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Crystalline–Amorphous Phase Transition of a Poly(ethylene glycol)/Cellulose Blend[†]

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ABSTRACT: Poly(ethylene glycol) (PEG)/cellulose (CELL) blends prepared from solutions in dimethyl sulfoxide–paraformaldehyde were studied with X-ray diffraction and thermal analysis. PEG in the blend was found to be crystalline at room temperature. However, when the temperature was raised to PEG's melting point, PEG blended with CELL did not melt into the liquid state as in the case of pure PEG but changed to an amorphous solid state. Infrared spectroscopy investigations suggested that there were quite strong intermolecular hydrogen bonds formed between PEG and CELL in the blends. PEG's molecules probably are tied to the semirigid CELL chains so strongly by the hydrogen bonds that they cannot change to a liquid state but change to the amorphous state by thermal vibration at high temperatures.

Introduction

Poly(ethylene glycol) (PEG), $H(OCH_2CH_2)_nOH$, is a crystalline solid at room temperature when n is greater than 16, or when its average molecular weight is greater than 800. The crystalline solid of PEG changes to the liquid state without going through a glass state when the temperature increases to the melting point. However, recent research[1] demonstrates that the phase change behavior of PEG in blends with CELL prepared from solutions in dimethyl sulfoxide–paraformaldehyde (DMSO–PF) is completely different. Instead of the solid–liquid phase transition of pure PEG, PEG blended with CELL exhibits a solid–solid phase transition at a temperature slightly below the melting point of pure PEG.

In the present paper, the structural features of this PEG/CELL blend and the mechanism of its solid–solid phase change are studied. These PEG/CELL blends were investigated with differential scanning calorimetry (DSC), thermomechanical analysis (TMA), wide angle X-ray diffraction (WAXD), and Fourier transform infrared spectroscopy (FTIR). The results are discussed in the context of the crystalline–amorphous transition of PEG. A probable scheme of the intermolecular hydrogen bonds in existence between PEG and CELL in the blend is proposed.

Experimental Section

Pulverized, washed, and dried wood pulp with a degree of polymerization of 839 was used as the cellulose sample. Samples of PEG with average molecular weights (MW) ranging from 600 to 8000 and reagent-grade DMSO and PF were purchased from Guangzhou Chemical Reagent Co., Guangzhou, China. All samples were stored over potassium hydroxide for more than 1 week before use.

The samples of CELL, PF, and DMSO were mixed in a ratio of 1/2/18 in weight. The mixture was stirred at a temperature of 110–130 °C until dissolution of cellulose was complete. Then the solution was cooled to 60 °C and filtered through a coarse fritted-glass funnel under reduced pressure with a mechanical pump. The resulting solution was visually clear, with a cellulose concentration of about 5.0 wt %, determined by a coagulation method.[2] PEG solutions from 5 to 40 wt % in DMSO were prepared by dissolving the polymer at 60 °C under continuous stirring.

The two solutions thus separately prepared were mixed and stirred at room temperature in the desired proportions, so that the relative composition of PEG/CELL in the mixed solution ranged from 95/5 to 50/50 in weight. The mixed solutions were undisturbed and stored for more than 2 h and then used to prepare PEG/CELL blends with a coagulation method similar to that described by Nishio and Manley.[2] The coagulants used were acetone and alcohol.

Transition points and the enthalpy of the phase changes of the solid blends were measured with a Perkin-Elmer differential scanning calorimeter (DSC-2C), heating and cooling at a rate of 5 °C/min in a range of 15–100 °C. A Shimadzu-1 thermomechanical analyzer (TMA) was used to detect the solid–liquid transition, that is, the melting of the solid samples. A small weight of 5 g was put on the upper surface of the sample and the displacement of the weight was recorded to an accuracy of ±0.001 mm. The sample was heated at a rate of 5 °C/min from 15 to 100 °C, more than 30 deg above the melting point of PEG. The solid–liquid transition, if it occurs, will be detected by a rapid shift of the displacement of this weight.

Wide angle X-ray 2θ scanning diffraction curves ranging from 5 to 40° were collected at selected temperatures with a Rigaku D/MAx-1200 X-ray diffractometer. The incident X-ray was Cu Kα with a power of 40 kV, 25 mA, passed through a nickel filter. A pulse-height discriminator was used to make further monochromatization.

FTIR investigation was conducted with a Nicolet-7199B spectrometer. The samples studied were dried and cut to a powder of about 0.2 mm in size. The powder sample was mixed with KBr and was pressed to give a pellet to be used as the FTIR analysis sample. The data of WAXD and FTIR were processed by computer.

Results and Discussion

(1) Visual Observation. Mixed solutions of PEG/CELL were optically clear in the PEG concentration range 5–40 wt % and at a CELL concentration of 5 wt %, over the range of mixture ratios from 95/5 to 50/50 (PEG/CELL). However, precipitation took place and the mixed solutions became turbid when the solutions contained more than 40 wt % PEG.

Solid blends obtained from the mixed solutions are hard and slightly white in color at room temperature. When the temperature rises to 50 °C, the blend becomes more and more transparent. It becomes quite transpar-

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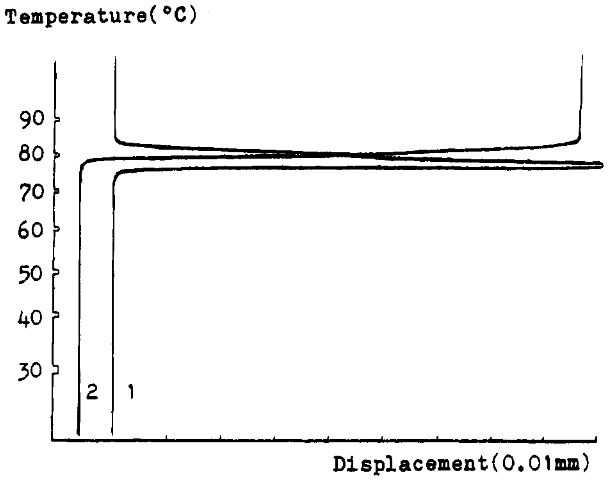

Figure 1. Thermomechanical analysis of a PEG sample with an average molecular weight of 4000: (1) differential displacement curve; (2) integral displacement curve.

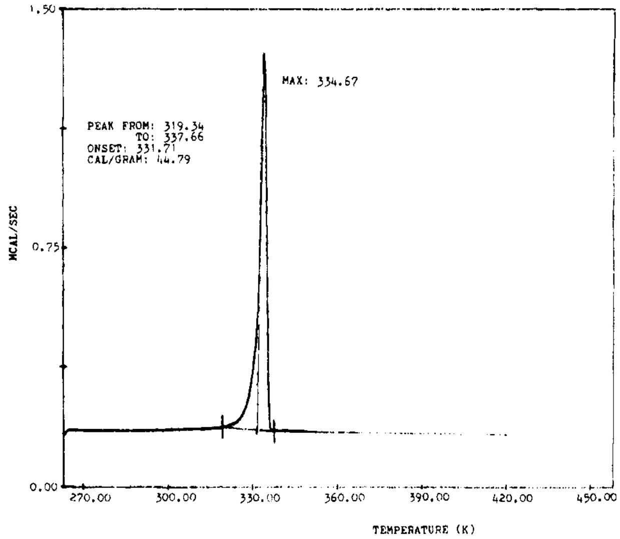

Figure 2. Differential scanning calorimetry of a PEG sample with an average molecular weight of 4000.

ent at about 60 °C and higher temperatures. Even up to 100 °C, the blend remains solid, as observed visually.

(2) Phase Change Investigations. Figure 1 shows the integral and differential TMA curves of a sample of PEG with an average MW of 4000. The peak in the differential curve and the rapid shift of the integral curve indicate that melting has occurred. Similarly, DSC measurement (Figure 2) indicates this melting as well as an enthalpy of 44.79 cal/g (187.4 J/g). The melting point shown in TMA is about 18 deg higher than that in DSC. This results from the different samples used in these two instruments. A cylindrical sample of 100–150 mg is required in TMA, whereas only 5–10 mg of a powder of about 0.3 mm in size is used in DSC. The melting of the larger sample in TMA is more difficult to complete than that in DSC because of the slower thermal transmission, and so the melting point shown is higher. In fact TMA is not a good method for measuring the melting point. It has been used here just for checking if the melting occurs or not.

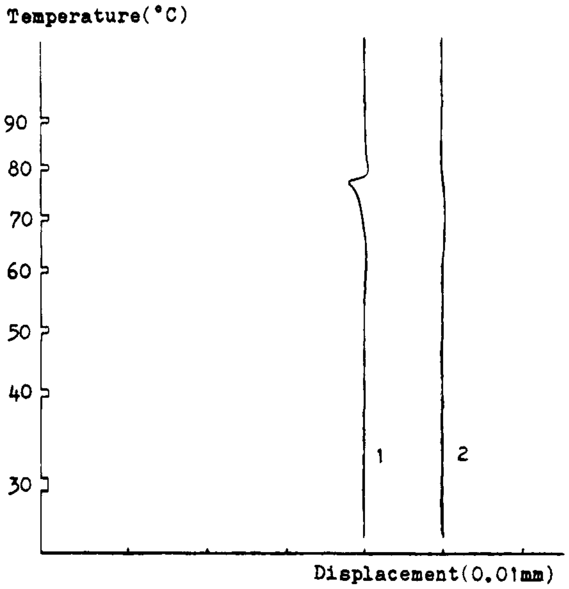

Figure 3. Thermomechanical analysis of PEG/CELL blend B1 with a composition ratio of 95/5 (PEG/CELL): (1) differential displacement curve; (2) integral displacement curve.

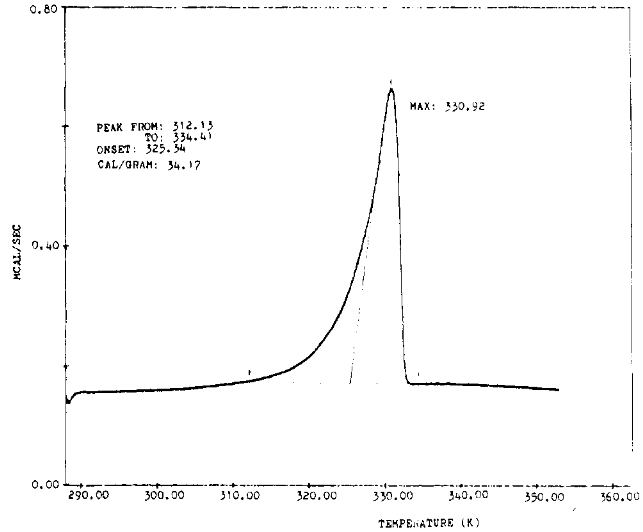

Figure 4. DSC curve (heating cycle) of PEG/CELL blend B1 with a composition ratio of 95/5 (PEG/CELL).

However, in contrast with the pure PEG, PEG in a blend with CELL does not change to the liquid state even at a temperature much higher than PEG's MP, as shown in Figure 3. The TMA curve of blend B1 (with a PEG/CELL ratio of 95/5) indicates that PEG in the blend remains in the solid state even when the temperature rises to 100 °C, over 40 deg above the MP of PEG.

On the other hand, the DSC measurement of B1 (Figure 4) shows a heat absorption at about 55 °C in the heating cycle, indicating that there is a phase transition taking place. This should be a solid–solid phase transition, since the sample has not melted to a liquid at that temperature, as indicated by the TMA analysis above. In the cooling cycle of DSC, a similar quantity of heat is released, as shown in Figure 5. Table 1 shows the transition temperatures (T_{tr}, regarded as the temperature of the onset point on the DSC curve) and enthalpy (ΔH) of the phase changes of PEG and the PEG/CELL blend.

The existence of a solid state phase transition of the PEG/CELL blend is evidenced by the TMA investigation as well. Figure 3 shows that there is a slight shrinkage, subsequently followed by an expansion in volume occurring in blend B1 at about 50–60 °C, which corresponds to the temperature range in DSC curves where the heat absorption takes place. It is well-known that a solid–solid phase change usually is accompanied by an expansion or a shrinkage in volume[3] of the sample.

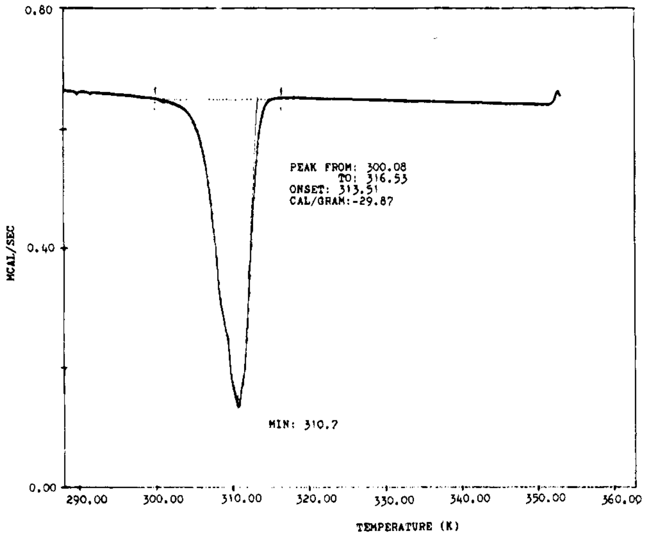

Figure 5. DSC curve (cooling cycle) of PEG/CELL blend B1 with a composition ratio of 95/5 (PEG/CELL).

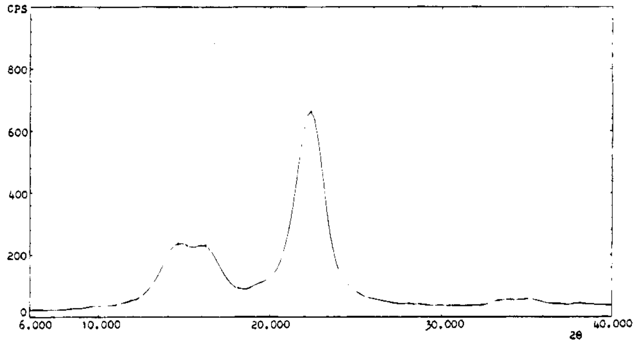

Figure 6. WAXD analysis of a sample of CELL—a wood pulp with a degree of polymerization of 839.

Table 1. Parameters of Phase Transition of PEG with MW 4000 and PEG/CELL Blend Sample B1 with a Composition Ratio of 95/5 Measured by DSC

		temp of transition (°C)[a]		enthalpy of transition Δ*H* (J/g)	
sample	phase transition	heating cycle	cooling cycle	heating cycle	cooling cycle
PEG	solid–liquid	58.5	48.1	187.2	180.1
B1	solid–solid	52.2	40.4	142.9	125.0

[a] The transition temperature was regarded as the onset temperature of DSC; see Figures 2, 4, and 5.

(3) Crystalline State Investigations. Figures 6 and 7 are WAXD patterns of the samples of CELL and regenerated CELL, respectively. The sample of CELL is a wood pulp as described above, and the regenerated CELL sample is obtained by dissolving the wood pulp in DMSO/PF and then precipitating it from this solution. Figure 6 shows that the wood pulp presents a typical crystalline CELL I pattern. However, after dissolving and regenerating, it becomes completely amorphous, as shown by Figure 7.

Figures 8 and 9 show the WAXD patterns of two samples, PEG with a MW of 4000 and PEG/CELL blend B1, respectively. Table 2 collects the WAXD data of the highest three peaks of these two samples. It is obvious that both pure PEG and PEG in the blend with CELL are crystalline at room temperature. Furthermore, they have the same unit cell, as demonstrated by their exactly identical X-ray diffraction spacings, as shown in Table 2. In other words, the crystal structure of PEG has not been changed by the procedure of blending, and therefore, there are no chemical changes at all. The only difference between these two samples shown by Table 2 is that the half-widths of the X-ray peaks of PEG in the blend with CELL are greater than those of pure PEG, indicating that the crystallite size of PEG becomes smaller after blending with CELL.

Comparing Figure 9 (the WAXD of PEG/CELL blend B1) with Figures 7 and 8 (WAXD of regenerated CELL and pure PEG), we learn that this PEG/CELL blend in fact is a mixture of PEG in the crystalline state with CELL in the amorphous state.

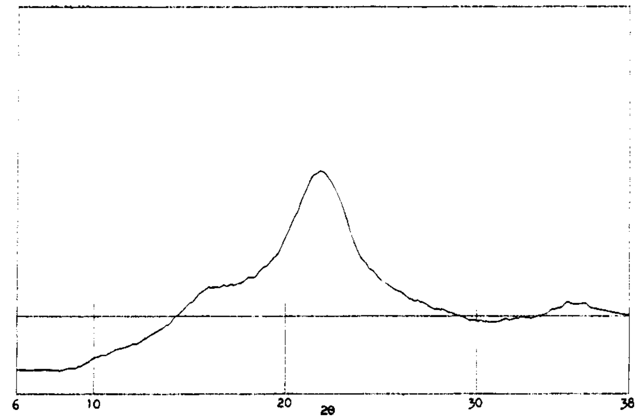

Figure 7. WAXD analysis of regenerated CELL.

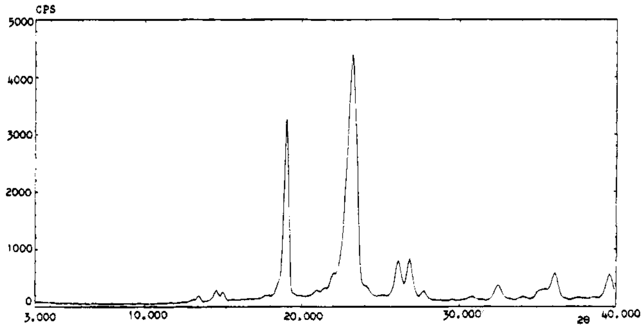

Figure 8. WAXD analysis of a sample of PEG with an average MW of 4000.

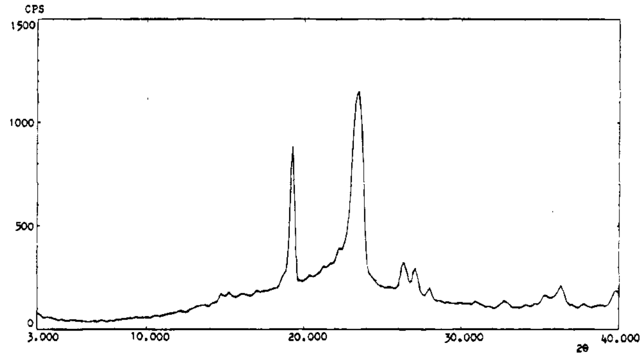

Figure 9. WAXD analysis of PEG/CELL blend sample B1 with a composition ratio of 95/5 (PEG/CELL).

Table 2. Highest Three Peaks of WAXD of PEG and PEG/CELL Blend B1 with a Composition Ratio of 95/5

sample	peaks	2θ (deg)	*d* (Å)	half-width	rel intens
PEG	1	23.22	3.83	0.75	100
	2	19.07	4.65	0.45	75
	3	26.12	3.41	0.53	19
B1	1	23.47	3.79	1.13	100
	2	19.27	4.60	0.53	77
	3	26.32	3.38	0.60	28

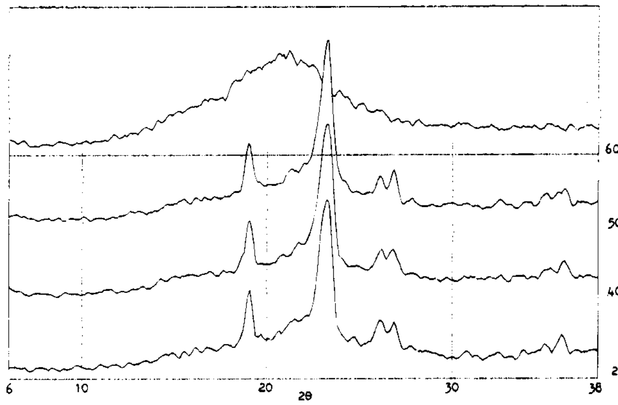

Figure 10. WAXD analysis of blend B1 at different temperatures.

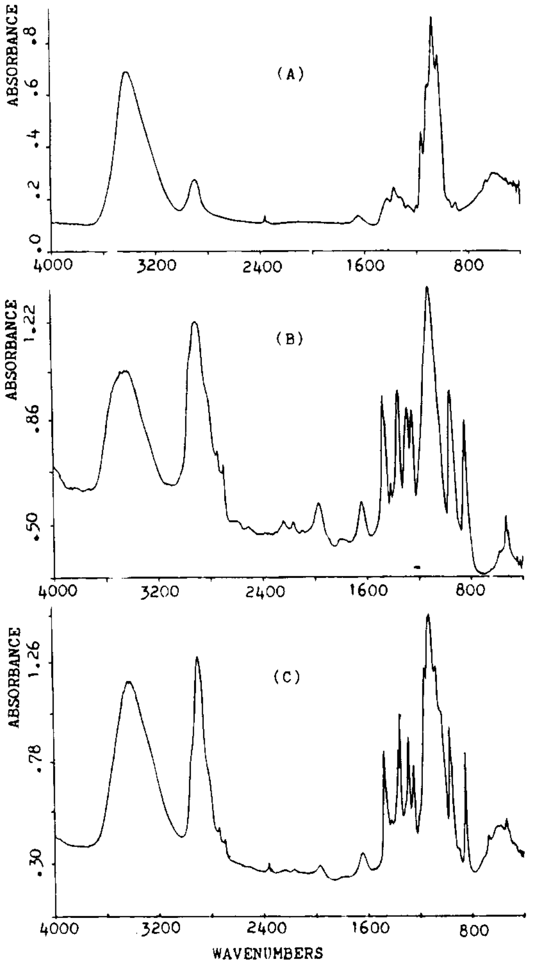

Figure 11. FTIR spectrum of regenerated CELL (A), PEG (B), and PEG/CELL blend B4.1 with a composite ratio of 80/20 (C).

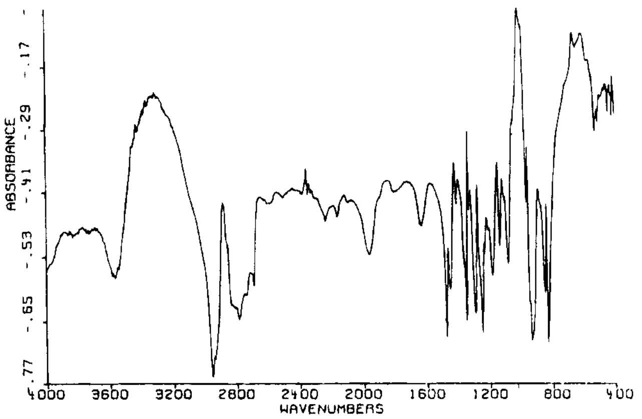

Figure 12. Differential FTIR spectrum of PEG to PEG/CELL blend B4.1 with a composite ratio of 80/20.

Table 3. Frequency Difference of the Stretching Band of the O–H and C–O Groups of CELL and CELL in PEG/CELL Blends

	O–H bond		C–O bond	
sample[a]	frequency (cm^{-1})	frequency diff	frequency (cm^{-1})	frequency diff
CELL	3401		1112	
D4.1 (B4.1 - PEG)	3194	−207	1015	−97
D4.2 (B4.2 - PEG)	3315	−86	1016	−96

[a] D4.1 and D4.2: the differential spectrum of PEG from B4.1 and B4.2, respectively. B4.1: a PEG (MW 1000)/CELL blend with a ratio of 80/20. B4.2: a PEG (MW 4000)/CELL blend with a ratio of 80/20.

Figure 10 shows the WAXD patterns of PEG/CELL blend B1 at several different temperatures. PEG in blend B1 maintains its quite perfect crystalline state when the temperature is not higher than 50 °C, as indicated by its high and sharp X-ray peaks. However, when the temperature rises to 60 °C, all the X-ray peaks disappear, and PEG in the blend becomes completely amorphous-as shown by the TMA analysis discussed above, it does not change to liquid, so it should be an amorphous solid. In other words, there is a crystalline–amorphous transition taking place at a temperature between 50 and 60 °C. As mentioned above, PEG/CELL blend B1 presents a solid-solid phase change at a temperature of 52.2 °C, indicated by DSC and TMA investigations. So we can come to the conclusion that the solid–solid phase change of the PEG/CELL blend in fact is a crystalline–amorphous transition of PEG in the blend. This is in agreement with the visual observations. As mentioned above, blend B1 becomes more transparent at temperatures of 60 °C or higher.

(4) Intermolecular Interactions in the Blend. In order to learn why the thermodynamic behavior of PEG in blends with CELL is so different from that of pure PEG, the intermolecular interaction of PEG and CELL in the blend has been investigated with FTIR. It has been well-known that the interactions between the components strongly affect the behavior of a polymer blend.[2,4,5]

Figure 11 shows the FTIR spectra of regenerated CELL, pure PEG, and PEG/CELL blend B4.1. It is demonstrated from Figure 11 that the spectrum of blend B4.1 is just an overlapping spectrum of regenerated CELL and PEG, and blend B4.1 is a mixture of the two components. No chemical reaction took place in PEG during the procedure of blending. This result agrees with the WAXD investigation described above.

A differential spectrum is obtained by subtracting the spectrum of PEG from the spectrum of blend B4.1 with a computer program attached in the instrument, as shown in Figure 12. This differential spectrum should be the spectrum contributed by CELL in blend B4.1. Comparing this differential spectrum with the spectrum of regenerated CELL (Figure 11), we can find that both stretching vibration bands of the O–H group and the C–O group in the blend shift observably to the direction of lower wavenumber. Table 3 indicates the frequency differences of the absorption band of the hydroxy group and carbonyl group, output by the instrument.

The shift of the carbonyl stretching band and hydroxy stretching band in a blend may result from the inter-

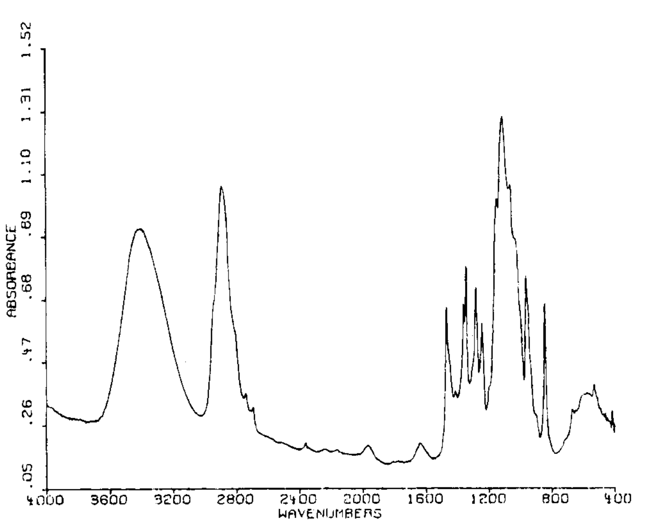

Figure 13. FTIR spectrum of PEG/CELL blend B4.1 with a composite ratio of 80/20 at a temperature of 85 °C.

molecular interaction, particularly from the intermolecular hydrogen bond.[5] The frequency difference is even considered as a measure of the average strength of the intermolecular hydrogen bond.[6] As shown in Table 3, the frequency differences between the stretching bands of CELL and those of CELL in PEG/CELL blends are equal to 86 and 207 cm^{-1}, depending on the molecular weight of PEG, indicating that the intermolecular interaction in the blend is quite strong. It is reasonable to suppose that there are quite strong intermolecular hydrogen bonds between PEG's end OH groups and CELL's latent OH group. It may therefore be assumed that the hydrogen bond fixes one end of the PEG molecules to the semirigid cellulose chains and makes the PEG molecules lose the freedom of translational motion. At the temperature of the melting point of PEG, about 60 °C, the energy of thermal vibration may not be great enough to destroy the hydrogen bond. This is probably why the PEG in the blend cannot change to a liquid state and changes to an amorphous state instead.

Figure 13 is the FTIR of blend B4.1 at a temperature of 85 °C. Comparing with the spectrum of B4.1 at room temperature (Figure 11C) we can find that there is no chemical change in B4.1 even when the temperature rises to 85 °C.

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