polymer mixing accompanied by an exothermic interaction between the two components.[14,15] In this case, the equation for the melting point depression can be represented as follows[14,16]:

$$\Delta T_m = T_m^0 - T_m = -T_m^0(V_{2u}/\Delta H_{2u})Bv_1^2 \quad (2)$$

where the subscripts 1 and 2 are amorphous and crystalline components, respectively, T_m^0 is the melting point of pure crystalline polymer 2, T_m is the melting point of the blend, v is the volume fraction, V_u is the molar volume of the repeating units, ΔH_u is the enthalpy of fusion per mole of repeating unit, and B refers to the interaction energy density characteristic of the two components and is related to the thermodyamic interaction parameter χ_{12} by

$$B = RT(\chi_{12}/V_{1u}) \qquad (3)$$

where R is the gas constant.

Using the observed data of the equilibrium melting point depression, a plot of ΔT_m *versus*
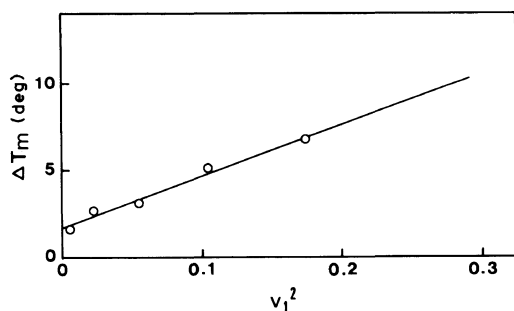
Figure 4. Melting point depression, ΔT_m, as a function of the square of volume fraction of cellulose, v_1^2, for CELL/PEO blends.

the square of volume fraction of CELL, v_1^2, was constructed as shown in Figure 4, where the solid line was drawn by the least-squares method assuming a linear relationship between ΔT_m and v_1^2. The volume fraction was calculated using the density data $\rho_1 = 1.51$ g cm^{-3} [17] and $\rho_2 = 1.09$ g cm^{-3} [18] given for cellulose with extremely low crystallinity and PEO melt (at 75°C), respectively. The straight line yields a slope 29.7°C and an intercept 1.7°C. The positive deviation from the origin is not beyond the usually observed limits 0.5—2.5°C attributed to a residual entropic effect,[16,19,20] which was neglected in the derivation of eq 2. From the slope of 29.7°C, we can evaluate the parameters B and χ_{12} by eq 2 and 3, respectively, as $B = -4.3$ cal cm^{-3} and $\chi_{12} = -0.67$ (at 348 K). For the assessment, $\Delta H_{2u}/V_{2u} = 49.7$ cal cm^{-3} [21] and $V_{1u} = 107.3$ cm^3 mol^{-1} were used, the latter being calculated from the molar mass (162.1) and a density (1.511 g cm^{-3}) for cellulose.

The fairly large negative values for the B and χ_{12} parameters strongly suggest the presence of favorable exothermic interactions between the two different polymers in the mixture. For elucidation of the details of these specific interactions, another measurement, e.g., Fourier-transform infrared spectroscopy, will be required. Further characterization of the CELL/PEO blends is now in progress in

the authors' laboratory.

REFERENCES

1. S. M. Hudson and J. A. Cuculo, *J. Macromol. Sci.-Rev. Macromol. Chem.*, **C18**, 1 (1980).
2. D. Gagnaire, D. Mancier, and M. Vincendon, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 13 (1980).
3. A. F. Turbak, R. B. Hammer, R. E. Davies, and H. L. Hergert, *Chemtech.*, 51 (1980).
4. C. L. McCormick and T. S. Shen, In "Macromolecular Solutions," R. B. Seymour and G. A. Stahl, Ed., Pergamon Press, New York, N. Y., 1982, pp 101—107.
5. A. El-Kafrawy, *J. Appl. Polym. Sci.*, **27**, 2435 (1982).
6. A. H. Jolan and R. E. Prud'homme, *J. Appl. Polym. Sci.*, **22**, 2533 (1978).
7. R. B. Seymour, E. L. Johnson, and G. A. Stahl, In "Macromolecular Solutions," R. B. Seymour and G. A. Stahl, Ed., Pergamon Press, New York, N. Y., 1982, pp 90—100.
8. N. D. Field and S. S. Song, *J. Polym. Sci., Polym. Phys. Ed.*, **22**, 101 (1984).
9. Y. Nishio, S. K. Roy, and R. St. J. Manley, *Polymer*, **28**, 1385 (1987).
10. Y. Nishio and R. St. J. Manley, *Macromolecules*, **21**, 1270 (1988).
11. Y. Nishio, T. Haratani, T. Takahashi, and R. St. J. Manley, *Macromolecules*, **22**, in press.
12. T. Tsutsui and R. Tanaka, *Kobunshi Ronbunshu*, **37**, 603 (1980).
13. J. D. Hoffman and J. J. Weeks, *J. Res. Nat. Bur. Stand.*, **66**, 13 (1962).
14. T. Nishi and T. T. Wang, *Macromolecules*, **8**, 909 (1975).
15. B. S. Morra and R. S. Stein, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 2243 (1982).
16. R. L. Imken, D. R. Paul, and J. W. Barlow, *Polym. Eng. Sci.*, **16**, 593 (1976).
17. J. A. Howsmon and R. H. Marchessault, *J. Appl. Polym. Sci.*, **1**, 313 (1959).
18. R.-J. Roe, *J. Phys. Chem.*, **72**, 2013 (1968).
19. D. R. Paul, J. W. Barlow, R. E. Bernstein, and D. C. Wahrmund, *Polym. Eng. Sci.*, **18**, 1225 (1978).
20. J. J. Ziska, J. W. Barlow, and D. R. Paul, *Polymer*, **22**, 918 (1981).
21. L. Mandelkern, F. A. Quinn, Jr., and P. J. Flory, *J. Appl. Phys.*, **25**, 830 (1954).