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Transformation from *α*- to *β*- phase in vinylidene fluoride–hexafluoropropylene copolymer nanocomposites prepared by co-precipitation method

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Nanocomposite materials on the basis of vinylidene fluoride–hexafluoro-propylene copolymer with Cloisite®15A were obtained by a co-precipitation method from dimethylsulfoxide solution. The addition of organically modified nanoclay was found to facilitate the transformation of the polymer crystals from *α*- to *β*- phase. The amount of *β*- phase calculated for the materials containing 6.0 mass % of modified nanoclay was more than 95%. At lower Cloisite®15A content, the *β*- phase also increased compared to that in the initial copolymer and was in the range 47–82%. The increase of the tensile strength and elongation at break of the nanocomposites was higher at lower content of nanoclay Cloisite®15A (38–39 MPa and 820–850% at 0.75–1.0 mass %, respectively). The reinforcing effect was lower for the nanocomposites with higher clay content owing to some clay platelets being partially exfoliated and stacked. This was confirmed by transmission electron micrographic observations of the nanomaterials obtained.

Keywords: nanoclay, nanocomposites, vinylidene fluoride-hexafluoropropylene copolymer, co-precipitation, phases

INTRODUCTION

Poly(vinylidene fluoride) (PVDF) and copolymers on its basis have been some of the most researched polymers, due to their ferroelectric properties. These polymers have different unit cells of varying polarity, because of their different crystal modifications. At least four different crystal modifications of PVDF with different molecular conformations and lattice parameters are known [1–3]. The most common, easily obtainable phase is the *α*- phase. It does not show net lattice polarization. In the *β*- phase, the molecules are configured in *all*-trans conformation. This imparts spontaneous lattice polarization to the *β*- phase crystals which results in ferroelectricity observed in PVDF. The *γ*- phase is a combination of alternating conformational units from the *α*- and *β*- phases, and the *δ*- phase is a polar version of the *α*- phase.

The crystal forms of PVDF are retained in many copolymers of VDF containing small amounts of comonomers [4]. The fluorine atoms in the copolymers produce steric hindrance which prevents the molecular chains from assuming conformations similar to the non-electroactive *α*-phase of PVDF. Many of the copolymers directly crystallize into the polar electroactive *β*- phase [3] which is responsible for the ferro-, pyro-, and piezoelectric behavior in PVDF and its copolymers [3, 5].

It is well known that films of vinylidene fluoride–hexafluoropropylene copolymer (VDF–HFP) with different HFP contents indicate prominent piezo-, pyro-, and ferroelectricity comparable to that in PVDF [6–9]. It was also found that these properties are highly dependent on the crystal structure and polymer chain orientation of the VDF–HFP copolymer [10].

Over the past decade, many researchers have reported a possibility to stabilize the *β*- phase in PVDF and its copolymers with HFP in the presence of layered silicates well scattered within the polymer matrix. The addition of nanoclays is a prerequisite for the improvement of the mechanical, piezo-, pyro- and ferroelectric properties [11, 12].

The aim of the present work is to obtain nanocomposite materials on the basis of vinylidene fluoride–hexafluoropropylene copolymer with organically modified nanoclay Cloisite®15A by a co-precipitation method from dimethylsulfoxide solution and to study some properties of the nanocomposites obtained.

EXPERIMENTAL

Materials

Vinylidene fluoride–hexafluoropropylene copolymer referred to as VDF–HFP is a copolymer (15 mol% of HFP comonomer) with melting temperature of 117ºC and melt index of 6.52 g/10 min (220ºC, load 98 N) in the form of powder, kindly supplied by Arkema, France. Cloisite®15A, organically modified montmorillonite nanoclay from Southern Clay Products Inc. was used. Cloisite®15A is a Na^+ montmorillonite clay modified with dimethyl, dehydrogenated tallow, quaternary ammonium (2M2HT) with d_{001} spacing of 31.5 Å and density of 1.66 g/cm^3. The modifier concentration of Cloisite®15A was 125 meq/100 g.

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The solvent used for the compositions was dimethylsulfoxide (DMSO), Sigma Aldrich. All the materials described above were used directly without any further modification or treatment.

Sample preparation

The co-precipitation method was used to prepare VDF–HFP copolymer nanocomposites containing 0.5, 0.75, 1.0, 1.5, 3.0 and 6.0 mass % of nanoclay Cloisite®15A. To obtain the nanoclay contents in the VDF-HFP copolymer mentioned, two premixes were made: one for the nanoclay and the other for the VDF–HFP, using DMSO as a solvent. The two premixes were sonicated using a Branson 8510 ultrasonication bath at 30–40°C for approximately 5 min. The final 10% solution was prepared by adding the contents of the nanoclay premix to the VDF–HFP copolymer premix and the product was sonicated again for 20 min. To the mixture obtained, 150 ml of deionized water were added. A stringy, white, translucent precipitate formed immediately. Then, the precipitate was removed and dried in a vacuum oven until constant weight. For most physical testings, the precipitated samples were pressed into films on a laboratory press PHI (England) between aluminum foils under the following conditions: sample thickness about 0.3 mm, temperature 200ºC, melting period at 200ºC – 3 min, pressing pressure – 12 MPa; cooling rate – 40ºC/min.

Fourier transform infrared spectroscopy (FT–IR)

Samples prepared as films were analyzed using a 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: $F_\beta^{IR} = A_\beta/(1.26A_\alpha + A_\beta)$, where: A_α and A_β are the heights of the peaks at 764 and 840 cm^{-1}, respectively, and the coefficient 1.26 represents the ratio of the absorption coefficients at 764 and 840 cm^{-1} [13].

Differential scanning calorimetry (DSC) measurements

The behavior under melting and crystallization in nitrogen atmosphere of samples with a mass of ca. 4 mg was analyzed using a simultaneous thermal analyzer „STA 449F3 Jupiter" (Netzsch, Germany) under the following conditions: first heating from 20 to 240°C at a 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 VDF–HFP copolymer [14].

Tensile properties

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

Transmission electron microscopy (TEM)

For the TEM experiments, JEOL JEM 2100 microscope was used. The observations were performed at 200 kV acceleration voltage. The samples were prepared by dropping and evaporating particle suspensions on a standard copper grid.

RESULTS AND DISCUSSION

Figs 1 A) and B) show DSC thermograms of heating and cooling of the initial VDF–HFP copolymer and the nanomaterials on its base with Cloisite®15A, prepared by the co-precipitation method in the temperature range from 80 to 160°C, at a scanning rate of 10°C/min in nitrogen atmosphere. The large endothermic peak present in all samples obtained from solution is related to the melting of *α*- and/or *β*- phase crystals (Fig. 1 A) while the exothermic peak observed at cooling was attributed to crystallization (Fig. 1 B). Table 1 shows the thermal characteristics, such as the temperature of melting T_m, the degree of crystallinity α for both heating processes of the initial VDF–HFP copolymer and the nanocomposites based on it with modified Cloisite®15A obtained by co-precipitation from DMSO solution.

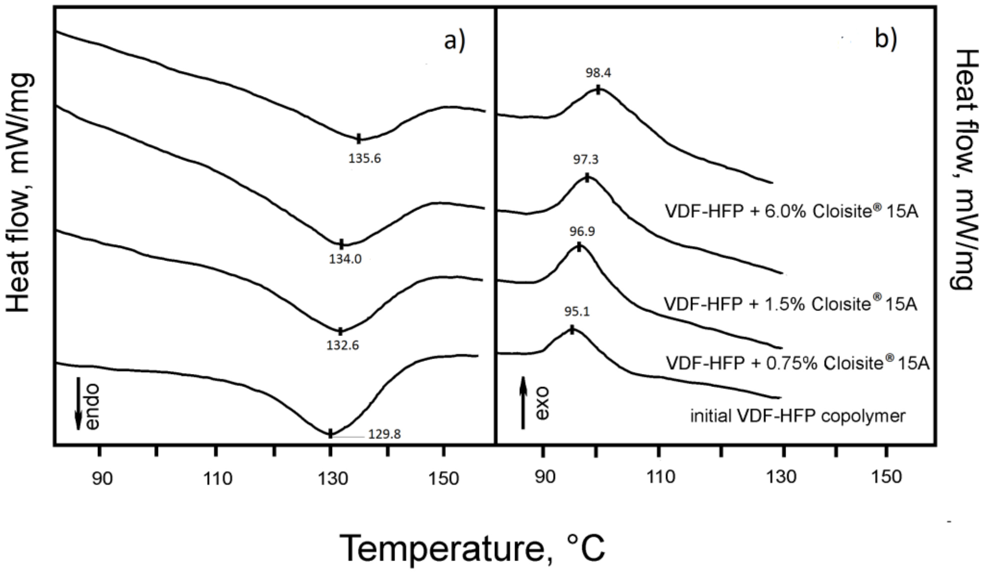

Fig. 1. DSC thermograms at: (A) heating and (B) cooling of the initial VDF–HFP copolymer and nanocomposite materials on its basis containing Cloisite®15A.

Table 1. DSC- thermogram values of the initial PVDF–HFP and its nanocomposites

Content of Cloisite®15A, mass %	Content of *β*- phase, %
0	26
0.5	47
0.75	54
1.0	54
1.5	57
3.0	82
6.0	95

It can be seen that the temperatures of melting T_m slightly increased during the first and second melting (by ca. 5°C) with the increase of organically modified nanoclay Cloisite®15A content from 0.5 to 6 mass %. For the initial copolymer, these temperatures were 129.8 and 129.7°C while for the materials with 6 mass % Cloisite®15A they were 135.6 and 133.2°C, respectively, during the first and second melting. The temperature of crystallization T_c also increased with the content of nano-filler in the compositions to reach 98.4°C. As it has been reported by Buckley *et al.* [15], the increase of the temperatures of melting and crystallization of the nanomaterials based on VDF–HFP copolymer is related to the formation of *β*- phase. The degree of crystallinity α of the series of samples based on VDF–HFP copolymer with nanoclay was found to decrease by 4–5% compared to these of the initial copolymer, due to the formation of a higher amount of *β*- phase [16].

The FT–IR spectra of the initial copolymer, organically modified nanoclay (Cloisite®15A) and films of VDF–HFP (15 mol%) copolymer co-precipitated from DMSO solution with different contents of Cloisite®15A are presented in Figure 2. The spectrum of the modified montmorillonite-Cloisite®15A showed the characteristic vibrational bands at 3633 cm^{-1} attributed to O–H silicate stretching [17]; 1640 cm^{-1} (related to O–H bending), 1042 cm^{-1} (owing of stretching vibration of Si–O–Si in silicate) and 917 cm^{-1} (from Al–OH–Al deformation of aluminates) [18]. The bands at 2921, 2851 and 1469 cm^{-1} were assigned to C–H vibrations of methylene groups (asymmetric stretching, symmetric stretching and bending, respectively) belonging to the surfactant chemical structure. The bands at 465, 521, 626, 722 and 796 cm^{-1} were attributed to the Si–O–Al bending vibrations [17], 847 cm^{-1} corresponds to Al–O–H and 1469 cm^{-1} – to the presence of ammonium salts [19]. The characteristic vibration bands of the initial VDF–HFP copolymer observed at 410, 489 (–CF_2-wagging), 510 (–CF_2-bending), 532, 614, 764, 797, 976, 1190 and 1406 cm^{-1} are a strong evidence for the existence of *α*- phase of VDF crystals [20]. The peak at 840 cm^{-1} is characteristic for –CF_2 symmetric stretching in the *all*-trans *β*-phase. It can be seen from Fig. 2 that the intensity at 840 cm^{-1} increases with the increase of Cloisite®15A content in the compositions.

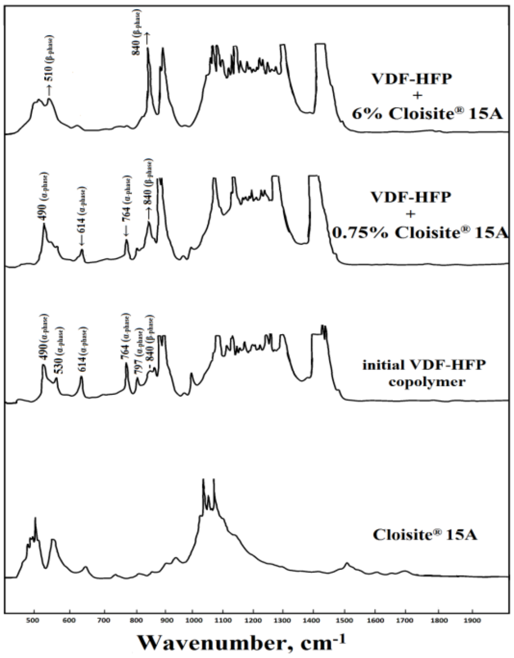

Fig. 2. IR–spectra of the initial copolymer, organically modified nanoclay (Cloisite®15A) and nanocomposite materials on their basis.

Another peak indicating for the change in conformation was registered at 764 cm^{-1}, which is characteristic of $–CF_2$ and C–C–C bending in the trans-gauche α- phase. Obviously, the intensity of this peak decreases with the increase of the amount of Cloisite®15A. Comparing the initial VDF–HFP copolymer with the materials containing Cloisite®15A, a new peak was observed at 510 cm^{-1} which confirms the crystal transformation from α- to β- phase. It should be noted that γ- phase was present in the materials containing 0.5–3 mass % of nanoclay Cloisite®15A, which indicates the transformation of the structure to a more polar phase. This can be explained with the inclusions of γ- together with β- phase.

The absorption bands at 764 and 796 cm^{-1} are mainly related to the presence of α- phase. According to [21], when the absorption bands of the γ- phase at 776 and 812 cm^{-1} are absent, the band at 840 cm^{-1} can be solely attributed to the presence of β- phase. Therefore, the relative fractions of the α- and β- crystalline phases can be calculated using the absorptions at 764 and 840 cm^{-1}, respectively.

The initial VDF–HFP copolymer mainly contains α- phase. With the addition of Cloisite®15A to the copolymer, the α- phase was fully transformed into β- phase. Furthermore, the amount calculated for nanomaterials with 6.0 mass % modified nanoclay was higher than 95%. At a Cloisite®15A content less than 6.0 mass %, the β-phase also significantly increased compared to that in the initial copolymer (47–82%) – Table 2. The tensile strength, elongation at break and *Young* modulus of the materials based on VDF–HFP copolymer with Cloisite®15A are shown in Table 3. It can be seen that the increase of the values of tensile strength (to 38.7 MPa) and elongation at break (to 848%) was higher at lower content of Cloisite®15A nanoclay (0.75−1.0 %, mass%), compared to that of initial VDF−HFP copolymer.

The reinforcing effect was lower for the nanocomposites with higher clay content owing to some clay platelets being only partially exfoliated and stacked (Fig. 3 B). The formation of β- phase in the compositions studied is also beneficial to the improvements of mechanical properties of the materials obtained (Table 3 and Fig. 2).

Table 2. Content of β- phase in the crystalline phase of initial VDF-HFP copolymer and its nanocomposites with Cloisite®15A prepared by co-precipitation method

Content of cloisite®15A,mass %	First melting		Second melting		Crystallization	
	T_m, °C	α, %	T_m, °C	α, %	T_c, °C	α, %
0	129.8	18.6	129.7	17.0	95.1	28.7
0.5	131.6	17.0	130.0	16.9	96.4	28.5
0.75	132.6	16.5	130.5	15.8	96.9	28.3
1.0	133.5	15.9	130.7	15.1	97.0	27.8
1.5	134.0	15.4	130.8	14.9	97.3	27.2
3.0	134.4	14.2	132.0	13.6	97.7	26.4
6.0	135.6	13.8	133.2	12.9	98.4	23.4

Table 3. Tensile parameters of the initial VDF-HFP copolymer and its nanocomposites.

Content of Cloisite®15A, mass %	Tensile strength, MPa	Elongation at break, %	*Young* modulus, MPa
0	27.2	795	125
0.5	34.8	831	143
0.75	37.9	848	170
1.0	38.7	823	215
1.5	36.2	807	190
3.0	35.2	805	156
6.0	33.6	750	154

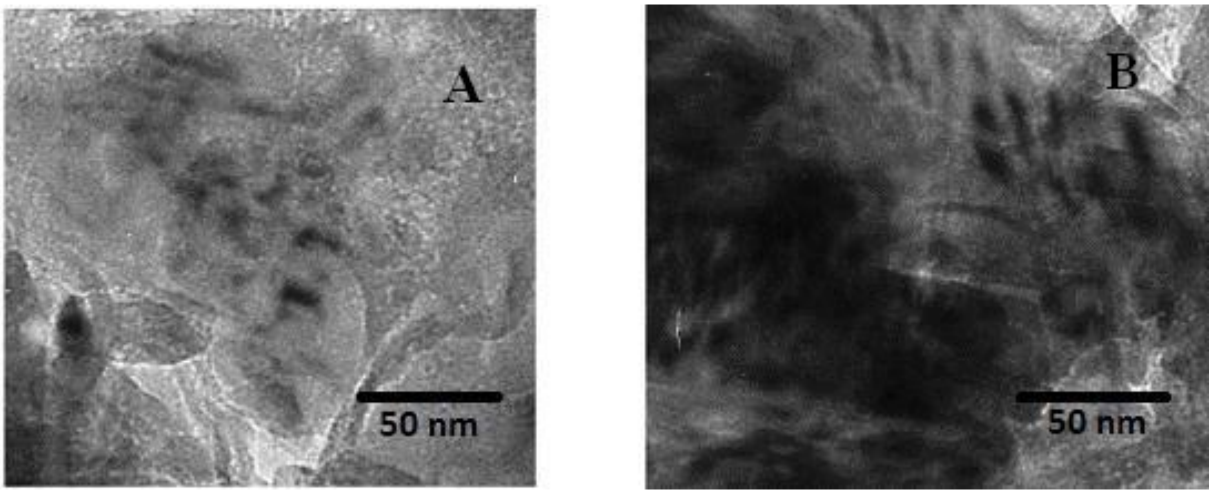

Fig. 3. TEM images of the nanocomposite materials based on VDF–HFP copolymer with 1.0 mass % (A) and 6.0 mass % (B) Cloisite®15A

CONCLUSIONS

Polymer nanocomposite materials containing up to 6.0 mass % of organically modified montmorillonite nanoclay Cloisite®15A were prepared by the co-precipitation method. The FT–IR analysis showed that the initial copolymer mainly contains the non-polar α- phase. The intensity of the peak at 840 cm^{-1} characteristic of –CF$_2$ symmetric stretching in the *all*-trans β- phase, increases with the Cloisite®15A content in the compositions. The intensity of the peak at 764 cm^{-1} which is characteristic of –CF$_2$ and C–C–C bending in the trans-gauche α- phase decreases with the increase of the nanoclay content. This proved the transformation of polymer crystals conformation from α- to β- phase. The highest content of β- phase (more than 95%) was calculated to be in the materials containing 6.0 mass % of Cloisite®15A. It was found that the values of the tensile strength and elongation at break of the nanomaterials obtained were higher at lower nanoclay content (0.75−1.0 mass %) and decreased to 33.6 MPa and 750%, respectively at 6.0 mass % of Cloisite®15A owing to poor exfoliation of the clay layers in the copolymer matrix.

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ТРАНСФОРМАЦИЯ НА α- В β- ФАЗА ПРИ ВИНИЛИДЕНФЛУОРИД-ХЕКСАФЛУОРОПРОПИЛЕНОВИ СЪПОЛИМЕРНИ КОМПОЗИТИ, ПОЛУЧЕНИ ПО МЕТОДА НА СЪУТАЯВАНЕТО

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(Резюме)

Нанокомпозитни материали на основата на винилиденфлуорид-хексафлуоропропиленов съполимер с Cloisite®15A са получени по метода на съутаяването из разтвор на диметилсулфоксид. Установено е, че добавянето на органично модифицирана наноглина улеснява трансформацията на полимерните кристали от *α*- в *β*- фаза. Количеството на *β*- фаза, изчислено за материалите, съдържащи 6.0 мас. % модифицирана наноглина е над 95%. При по-ниско съдържание на Cloisite®15A, *β*- фазата нараства в сравнение с тази в изходния съполимер и е в интервала от 47–82%. Повишаването на издържливостта на опън и удължението при счупване на нанокомпозитите е по-високо при по-ниско съдържание на наноглина Cloisite®15A (съответно 38–39 MPa и 820–850% при 0.75–1.0 мас. %). Усилващият ефект е по-слаб за нанокомпозити с по-високо съдържание на глина поради частичното ексфолиране и слепване на някои от глинестите плочки, доказано чрез трансмисионна електронна микрография на получените наноматериали.