Structural Properties of CrF_3- and $MnCl_2$-Filled Poly(vinylalcohol) Films

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ABSTRACT: Poly(vinylalcohol) (PVA) films filled with different filling levels of CrF_3 and $MnCl_2$ have been prepared by the casting method. Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) analysis were used to study the changes in structure properties that occur due to filling. The changes occurring in the measured parameters with increasing the filler content was been interpreted in terms of the structural modification of the PVA matrix. It was found that all studied samples had the main melting temperature due to the main crystalline phase of PVA. The intensity and position of this peak depended on the filling level. On the other hand, the samples of CrF_3-filled PVA films with filling level $W \geq 10$ wt % revealed another melting temperature, indicating the presence of a new crystalline phase besides the main crystalline phase. Changes occurring in the degree of crystallinity of the studied samples were discussed. The calculated degree of crystallinity was formulated numerically to be an exponential function of filling level. The X-ray diffraction patterns of the studied samples confirmed the DSC results. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 516–521, 2003

Key words: $MnCl_2$; CrF_3; poly(vinyl alcohol); X-ray diffraction; differential scanning calorimetry

INTRODUCTION

Metal halide doped polymers have been the subject of both theoretical and experimental interests because of their increasing technological importance. Doping polymers with transition metal halides has a significant effect on its physical properties. The change in physical properties of the polymers due to doping depends on the chemical nature of the doping substances and the way in which they interact with the host matrix.[1–3] We may select the suitable type and doping level of transition metal halide to prepare a doped polymer with a desired physical property.[4]

Poly(vinylalcohol) (PVA) is a nontoxic water-soluble synthetic polymer, which is widely used in biochemical and medical applications due to its compatibility with the living body.[5] Water-soluble PVA is rendered insoluble by the introduction of crosslinks into the specimen. PVA has good film-forming, highly hydrophilic properties, and has been studied as a membrane in various ways. PVA has been exploited recently as a substrate for enzyme immobilization in the form of photocrosslinkable PVA.[6] PVA gels can be prepared from aqueous solutions by repetitive freezing and throwing.[7]

The film obtained by casting a PVA aqueous solution has a 100% amorphous structure. PVA hydrogels prepared by freezing the concentrated aqueous PVA solution exhibits, however, a diffraction pattern from the (101) spacing corresponding to 4.55 Å.[8] An important feature of the semicrystalline PVA polymer is the presence of crystalline and amorphous regions. These two regions are well separated by portions of intermediate degree of ordering that enhances the macromolecule to run through several crystalline and amorphous phases.

A crystalline polymer may be regarded as an amorphous matrix in which small crystallites are randomly distributed. However, it is more natural to treat a crystalline polymer as a specific sufficiently imperfect crystalline lattice in which the voids are filled with amorphous matter.[9] The role of amorphous regions may be played by sites saturated with crystal defects, which form chain-folded crystals. The importance of the semicrystalline PVA polymer arises from the role of the OH group and the hydrogen bond.[10]

Physical properties of PVA doped with some transition metal salts have been investigated.[11–13] The present work studies the effect of both filler concentration and the nature of metal halides on structure modification of PVA films.

EXPERIMENTAL PROCEDURES

Sample preparation

The PVA and metal halides used in this work were supplied by Aldrich Chemical Co., USA. The present PVA films with different amounts of chromium fluo-
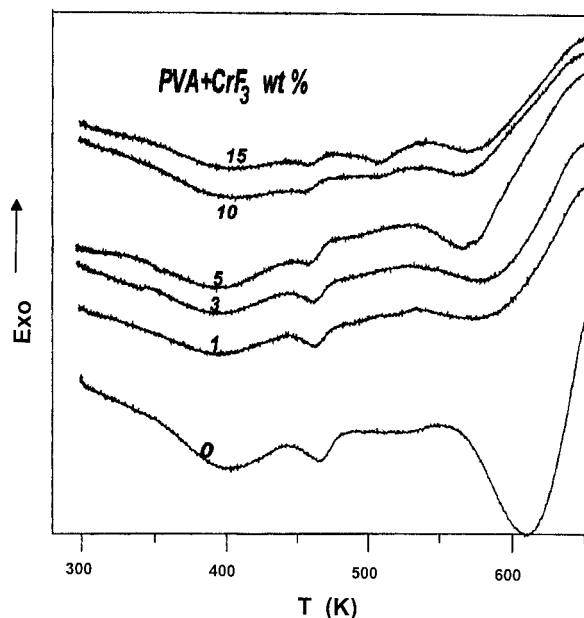
Figure 1 DSC curves for PVA films filled with different filling levels of CrF$_3$.

ride and manganese chloride were prepared by the casting method as follows[11]: PVA powder was dissolved in distilled water and then heated gently, using a water path, for complete dissolution. Chromium fluoride or manganese chloride also was dissolved in distilled water and added to the polymeric solution. The solutions were left to reach a suitable viscosity, after which they were cast in glass dishes and left to dry in a dry atmosphere at room temperature. Samples were transferred to an electric air oven held at 60°C for 48 h to minimize the residual solvent. The thickness of the obtained films was in the range of 0.1–0.2 mm. PVA films filled with CrF$_3$ mass fractions 0, 1, 3, 5, 10, and 15% and PVA films filled with MnCl$_2$ mass fractions 0, 10, 15, 20, 25, 35, and 40% were prepared. The filler concentration W (wt %) was calculated from the equation

$$W \text{ (wt \%)} = \frac{w_f}{w_p + w_f} \times 100 \qquad (1)$$

where w_f and w_p represent the weight of filler and polymer, respectively.

Physical measurements

Differential scanning calorimetry

The thermal analysis of PVA films filled with different mass fractions of metal halide were performed by differential scanning calorimetry (DSC) using a Stanton Redcroft Model DTA 673-4 apparatus. A heating cycle was made from room temperature up to 650 K using a programmed heating range of 10 K/min. The

values of the glass transition temperature and melting point were obtained. The change of the degree of crystallinity can be detected by calculating the endothermic thermogram area of DSC.

X-ray diffraction

X-ray diffraction (XRD) diagram of the studied samples were recorded with a Philips PW 1050/80 diffractometer. Ni-filtered CuK$_\alpha$ radiation generated 30 kV and 30 mA. The radiation was incident on the sample, which was scanned at 1°/min over a range of 2θ from 5° to 40°.

RESULTS AND DISCUSSION

Differential scanning calorimetry

The thermal behavior of PVA films filled with different fractions of CrF$_3$ was studied by DSC in the temperature range of 298–630 K (Fig. 1). From this figure we can observe that pure PVA films displayed three transitions at 351, 443, and 467 K, in addition to another endothermic peak at 610 K, which indicates the thermal degradation of the polymer. These transitions can be interpreted as follows[5,13,14]: The transition at about 351 K is attributed to the glass transition (T_g) relaxational process resulting from micro-Brownian motion of the main-chain backbone. The exothemic peak at about 443 K is broad and shallow, and attributed to the α relaxation associating with the crystalline region. The endothermic peak at 467 K has been attributed to the melting temperature (T_m) of pure PVA.

It is observed from Figure 1 that the thermal behavior of PVA films filled with mass fractions < 10 wt % CrF$_3$ is similar to that of pure PVA films. The magnitude of thermal degradation temperature (T_D) of the pure PVA is greater than those of the filled samples (Table I). It is suggested that the addition of CrF$_3$ to PVA films decreases the thermal stability. The position of T_g for PVA films filled with different amounts of CrF$_3$ samples is shifted slightly toward lower temperatures as compared with that of the unfilled one (Table I). This also suggests that the segmental mobility of amorphous pure PVA increases due to addition of CrF$_3$ and become less rigid segments. This indicates

TABLE I
The Transition Temperatures of DSC Thermogram for PVA Films Filled with Different Filling Levels of CrF$_3$

W (wt %)	T_g (K)	T_α (K)	T_D (K)	T_{m1} (K)	T_{m2} (K)
0	351	398	610	467	—
1	350	399	590	463	—
3	347	400	583	460	—
5	346	403	572	457	—
10	345	405	571	456	508
15	344	406	570	455	509
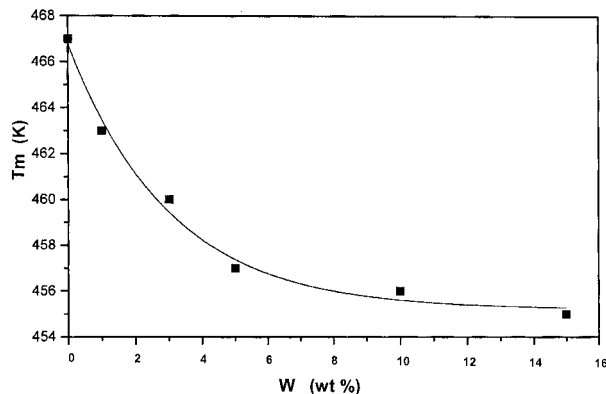
Figure 2 The filling level dependence of the melting temperature of CrF_3-filled PVA films.

W (wt%)	0	1	3	5	10	15
Crystallite Thickness (Å)	96	86	80	74	72	71

that the CrF_3 filler acts as plasticizer. Increasing CrF_3 content results in a decrease in both T_g and T_D of PVA films, indicating that the CrF_3 molecules greatly affect the PVA structure.

With respect to α-relaxation temperature T_α for PVA films filled with different amounts of CrF_3, Figure 1 shows that the value of T_α is slightly increased and its peak intensity is decreased with increasing the filling levels of CrF_3. The change in position of T_α may be mainly due to the effect of filling on the orientation of the crystals, crystallinity, and microstructure of the sample. It is known that the changes in the crystalline structure and morphology affect the magnitude and position of the α relaxation in PVA.[15] It is expected that T_α could be influenced by the size and perfection of the crystals, and thus their melting point. The magnitude of the relaxation may be affected by the orientation of the crystals and the crystallinity and microstructure of the sample. If the α relaxation in PVA is associated with a particular movement, its intensity will vary with crystal orientation. Thus, if the motions were perpendicular to the chain axis, the detected magnitude of the transition would decrease as the orientation of the crystals along the chain axis increases. Also, it is found that the α-relaxation magnitude depends on the density and perfection of crystal packing.[16] On the other hand, Popli et al.[17] measured T_α of polyethylene (PE) samples by dynamic mechanical analysis at 3.5 Hz. They reported that T_α depends on the crystal thickness.

A reduction of T_m of PVA crystals is evident with the increase of the CrF_3 filling levels (Table I). This behavior is illustrated in Figure 2, where T_m is plotted against filling levels of CrF_3. The distribution of melting temperatures were converted to a distribution of crystallite thickness using the Thomson–Gibbs' equation,[18]

$$T_m = T_m^o \left(1 - \frac{2\sigma_e}{\Delta H\, L} \right) \qquad (2)$$

where T_m is the observed melting temperature of a crystal of lamellar thickness L, T_m^o is the equilibrium melting temperature of an infinitely thick crystal, σ_e is the surface area of the chain folds, and ΔH is the heat of fusion per unit volume of the crystals. The values of $\sigma_e/\Delta H$ used for PVA was 3.3×10^{-8} cm and $T_m^o = 501.5$ K.[14] The calculated values of a crystal lamellar thickness (Table II) imply that the crystal structure of PVA films filled with different contents of CrF_3 is basically different from that of the ordinarily obtained PVA films. The endotherm of T_m form becomes less sharp with increasing the CrF_3 amount, which indicates the decreases in the size of the crystallite and/or the order of molecular packing in the crystallite.

The heat required for melting the sample ΔH (heat of fusion) was obtained by integrating the area under the melting peak. Figure 3 shows the variation of ΔH for PVA films filled with different filling levels of CrF_3 (W). The ΔH values decrease exponentially with increasing the filling levels of CrF_3. This can be interpreted by considering that CrF_3 molecules induce defects in a crystalline phase in PVA. The present results suggest the following numerical formula for the dependence of ΔH on W,

$$\Delta H = \Delta H_0 + A \exp(-W/B) \qquad (3)$$

where ΔH_0, A, and B are constants. The present variation of ΔH could attributed mainly to the variation of
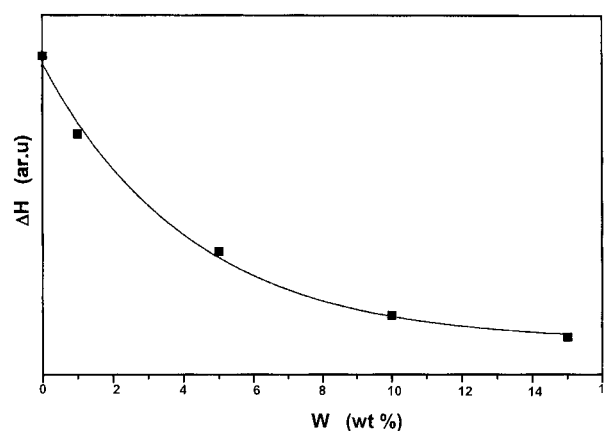
Figure 3 The filling level dependence of the heat of fusion of CrF_3-filled PVA films.

the degree of crystallinity.[19] This is be clarified in XRD section of the present work.

For films with filling levels of CrF$_3$ ≥ 10 wt %, an additional melting peak appeared at the higher temperature of the ordinary peak (Fig. 1). The endotherm of the high T_m form becomes sharper with increasing the amount of CrF$_3$, which indicates an increase in the size of the crystallite and/or the order of molecular packing in the crystallites. Such two-peak melting curves have been reported by Cha et al.[20] The two endotherms of their DSC curve for highly drawn PVA fibers were clearly separated peaks. The high T_m form is thought to be another kind of crystallite. Also, the DSC curves of drawn special PVA films after aging for more than 30 days showed another melting peak at the higher temperature of the ordinary peak.[21]

A fusion curve having dual or multiple peaks also has often been reported for other polymers such as polyethylene[22] and Nylon-66,[23] together with abnormally high melting temperature, when the polymers are crystallized at very high pressure or under conditions giving rise to high molecular orientation. The structure and physicochemical properties of PVA film have been studied when stretched at the amorphous state, followed by annealing.[24] It was found that the PVA film showed a dual fusion curve and a very high melting temperature. Thus, the dual fusion curve and the high melting temperature seem to be general characteristics of polymer crystallized under the condition that induces high molecular orientation, regardless the polymer type. This dual peak strongly indicates the presence of a dual structure or a very high ordered crystalline phase of large dimensions in addition to the normal crystalline region.

The thermal behavior of PVA films filled with different filling levels of MnCl$_2$ was observed by DSC (Fig. 4). This figure shows no major changes in the general shape of DSC curves of PVA films filled with CrF$_3$. It is interesting to note that in case of MnCl$_2$ there is one melting peak; its area decreases with increasing filling level and the peak disappears at filling level W ≥ 25 wt %. This indicates that the main crystalline phase decreases with increasing the filling level and the samples become completely amorphous for W ≥ 25%. Also, another crystalline phase has not been formed as in the case of CrF$_3$, although in this case we used high concentrations of MnCl$_2$. From Figure 4 we see that T_m also increases with increasing MnCl$_2$ content, although usually this value decreases with decreasing the degree of crystallinity. This result is very unusual and the discrepancy suggests that the crystallites of PVA are more highly organized in the filled films than in the pure PVA homopolymer, i.e., there is an increase in crystallite size and a difference in density between the crystalline and amorphous regions.
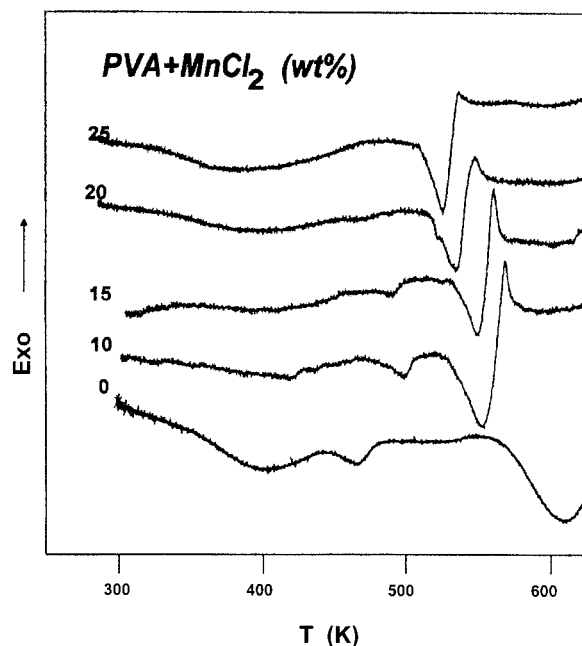

Figure 4 DSC curves for PVA films filled with different filling levels of MnCl$_2$.

The crystallite size (V) was calculated from Sherrer's equation[25] by using a (101) plane,

$$V_{hkl} = \frac{R\lambda}{\beta\cos\theta} \qquad (4)$$

where hkl is the index of the plane, $R = 1$, $\lambda = 1.54$ Å, and β is the half width of the 101 plane. Figure 4 shows the value of β decreases with increasing the amount of MnCl$_2$. This means that the crystallite size of PVA increases with increasing MnCl$_2$ content. This result supports the above discussion.

X-ray diffraction

Figure 5 displays the X-ray diffraction scans of pure PVA and PVA containing different levels of CrF$_3$. It is obvious that there is no significant effect on the general shape of the X-ray pattern. The observed spectra characterize a semicrystalline polymer possessing a clear crystalline peak for all studied samples at a scattering angle $2\theta \cong 19.2°$ corresponding to a (101) spacing.[26] A reduction of area under the crystalline peak or its height is evident with the increase of CrF$_3$ content. It is known that the area under the crystalline peak or its height can be taken as a measure of the degree of crystallinity (X). The calculated values of the height of the main peak (101) are plotted as a function of the filling level of CrF$_3$, as shown in Figure 6. We can see that the peak height decreases exponentially with increasing filling level. This means that the degree of crystallinity decreases exponentially due to the addi-
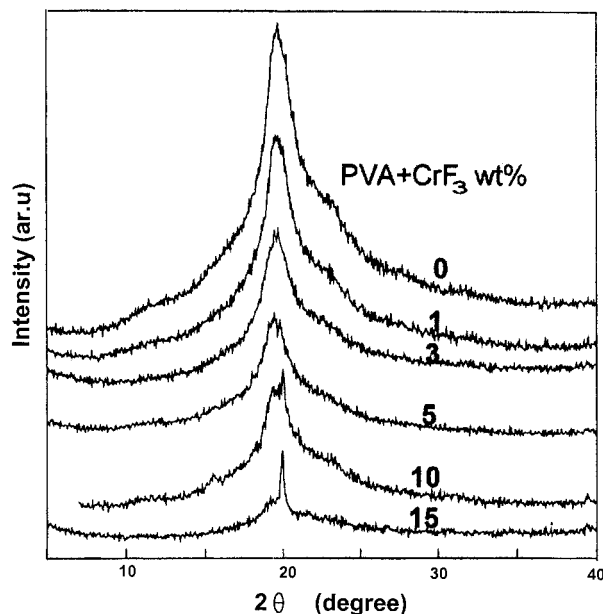
Figure 5 X-ray diffraction scans of various CrF_3 filling levels for PVA films.

tion of CrF_3. It is found that the degree of crystallinity (X) depends on the filling level (W) according to the following formula,

$$X = X_o + A_1 \exp(-W/B_1) \qquad (5)$$

where X_o, A_1, and B_1 are constants. From eqs. (3) and (5) we can see the similarity of the filling level dependence of heat of fusion and the corresponding dependence for crystalline peak height. Also, the degree of crystallinity may be considered as an indicator for filling level.

It is remarkable, in Figure 5, that for samples containing 10 and 15 wt % CrF_3, there is a sharp peak superimposed on the main peak at $2\theta = 20.2°$. This peak belongs neither to PVA nor to CrF_3 crystalline spectra, but it may arise from scattering atomic planes
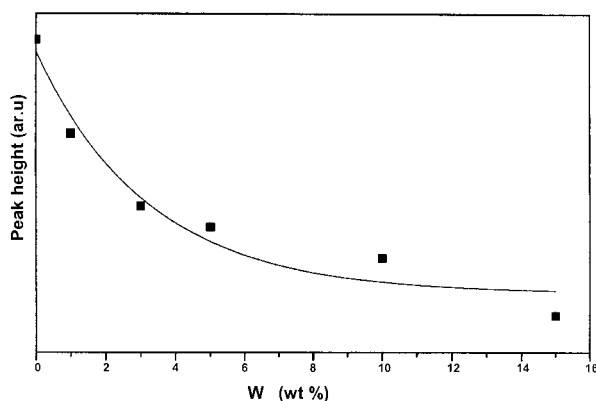

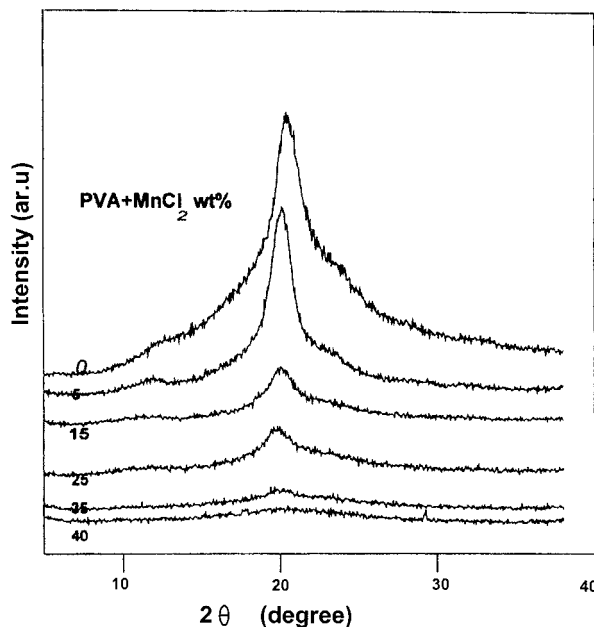**Figure 6** The filling level dependence of the height of the main peak in XRD pattern of CrF_3-filled PVA films.

Figure 7 X-ray diffraction scans of various $MnCl_2$ filling levels for PVA films.

of some crystalline patterns of the PVA–Cr^{3+} complex. The appearance of two melting points (T_{m1}, T_{m2}) in DSC scans for filling levels of CrF_3 $W \geq 10$ supports the existence of two crystalline phases. The first crystalline phase is the main phase of PVA, which decreases with increasing CrF_3 content due to the induced defects, and the second crystalline phase, which characterizes the PVA–Cr^{3+} complex. Similar results[27] have been observed for PVA filled with 5 wt % $CrCl_3$ irradiated by low level fast neutron. They reported that the addition of $CrCl_3$ to PVA could cause structural variations in the polymeric network. These variations are most probably related to the interaction between the negatively charged hydroxyl groups and positive chromium ions.

Figure 7 represents the XRD pattern for PVA filled with different levels of $MnCl_2$, from which we can notice that the main peak has neither changed in shape nor in position, but the intensity of the main peak decreases exponentially with increasing the filling level. The filling level dependencies of the height of the main peak (101) for $MnCl_2$-filled PVA films is similar to that for CrF_3-filled PVA films (figure not shown here). At high concentrations ($W \geq 35$), the filled PVA films become completely amorphous. Das et al.[28] measured the X-ray diagrams for the PVA and fluorinated PVA. They reported that PVA becomes highly amorphous after fluorination. Although PVA is atactic, it possesses a certain regularity in its virgin state. However, on fluorination, its crystalline order is lost due to incorporation of fluorine and unsaturation. Referring to Figure 7, we can observe that no new crystalline phases appears due to filling with $MnCl_2$,

contrary to the filling with CrF$_3$. The appearance of one melting peak in the DSC scans—its area decreases with increasing MnCl$_2$ content and it disappears for high concentrations—confirms this results. This means that the structural modifications depend on the filling level and the nature of filler. We can obtain PVA films with the desired crystallinity by addition of MnCl$_2$ with certain levels. Also, we can obtain amorphous PVA films with addition of MnCl$_2$ with concentrations of $W \geq 25$ wt %. On the other hand, PVA films can be obtained with the dual crystalline phase by using CrF$_3$ with filling levels $W \geq 10$ wt %.

CONCLUSION

From the analysis of DSC curves and X-ray diffraction of filled PVA films, it may be said that the structural changes take place after filling with CrF$_3$ and MnCl$_2$ as a result of defect formation. From the DSC curves, we notice the following: (1) increasing filler content results in a decrease in both T_g and T_D of PVA films, indicating that the filler acts as plasticizer; (2) for all investigated samples, there is a main melting peak due to the main crystalline phase of PVA; (3) the main melting peak area decreases exponentially with increasing filling level, indicating a reduction of degree of crystallinity; (4) films with CrF$_3$ filling level $W \geq 10$ wt % show an additional melting peak indicating the presence of dual structure. The X-ray analysis showed that no significant peaks, characterizing CrF$_3$ or MnCl$_2$ crystals, were detected. The degree of crystallinity of the main phase, detected by X-ray diffraction, decreases exponentially with increasing the filling level. It is observed that the degree of crystallinity can be used as a measure of filling level. Also, the X-ray diffraction confirmed the presence of two different crystalline phases for CrF$_3$ filling level $W \geq 10$ wt %, which agrees with the DSC findings. The similarity of the filling level dependence of melting peak area and the corresponding dependence for the height of the main peak (101) confirm each other. Thus, it may be concluded that the crystalline structure changes in PVA due to filling depends on the chemical nature of the filling substances and the way in which they interact with the host matrix. We may select the suitable type and filling level of filler to prepare filled PVA films with a desired crystalline structure.

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