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Crystallization of water in swollen poly(vinyl alcohol)-poly(vinyl pyrrolidone) blends

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Summary

Water molecules sorbed in pure poly(vinyl alcohol) and poly(vinyl pyrrolidone), as well as in their blends is found to be only partially crystallizable. The fraction of non-crystalizable water is shown to vary with the blend composition. Such variation is explained by the newly proposed Tg-regulation effect when the swollen blend materials is cooled down. A part of the sorbed water cannot crystallize due to the fact that during cooling the amorphous polmer-water phase is frozen before the water crystallization temperature is reached.

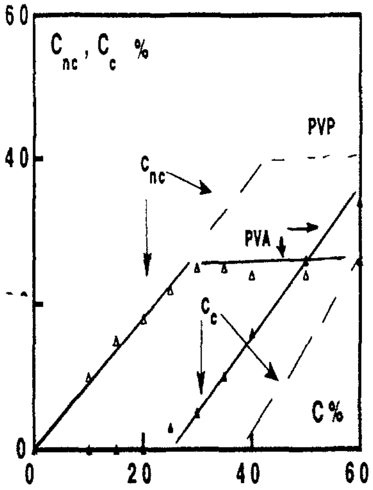
Introduction

Poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone) (PVP) as well as their blends were reported to be good materials for membrane dense active layers for organic solvent dehydration by pervaporation (1-3). This separation process involves a selective water sorption, from the liquid mixture, in the membrane material at one face followed by molecular diffusion of water (and organic solvent) to the other face; the membrane separation properties should be controlled by the sorbed-water properties. The latter properties can be studied by different methods , among which the differential scanning calorimetry (DSC) .Using this technique Higuchi et al (4) reported that water exists in PVA in at least two states : the bound and unbound states. In the first state ,water in polymer when cooled does not crystallize whereas in the second state it does; the non-crystallizable water is determined from the difference between the total sorbed amount and the measured crystallizable water amount (5). Gref et al (6) showed that water molecules in PVA can only crystallize when its content exceeds a critical, value, C^* which depend on the degree of acetylation. Ling and Zhang (7) reported C^* for a series of hydrophilic polymers. We recently proposed an alternative mechanism to explain the water non-crystallizability in a polymer material in DSC experiments (8). The mechanism, called the Tg-regulation effect, suggest that water cannot crystallize during the cooling down process because the water-polymer system is frozen in the glassy state before the water crystallization temperature is reached. The aim of the present work is to study the validity of this mechanism in the PVA-PVP-water systems.

Experimental

Materials :

All materials were prepared in film ,formed by the solution technique. PVA and PVP were dissolved in water (for PVP) or boiling water (for PVA). Solutions of polymer blends of different compositions were obtained by mixing 8 wt.% feed solutions of pure polymers in appropriate proportions. The films were made by casting polymer solutions on a



ig. 1 : Variations of the crystallizable Cc) and non-crystallizable (Cnc) water ontent as a function of the total sorbed-water content in pure PVA (continuous line) and pure PVP (dashed line).

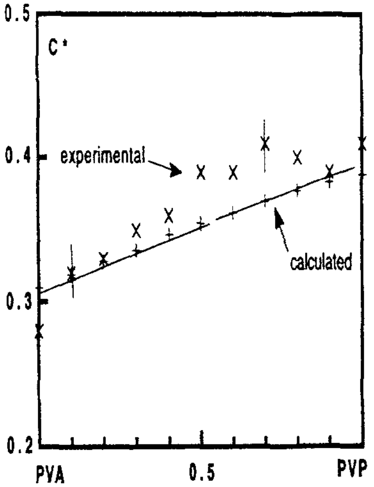


Fig. 2 : Variation of the critical-water content C^* as a function of the PVP wt. content in PVA-PVP blends. Points : experimentally determined C^* values ; line : theoretical C^* values determined according to the described procedure.

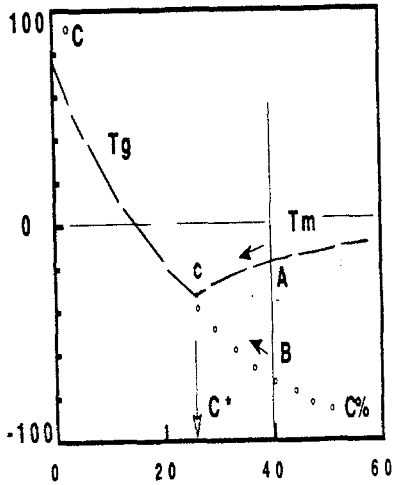


Fig. 3 : Variations of the glass transition temperature Tg and the ice melting temperature Tm of crystallizable water in the water-PVA system as a function of the water content in the system.

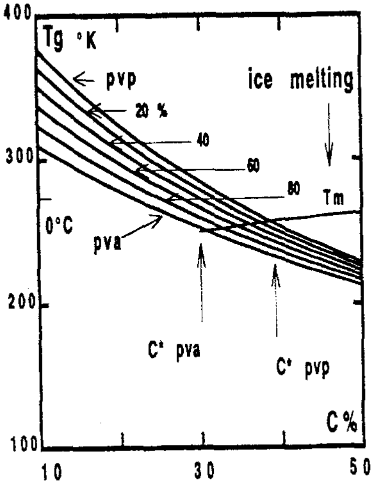


Fig. 4 : Calculated Tg curves for PVA-PVP blends of different compositions (with the Fox equation), and the ice melting temperature Tm curve for the blends. Intersection point abscissas give the C^* values for the different blends.

poly(methylmethacrylate) plate by means of a "Gardner knife", and then drying the liquid films at 60°C.

DSC operating conditions :

All films were dried under vacuum and stored in dry atmosphere. A precise water amount was added to a weighed sample placed in a DSC pan which is immediately and hermetically sealed. The added water amounts in all cases were smaller than the saturation level of the polymer materials. The sample were left to reach complete water absorption in the sealed pan, then studied in the DSC apparatus (Mettler model 3000). The amounts of crystallizable water were calculated from the ice melting peaks (Tm melting temperature) by assuming the melting enthalpy for the ice in the polymer material to be the same as that of free ice after correction ($C_p\Delta T$). The non-crystallizable-water amount for a swollen sample was deduced from the total sorbed amount and the crystallizable-water amount (if any).

Results and discussion

Fig. 1 shows the variations of the content in non-crystallizable water (in wt.%) in pure PVA and pure PVP as a function of the total water content in the polymer. It can be seen that above the critical value C^*, the content of this type of water remains constant and equal to C^*. It should be reminded that below the C^* value, no crystallizable water was detected. The plot of the experimentally determined critical water content C^* as a function of the PVP content (wt.%) in PVA-PVP blends (Fig. 2) exhibits an increase in the C^* value with the PVP content, which tends to level off at high PVP contents. The C^* values for pure PVA and pure PVP corresponds respectively to one and four water molecules per monomer unit, i.e. per polar group. Although the number of one water molecule per hydroxyle group can be explained by the formation of 1-1 hydrogen bonded complex, no realistic structure for hydrogen bonded complex four water molecules and one amide group in PVP and for the other polymers (7).

Let us apply the Tg-regulation effect (8-10) which is illustrated in Fig. 3. Briefly, when the water-polymer system is cooled down below 0°C, water molecules tend to gather together to form ice crystals, but it ability to gather together is prevented if the system is frozen into the glassy state. Below Tg,experiments on polymer and inorganic systems show that crystallization cannot occur because of the low mobility of the components.. As the variations of the Tg of PVA-water and PVP-water systems with the water content are well predicted by the Fox equation (11) we assume that the same equation can be applied to the water-polymer bend systems. The water Tg-value was taken to be -125°C (12), while those for blends of different compositions have been measured ; they also obey to the Fox equation. A series of curves of Tg *versus* water content were then generated by caculations for blends of different compositions (Fig. 4). The ice melting curvesTm (c) for PVA and in PVP-water systems are very similar (7,8), so that in this work we assume that an unique curve Tm (c) represents the variation of ice melting temperature for the pure swollen polymers and their blends. This Tm curve intersect the series of Tg(C) curves of the swollen blends at point C, whose abscissas represent the critical C^* values of the blends. When these theoretically determined C^* values are plotted as a function of the PVP content in blends, a good agreement with the experimentally-determined C^* is observed (Fig. 2).

The results indicate that the Tg-regulation effect applies to PVA-PVP blends. For water contents in the blends $C < C^*$, the water-polymer blend systems are frozen in the glassy state upon cooling before the *liquidus* line (Tm (c) is reached,therefore water molecules cannot crystallize below Tg. Above C^*, the Tm (c) curves is crossed first upon cooling and water starts to crystallize. As the crystallization proceeds (at constant cooling rate), the water content in the polymer materials decreases, leading to a decrease in the swollen materials Tg. During the process, the system Tm and Tg values describe respectively the AC and BC segments in Fig. 3, and the crystallization process stops when Tg becomes equal to Tm (at point C). The remaining amount of non-crystallizable water in the materials corresponds then to the C^* value of the specific blend.

In summary, the change in the critical C^* value of non-crystallizable water with the blend composition in DSC studies of water in PVA-PVP blend materials can be accounted for by the Tg-regulation effect. The C^* values can be predicted by using the Fox equation for water-materials mixture and a unique ice melting curve for water in these materials.

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