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Nanocomposites based on layered silicate and miscible PVDF/PMMA blends: melt preparation, nanophase morphology and rheological behaviour

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Abstract

Polyvinylidene fluoride (PVDF)–organoclay nanocomposites were prepared by melt-extrusion using polymethylmethacrylate (PMMA) as an interfacial agent. These nanocomposite materials were analysed with respect to their morphological and rheological properties. The nanophase morphology development and nanophase dispersion were studied using TEM. A fine dispersion of partially to nearly fully exfoliated silicate layers in miscible PVDF/PMMA blend matrices was observed when organophilic montmorillonite was used. Increasing the amount of PMMA in the PVDF/PMMA blend leads to high degree of exfoliation.

The rheological behaviour of intercalated/exfoliated PVDF/PMMA nanocomposites containing various concentrations of organophilic silicate was also investigated. At low frequencies, the storage modulus is increasing with increasing PMMA content and the frequency dependence of the storage modulus gradually changes from liquid-like to solid-like for nanocomposites when 10 wt% of PMMA is added, indicating formation of a network structure.

Dynamic mechanical investigations show a dramatic increase of the storage modulus in the rubbery plateau compared to conventional mineral fillers, as a result of the network structure. Due to the 'nano'-sized dispersion, property efficiency is already realized at low loading levels (3–5 wt%).

Keywords: Polyvinylidene fluoride/polymethylmethacrylate; Melt intercalation; Nanocomposites

1. Introduction

The development of polymer nanocomposites, particularly polymer-layered silicate nanocomposites, is one of the latest evolutionary steps in polymer technology. Nanocomposites offer attractive potential for diversification and application of traditional polymeric materials [1–6].

The many useful properties of polymers such as mechanical properties (stiffness, strength, toughness and impact resistance [7–10]), gas permeability resistance [11, 12], chemical inertness [13], thermal stability [7,14,15] and melt-processability can be built into new materials via nanocomposites with thermoplastic polymers. The enhanced properties are mainly ascribed to the nanoscale morphology of these composite materials [16–19].

The melt-intercalation approach is considered as an attractive method for preparing polymer nanocomposites [20]. It consists of inserting the thermoplastic polymer melt into the interlayer space of the mineral layers to form ordered nanocomposites. Interestingly, these nanostructured materials can be prepared using conventional melt-processing techniques such as extrusion [21,22].

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 [1–3].

Layered minerals are hydrophilic and most polymers are hydrophobic. To enhance the mineral–polymer interaction, preintercalating long chain alkyl ammonium ions as

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surfactant can modify the mineral, so that it becomes organophilic [1]. Depending on the interaction between the layered mineral and the surfactant, different types of nanocomposites ranging from intercalated to exfoliated can be elaborated. It was shown, recently, that using appropriate premade block or graft copolymers as compatibilizing agent can also improve the interfacial interaction between the matrix polymer and the layered mineral [15]. Block or graft copolymers having one part that is chemically identical or completely miscible with the matrix polymer, and another part that is compatible with the mineral, are used to decrease the surface energy of the layered inorganic material and to improve the wetting characteristics with the polymer. It has been reported by Hasegawa et al. [23–25] that polypropylene and polystyrene containing exfoliated silicate layers were successfully prepared by using non miscible functional polymers containing a small amount of functional groups as compatibilizers to enhance the affinity of the polymer with respect to the organosilicate.

The purpose of the present paper is to investigate another strategy to improve the mineral–polymer adhesion. It would consist of using a homopolymer as compatibilizer agent which is completely miscible with the matrix polymer and presents an adequate affinity with the mineral to act as a potential interfacial agent during melt-processing. As a prerequisite condition for this purpose, the polymer, selected as a compatibilizer, is required to exfoliate the silicate layers during melt-mixing. As a model system we selected polyvinylidene fluoride (PVDF)/clay in which the silicate layers are not exfoliated during melt-mixing. Polymethylmethacrylate (PMMA) is considered as a potential interfacial agent since it is known to be miscible with PVDF [26,27], and it was reported that it has the ability to exfoliate the silicate layers [28–30].

This study deals with the beneficial effect that PMMA can have on the nano-phase morphology of these composites.

2. Experimental

2.1. Materials and preparation

The Na^+-montmorillonite clay with a cation exchange capacity of 98 mequiv./100 g (Cloisite Na^+) and the organophilic clay (Cloisite 20A) have been supplied by Southern Clay. The organophilic clay is prepared via ion exchange reaction between Na^+-montmorillonite and dimethyldioctadecylammonium chloride. The main characteristics of the polymers used in this study are listed in Table 1.

Polymer composites with different clay contents were extruded at 230 °C for 10 min with a rotation speed of 80 rpm and under nitrogen atmosphere using a twin-screw mini-extruder designed by DSM-Research. The polymers were previously dried overnight in a vacuum oven at 70 °C to remove water. A two-step mixing procedure was used to prepare the PVDF nanocomposites. PMMA–organoclay master batches with different contents of silicate were first prepared by melt-mixing, and subsequently melt-mixed with PVDF. One step mixing was also considered.

2.2. Characterization methods

Ultrathin sections of the composites with a thickness of approximately 60–100 nm were cut under cryogenic conditions with a Leica Ultramicrotome equipped with a diamond knife. Transmission electron microscopy (TEM) was carried out with a Philips CM20 apparatus using an acceleration voltage of 70 keV. Due to the high electron density difference between the silicate and the polymers, staining of the samples is not needed.

The rheological properties of the neat PVDF and the PVDF/PMMA composite series with different contents of PMMA were measured by Rheometrics RMS800 in an oscillatory mode with parallel plate geometry using 25 mm diameter plates at 200 °C. All measurements were carried out under nitrogen. The strain region in which the material can be regarded as linear viscoelastic was determined by amplitude sweep experiments, it is in the order of 10%. Samples (for the rheological testing) with a plate geometry of 25 mm diameter and ranging from 0.8 to 1 mm thickness were prepared by compression molding at 220 °C. The data of both thinner and thicker samples were closely matching, which indicates that the surface has no influence on the structure of the nanocomposites.

Dynamic mechanical properties were measured on a DMTA 2980 TA instruments, using a film specimen in the tensile mode at an oscillation frequency of 1 Hz and at temperatures ranging from 20 to 160 °C with a heating rate of 5 °C min^{-1}.

3. Results and discussion

3.1. Micro- and nanophase morphology

It should be noted that no difference in morphological structure is observed between samples prepared by the two-step or one-step mixing procedures.

Transmission electron microscopy (TEM) was used to examine the phase morphology development of the composites based on PMMA, PVDF and PVDF/PMMA blends as matrix. The overall silicate loading was 5 wt% for all composites. The TEM micrographs are displayed in Figs. 1–3, where the dark domains represent the silicate layers in the polymer matrix.

Fig. 1a and b illustrates the TEM micrographs of PVDF–MMT and PMMA–MMT composites, respectively, containing 5 wt% of hydrophilic MMT. A micron-scale dispersion of primary particles aggregates is observed in both PMMA and PVDF matrices, as a result of the high

Table 1
Main characteristics and origin of the polymers used in this study

Polymers	Abbreviation	Commercial designation	Source	Molecular weight M_w (10^{-3})	M_w/M_n	T_g[a] (°C)	Density (g cm^{-3}) (23 °C)
Polymethylmethacrylate	PMMA	Diakon	ICI	60[b]	1.6[b]	118	1.08
Polyvinylidene fluoride	PVDF	Solef 1008	Solvay	110	1.8	−45	1.7

[a] Determined by dynamic mechanical analysis (DMA) at 1 Hz.
[b] Determined by SEC with a polystyrene calibration.

interfacial tension between the hydrophobic polymers and the hydrophilic montmorillonite. In sharp contrast, mixing PVDF with organophilic MMT leads to a relatively fine dispersion of silicate particles but it failed to exfoliate the silicate layers (Fig. 2a and b). However, PMMA–organophilic MMT composites exhibit a very fine dispersion of nearly individual silicate platelets (Fig. 2c and d). The high-magnification image of PMMA nanocomposites (Fig. 2d) shows individual layers as well as stacks containing parallel oriented layers with various degrees of intercalation. The intercalation of PMMA chains between the silicate layers is enhanced by the strong polar interaction developed between the oxygen groups of the silicate and the oxygen groups of PMMA. Obviously, the large interlayer distance in the PMMA–organophilic MMT nanocomposites was accompanied by a weakening of the silicate interlayer interactions leading to the formation of a partially exfoliated structure during melt-extrusion.

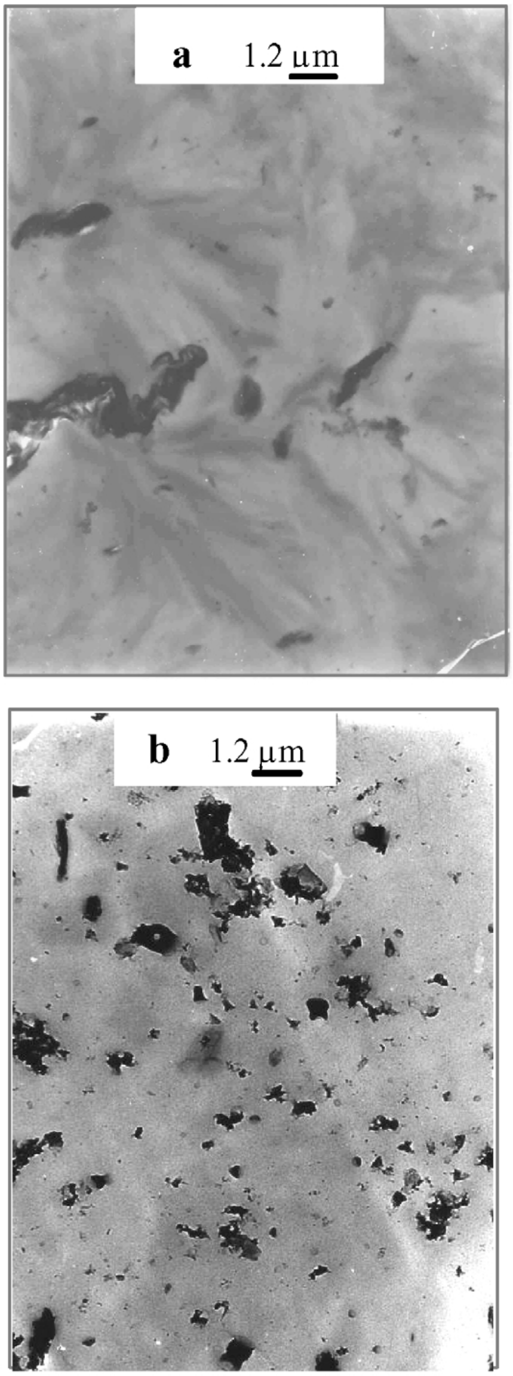

Fig. 1. TEM micrographs of PVDF (a) and PMMA (b) with 5 wt% of hydrophilic MMT prepared by melt-extrusion.

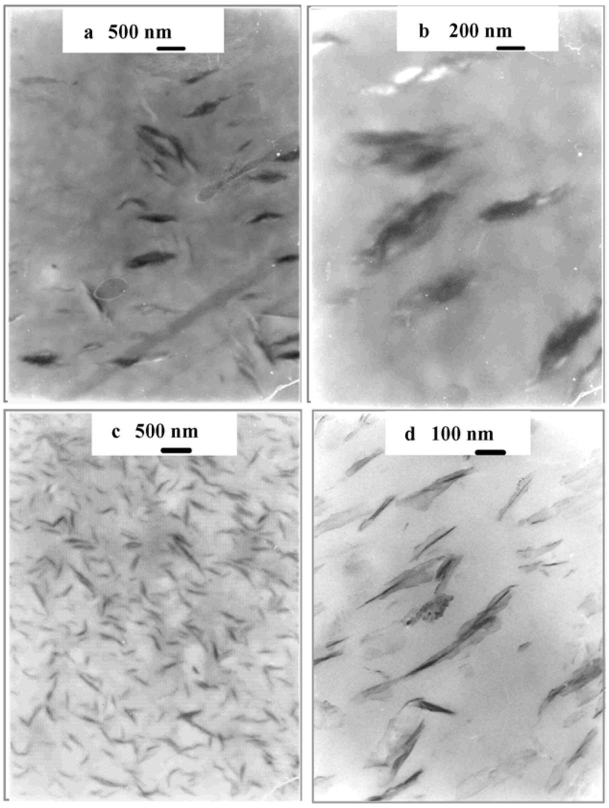

Fig. 2. TEM micrographs of PVDF (a and b) and PMMA (c and d) with 5 wt% of organophilic MMT prepared by melt-extrusion.

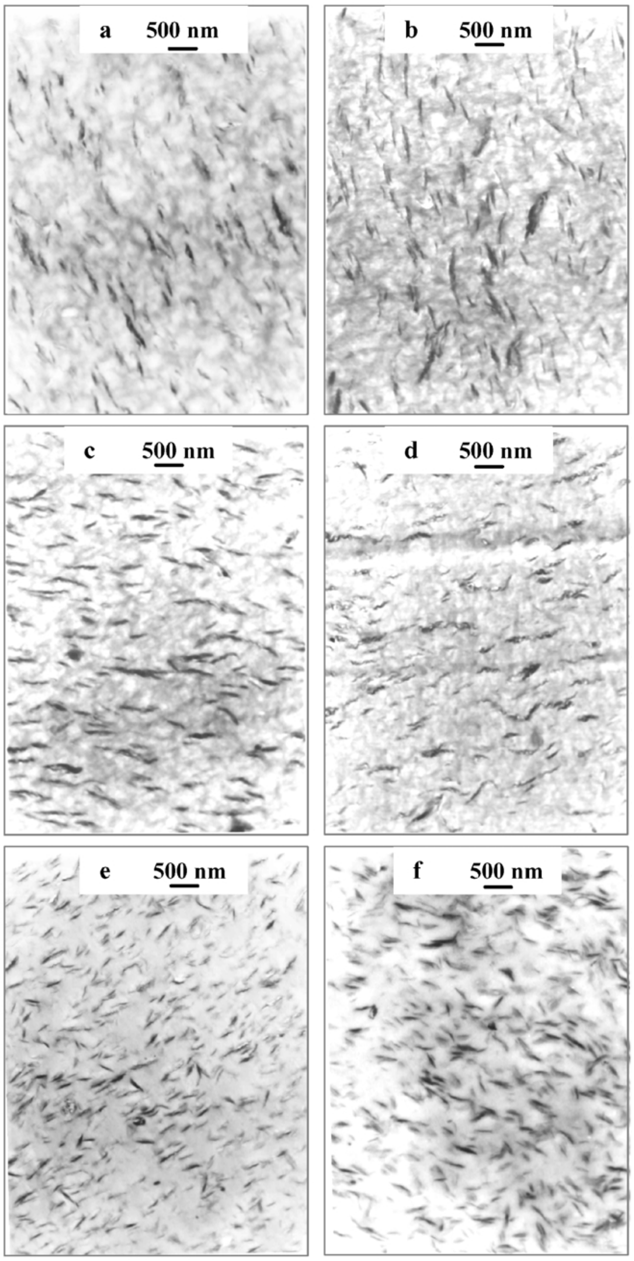

Fig. 3. TEM micrographs of 95/5 (a), 90/10 (b), 85/15 (c), 80/20 (d), 60/40 (e) and 45/55 (f) PVDF/PMMA blends with 5 wt% of organophilic MMT prepared by melt-extrusion.

Fig. 3 shows the TEM micrographs of the PVDF/PMMA–organophilic MMT nanocomposites containing 5 wt% of organophilic MMT. The content of PMMA in the miscible PVDF/PMMA blend matrix is 5, 10, 15, 20, 40 and 55 wt%, respectively. From Fig. 3a, it is clear that blending PVDF with only 5 wt% PMMA leads to a regular and homogeneous dispersion of intercalated and delaminated silicate layers, compared with the neat PVDF–organophilic MMT composites (Fig. 2a). In addition, these nanomorphologies are very similar to those of PMMA–organophilic MMT nanocomposites (Fig. 2c). The premixing of PVDF with an increasing amount of PMMA from 10 to 55 wt% does not basically affect the nano-morphology dispersion (Fig. 3, micrographs: b, c, d, e and f). This observation emphasizes the beneficial effect of PMMA as a compatibilizer, which preferably intercalates between the silicate layers to the point where the silicate interlayer interactions become significantly weakened. Hence a partially exfoliated structure is generated as a result of the shear forces applied during melt-extrusion. It should be noted that high shear forces have no more effect on the nano-morphology dispersion.

3.2. Rheological behavior

The investigation of the rheological properties is another interesting tool to identify the intercalated–exfoliated type of structure and to examine the ability of PMMA to enhance the nano-dispersion of the silicate layers in the PVDF/PMMA matrix. The melt-state rheological experiments are used in combination with TEM analysis to assess the relative dispersion of the silicate layers in these nanocomposite materials. The frequency dependence of the storage modulus (G') and the dynamic viscosity measured at 200 °C for both PVDF and PMMA homopolymers are shown in Fig. 4a. According to Cox and Mertz [31], the dynamic viscosity–frequency plots are equivalent to shear viscosity versus shear rate plots. Fig. 4b shows the frequency dependence of the storage modulus (G') measured at 200 °C for both PVDF/PMMA–hydrophilic MMT microcomposites and PVDF/PMMA–organophilic MMT nanocomposites containing increasing amounts of PMMA in the PVDF/PMMA blend matrix. It should be noted that prolonged heating of the samples in the rheometer with flowing N_2 did not result in any changes in the viscoelastic data. In addition, the data for the unfilled PVDF/PMMA blends are almost similar to those obtained for the PVDF/PMMA–hydrophilic MMT microcomposites (not shown in Fig. 4b). In the whole frequency range, PVDF is much less elastic than PMMA at 200 °C (Fig. 4a), which explains the slight increase of G' of PVDF/PMMA–hydrophilic MMT microcomposites with increasing PMMA content at 200 °C (Fig. 4b, filled symbols). The frequency dependence of G' for the microcomposites containing hydrophilic MMT (filled symbols) exhibits the normal response of a conventional filled thermoplastic polymer, with a liquid-like behavior at the lowest frequencies (below 0.1 rad s^{-1}). In sharp contrast, the storage modulus for the nanocomposites containing organophilic MMT (open symbols) increases strongly with increasing PMMA content in the frequency range of 0.02 to1 rad s^{-1}. Furthermore at low frequencies (corresponding to a regime where the unfilled polymer exhibits liquid-like behavior), the storage modulus for these nanocomposites shows a diminished frequency dependence with increasing PMMA content. From Fig. 4c which represents the dependence of G' on the PMMA content in the PVDF/PMMA matrix at 0.1 and 0.03 rad s^{-1}, it can be seen that G'

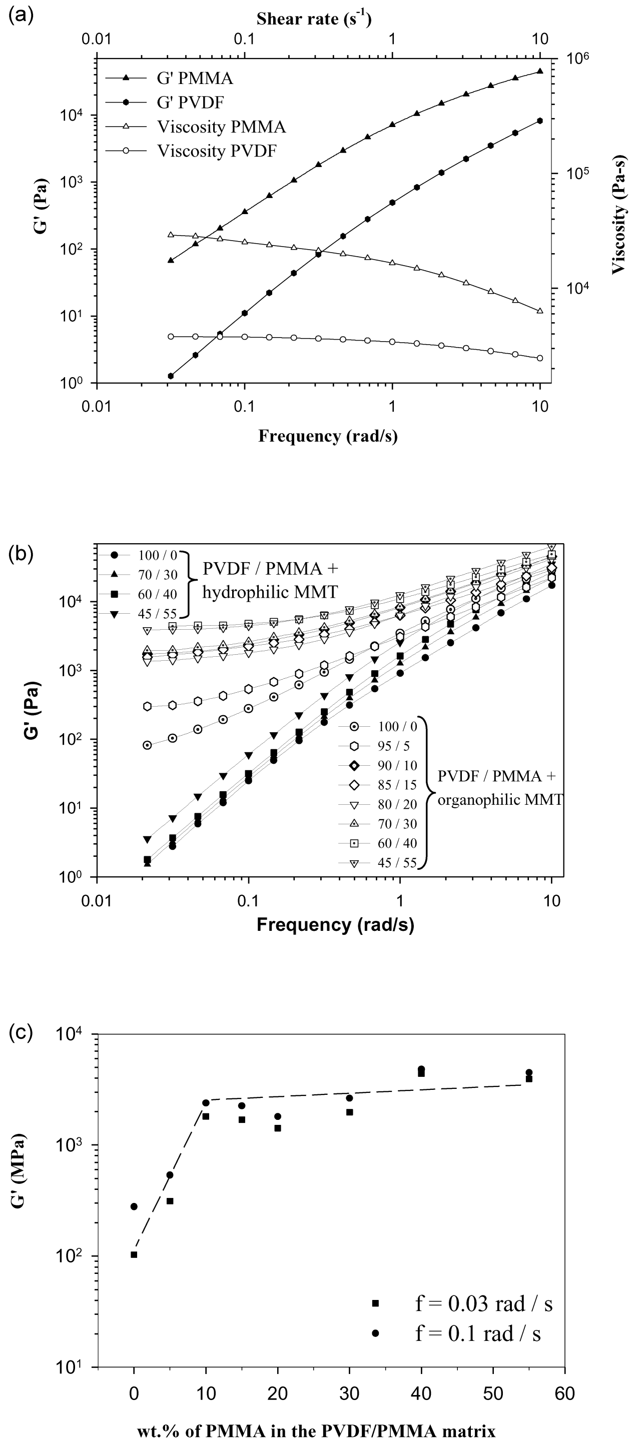

Fig. 4. (a) Shear storage modulus versus frequency and shear viscosity versus shear rate for PVDF and PMMA homopolymers at 200 °C. (b) Shear storage modulus versus frequency for various PVDF/PMMA micro- and nanocomposites containing 5 wt% of silicate and with several PMMA contents ($T = 200$ °C). (c) Shear storage modulus versus PMMA content in PVDF/PMMA nanocomposites containing 5 wt% of organophilic MMT at 0.03 and 0.1 rad s^{-1} ($T = 200$ °C).

increases rapidly to reach a plateau value when 10 wt% of PMMA is added to PVDF. At this PMMA content, the nanocomposites behave solid-like in the low frequency region. Beyond a PMMA content of 10 wt%, the storage modulus becomes nearly independent on both PMMA content and frequency (Fig. 4b). At high frequencies (5–10 rad s^{-1}), where the polymer chains are not fully relaxed, the viscoelastic behavior of the nanocomposites remains almost unaffected by the addition of PMMA, with the exception of a monotonic increase in the modulus value.

Based on the dynamic oscillatory shear experiments, it is clear that the addition of PMMA to PVDF in the presence of the organophilic layered silicate has a profound influence on the long-time relaxation of the nanocomposites (at low frequencies). With increasing PMMA content at a given silicate loading (5 wt%), the liquid-like relaxation observed for the conventional filled composites (microcomposites) gradually changes to a solid-like behavior for nanocomposites. This behavior can be attributed to the retardation of molecular relaxation processes induced by the confined geometric effect [32,33]. Solid-like behavior at low frequencies has been recently observed in both polycaprolactone and polyamide exfoliated nanocomposites with low silicate contents (3–5 wt%) [34,35]; it was attributed to the percolation of a three-dimensional filler network structure comprising a random orientation of exfoliated layers. Our observations clearly indicate that PMMA exhibits a strong interfacial activity enhancing the exfoliation of the silicate layers in the blend matrix, leading to the formation of a percolated network structure of the exfoliated layers, which is in a good agreement with the morphological investigations.

The melt-state steady shear viscoelastic behavior has been also studied for these composite systems. The steady shear viscosity (η) as a function of shear rate ($\dot{\gamma}$) for PVDF/PMMA microcomposites and nanocomposites with various PMMA contents is shown in Fig. 5. Over the whole shear rate range (0.02–10 s^{-1}), the viscosity of the nanocomposites is much higher than that of the

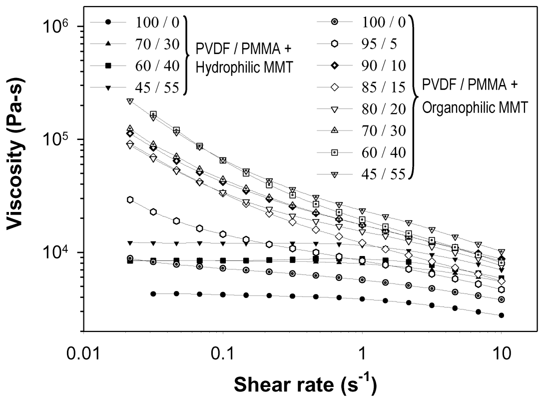

Fig. 5. Shear viscosity versus shear rate for various PVDF/PMMA micro- and nanocomposites containing 5 wt% of silicate and with several PMMA contents ($T = 200$ °C).

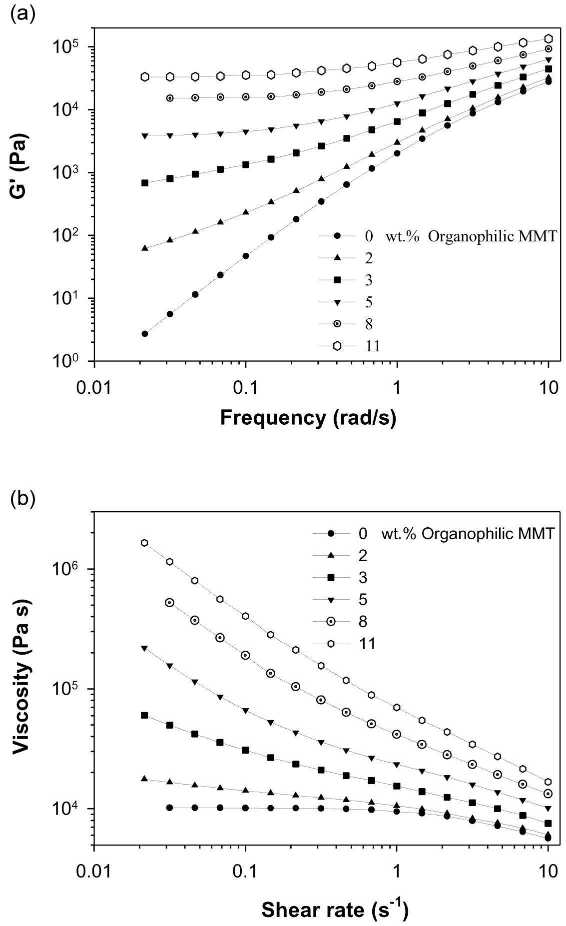

Fig. 6. (a) Shear storage modulus versus frequency for 45 PVDF/55 PMMA nanocomposites containing various contents of organophilic MMT ($T = 200$ °C). (b) Shear viscosity versus shear rate for 45 PVDF/55 PMMA nanocomposites containing various contents of organophilic MMT ($T = 200$ °C).

microcomposites. At low shear rates ($\dot{\gamma} < 0.1\ \mathrm{s}^{-1}$), the nanocomposites containing more than 5 wt% of PMMA exhibit a solid-like behavior, with a higher viscosity than that of 100/0 and 95/5 PVDF/PMMA-composites. This enhancement of the shear viscosity arises from the intercalation/exfoliation and dispersion of layered silicates in the polymer matrix leading to a network structure [36]. These results are an additional confirmation that nano-dispersion of the individual silicate platelets is not only related to the surfactant in the organophilic MMT but also to the presence of the PMMA as a potential interfacial agent. At high shear rates ($\dot{\gamma} \sim 10\ \mathrm{s}^{-1}$), the viscosity and shear thinning rate for the nanocomposites are comparable with those of conventionally filled polymers due to the preferential orientation of the silicate layers parallel to the flow direction [35].

Fig. 6a and b show the effect of the organophilic MMT content on the storage modulus vs. frequency and viscosity vs shear rate curves for 45 PVDF/55 PMMA nanocomposites. At high shear rates ($10\ \mathrm{s}^{-1}$) and high frequencies ($10\ \mathrm{rad\ s}^{-1}$) the silicate content affects only slightly the melt viscosity and the storage modulus. However, at low frequencies (less than $1\ \mathrm{rad\ s}^{-1}$) and at low shear rates (less than $1\ \mathrm{s}^{-1}$), respectively, the influence of the silicate content on G' and η is significant. While the polymer matrix shows a liquid-like relaxation at low frequencies, the nanocomposites containing more than 2 wt% silicate exhibit a solid-like behavior. A similar trend has been observed by Krishnamoorti et al. [37]. They observed that the shear viscosity of the nanocomposites increased monotonically with clay loading and the nanocomposites display a shear thinning behavior at low shear rates (even though the viscosity of the pure polymer matrix is shear rate independent). The presence of the silicate layers and the lack of complete relaxation of the chains contribute to the solid-like response at low frequencies. On the basis of mesoscopic structure at low clay concentrations, it is suggested that, beyond a critical volume fraction, the tactoids (clay crystallites) consisting of intercalated silicate platelets as well as individual layers are incapable of freely rotating and are prevented from complete relaxation when subjected to shear. This incomplete relaxation due to the percolation leads to the solid-like behavior observed in the exfoliated nanocomposites [36]. Thus, it is appears that intimate contact between the polymer and the silicate layers alters the relaxation processes of the polymer, leading to the low frequency plateau in the shear modulus with increasing clay loading [38]. From Fig. 7 it is observed that the shear storage modulus of PVDF/PMMA nanocomposites containing 40 and 55 wt% of PMMA increases sharply after a critical silicate content of 2 wt% and becomes independent of the PMMA content in the PVDF/PMMA matrix at about 5 wt% of silicate.

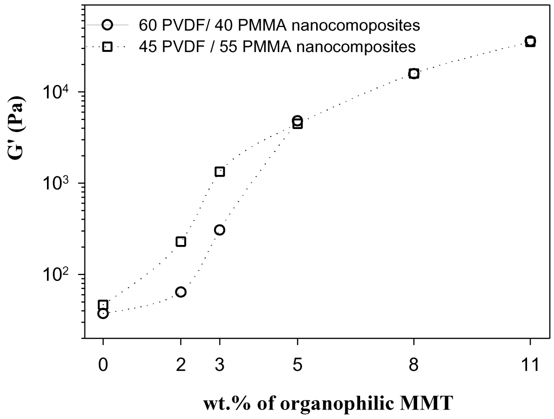

Fig. 7. Shear storage modulus versus organophilic MMT content for PVDF/PMMA nanocomposites containing 40 and 60 wt% of PMMA ($f = 0.1\ \mathrm{rad\ s}^{-1}$, $T = 200$ °C).

3.3. Dynamic mechanical behavior

The temperature dependence of the storage modulus using dynamic mechanical analysis for the (45 PVDF/55 PMMA) blend, the (45 PVDF/55 PMMA)–hydrophilic MMT and the (45 PVDF/55 PMMA)–organophilic MMT

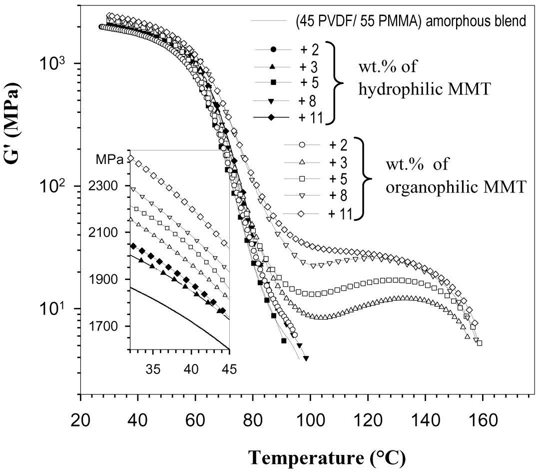

Fig. 8. Storage modulus–temperature curves obtained by dynamic mechanical analysis (1 Hz, 5 °C $\min^{-1}$) for 45 PVDF/55 PMMA micro- and nanocomposites with different content of silicate.

composites containing different contents of silicates has also been used to evaluate the micro- and nanodispersion of the silicate in the matrix. It should be noted that no crystallization of PVDF occurs at this blend composition. The dynamic mechanical investigations (Fig. 8) show that the 45/55 PVDF/PMMA blend exhibits a major transition at 74 °C, in agreement with a single composition-dependent T_g of a miscible blend, intermediate between the T_gs of the neat components. However, the PVDF/PMMA nanocomposites exhibit a T_g at slightly higher temperature than the unmodified polymer. The hydrophilic MMT microcomposites based on PVDF/PMMA exhibit the same behavior as the matrix with a slight increase of the storage modulus in the glassy, glass-transition and rubbery regions, as a normal material response of a simple filled thermoplastic polymer. In sharp contrast, the (PVDF/PMMA)–organophilic MMT nanocomposites exhibit a clear increase in glassy modulus, and a dramatic extension as well as elevation of the rubbery plateau as a result of the network structure. In fact, at 40 °C, still well within the glassy region, the storage modulus G' of the 3 wt% nanocomposite is approximately 20% higher compared with the PVDF/PMMA matrix. In the rubbery state (above the T_g at 95 °C, which is the limit temperature of the rubbery state for the unfilled matrix), the 3 and 11 wt% nanocomposites exhibit storage moduli that are 2 and 8 times higher, respectively, than that of the unfilled matrix. The dependence of G' on the silicate content for the 45 PVDF/55 PMMA nanocomposites at 95 °C is summarized in Fig. 9. Up to an organophilic MMT content of 2 wt%, the G' of the nanocomposite is similar to that of the matrix. Beyond 2 wt%, G' increases strongly and linearly with a slope of approximately 3. Due to the 'nano'-sized dispersion and the high aspect ratio of the silicate layers, dynamic mechanical property enhancement is already realized at low loading levels (3–5 wt% silicate).

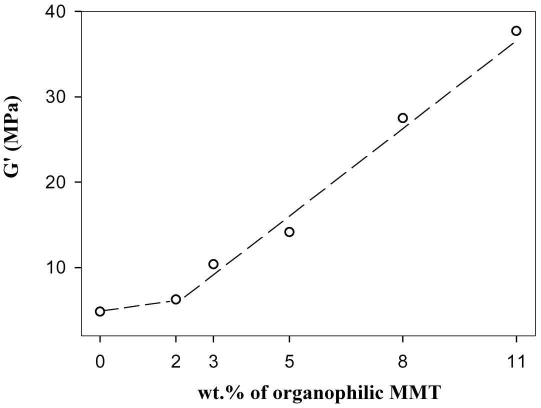

Fig. 9. Storage modulus versus silicate content for 45 PVDF/55 PMMA nanocomposites obtained by dynamic mechanical analysis (1 Hz, 5 °C $\min^{-1}$) at 95 °C.

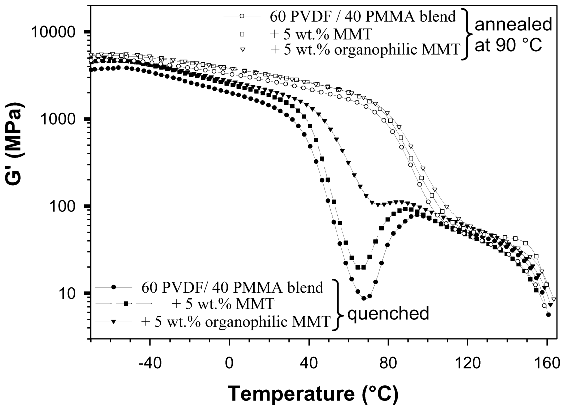

Fig. 10. Storage modulus–temperature curves obtained by dynamic mechanical analysis (1 Hz, 5 °C $\min^{-1}$) for 60 PVDF/40 PMMA micro- and nanocomposites containing 5 wt% of silicate.

Fig. 10 shows the temperature dependence of the storage modulus for the 60 PVDF/40 PMMA blend, the 60 PVDF/40 PMMA–hydrophilic MMT microcomposite and the 60 PVDF/40 PMMA–organophilic MMT nanocomposite containing 5 wt% of silicate, directly quenched after melting. The annealed samples at 90 °C for 4 h are also investigated. The temperature dependence of G' for all quenched samples exhibits two transitions at 50 and 90 °C. The lower transition temperature is assigned to the T_g of the PVDF/PMMA amorphous phase, whereas the higher one is attributed to the onset of crystallization of PVDF within the blend since PVDF crystallizes at this blend composition.

The conventional microcomposite, previously quenched, exhibits the same behavior as the matrix phase with a slight increase in the storage modulus. However, the quenched nanocomposite display significant enhancement of the storage modulus compared with both the matrix and the conventional microcomposite, as a result of the network structure. The quenched as well as the annealed samples exhibit a high modulus in the rubbery plateau; this behavior is mainly due to the presence of the PVDF crystalline phase acting both as a rigid filler and physical crosslink.

4. Conclusions

PVDF/PMMA–MMT nanocomposite materials were prepared by melt-extrusion. The ability of PMMA as an interfacial agent is investigated with respect to the morphological, rheological and dynamic mechanical properties of these materials. A fine dispersion of intercalated/exfoliated silicate layers in both PMMA and PVDF/PMMA matrices was observed when the organophilic montmorillonite was used. The intercalation/exfoliation is greatly enhanced by the presence of only 5 wt% of PMMA in the PVDF/PMMA matrix.

From the rheological measurements, an increase in shear viscosity and storage moduli of the nanocomposites with increasing both PMMA and silicate content was observed. Furthermore, PVDF/PMMA nanocomposites exhibit a solid-like behavior at lower frequency indicating the formation of a percolated network structure. 10 wt% of PMMA in PVDF/PMMA nanocomposites is considered as the optimal concentration.

The dynamic mechanical properties of PVDF/PMMA–MMT nanocomposites display a significant increase of the storage modulus in the rubbery plateau, indicating network formation of the silicate layers. This network was not observed in the case of the conventional microcomposites.

On account of the 'nano'-sized dispersion, an increase in the rheological and dynamic mechanical properties is already realized at low loading levels (3–5 wt%).

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