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Morphological studies on the blends of polyethyleneoxide and cellulose ethers

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Summary

The blends of the water soluble polymers, PEO/HPC and PEO/CMC show crystallization of PEO over a wide composition range. The crystallinity of the PEO fraction decreases drastically beyond an HPC concentration of 70%, whereas it persists throughout the composition range in the case of the blend with CMC. This leads to the conclusion that at low concentrations, PEO is more compatible with HPC than with CMC. The films of the blends exhibit a skin as seen in the cross-sections of the films. Calorimetric studies show that annealing above T_m of PEO or prolonged annealing below T_m causes disorder of the PEO crystalline domains.

Introduction

A number of studies have been reported in the literature on the morphological characteristics of polymer blends in which one of the polymer components is crystallizable. Polyethyleneoxide (PEO) or poly(ε-caprolactone) has been used as the crystallizable polymer in most of these efforts (1-4). Blends of cellulose with vinyl polymers have also been studied recently. The morphological studies of blends of cellulose with polyvinylalcohol, polyacrylonitrile and PEO have been reported (5-7). It is well known that cellulose is notoriously insoluble in common organic solvents and blends in these cases had to be prepared by treatment with N,N-dimethylacetamide-lithium chloride.

In this paper, we describe the studies on blends of PEO with hydroxypropylcellulose (HPC) and carboxymethyl cellulose (CMC). Studies on crystalline/amorphous polymer blends are traditionally conducted on isothermally crystallized samples and are important for a fundamental understanding of these systems. However, the morphologies of as cast films have a bearing on industrial processes and applications and hence the present paper deals with observations on as prepared and annealed films. Although HPC can be crystallized and the crystal structure is known (8), under the conditions of the present experiments, the HPC component remains amorphous. The PEO/HPC and the PEO/CMC systems differ from the studies cited above in some respects. In the case of PEO/PMMA or PEO/PVAc blends, the polymer chain skeletons are of similar cross section, and belong to the polyolefin family.

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These blends were prepared from non-aqueous (chloroform) solutions or by compression molding. In the case of PEO/HPC and PEO/CMC blends, all these polymers are water soluble. In addition, the skeletal sizes of HPC and CMC are significantly bulkier (in terms of the glucose unit and the substituents) than that of PEO.

Experimental

A PEO sample of M_w = 300,000 and an HPC sample with M_w = 300,000 and molar substitution of 3 were purchased from Polysciences Inc. and Scientific Polymer Products, respectively. A CMC sample of M_w = 250,000 and fractional substitution of 0.7 was purchased from polysciences Inc. Separate master solutions of PEO, HPC and CMC were prepared with distilled water, with a concentration of 1% (wt) of the polymer, with stirring for 20 hrs. The solutions were then allowed to stand for at least two days. The PEO/HPC blends of required composition were prepared by mixing the two master solutions in the appropriate ratios, stirring for 1hr and let stand for a day before casting the films. The films were prepared at room temperature. A polycarbonate petri dish was chosen as the substrate due to the ease it offered in peeling off the dried film, as opposed to a glass substrate. Films for optical microscopy were prepared by depositing a drop of the solution on a microscope slide and allowing it to dry under room conditions. The films of PEO/CMC blends were prepared in the same manner.

The films were characterized by differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and optical microscopy. Thermal analysis was performed on a Perkin Elmer DSC II differential scanning calorimeter. The crystallinity of the PEO fraction was calculated from the enthalpy of fusion, by taking the literature value (9) of 53 cal/gm for the enthalpy of fusion of 100% crystalline PEO. Scanning electron micrographs were recorded on a Philips 505 SEM. Some of the films were examined in cross-section on the SEM. Samples for this purpose were prepared by immersing the film in liquid nitrogen for 30 seconds and fracturing it with a pair of tweezers. The optical micrographs were recorded using a Zeiss Axioplan polarizing optical microscope. The films were studied as cast, after annealing at 70°C (near the T_m of PEO) for 1hr and annealing at $52 \pm 2°$ C, (below the T_m of PEO) for periods ranging from 1 to 72 hrs.

Results and discussion

PEO/HPC blends

Figure 1 shows the variation of $\Delta H_{f,b}$ of the blend and $\Delta H_{f,peo}$ of the PEO fraction as a function of the blend composition. The value of $\Delta H_{f,b}$ decreases monotonically with an increase in the fraction of HPC. This behavior is similar to that observed in the case of isothermally crystallized blends of PEO with polycarbonates (10) and PVAc (4). It was also seen in the work of Ong and Price (11) with blends of poly(ε-caprolactone) and PVC. The $\Delta H_{f,peo}$ does not show any significant change up to an HPC concentration of 60%. The crystallinity of PEO as a function of blend composition, shown in Figure 2 follows the same trend. In blends of these compositions, which are rich in PEO, it can be expected that the amorphous HPC is accommodated in the inter-lamellar regions within

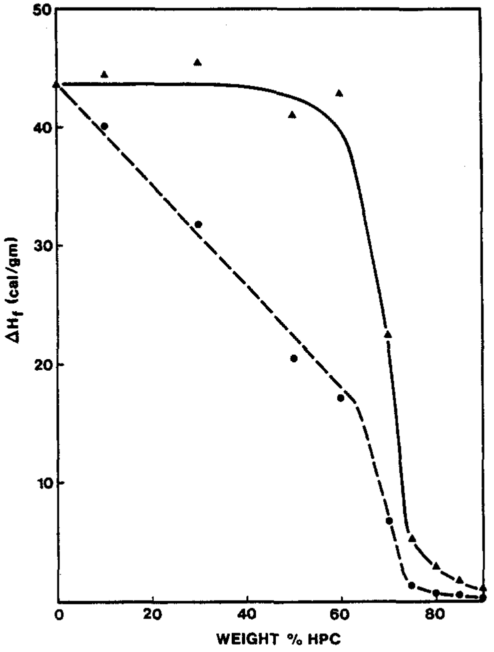

Figure 1. Variation of the enthalpy of fusion of the PEO/HPC blend (●) and of the PEO fraction (▲) are shown as a function of HPC concentration.

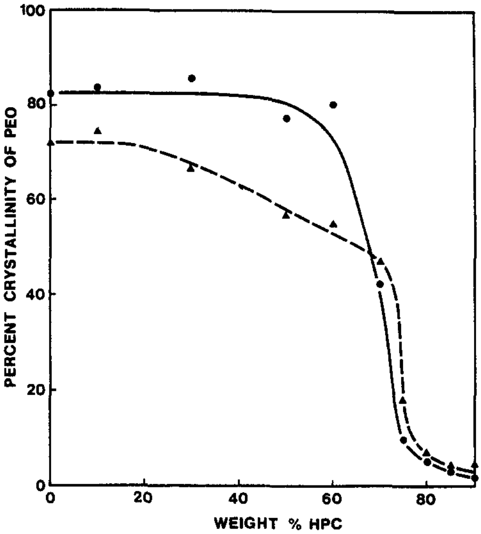

Figure 2. Variation of the crystallinity of the PEO fraction is shown as a function of HPC concentration, before (●) and after annealing at 70°C for 1 hr(▲).

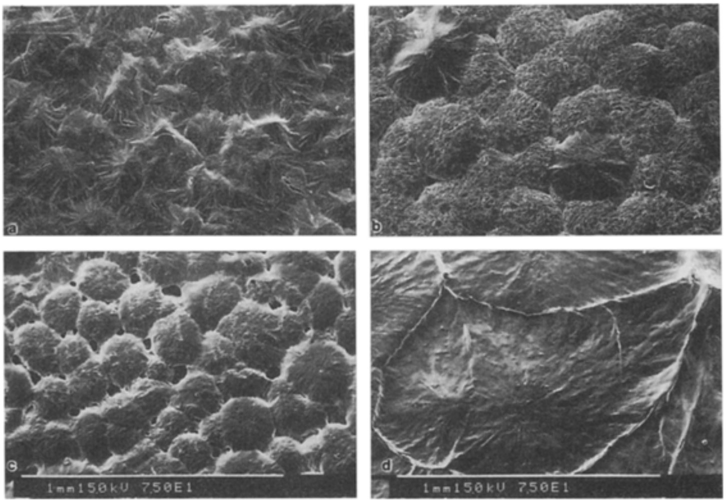

Figure 3. Micrographs of the PEO/HPC blend for the following compositions : (a) 100/0, (b) 90/10, (c) 70/30 and (d) 50/50.

the spherulitic domains as well as inter-spherulitic regions. Progressive coarsening of the spherulites and their sparsity, as the HPC concentration increases, is seen in Figure 3. Between an HPC concentration of 60-70%, there is a drastic reduction in the fraction of crystalline PEO. This can be interpreted as due to the diffusion of PEO into the HPC rich matrix. The corresponding micrograph showed absence of spherulitic texture. Such a decrease in the crystallinity was also observed by Ong and Price (11) between 50 and 60% PVC

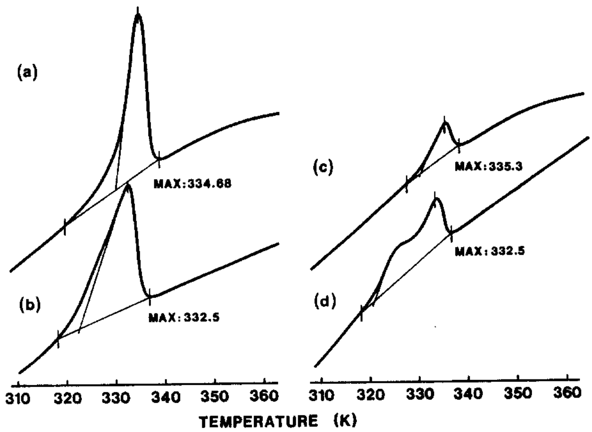

Figure 4. The melting peak profiles for (a) 30/70 PEO/HPC blend before annealing, (b) after annealing at 70°C for 1 hr, (c) 25/75 blend before annealing, and (d) after annealing.

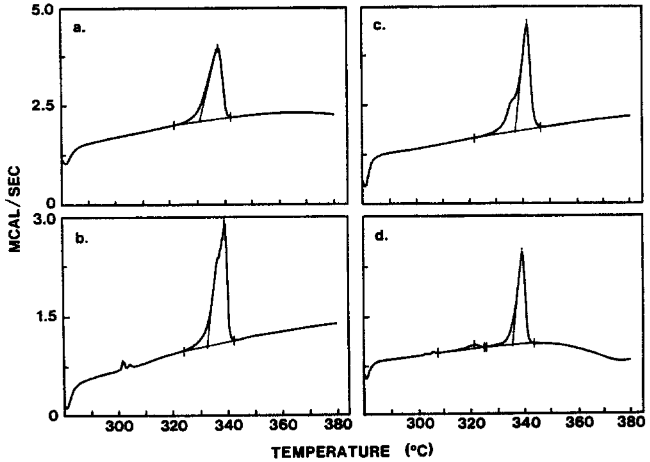

Figure 5. Changes in the melting peak profile are shown for the 30/70 PEO/HPC blend after annealing at 52°C for (a) 1hr, (b) 3hrs, (c) 9hrs and (d) 72 hrs.

concentration in the PCL/PVC blends. This behavior contrasts with the results of Kalfoglou et al (4) on isothermally crystallized PEO/PVAc blends in which the fraction of crystalline PEO remains constant throughout the composition range. The crystallinity of PEO upon annealing the blends at 70°C for 1 hr is shown in Figure 2. Up to an HPC concentration of 60%, there is a gradual decrease in the crystallinity and a sharp drop thereafter. It is also seen that in this range, there is a decrease in the crystalline PEO fraction compared to the initial sample. The decrease is more pronounced as the HPC concentration increases beyond 60%. Since the temperature of annealing in this case is close to the melting point of PEO, the enhanced diffusion of HPC in the inter-lamellar regions of the spherulites contributes to the observed reduction in the crystallinity and an increase in disorder, as shown by calorimetric studies. Figure 4 shows the DSC traces for two of the blend compositions, before and after annealing. The maximum of the melting endotherm shifts to lower temperature upon annealing, for all compositions. In addition, for the PEO/HPC:30/70 blend, the peak becomes broader, with a shoulder developing at the lower temperature. Similar broadening was seen for the 40/60 blend, with a pronounced low temperature tail. For the 25/75 blend, the endotherm becomes broader upon annealing, with a low temperature peak developing. The broad endotherms with multiple peaks can be rationalized on the basis of diffusion of PEO in the amorphous HPC matrix, resulting in poorly formed microcrystalline regions.

Annealing at 52°C for various lengths of time did not cause any significant change in the crystallinity. However, prolonged annealing at this temperature resulted in changes in the shape of the melting endotherms at low PEO

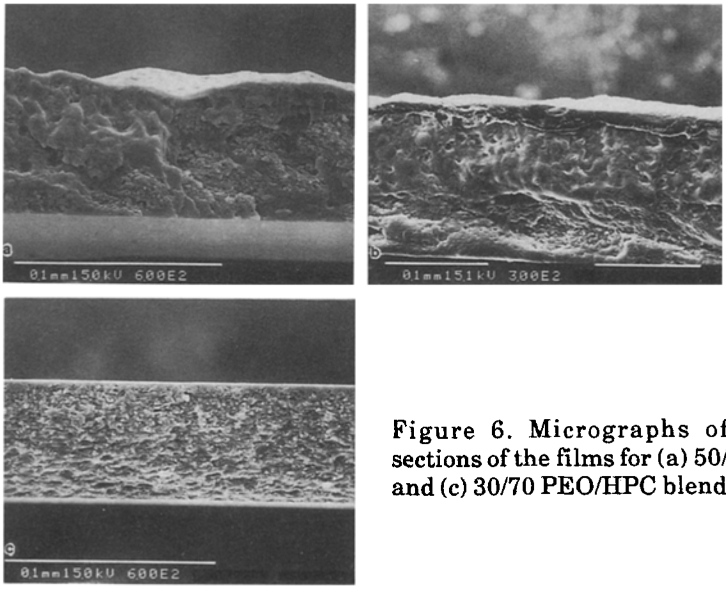

Figure 6. Micrographs of the cross sections of the films for (a) 50/50, (b) 40/60 and (c) 30/70 PEO/HPC blends.

concentrations. This is illustrated in Figure 5 for the 30/70 blend. Upon annealing for 3 hrs, a low temperature shoulder develops in the melting endotherm. This shoulder shifts to lower temperature after 9 hrs of annealing, and after 72 hrs, multiple low temperature peaks appear. Similar behavior was noted for the 15/85 blend upon annealing for 72 hrs. The slight decrease in the enthalpy of fusion with annealing rules out the possibility of developing perfection of PEO crystallites. Thus, annealing at 52°C for extended periods of time enhances the diffusion of PEO into the HPC domain, resulting in less ordered crystalline regions. Based on these observations, it may be concluded that annealing improves the miscibility of this blend.

The SEM micrographs of the cross sections of the films, (prepared by freeze-fracturing) are shown in Figure 6 for a few of the blend compositions. For the 50/50 and 40/60 blends, two types of textures are seen : one, a smooth agglomerated structure and the other, fibrous or porous. In addition, these samples exhibit a skin on the top of the film. The fibrous texture as well as the skin are less pronounced as the fraction of PEO in the film decreases, as seen for the 30/70 blend. The observation that the thickness of the skin decreases with an increase in HPC content leads to the conclusion that it is PEO enriched. Such enrichment of the surface by one of the components has also been observed in the case of films of blends of PEO and polystyrene as well as their diblock copolymers (12). However, attenuated total internal reflection IR spectroscopy did not confirm if the skin constituent is uniquely PEO or HPC. The effect of the drying protocol on the thickness of the skin has not been investigated here.

PEO / CMC Blends

Figure 7 shows the variation of $\Delta H_{f,b}$ of the blend and $\Delta H_{f,peo}$ of the PEO fraction as a function of the CMC concentration in the blend. The $\Delta H_{f,b}$ of the blend decreases monotonically throughout the entire concentration range. Up to a CMC concentration of 60% the values of $\Delta H_{f,b}$ are similar to those in Figure 1 for the PEO/HPC blend. The drastic reduction in $\Delta H_{f,b}$ which occurred for the PEO/HPC blend between 60 and 70% HPC, is not seen here. For example, for the 30/70 PEO/HPC blend, the value of $\Delta H_{f,b}$ is 5 cal.gm^{-1} whereas it is 12.5 cal.gm^{-1} for the PEO/CMC blend with the same composition. The value of $\Delta H_{f,peo}$ does not vary significantly up to a CMC concentration of 80% and drastic reduction is seen thereafter. This again is different from the behavior exhibited by the PEO/HPC blend. For a 30/70 PEO/HPC blend, the value of $\Delta H_{f,peo}$ is 22 cal.gm^{-1} whereas it is 42 cal.gm^{-1} for the 30/70 PEO/CMC blend. Even for a blend with 90% CMC, the $\Delta H_{f,peo}$ is 8 cal.gm^{-1}which amounts to about 16% crystallinity. Thus, the crystallinity of PEO in the PEO/CMC blend persists for all compositions.

The crystallinity of the PEO fraction as a function of the blend composition is shown in Figure 8. The same differences as above are noted between the PEO/HPC and PEO/CMC cases. For the 30/70 PEO/HPC blend, the crystallinity is 40% and it reduces to close to zero with an HPC concentration of 80%. However, with the PEO/CMC blend, the crystallinity is 70%, even for the 20/80 composition. A significant reduction in crystallinity is seen between a CMC concentration of 80 and 90%. Upon annealing at 70°C for 1 hr,the crystallinity reduces by about 10% up to a CMC concentration of 80% and the reduction is significant for the 15/85 PEO/CMC blend. The changes in the DSC profiles which were seen with the PEO/HPC blends with prolonged annealing were not observed in the case of the PEO/CMC blend.

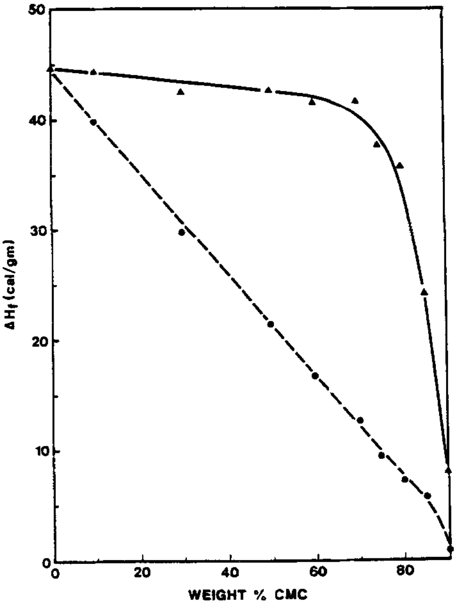

Figure 7. Variation of the enthalpy of fusion of the PEO/CMC blend (●) and of the PEO fraction (▲) are shown as a function of CMC concentration.

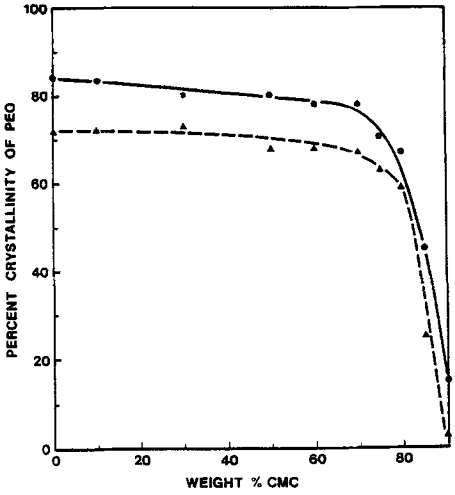

Figure 8. Variation of the crystallinity of the PEO fraction is shown as a function of CMC concentration, before (●) and after annealing at 70°C for 1 hr(▲).

SEM micrographs of films with high PEO concentrations (up to 50%) showed significant cracking along the spherulite interfaces, and propagating through the bulk of the film. Annealing the films at 70°C for 1 hr did not show any significant change in the surface morphology although it seemed to heal the bulk cracks. As the CMC concentration increases, the cracks are less pronounced. The skin which was present in the PEO/HPC blends in cross section is also seen in the case of the PEO/CMC blends. Here again, the skin becomes less pronounced as the CMC concentration increases.

Conclusions

The blends of the water soluble polymers, PEO/HPC and PEO/CMC show crystallization of PEO over a wide composition range. The crystallinity of the PEO fraction decreases drastically beyond a HPC concentration of 70%, whereas it persists throughout the composition range in the case of the blend with CMC. This leads to the conclusion that at low concentrations, PEO is more compatible with HPC than with CMC. The films of the blends exhibit a skin which is clearly seen in the cross-sections of the films. Although it is believed that the skin is PEO rich, the experiments performed in this study were not conclusive. The film preparation protocol such as the thickness and the drying conditions would no doubt affect the final morphology.

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