

Polymorphism in Intercalated Poly(vinylidene fluoride)/Clay Nanocomposites

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ABSTRACT: Polymorphism in poly(vinylidene fluoride) (PVDF)/clay nanocomposites was studied. Poly(vinylidene fluoride)/clay nanocomposites were prepared with melt intercalation. The samples were characterized with X-ray diffraction, differential scanning calorimetry, and Fourier transform infrared spectroscopy. The nanocomposite exhibited the β form. Thermal annealing performed at 125 and 185°C showed that the β form of PVDF was stable. The

stability of the β form of PVDF was ascertained from these studies. The β form of PVDF in the nanocomposites could be due to crystallization in the constrained phase. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2036–2040, 2003

Key words: annealing; differential scanning calorimetry (DSC); nanocomposites; polymorphism; WAXS

INTRODUCTION

Polymer/clay nanocomposites are very interesting because of their unique properties with respect to conventional filled polymers. The incorporation of nanoscale clay layers into the polymer matrix has a profound effect on the crystallization behavior and crystalline morphology and improves the thermal and mechanical properties of polymers. The crystallization rates are enhanced in nylon,¹ polypropylene (PP),² poly(ethylene terephthalate),³ and many other polymer nanocomposites, and polymorphism can be observed in nanocomposites of nylon 6¹ and PP.⁴ In nylon 6, the addition of saponite results in the γ phase of nylon. The polymorphic behavior, moreover, depends on the saponite content and the cooling rates employed.¹ The α and γ forms coexist, and the observed toughness in nylon 6 nanocomposites can be ascribed to the presence of the γ phase. In PP/clay nanocomposites, the γ phase is located in the proximity of the silicate layer, whereas the α phase exists in the bulk.⁴ The existence of the γ phase in PP/clay has also been observed by Nam et al.⁵

In an earlier communication, we reported poly(vinylidene fluoride) (PVDF)/clay nanocomposites prepared by the melt intercalation process, and we noted the superior properties of these nanocomposites.⁶ The objective of this investigation was to elucidate the effect of the incorporation of clay on the crystal structure of PVDF. X-ray diffraction (XRD), differential scanning calorimetry (DSC), and Fourier transform

infrared (FTIR) spectroscopy were used for this investigation.

EXPERIMENTAL

Solef 1008 PVDF (or P), supplied by Solvay (Brussels, Belgium), was used for this study. The weight-average molecular weight of PVDF was 100×10^3 , and the ratio of the weight-average molecular weight to the number-average molecular weight was 2.5. The organically modified bentonite clay sample in this study was Cloisite 6A, which was generously donated by Southern Clay Products (Gonzales, Texas). The clay was organically modified with a tallow compound, dimethyl dihydrogenated tallow quaternary ammonium chloride (6A). The cation-exchange capacity of the clay was reported to be 140 mequiv/100 g, and the organic content was 47% (according to the company data sheet). The melt compounding of PVDF/6A clay nanocomposites was performed with a Brabender plasticorder batch mixer at 200°C and 60 rpm for 5 min. The clay was dried in an air circulatory oven at 60°C for 8 h before the compounding. Four compositions, containing 1.5, 3, 5, and 7 wt % clay (PNC1.5, PNC3, PNC5, and PNC7, respectively), were prepared. The films used for XRD and annealing were prepared by compression molding at 200°C with a Carver model F-15181 press. The structure of the clay in the polymer matrix was evaluated with XRD measurements. A Rigaku Dmax 2500 X-ray diffractometer with Cu K α radiation with a wavelength 1.54 Å and an energy of 8.05 keV was used for this purpose. The basal spacing of PVDF was estimated from the XRD patterns with Bragg's law. FTIR spectra were taken with a Nicolet Dmax spectrometer in the diffused

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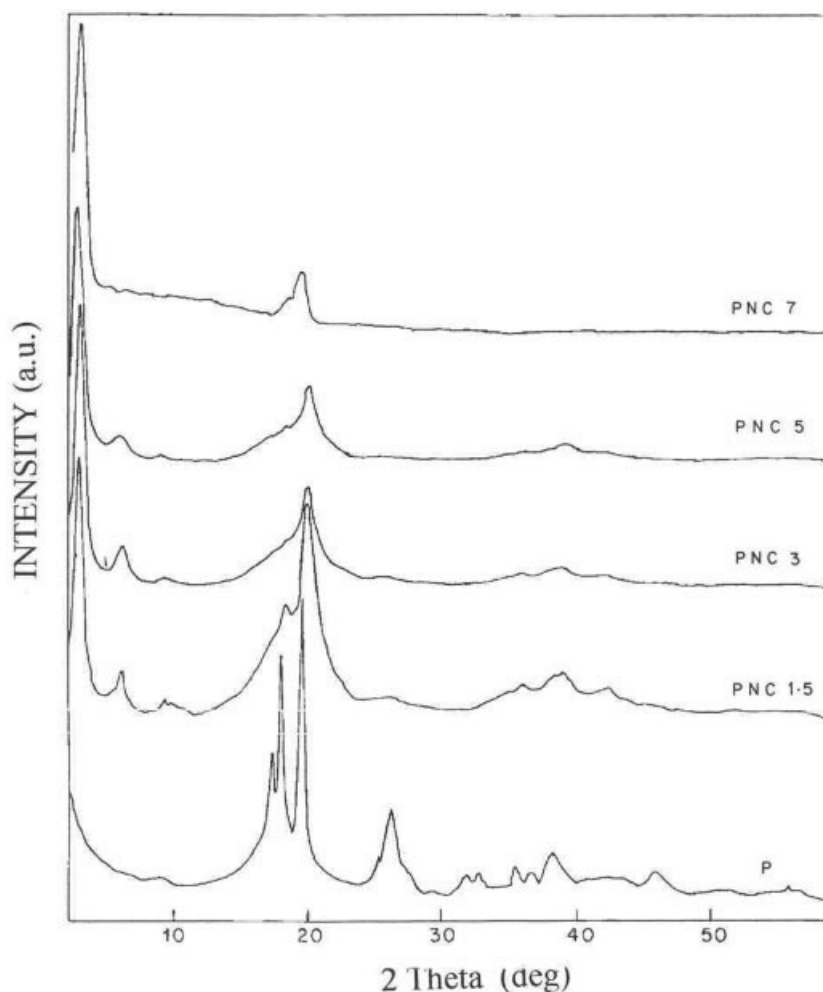


Figure 1 XRD patterns of pristine PVDF exhibiting the α form and PVDF/clay nanocomposites exhibiting the β form.

reflection mode. A PerkinElmer DSC-2 equipped with thermal analysis data station (TADS) was used for the melting studies. The samples were heated and cooled at a rate of 10°C/min, and the melting and crystallization parameters were determined from the heating and cooling scans, respectively.

Annealing is also known to bring about changes in PVDF. We performed thermal annealing to study the structural changes in PVDF/clay nanocomposites. The pristine PVDF and the nanocomposites were annealed at 125 and 185°C under atmospheric pressure for 24 h in air.

RESULTS AND DISCUSSION

In this study, the effect of silicate layers on possible polymorphism has been investigated. PVDF exhibits polymorphism and is known to crystallize in four different forms: α , β , γ , and δ . The most readily formed crystal structure is the α form, and it can be obtained via cooling from the melt. On orientation, it converts into the β form, which is very important

because of its piezoelectric and pyroelectric effects. The α form consists of a series of nonpolar antiparallel chains, whereas the β form consists of a series of polar parallel chains. Another structure, the γ form, is obtained by crystallization from some highly polar solvents, high-temperature annealing, or high-pressure crystallization. This conformation is intermediate between the α and β phases. The mechanical orientation of the γ form yields the β phase. The δ phase is obtained by the polarization of the α phase under a high electric field (ca. 1.25 MV/cm at room temperature).⁷⁻⁹ The transformation of the polymer melt to the α form is kinetically favored, whereas the β form is favored for energetic reasons.⁹ Some substrates are known to induce β formation when crystallized from melt.⁹

An XRD pattern confirming the intercalation of PVDF is discussed in a previous publication of ours.⁶ The X-ray pattern of film P shown in Figure 1 indicates the predominant presence of the α phase, as evidenced by the characteristic peaks at 2θ values of 17.3 (020), 18.15 (110), 26.8 (021), and 38.8° (002).¹⁰ As for the

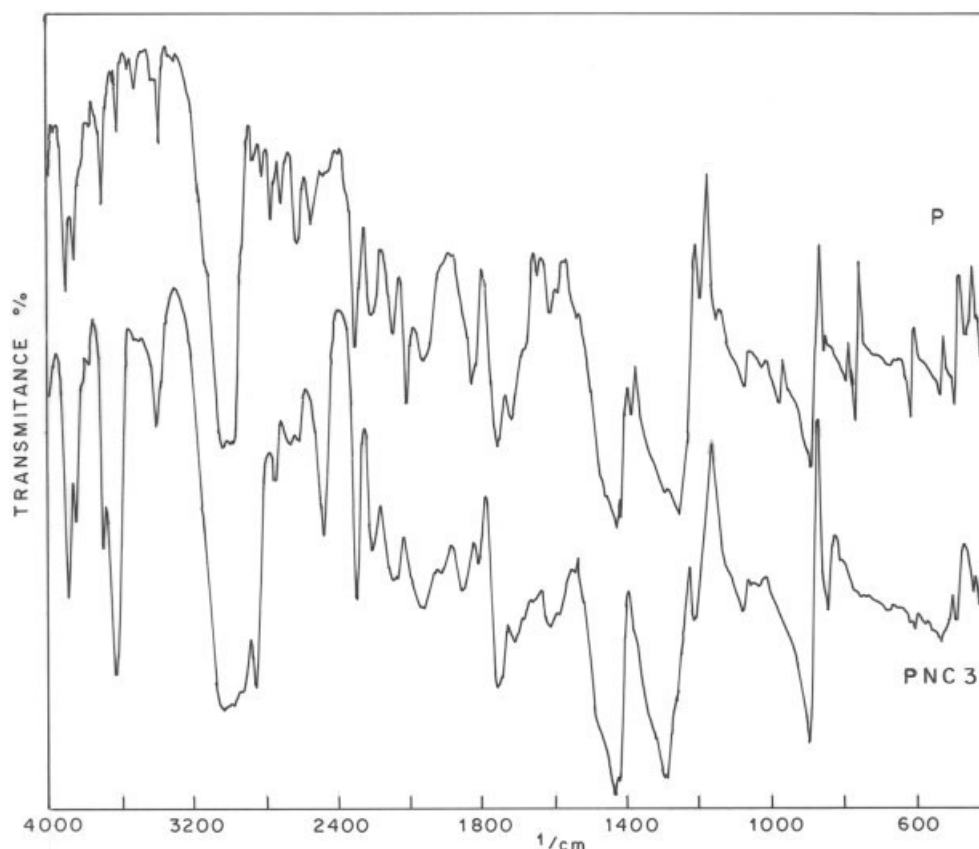


Figure 2 FTIR spectra of PVDF and one nanocomposite.

nanocomposites, the compositions do not exhibit the characteristic peaks of the α form in the XRD patterns like the pristine polymer but instead show a single peak at $2\theta = 20.5^\circ$ corresponding to (110) and (200) planes of the β form of PVDF.¹¹ The XRD pattern is significantly different from that observed for PVDF, and the characteristic peaks of the α form are no longer visible for the PVDF/clay nanocomposites. Therefore, the addition of clay seems to promote the formation of the β phase in PVDF. The presence of the β form of PVDF in these composites is noteworthy because it is the form with high polarizability.

The FTIR studies of P and PNC have been carried out to ascertain the presence of the β form of PVDF. In the pure PVDF films, the bands obtained at 495, 538, 769, 798.5, and 981.7 cm^{-1} can be assigned to the α

form. The band at 769 cm^{-1} is assigned to the CF bending mode and the skeletal bending of C(F)—C(H)—C(F). The peaks at 981 cm^{-1} are assigned to the CH_2 twisting mode.

For the nanocomposites, the bands obtained at 510 (CF bending), 846.7 (CH_2 rocking), and 896.8 cm^{-1} can be assigned to the β form of PVDF. The bands at 510 and 847 cm^{-1} are assigned to CF bending and CH_2 rocking, respectively. The absence of the γ form can be confirmed by the absence of the CH_2 twisting band at 950 cm^{-1} .^{12–14} Figure 2 shows the FTIR spectra of PVDF and PVDF/clay nanocomposites.

The melting has been studied with DSC. A thermal analysis of the PVDF/clay nanocomposites indicates that the melting temperature (T_m) of PVDF is increased from 172 to about 178°C for all four composi-

TABLE I
Melting Parameters for PVDF and PVDF/Clay Nanocomposites (as Compounded and Annealed Samples)

Sample identification	As compounded		Annealed at 125°C		Annealed at 185°C	
	T_m (°C)	ΔH_f (cal/g)	T_m (°C)	ΔH_f (cal/g)	T_m (°C)	ΔH_f (cal/g)
P	172	11.7	174	10.5	173	13.4
PNC1.5	178	11.2	180	8.8	183	13.6
PNC3	178	10.4	180	8.8	182	13.9
PNC5	179	9.8	182	8.8	183	13.4
PNC7	180	8.5	180	8.5	180	15.1

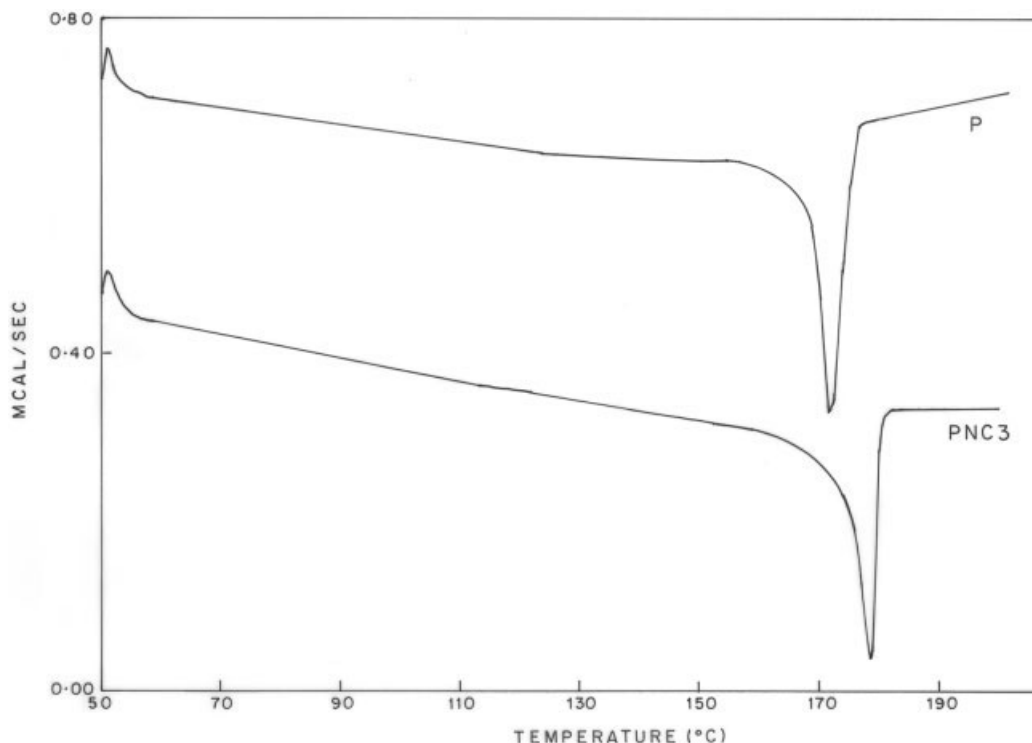


Figure 3 DSC melting curves of PVDF and one nanocomposite.

tions (Table I). T_m of PVDF can be observed at 172°C, corresponding to the α form of PVDF, whereas in the PVDF/clay nanocomposites, T_m shifts to a higher temperature (178°C). The DSC melting curves of PVDF and PVDF/clay nanocomposites are shown in Figure 3. The high-temperature melting peak is ascribed to the presence of the β form of PVDF. The crystallinity of PVDF is reduced in the composites in comparison to that of the pristine polymer. The heat of fusion (ΔH_f) decreases from 11.7 to 10.5 cal/g for the composite containing 3% clay.

Therefore, the DSC data show that the incorporation of clay into PVDF results in the formation of the β phase. These results are qualitatively consistent with the XRD results.

Thermal annealing of PVDF and PVDF/clay nanocomposites

The annealing of PVDF and PVDF nanocomposites has been carried out to ascertain the thermal stability of β crystals formed in the nanocomposites. The two annealing temperatures, 125 and 185°C, are such that the former is above the glass-transition temperature and the latter is above T_m ; this ensures enough molecular mobility in the polymer. As can be seen from Figure 4, PVDF remains in the α form, as evidenced by the presence of the characteristic peaks at 2θ values of 17.3 (020), 18.15 (110), 26.8 (021), and 38.8° (002). The β form of PVDF also remains unchanged even after annealing in PNC. This

result is of particular interest because the stability of the β phase is important from a processing point of view in the downstream processing of the composites.

With annealing at 125°C, which is below T_m of the nanocomposites, no changes can be observed in the crystal structure of pristine PVDF and the nanocomposites. After the annealing of samples at these temperatures for 24 h, PVDF in the nanocomposites remains in the β form, as evidenced by XRD patterns and the T_m peak values observed from the DSC curves. A part of the history is recorded in the crystalline phase and can be deleted only through annealing at a temperature above T_m . It has been reported that the annealing of α -phase films at 185.8°C and atmospheric pressure leads to transformation into the γ phase.⁹ In PVDF/clay nanocomposites, however, the γ phase of PVDF is not observed from the XRD patterns and DSC T_m peaks.

PVDF has also been reported to crystallize in the β form in PVDF/PMMA blends by Yang et al.¹⁵ However, the observed β form was thermodynamically metastable, as evidenced by its transformation into a stable form after annealing. The β form was a result of crystal growth in limited space and time. In our study, we have found that the β form induced by the presence of clay remains stable even after annealing.

CONCLUSIONS

The dispersion of nanometer clay layers in PVDF brings about changes in the crystallization behavior so that the

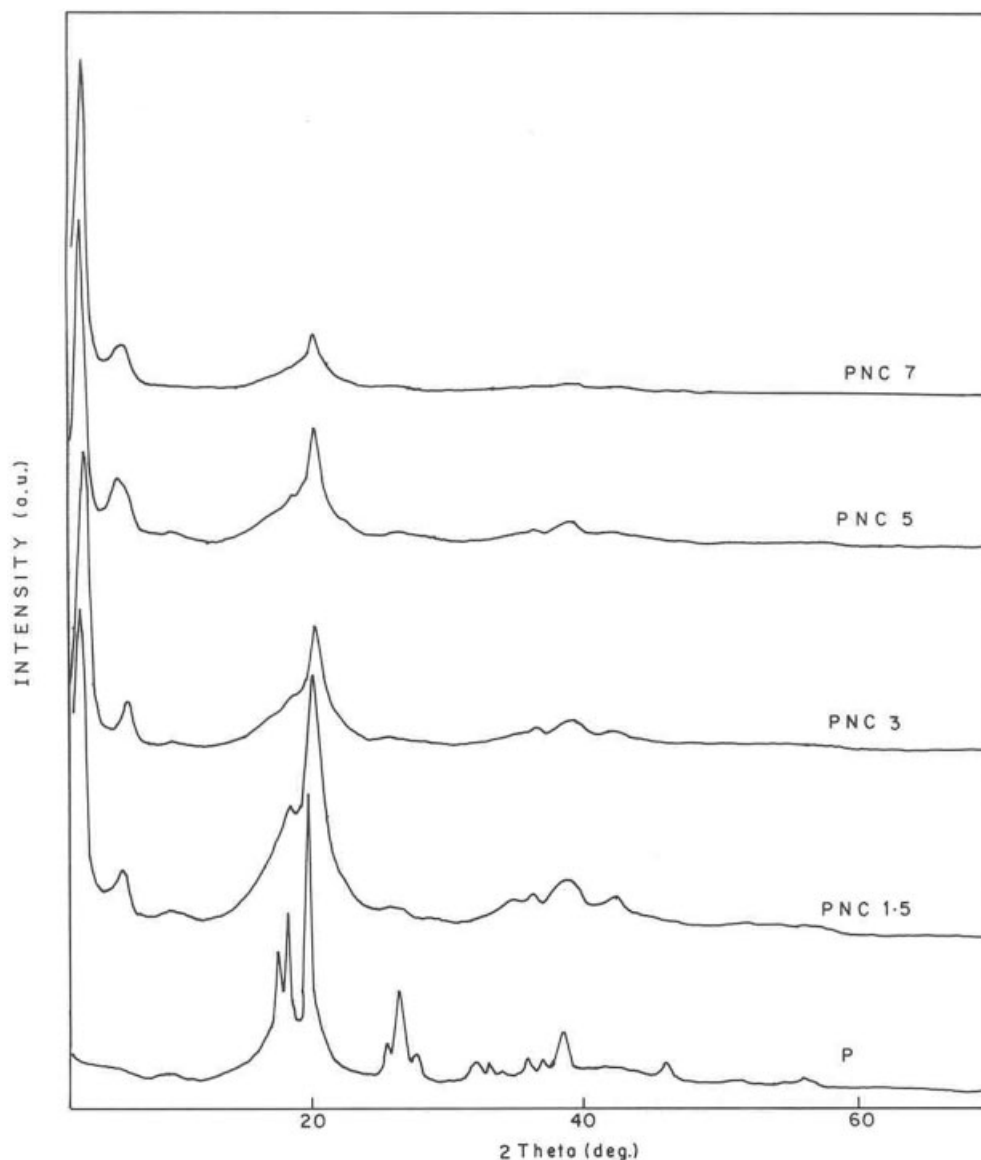


Figure 4 XRD patterns of samples annealed at 185°C.

β form of PVDF is formed. The nanometer-size clay layers induce heterophase nucleation, as evidenced by crystallization at a higher temperature than that for the pristine polymer.⁶ The results of this study indicate that PVDF crystallizes in the β form in PVDF/clay nanocomposites, and that form is stable even after annealing.

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