Nanostructure and morphology of Poly (Vinylidene Fluoride)/ Poly Methyl (Methacrylate)/Clay Nanocomposites: Correlation to micromechanical Properties

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Abstract

Nanocomposites based on poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA) with untreated clay were prepared in one step by reactive melt extrusion. Chemical reactions took place between the polymer matrices, the inorganic clay particles, and three reactive agents, leading to the PVDF/PMMA/clay nanocomposites. The microstructure modifications were characterized by differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS). The mechanical behavior was investigated by tensile experiments, impact tests and microhardness measurements. The morphological characterization was carried out by optical and atomic force microscopy (AFM). The decrease of the melting and crystallization temperatures of the PVDF with increasing PMMA content is attributed to the interactions between the oxygen of the PMMA carbonyl group and the PVDF's hydrogen atom. WAXD analysis shows that there is neither an intercalation step nor total exfoliation in any composition. As the PMMA content increases, WAXS diagrams show, either the PVDF α -crystallographic form, both, α - and β -forms, or only the β -form. For PMMA contents higher than 40wt %, the materials became amorphous. The microhardness of the samples decrease for a PMMA content up to 20wt %. The study by optical microscopy and AFM illustrates the significant effect of the clay presence on the films surface morphology.

Key words: PVDF, PMMA, Clay, Nanocomposites, Exfoliation, reactive melt-mixing.

1. Introduction

Polymer clay nanocomposites exhibit better physical properties as compared with conventional composites, especially at lower filler loadings (e.g., less than 5 wt %) [1]. They show higher Young's modulus, improved thermal stability, better solvent resistance, an enhanced ionic conductivity and a reduced gas permeability [2-7]. Poly (vinylidene fluoride) (PVDF) and poly (methyl methacrylate) (PMMA) are known to be molecularly miscible in the molten state [8]. Many PVDF/PMMA blends have been prepared via solution cast. Dielectric measurements were carried out by Moon et al. to investigate the phase behavior and the structure of the blend system [9].

The homogeneity and the miscibility of the PVDF/PMMA blend has been studied in the past [10-17]. Thus, Jarray et al. [12] reported that PVDF crystals were formed in the PMMA matrix. Results show that the PVDF crystallization decreases with increasing the PMMA concentration. For instance, E. Benedetti and al. [14] found that the PMMA limits the PVDF spherulite growth-rate. Furthermore, the influence of polymer blending with PMMA on the crystalline structure of PVDF also has been recently reported [18]. The performance improvements of thermoplastic polymer nanocomposites depend to a large extent on the distribution and arrangement of the mineral layers as a result of intercalation and/or exfoliation, and on the interfacial bonding between the mineral layers and the thermoplastic polymer [19–21].

The present study deals with the modification of a previous method that was developed and patented by Bouhelal in 2009 [22]. This method has demonstrated its great efficiency in the formulation of polymer/clay nanocomposites in only one step [23-27] by using a reactive melt extrusion process.

The materials used in this method are: PVDF, PMMA, dicumyl peroxide, sulfur (S) and a specific activator, tetra methyl thiuram disulfide (TMTD). The clay of preference is montmorillonite (MMT).

The main principle of the method developed and patented by Bouhelal in 2009 [22], is the generation of macroradicals provided by the peroxide, that decomposes (homolytic reaction) under the appropriate processing conditions. As a result of this reaction, the polymer chains are linked by sulfur atoms through the formation of a three dimensional network. In the presence of clay, the complete process becomes more complicated.

In our study, we have used dicumyl peroxide as one of the ingredients of the so called “active agents” (see below). The other “active agents” are sulfur and an activator (TMTD, in our case). The rest of the components of the system studied are: PVDF, PMMA, and clay (in our case, raw montmorillonite).

As a consequence of the preparation process of the composites, several chemical reactions occur, which, eventually, could lead to the partial or total clay exfoliation.

Thus, according to recent findings, the clay exfoliation could take place:

- 1) Either by gas production after the peroxyde decomposition. This gas could be trapped in between the interlamellar clay spaces, thus giving rise to an increase of the interlamellar distance, favouring the penetration of the polymeric chains between the platelets. [28]
- 2) Or by intramolecular scission of the polymeric chains, scission also originated as a consequence of the thermal decomposition of the dicumyl peroxide. This process also facilitates the insertion of the chains between the interlamellar spaces [29].

Further details about the above described methods are given in references [25-27].

The aim of the present work is to examine the structure of the novel PVDF/PMMA chains and confirm whether total exfoliation appears for a certain content of clay in the PVDF and PMMA matrices. As it is well known, a perfect exfoliation of the clay particles could provide the best final properties.

2. Experimental

2.1 Materials

- Poly (vinylidene fluoride) (Hylar 5000), which was generously donated by Ausimont, Italy; it was used as received. Density = 1.76 g.cm^{-3} at 25°C . Melting temperature $T_m = 160^\circ\text{C}$. Glass transition temperature $T_g \approx -35^\circ\text{C}$.
- Polymethyl methacrylate (Vedril S.P.A.) from Montedison Group, Italy, was used as received without further purification. Density = 1.19 g.cm^{-3} at 25°C . Deflection temperature $T = 105^\circ\text{C}$.
- Raw Montmorillonite (called Maghnite). This unmodified clay, (from the Algerian region of Maghnia) was supplied by ENOF, Algeria. The cation exchange capacity, CEC, of this montmorillonite is about $1.15 \times 10^{-3} \text{ mol/g}$ [30].
- Dicumyl peroxide (DCP), 96 wt % activity, was supplied by ACROSS (Belgium).
- The sulfur vulcanizing agent (S) was supplied by Wuxi Huasbeng Chemical Additives Factory (China).
- The activator used was « Super accelerator 501 » (tetramethyl thiuram disulfide TMTD); supplied by Rhône-Poulenc (France).

In what follows, the blend of peroxide, sulfur and activator will be designed as “active agents”.

2.2 Sample preparation

The clay was separated from the raw material by means of washing with distilled water followed by centrifugation. It is not necessary to perform any other chemical treatment or purification step. The dried clay (100°C , 24 h) is then screened through sieves (granular size, $63 \mu\text{m}$ or less).

At this step, the clay is ready to be mixed with the “active agents”. The “active agents” are dissolved in acetone; then, well mixed with the dried clay, and left during 24 hours before being used. The formulations are as follows: the chosen sulfur concentration (in wt %) was always equal to that of peroxide, and the activator was 1/4 of the sulfur or peroxide concentration. The “active agents” were added in a concentration of 1/10 of the clay.

This “activated” clay was blended with the polymer matrix for different weight contents. The compounding is made by reactive melt mixing by using a Plastograph. See Fig. 1 from reference [25] illustrating the scheme of the one-step reactive extrusion process.

The materials were formulated with various amounts of clay in order to identify the best conditions enabling to obtain the optimal particle exfoliation in the polymer matrix at the nanometric scale. According to the previous results, PVDF with 4 wt% clay showed good mechanical properties [25]. Therefore, this composition was chosen to blend it with that of PMMA 4 wt% clay, provided that this amount of clay gave rise to enhanced properties for both polymer matrices. We shall call these compositions nPolymerx (x = 4 wt % clay).

These two main compositions have been prepared separately via a melt compounding method using a Plastograph at 200 °C with a screw speed of 45 rpm for 5 min for the nPVDF4 nanocomposite, and at 230 °C with a screw speed of 45 rpm for 5 min for the nPMMA4 nanocomposite.

Nanocomposites (nPVDF4/nPMMA4) 90/10, 80/20, 70/30, 60/40 and 50/50 were prepared by mixing the two initial compositions (nPVDF4 and nPMMA4) in the Plastograph (Brabender) at 230 °C with a screw speed of 45 rpm for 5 min.

A laboratory compression molding equipment was used to prepare films of about 1 mm thickness for all the formulations. Different measurements and analyses, such as DSC, WAXS and tensile and micro and macro-mechanical measurements, as well as morphological studies of the surface roughness, were performed on those films.

2.3. Microstructural characterization techniques

2.3.1 Differential scanning calorimetry (DSC)

Thermograms of all the samples were obtained by using a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC), calibrated with indium standard. The calorimetric runs were performed using 5-10 mg of sample with a heating rate of 10°C/min in the 40 to 200°C

temperature interval under a constant flux of nitrogen of 0.1 L/min. All DSC curves are baseline substrated and normalized to 1 mg of sample. The first heating scan was analyzed to identify the thermomechanical history underwent during the chemical formulation and compression molding. Second heating scans have not been performed.

2.3.2 Wide angle X-ray diffraction (WAXS)

Wide angle X-ray scattering (WAXS) experiments were performed using a Seifert diffractometer equipped with a $\text{CuK}\alpha_1$ ($\lambda = 0.1542$ nm) monochromator in the reflection mode. The following conditions were employed: 40 kV; 35 mA; angular range: 5° - 35° (2θ); scan rate: $0.02^\circ/\text{s}$; slits: 0.3 and 0.2.

2.4. Mechanical behavior and properties

2.4.1. Uniaxial tensile testing

The tensile tests were conducted at room temperature on a Universal Testing machine (Zwick Roell Proline). The tests were made on $4 \times 1 \text{ cm}^2$ size samples, with a thickness of about 1 mm. The crosshead speed (initial strain rate) was 5 mm/min and the grip length 40 mm. In each case five samples were tested and the average of five readings was taken. The tensile strength at the yield point, the Young's modulus and the elongation at break were derived from the stress strain curves.

2.4.2. Impact testing

The impact strength tests were conducted at room temperature on a Universal Testing machine Resil Impactor, initially developed and commercialize by CEAST (Italy) and recently acquired by INSTRON in 2008. In each case five samples were tested and the average of five readings was taken.

The standard test method for determining the Charpy impact resistance of notched and un-notched specimens of (nPVPDF4/nPMMA4) with different compositions was used. The notch was machined out using a specially made milling cutter with an angle of 45°. The depth value is between 1 mm and 10 mm.

2.4.3. Microhardness testing

Microindentation measurements were performed at room temperature (23°C) using a Leitz (Wetzlar, Germany) microindentation tester equipped with a Vickers square-based diamond indenter. Loads of 0.5 and 1N were applied for 6 s and subsequently released to measure the residual area of indentation.

The microhardness H value was derived from the residual projected area of indentation according to the well-known expression [31]:

$$H = kP/d^2 \quad (1)$$

where d is the length of the impression diagonal (m), P is the applied contact load (N), and k is a geometrical factor equal to 1.854. The hardness measurements were averaged over 8-10 indentations on each sample.

2.5. Morphological characterization

2.5.1. Optical Microscopy

The images were recorded using a Asylum Research-Model MFP-3D microscope and a numeric CCD camera KAPPA.

2.5.2. AFM Microscopy

The surface morphology was observed using an atomic force microscope (AFM). The images were recorded using an AXIOSCOPE 40 microscope with a frequency of 1 Hz and at a scale of 50 μm .

The RMS roughness (root-mean-square height deviation) of the samples was obtained directly from the software of the AFM.

3. Results and Discussion

3.1 Microstructure Characterization (DSC and WAXS)

In order to identify the modification of the semicrystalline microstructure of PVDF induced by the incorporation of clay fillers and to characterize their distribution through the polymer matrix, DSC and WAXS analyses were performed on each compression molded film.

DSC heating and cooling curves for (nPVDf4/nPMMA4) compositions from 100/0 to 50/50 are plotted in Figs. 1a (heating) and 1b (cooling). The corresponding data are listed in Table 1.

The addition of an amorphous or semi-crystalline polymer to another semi-crystalline polymer generally modifies the crystallinity of the latter, at least when their amorphous phases are miscible. The decrease in the melting point of PVDF resulting from the incorporation of PMMA has been reported previously, and was attributed to the interactions of semi-crystalline PVDF with amorphous PMMA [32]. Thus, as it is indicated in Table 1, both, the melting temperature (T_m), and the crystallization temperature (T_c) of the PVDF component decrease with increasing PMMA. The crystalline lamellar thickness l_c , was calculated from the melting temperature T_m through the Thomson-Gibbs equation [33]:

$$T_m = T_m^0 [1 - (2\sigma_e / \Delta H_m^\infty \rho_c l_c)] \quad (2)$$

In this expression T_m^0 is the PVDF equilibrium melting point: 483.2°K [34]; ΔH_m^∞ is the melting enthalpy for an infinitely thick PVDF crystal: 104.7 J/g [34]; σ_e is the surface free energy of the PVDF α -crystals, with a value of 38.0 erg/cm² [35]; and ρ_c is the crystalline density of the α -phase of PVDF: 1.925 g/cm³ [36]

The l_c values, calculated from eq. (2), diminish from 3.56 nm to 2.90 nm (60/40 composition), in a parallel way to T_m (see Table 1).

From the experimental melting enthalpies ΔH_m , derived for every composition, the DSC crystallinities have been calculated from the expression: $\alpha_{DSC} = \Delta H_m / w \cdot \Delta H_m^\infty$. In this formula, w is the weight fraction of PVDF in every sample, and ΔH_m^∞ is the melting enthalpy for an infinitely long PVDF crystal. In addition to this, the value of ΔH_m^∞ is the same for both α - and β -crystallographic forms, that is: 104.7 J/g [34]. In Table 1 it can be seen that the PVDF degree of crystallinity is strongly affected by the presence of nPMMA4 amounts equal or higher than 30 wt%. Furthermore, the melting temperature depression from 160 to 147 °C indicates that the PVDF crystallites become smaller in size, and probably, less perfect [37].

The decrease of T_c of the PVDF in their blends with PMMA content, irrespective of the cooling rate used, could be attributed to intermolecular interactions between the carbonyl group of PMMA ($-\text{[CH}_2\text{-C(CH}_3\text{)(COOCH}_3\text{)]n-}$) and the hydrogen atoms of PVDF ($-\text{[CH}_2\text{-CF}_2\text{]n-}$) as reported in [32, 37-41]. The PMMA chains reduce the PVDF segments mobility because of these specific interactions when the temperature is close to the PMMA glass transition temperature (about 106° C). Whereas this reduced mobility favors the nucleus formation and beta phase nucleation, it depresses drastically the crystallite growth around the PMMA glass transition temperature.

In nPVDF4/nPMMA4 blends with lower nPMMA4 content, the crystallization process is only slightly affected, and the PVDF crystallization from the melt occurs. In these conditions, the nucleation of the alpha phase is more stable and favorable [38].

The cooling thermograms (Fig. 1b) show that the crystallization temperature decreases from 139 °C for pure PVDF to 133 °C for 90/10 composition, and down to 100 °C for the 60/40 composition. When the nPMMA4 content is higher than 40 wt%, no crystallization peak can be detected. This is also an indication that the crystallinity decreases with the addition of PMMA. This result was in agreement with the WAXS analyses, as indicated below.

In all the (nPVDf4/nPMMA4) compositions, the diffraction peak appearing at $2\theta = 6.8-7.4^\circ$ on the WAXS diffractograms (see Fig. 2) corresponds to the $d_{(001)}$ spacing of clay. This means that no partial intercalation takes place in any of the compositions. Moreover, there is no total exfoliation for any composition. In addition to this, whereas compositions 100/0 and 90/10 only show the reflections characteristic of the α -form (at 17.6, 18.4, 19.95 and 26.9 ° of 2θ , respectively), for the composition 80/20 the reflections of both, α - and β -forms, appear. In the composition 70/30 only the β -form (reflection at 20.75 ° of 2θ) is evident. On the other hand, compositions 60/40 and 50/50 are completely amorphous, at least from the WAXS point of view. Thus, from the diffractograms analysis, it is also clear that increasing amounts of nPMMA4 strongly inhibits the crystallization ability of the nPVDf4 component, in agreement with the DSC findings.

3.2 Micro- and macromechanical properties

3.2.1. Microhardness

Figure 3 shows the variation of the microhardness H as a function of the compositions for the investigated blends. We observe that H decreases from 94 down to 64 MPa for the nPVDf4/nPMMA4 80/20 composition. Then, H increases again, reaching a maximum value of 90 MPa for the 50/50 composition. Hardness values found for the different compositions are also included in Table 2.

On the other hand, for all the studied blends, the Young's modulus E values correlate quite well with those of the hardness H, in accordance with previous studies on different samples of polyethylene [42] (see Fig. 4).

3.2.2. Tensile resistance

The Young's modulus, the yield point, and the stress and strain at break are reported in Table 2 for all the compositions.

From these results, it can be inferred that blending the nPVDF4 and the nPMMA4 in different proportions has significantly affected the tensile properties of the resulting nanocomposites. We can see in Table 2 that the 70/30 composition has the highest value of the tensile strength (98 N) and the maximum stress (28.6 MPa) and elongation at break (621%) values. This is attributed to the interaction between the PMMA-carbonyl groups and the PVDF-hydrogen atoms and also, between the polymer chains and the clay nanolayers. On the other hand, the 50/50 composition also shows tensile strength and tensile stress values very close to those of 70/30 composition, together with the maximum Young's modulus, 295 MPa.

3.2.3. Impact strength

Table 3 shows the impact strength values of the nanocomposites with different nPMMA4 content. It can be seen that the 70/30 composition presents the highest impact strength value. However, all composition's values are lower than that of nPVDF4.

3.2.4. Relation between microstructure and micromechanical properties

The hardness of a polymer can be expressed in terms of its crystalline H_c and amorphous H_a components, according to the additivity law [43]:

$$H = H_c \alpha + H_a (1 - \alpha) \quad (3)$$

In this expression, α is the degree of crystallinity of the polymer. On the other hand, the crystal hardness H_c is related to the crystal thickness l_c through the expression [44]:

$$H_c = H_c^\infty / (1 + b/l_c) \quad (4)$$

where H_c^∞ is the hardness of an infinitely thick crystal, and the b -parameter is defined as [44]:

$$b = \sigma_e / \Delta h \quad (5)$$

where σ_e is the surface free energy, and Δh is the energy required for the plastic deformation of the crystals. In the 100/0 to 80/20 compositions, due to the lowering value of l_c , H_c slowly diminishes, and so does H . This is explained by the miscibility of the PVDF with the PMMA. Thus, the addition of the latter increases the segmental mobility of PVDF chains, resulting in the observed decrease of the H value for the first compositions.

However, from the composition 70/30 onwards, H gradually increases again. This behavior is probably due to the fact that the material becomes gradually amorphous. Thus, for the last compositions, by applying the additivity law [31], and assuming that $H_{PVDF} \approx 0$, the total hardness of the material can be expressed as:

$$H = H_{PMMA} (1 - \Phi_1) \quad (6)$$

where $H_{PMMA} = 176$ MPa [45]. The values so calculated agree very well with the experimental ones: 85.4 and 88 MPa for 60/40 and 50/50 compositions, respectively.

3.3 Morphological characterization

3.3.1. Optical Microscopy

One of the most important requirements for improving the properties of nanocomposites is to achieve the exfoliation, or a homogeneous dispersion of the filler used. The objective of the optical microscopy is to visualize the dispersion of the fillers in the polymer matrix. Figure 5 shows the optical microscopy images of nanocomposites (nPVDf4/ nPMMA4). From this figure, it is clearly seen that, for the 50/50 composition, the clay was homogeneously dispersed, while the other compositions presented inhomogeneous aggregates.

3.3.2. AFM Microscopy

Figures 6 and 7 represent the AFM topographic images of different (nPVDf4/nPMMA4) nanocomposites. Compositions (d) and (f) have the lowest values of the surface roughness, as indicated in Table 3.

Summary and Conclusions

- The DSC analysis shows a decrease of the melting and crystallization temperatures for the PVDF component as the nPMMA4 content increases. This effect is due to the interactions between the oxygen of the carbonyl group of the PMMA and the PVDF's hydrogen atoms. For higher nPMMA4 (> 40%) contents, neither the melting nor the crystallization peak are detected, indicating that the crystallinity decreases with the incorporation of nPMMA4. This is in good agreement with the results of the WAXS analysis.
- For all the (nPVDf4/nPMMA4) compositions, the diffraction peak appearing at $2\theta = 6.8-7.4^\circ$ on the WAXS diffractograms corresponds to the $d_{(001)}$ spacing of clay. This means that no partial intercalation step takes place in any of the compositions. Moreover, there is no total exfoliation for any composition.

- For some compositions, the addition of nPMMA4 improves the tensile properties of the nanocomposites. Thus, the 70/30 composition shows the maximum values of the tensile strength, tensile stress and elongation at break, whereas 50/50 composition exhibits the highest value of the Young's modulus. This is attributed to the interaction between the carbonyl group of PMMA and the hydrogen atoms of PVDF due to their miscibility, and also, to the miscibility between the polymer chains and the clay nanolayers.
- The decrease of H for the PVDF/PMMA compositions between 100/0 and 80/20 could be explained by the diminishing value of the PVDF crystal thickness, l_c . For higher PMMA contents, H increases, probably because the PVDF becomes amorphous, and only the PMMA component has an effect on the H value in this composition range.
- The optical microscopy images indicate that only for the 50/50 composition, the clay is homogeneously dispersed.
- Finally, the morphological study of surface roughness by atomic force microscopy (AFM) shows the significant effect of the clay. Thus, compositions 70/30 and 50/50 present the lowest roughness values (between 40 and 50 nm).

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(a)

(b)

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Table 1: DSC (first scan) results of (nPVDf4/nPMMA4) nanocomposites.

Sample	Heating						Cooling	
nPVDF4/nPMMA4	T _c (°C)	ΔH _c (J/g)	T _m (°C)	l _c (nm)	ΔH _m (J/g)	α _{DSC}	T _c (°C)	ΔH _c (J/g)
100/0			159	3.56	39	0.39	137	-45
90/10			158	3.49	40	0.44	133	-40
80/20			156	3.36	32	0.40	127	-31
70/30			152	3.13	24	0.34	118	-22
60/40	103	-5	147	2.90	14	0.11	100	-5
50/50			---		---	0.00	--	--

Table 2: Tensile properties and hardness values of (nPVDf4/nPMMA4) nanocomposites.

Samples nPVDf4/nPMMA4	Tensile strength (MPa)	Tensile Stress (MPa)	Modulus E(MPa)	Elongation at break (%)	H (MPa)
100/0	49.1	17.4	636	351	89±7
90/10	40.5	26.9	570	536	84±5
80/20	57.9	14.9	98.4	224	64±8
70/30	98.0	28.6	57.3	621	73±6
60/40	55.3	18.0	57.2	176	74±6
50/50	89.5	28.3	295	22.2	90±12

Table 3: Impact strength and roughness values of (nPVDf4/nPMMA4) nanocomposites.

Samples nPVDf4/nPMMA4	Impact strength $a_n \cdot 10^4 \text{ J/m}^2$	Roughness (nm)
100/0	14.5	78
90/10	2.5	196
80/20	6.1	90
70/30	10.3	54
60/40	9.5	99
50/50	1.8	43

Figure captions

Fig.1: (a) Heating thermograms of nPVDF4/nPMMA4 nanocomposites with compositions 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50 (b) Cooling thermograms of the same samples.

Fig. 2: WAXS diagrams of the same nanocomposites as in Fig. 1.

Fig. 3: Dependence of hardness on the composition for the above cited nanocomposites.

Fig. 4: E-H relationship for the nPVDF4/nPMMA4 nanocomposites included in this study.

Fig. 5: Optical microscopy images of nanocomposites (nPVDF4/nPMMA4): (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30, (e) 60/40 and (f) 50/50.

Fig. 6: AFM topographic images in two dimensions of the same (nPVDF4/nPMMA4) compositions as in Fig. 5

Fig. 7: AFM topographic images in three dimensions of the same (nPVDF4/nPMMA4) compositions as in Figs 5 and 6.