SYNTHESIS AND CHARACTERIZATION OF POLY(VINYLIDENE FLUORIDE-*CO*-HEXAFLUOROPROPYLENE)/CLOISITE 30 B NANOCOMPOSITES BY MELT MIXING

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ABSTRACT

In this research, poly(vinylidene fluoride-*co*-hexafluoropropylene)/nanoclay composites was prepared by copolymer melt mixing with Cloisite[®] 30 B at concentrations 0 – 10.0 mass%. The blends were characterized by Fourier transform infrared spectroscopy, X-ray diffraction analysis, Differential scanning calorimeter measurements and tensile properties.

The temperatures of melting and crystallization were found to increase with the increase of filler content. The tensile properties of the composite studied remained the same at Cloisite[®] 30 B contents up to 6.0 mass%. In the nanocomposites containing 0.75, 1.5, 3.0 and 10.0 mass%, mixed structure was observed (intercalated/exfoliated) while at 6.0 mass% Cloisite[®] 30 B – there was only exfoliated structure. The content of ☐☐phase increased with the increase of the organically modified filler to reach 68% of the crystalline phase of the polymer at 10.0 mass% Cloisite[®] 30 B.

Keywords: nanoclay, nanocomposites, poly(vinylidene fluoride-co-hexafluoropropylene), β-phase, properties

INTRODUCTION

Polymer layered silicate nanocomposites are of great importance for the manufacturing of materials of high performance properties because of the formation of intercalated structure with layered silicate using conventional processing technology [8]. Because of the rigid structure of clay layers and their high aspect ratio, they have been proven to be very effective in the improvements of the mechanical properties of nanocomposites even at very lower nanoclay additions [4].

Natural montmorillonite is one of the most often used layered silicates for obtaining polymeric nanocomposites. Montmorillonite is hydrophilic which makes it difficult to disperse it homogeneously in organic polymers [5]. In order to render the montmorillonite clay layers more compatible with polymer chains, it is necessary to carry out surface modification of hydrophilic silicate surface to make it organophilic. An efficient method to achieve this is to use ion-exchange reactions of substitution of sodium and calcium cations present in the inter-layer space or clay galleries by alkylammonium or alkylphosphonium cations [1]. Thus, polymers and polymer molecules are able to intercalate within their interlayer space or galleries [2, 11]. Such organomodified clays are commercially available in several varieties and are compatible with many polymeric materials [11].

The aim of the present work is to obtain nanocomposite materials on the basis of poly(vinylidene fluoride-*co*-hexafluoropropylene) with organically modified nanoclay based on montmorillonite (Cloisite[®] 30 B) by melt mixing and study some properties of the nanocomposites obtained.

EXPERIMENTAL
Materials
Poly(vinylidene fluoride-*co*-hexafluoropropylene) referred to as PVDF–HFP is a copolymer (15 mol% HFP comonomer) with melting temperature 117ºC and melt index 6.52 g/10 min (220ºC, load 98 N) as powder was kindly supplied from Arkema, France.

Cloisite® 30 B, organically modified montmorillonite nanoclay was supplied by Southern Clay Products Inc. The organic modifier of Cloisite® 30 B contains methyl, tallow, bis-2-hydroethyl quaternary ammonium cation and chloride anion with concentration 90 meq/100 g clay. Almost 65 % of the chains have 18 carbon atoms, ~ 30 % have 16 carbon atoms and ~ 5 % – 14 carbon atoms in the tallow structure. The basal spacing of Cloisite® 30 B is 18.5 Å.

Sample Preparation

The compositions containing 0.75, 1.5, 3.0, 6.0 and 10.0 mass% of nanoclay Cloisite® 30 B were mixed with PVDF–HFP and homogenized as powder by stirring at 50 – 60°C for 10 min and then twice in a "Brabender" at 200°C. They were pressed on a laboratory press PHI (England) between aluminium foils under the following conditions: samples thickness about 1 mm, temperature 200ºC, melting period at 200ºC – 3 min, pressing pressure – 12 MPa; cooling rate – 40ºC/min.

Melt Index

The melt indices of the initial polymer and the nanomaterials based on it were determined by the *MFI* (g/10 min) method on an apparatus MFI 3350 Prodemat (France) at temperature of 200ºC and load 98 N.

X-ray Structure Analysis

The X-ray diffraction patterns were taken by X-ray diffractometer with generator Iris-M (Russia) and goniometer URD-6 (2θ) (Germany) at atmospheric pressure, room temperature, Ni-filtered Cu target K_α radiation in the interval 2θ = 4 – 50°.

Fourier Transform Infrared Spectroscopy

Samples prepared as films were analyzed using spectrophotometer produced by "Bruker" (Germany) in the interval 4000–400 cm^{-1} with Tensor 27. To determine the relative quantity of the *β*- phase, the heights of the series of peaks were determined by simulation of the spectrum observed. This was done using OPUS–65 software which automatically corrects the baseline. For each sample, the fraction of the *β*- crystalline phase (F_β^{IR}) was calculated by the formula: $F_\beta^{IR} = A_\beta /(1.26 A_\alpha + A_\beta)$, where: A_α and A_β – are the heights of the peaks at 764 and 840 cm^{-1}, respectively while the coefficient 1.26 represents the ratio of the absorption coefficients at 764 and 840 cm^{-1} [10].

Differential Scanning Calorimeter Measurements

The behavior under melting and crystallization in nitrogen atmosphere of samples with mass ca.4 mg was analyzed using simultaneous thermal analyzer „STA 449F3 Jupiter" (Netzsch, Germany) under the following conditions: first heating from 20 to 240°C at rate of 10°C/min, isothermal period of 1 min at 240°C (to remove any traces of crystalline structure) followed by cooling to 20°C and second heating to 240°C at the same rate. The degree of crystallinity of the samples was calculated at $\Delta H_{100\%} = 104.7$ J/g for 100% crystalline PVDF–HFP [9].

Tensile Properties

The tensile strength (σ), elongation (ε) and the other characteristics of the initial PVDF–HFP and the nanocomposite materials based on it were measured on a dynamometer INSTRON 4203 (England) at speed of 100 mm/min and room temperature.

RESULTS AND DISCUSSION

At least four polymorphous crystalline phases of polyvinylidene fluoride (PVDF) are known. The one with the highest polarity is the *β*- phase while *γ*- and *δ*- phases are less polar and the *α*-phase in non-polar. It was established also that the low content of hexafluoropropylene (up to 10 – 15 mol%) in PVDF–HFP changes the symmetry off the crystal lattice only slightly, compared to the one of PVDF [3, 7, 12]. This allows the copolymer to be analyzed similarly to the homopolymer. In the XRD patterns, certain interest arouse the peaks at 2θ = 18.4, 19.9 and 26.5° (corresponding to *α*-

phase) and $2\theta = 20.2 - 21.1°$ (corresponding to β- phase) in the absence of γ- phase, as it has been observed by the IR studies. The increase of the intensities of the peaks at $2\theta > 20.2°$ and the simultaneous decrease of the intensity at $2\theta = 18.4°$ with the increase of filler content, as well as the appearance of a general peak shifted to the higher values of the reflection angle, is an obvious indication for increased content of β- phase (Fig. 1).
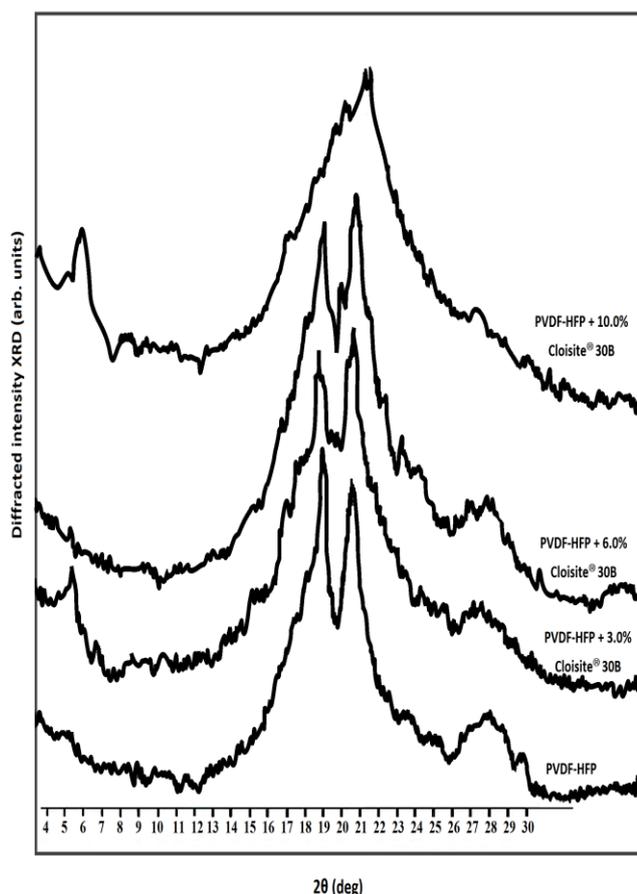
Fig. 1. X-ray diffraction patterns of the initial PVDF–HFP and its nanocomposites
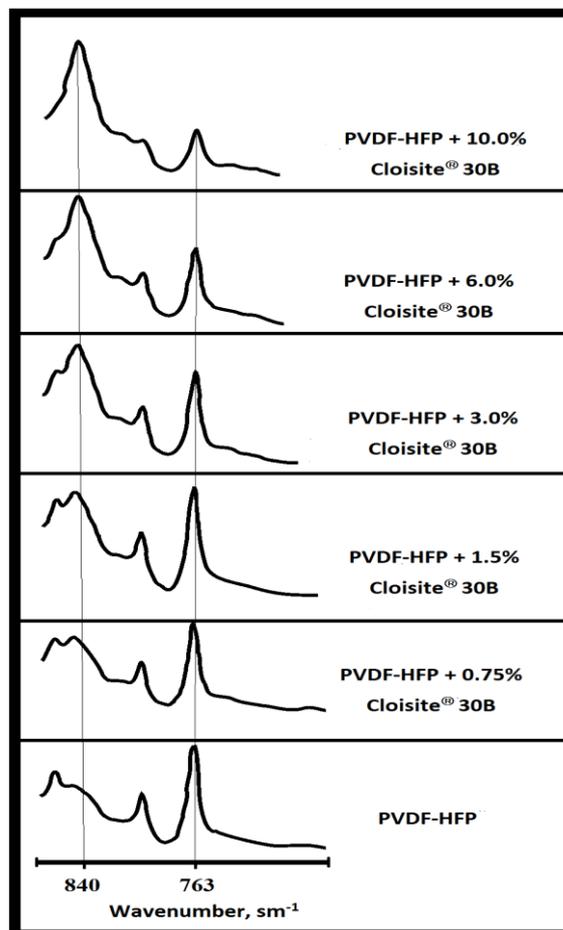
Fig. 2. IR– spectra of the initial PVDF–HFP and its nanocomposites

It was confirmed also by the β- phase content quantitatively calculated from the IR spectra of the nanocomposites obtained, shown in Table 1 and Fig. 2. From the intensity in the X-ray patterns at low angles of the diffracted rays ($2\theta = 1 - 10°$), a qualitative assessment of the microstructure of the nanocomposites obtained can be made. It can be seen in Fig. 1 that the peak at $2\theta = 4.9°$ was not observed for the composite containing 6.0 mass% Cloisite® 30 B while it is present at both higher and lower filler content. It means that the nanofiller used in the composite with 6.0 mass% filler was fully delaminated (exfoliated) to its initial nanometric size. Besides, the particles of the layered silicate filler were at such distance from each other that its periodicity disappeared. This is possible when the electrostatic forces of interaction between the filler layers are fully screened by the polymer chains. The structure obtained is exfoliated. When these forces are not fully screened, it is the case for the composites containing 3.0 and 10.0 mass% Cloisite® 30 B (Fig. 1), the arranged multi-layer morphology and its periodicity are registered on the X-ray pattern. For these composites, as well as these with 0.75 and 1.5 mass% filler content, the structure observed was mixed – intercalated/exfoliated.

The melt flow index (Table 2) decreased with the increase of filler content for all the samples to reach 3.5 g/10 min at nanofiller content of 10.0 mass%.

The tensile properties of the materials obtained on the basis of PVDF–HFP and Cloisite® 30 B (Table 2) decreased with the increase of nanofiller content.

Table 1. Content of β- phase in the initial PVDF–HFP and its nanocomposites

Cloisite® 30 B, mass%	β- phase, %
0	30
0.75	36
1.5	43
3.0	50
6.0	55
10.0	68

Table 2. Tensile parameters of the initial PVDF–HFP and its nanocomposites

Cloisite® 30 B, mass%	MFI, g/10min	σ, MPa	ε, %	M, MPa	E, J
0	6.5	29.8	780	215	15.7
0.75	4.9	28.0	790	120	11.6
1.5	5.0	28.0	760	184	11.8
3.0	4.9	27.9	770	186	11.8
6.0	3.7	23.7	700	208	9.8
10.0	3.5	14.5	550	220	3.5

The DSC thermograms of the materials studied showed endothermic asymmetric peaks of melting during the first and second meltings. The wider peak for all the samples during the second melting indicated for a hindered process which was due to the refined crystalline phase after the first melting and the slow recrystallization. Logically, it was found also that the increase of filler content decreased the degree of crystallinity because of the enhanced steric disturbances. This was due to the decreased area of the exothermic peak under cooling. Table 3 shows the melting temperatures (T_m) during the first and second meltings along with the corresponding enthalpies (ΔH_m), as well as the temperature (T_c) and enthalpy (ΔH_c) of crystallization. It can be seen that T_m by the first and second melting and T_c increased while ΔH_m by first and second melting and ΔH_c decreased with the increase of the degree of filling with Cloisite® 30 B.

Table 3. DSC- thermogram values of the initial PVDF–HFP and its nanocomposites

Content of Cloisite® 30 B, mass%	First melting		Second melting		Crystallization	
	T_m, °C	ΔH_m, J/g	T_m, °C	ΔH_m, J/g	T_c, °C	ΔH_c, J/g
0	132	27.7	132	25.1	95.5	29.6
1.5	140	21.1	142	21.9	105.7	22.4
6.0	141	19.6	142	20.6	106.8	21.2
10.0	136	20.7	140	21.9	105.4	19.8

The aim of our further studies will be the preparation of nanocomposite materials by mixing in solution of PVDF–HFP and nanofillers followed by precipitation. This method suggests preparation of nanomaterials with tensile properties better than these of the initial copolymer.

CONCLUSIONS

The use of organically modified nanoclay Cloisite® 30 B as filler in poly(vinylidene fluoride-*co*-hexafluoropropylene) resulted in increased content of *β*- phase and formation of two types of structures in the nanocomposites obtained – mixed (intercalated/exfoliated) and fully exfoliated.

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