Mechano-chemical Preparation of Novel Cellulose-Poly(ethylene glycol) Composite

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A new type of cellulose composite was mechano-chemically prepared by ball-milling mixtures of cellulose and poly (ethylene glycol) (PEG). The composites are probably formed by insertion of PEG molecules among cellulose crystalline molecular-chains, and accordingly the compatibilization of cellulose and PEG through the formation of hydrogen-bonds, exhibiting a different mode of orientation of cellulose from that of similar blends from solution systems.

Cellulose exhibits no thermoplasticity and is insoluble in ordinary solvents owing to the tight inter- and intra-molecular hydrogen-bondings, and thus its applications have been limited to the areas of paper and rayon employing a suspension or solution system. To make extensive use of cellulose possible as a new industrial material, we have already developed biodegradable films derived from an aqueous suspension of micro-fibrillated cellulose and chitosan in acetic acid.[1-3] In this study, we demonstrate a mechano-chemical preparation of a novel composite of cellulose with poly (ethylene glycol) (PEG) under a dry- and solid-state.

Composites of cellulose with PEG were obtained by ball-milling mixtures of CF11[4] (degree of polymerization (DP) = 220; molecular weight (MW) = 3.6 x 10^4) and PEG (average MW = 2 x 10^6, 2 - 20 wt%).[5] Differential scanning calorimetry (DSC) measurement[6] showed that these products have one endothermal peak, because of a thermal phase transition of the PEG fraction. The transition temperature (onset) and enthalpy (ΔH) of the PEG fraction in the product decrease with a decrease in the PEG content as shown in Figure 1, although these behaviors were not observed in simple mixtures of CF11 and PEG with no ball-milling. To make clear the thermal behavior of PEG in the product, cellulose and PEG in the product were separated by washing with water and centrifuging, followed by vacuum drying. There are hereafter denoted as washed cellulose and extracted PEG, respectively.[7] Cellulose essentially has no melting point. The extracted PEG from the product with a PEG content = 20 wt% exhibited a sharp melting endothermal peak with the onset temperature at 62 °C, the maximum at 71 °C, and a melting enthalpy of 173.5 J/g. The melting temperatures (onset and maximum) and enthalpies of the extracted PEG from the products with PEG contents up to 20 wt% were nearly equal to one another, respectively. It has been reported that cellulose - PEG blends obtained from their solution exhibits a melting point depression, and a solid-solid phase transition of PEG.[8-10] The changes of melting point and phase transition observed in many synthetic polymer blends are due to miscibility.[11] A similar thermal behavior of PEG in the products suggests strong interactions between cellulose and PEG and thus a compatibilization of cellulose with PEG.

The interactions caused between cellulose and PEG in the products were examined from FT-IR and Raman spectroscopy. Both spectra of the product were described roughly by superposition of spectra of amorphous cellulose and PEG extracted from the product, and exhibited no new peaks due to the formation of covalent bonds between cellulose and PEG.

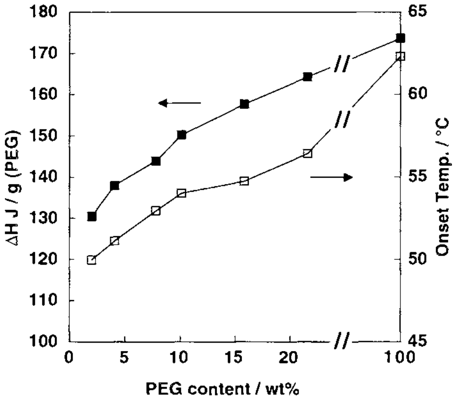

Figure 1. PEG content dependence of the enthalpy (ΔH) (■) and onset temperature (□) of the cellulose – PEG product.

Figure 2 shows IR spectra of the products in the range of OH stretching vibration bands. The product from pure cellulose (Figure 2(b)) gives a broader IR band than that of original CF11. The extracted PEG samples from the products exhibit almost the same spectra as in Figure 2(a). The OH stretching band of the product shifts to lower wavenumbers with an increase in the PEG content. A similar band shift of the OH band was also observed in the Raman spectra. Simple mixtures of CF11 and PEG with no ball-milling did not exhibit such band shifts of the OH bands. These band shifts are probably due to the formation of hydrogen-bonds between cellulose and PEG in the products.

In order to understand the mechanism for the compatibilization of cellulose with PEG in a dry- and solid-state, we examined the crystal structures of cellulose and PEG in the products by wide-angle X-ray diffraction (WAXD). Figure 3 shows WAXD patterns of the products. The product from CF11 and 0 wt% PEG (cellulose only) has a broad peak at 2θ = ca. 20 ° in Figure 3(c) and is completely amorphous (crystallinity index (CI)[4] = nearly 0 %), quite different from original CF11 (CI = 93%) in Figure 3(b). In Figure 3(d), cellulose in the product with 20 wt% PEG is almost in an amorphous state (CI = ca. 9%); the other products exhibit low CI values for the included cellulose ranging from 0 to 11%. On the other hand, PEG in the product with 20 wt% PEG remains crystalline (Figure 3(d)) and the degree of crystallinity is almost the same as that of the extracted PEG (Figure 3(a)). This supports the opinion that PEG in the product does not undergo any chemical change except for a decrease in MW.[7] No chemical change of PEG in the product was supported by IR or Raman spectra. PEG in the blends from solution system is also crystalline and has the same unit-cell as original PEG.[10]

The washed cellulose from the product with 20 wt% PEG has stronger and sharper X-ray diffraction peaks than those of cellulose in the product (Figures 3(d) and 3(e)). The CI value of the washed cellulose increases to about 50%, indicating intensive recrystallization of cellulose after extracting PEG from the product. The recrystallization increased with an increase in

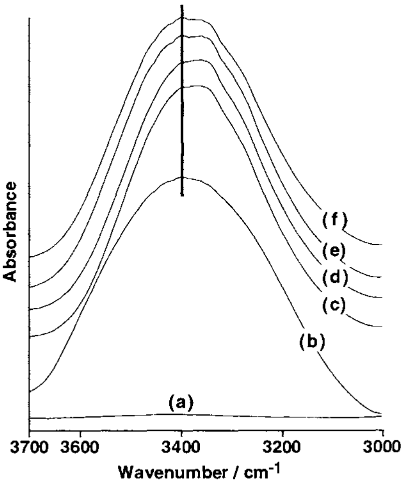

Figure 2. IR spectra of the products from cellulose - PEG mixtures: (a), the extracted PEG from the product with 20 wt% PEG; (b), CF11+0 wt% PEG; (c), CF11+4 wt% PEG; (d), CF11+8 wt% PEG; (e), CF11+15 wt% PEG; (f), CF11+20 wt% PEG.

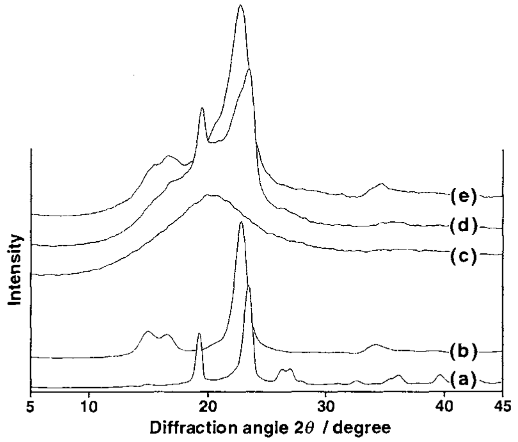

Figure 3. WAXD patterns of the products from cellulose - PEG mixtures and of reference samples: (a), the extracted PEG from the product with 20 wt% PEG; (b), original CF11; (c), CF11+PEG 0wt% (cellulose only); (d), CF11+PEG 20wt%; (e), the washed cellulose from the product with 20 wt% PEG.

the PEG content, the CI value ranging from 30 to 50%. The WAXD pattern of the washed cellulose is in agreement with a typical crystalline cellulose I pattern (Figure 3(e)). The similarity to the pattern of original CF11 (Figure 3(b)) suggested that the recrystallization proceeds through a crystalline cellulose I type. It is noted that no recrystallization of cellulose was observed even if the amorphous cellulose obtained from CF11 + 0 wt% PEG (Figure 3(c)) was washed with water. These results suggest that, when a mixture of cellulose and PEG is milled, the mechanical stress principally makes cellulose amorphous to cause insertion of parts of PEG molecules among the cellulose molecular-chains with other parts of PEG molecules in crystalline state assembling on the surface of cellulose molecules, and accordingly the formation of hydrogen-bonds between cellulose and PEG induces the compatibilization between cellulose and PEG. The marked recrystallization of the washed cellulose in a cellulose I type after extracting PEG from the product implies that cellulose in the product maintains a molecular orientation close to the cellulose I type.

Cellulose in the blends of cellulose and PEG obtained from their solutions recrystallizes to a cellulose II type on extracting PEG from the blends with water.[12] Recrystallization to a cellulose II type is usually observed for regenerated cellulose obtained through a dissolving process, because a cellulose II type is thermodynamically more stable than a cellulose I type. The crysallization of cellulose molecules in the blends through a cellulose II type may be due to random orientation of cellulose molecules, which is different from the orientation of cellulose in the products described above. Accordingly, the compatibilization of cellulose with PEG by milling results from a specific mechano-chemical mechanism in a dry- and solid-state, quite different from the case of the blend obtained in a solution system.

In conclusion, the new cellulose composites were mechano-chemically prepared by ball-milling mixtures of cellulose and PEG under a dry- and solid-state. The compatibilization of cellulose and PEG is probably caused by insertion of parts of PEG molecules among cellulose molecular-chains, followed by the formation of hydrogen-bonds between OH groups of cellulose molecules and ether oxygens of PEG molecules. The composites have a different mode of orientation of cellulose from that of similar blends obtained from solution systems. New composites of cellulose with PEG produced by a milling method without solvents will intensively facilitate the development of functional celluloses and their new utilization.

References and Notes

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4 CF11 (Whatman) was used as a pure fibrous cellulose sample without further purification. The crystal structure of CF11 is native cellulose I type, with a crystallinity index (CI) of 93%. The DP value of cellulose was calculated from the intrinsic viscosity of a 0.5 wt% Cu - ethylenediamine solution; *TAPPI Standard Methods T-230 om-82* (1982); H. Sihtola, B. Kyrklund, L. Laamanen, and I. Palenius, *Paperi ja puu*, **45**, 225 (1963). MW of cellulose is calculated by follow equation; MW = 162 ($C_6H_{10}O_5$) x DP. The CI value of cellulose was calculated from wide-angle X-ray diffraction; A. Isogai and M. Usuda, *Sen'i Gakkaishi*, **46**, 324 (1990).

5 The products were prepared as follows. Vacuum-dried mixtures of CF11 and PEG (2 - 20 wt%) were milled in a vibratory ball mill (C.M.T Ltd., Japan, TI-500DX) at -25 °C to prevent PEG from melting under an airtight condition. After milling for 300 min, the product was warmed up to room temperature in a dry condition.

6 The DSC measurements were performed on 5 - 10 mg of the products or PEG at a heating rate of 10 °C / min over a range of -50 – 100 °C.

7 DP values of the washed cellulose were 199 – 209 (MW = 3.2 – 3.4 x 10^4), and MW values of the extracted PEG were approximately 1.5 x 10^5.

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