Structure and Dynamics of Polyethylene/Clay Films

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ABSTRACT: The relationships between structure and rheology of polyethylene/clay hybrid composite blown films were investigated through rheological tests both in shear and elongational flow. Two polymer matrices (low density polyethylene, LDPE and linear low density polyethylene, LLDPE) with different relaxation kinetics were used. Independently from the matrix, morphological analyses (TEM, XRD, and SEM) indicate that the hybrid structures are similarly constituted of delaminated platelets or tactoids having a relevant degree of orientation along the draw direction. This strongly affects the rheological behavior of materials. However, despite the similarities emerged from morphological analyses, both shear (steady shear and oscillatory) and elongation measurements show a negligible effect upon the rheology of LDPE-based nanohybrids. Conversely, relevant increases of shear viscosity, dynamic moduli and melt strength of LLDPE-based nanohybrids have been detected. The effects of homopolymer relaxation kinetics have been investigated by means of stress relaxation tests. The results obtained seem to be consistent with the existence of a roughly bimodal population of dynamical species: a matrix component behaving like the homopolymer, and a fraction interacting with the filler, whose rheological behavior is controlled by the particles and their interactions with the polymer. Mechanical properties of hybrid films were also investigated. Differently from what happens in the melt state, the solid-state properties mainly depend on the filler amount. The relative increases of tensile modulus and melt strength are of the same order of magnitude for both the matrices used, indirectly confirming the similarities in hybrids structures. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4749–4758, 2006

Key words: structure-rheology relationships; films; polyethylene (PE); rheology; nanolayers

INTRODUCTION

Polyethylene (PE) films are used for flexible food packaging, garbage bags, liners, and agricultural films. Improvement in macroscopic polyethylene film properties, such as enhancement of mechanical and barrier properties and reductions in thermal expansion coefficient, can be obtained by adding small quantity of organoclay.[1,2] In recent years, most studies have shown that organically modified clays can be well dispersed in polar polymers like polyamides using appropriate processing techniques and conditions.[3,4] Conversely, for the more commonly used polyolefins, like polyethylene and polypropylene, the obtaining of nanocomposites characterized by an enhancement of their final properties appears much more difficult, because of the lack of suitable interactions of hydrophobic polyolefins with the polar surface of the clays.[2,5] The fillers should not affect the film clarity, dispersion and orientation of filler and the process-ability of materials. Therefore, the study of rheological properties of polymer melt layered-silicate composites become more and more a critical issue to gain a fundamental understanding of processability and morphology for these materials. Rheology represents a sensitive tool to provide information about the structure of materials. Linear oscillatory low-frequency behavior is representative for the unperturbed structure in the hybrid. Often, it has been proposed that the formation of a superstructure of the dispersed layers in the polymer matrix governs the linear viscoelastic properties of layered-silicate-based nanocomposites.[6,7] On the other hand, the steady shear flow behavior allows inferring important remarks related with the processability of the materials. At high shear rates or prolonged action of slow shear forces, the silicate layers do increasingly align in parallel, leading to the observation of pronounced shear-thinning.[8,9] Often, the extent of this shear-thinning has been correlated to the concentration of clay platelets.[10] Finally, the response to the nonisothermal elongational flow is a key issue for the preparation of film by film-blowing.

In this work, the response of PE/silicate-layered nanocomposite films to external flow and the resulting mechanical properties have been investigated. The overall objective of this article is to map out the mor-

phology-rheology and the morphology-mechanical properties behaviors of two commercial grade polyethylene/clay composite films. The effect of clay on two different types of polyethylene, low density polyethylene (LDPE) and linear low density polyethylene (LLDPE), was investigated.

EXPERIMENTAL

Materials

The materials used in this work were two samples of film-grade polyethylenes, a linear low density polyethylene (Clearflex FG166, $M_w = 130,000$ g mol^{-1}, $M_w/M_n = 3.8$; MFI$_{190/2.16} = 0.27$ g 10 min^{-1}, and $\rho = 0.918$ g cm^{-3} at room temperature) and a low density polyethylene (Riblene FC30, $M_w = 175,000$ g mol^{-1}, $M_w/M_n = 5.76$, MFI$_{190/2.16} = 0.28$ g 10 min^{-1} and $\rho = 0.922$ g cm^{-3} at room temperature), both from Polimeri Europa. To produce polyethylene/clay hybrid films, two commercial PE-based nanocomposite masterbatches, named Nanoblend 2101® and Nanoblend 2001® and supplied by PolyOne, were blended with the homopolymers. Nanoblend 2101® and Nanoblend 2001® contain 40% wt/wt of MMT clays dispersed into LLDPE and LDPE, respectively. The clays are surface-modified with polyethylene-*graft*-maleic anhydride to help their dispersion into the polymer matrices. The masterbatches, defined as intercalated by suppliers, were compounded with FG166 and FC30 to produce LLDPE- and LDPE-based nanohybrid films at 2, 4, and 8% wt/wt of clays.

Melt compounding

The compounding and the production of the films were carried out in a Brabender single screw extruder ($D = 19$ mm, $L/D = 25$) attached to a Brabender Plasticorder PLE 651 and equipped with a die for film and a Brabender film blowing unit. The thermal profile was 120–140°C, 140–150°C, and 150–160°C and the screw speed was 80 rpm. The drawing speed of the film was kept constant at about 3 m min^{-1}. The final thickness of the films was in the range 100–110 μm.

Mechanical characterization

Mechanical tests were carried out with a universal Instron machine mod 4443, according to ASTM D882. Average values for tensile strength (TS) and elongation at break (EB) have been calculated. The reproducibility of the results was ±5%.

The ball drop tests were carried out in CEAST (Italy) machine mod 6205/000, according to ASTM D1709. At least 10 samples were tested and the reproducibility was about ±3%.

Rheological characterization

The rheological behavior of materials was investigated both in steady shear and oscillatory flow. A strain-controlled rotational rheometer (ARES L.S., Rheometric Scientific™) was used to measure the dynamic moduli and steady shear viscosities of materials. All tests were carried out using 25 mm diameter parallel plates fixture in inert atmosphere at 160°C. Samples were obtained by superposing five blown films, and inserting them between the rheometer plates. The samples were heated up to the testing temperature and then they were squeezed to obtain ∼ 0.6-mm thickness disks.

To evaluate the steady shear viscosities, the minimum time required to reach a steady state at a given shear rate was established during preliminary tests. Because of the onset of melt fracture phenomena appearing at high shear rates, the viscosity data were collected from 0.01 to a maximum of 10 s^{-1}. Following to the results of linearity check tests, linear viscoelastic moduli were evaluated through frequency scans from 0.01 to 100 rad s^{-1} with amplitude of 1%. To evaluate the effects of clay alignment on hybrid flow properties, rheological tests were also carried out upon samples mixed for about 3 min at 160°C (Rheocord 600p, Haake), with the purpose to obtain a random distribution of silicate layers or their tactoids. Linear stress relaxation measurements were performed submitting the samples to a single step strain $\gamma_0 = 1\%$ at time $t = 0$, and the shear stress evolution during time $\sigma(t)$ was measured to obtain the modulus $G(t)$. Finally, a double-bore capillary rheometer (RH7, Bohlin Instruments) was used to extent the range of investigated steady shear rate up to ∼ 10^5 s^{-1}. Both the Bagley and Mooney–Rabinowitsch corrections were performed for the capillary data by using a zero-length capillary.

A capillary viscometer, Rheologic 1000, (CEAST, Italy) equipped with a drawing system was used to investigate the rheological behavior in nonisothermal elongational flow. The capillary diameter was 1 mm and the length-to-diameter ratio was 40. The force in the molten filament at breaking is measured directly and is known as melt strength, MS. The breaking stretching ratio, BSR, was calculated as the ratio between the drawing speed at breaking and the extrusion velocity at the die. The data were collected at 160°C.

Morphological analyses

To obtain morphological information about the microstructure of composites, transmission electron micrographs (TEM) were taken from 60 to 100 nm thick, microtomed sections of polymer-clay composite blown films by using a Philips EM 208 TEM with 100 keV accelerating voltage. WAXD analyses were performed

using a diffractometer (Siemens D-500 Krystalloflex 810) in the reflection mode with an incident X-ray wavelength of 0.1542 nm (Cu Kα) and at a scan rate of 1.0° min^{-1}. The specimens for WAXD were prepared by compression molding ($D = 20$ mm; thickness 2 mm) using a laboratory Carver press preheated to a temperature of 190°C. Furthermore, scanning electron microscope (SEM, Leica 420) was used to detect the presence of clay stacks, recognized through energy dispersive X-ray spectroscopy (EDS EDAX, Oxford mod. INCA 200). The samples for SEM investigations were obtained using the rheometric apparatus, by melting five superposed blown films at 160°C for 3 min and squeezing them between parallel plates, previously covered with antiadhesive PTFE sheets to make the sample removal easier after the treatment.
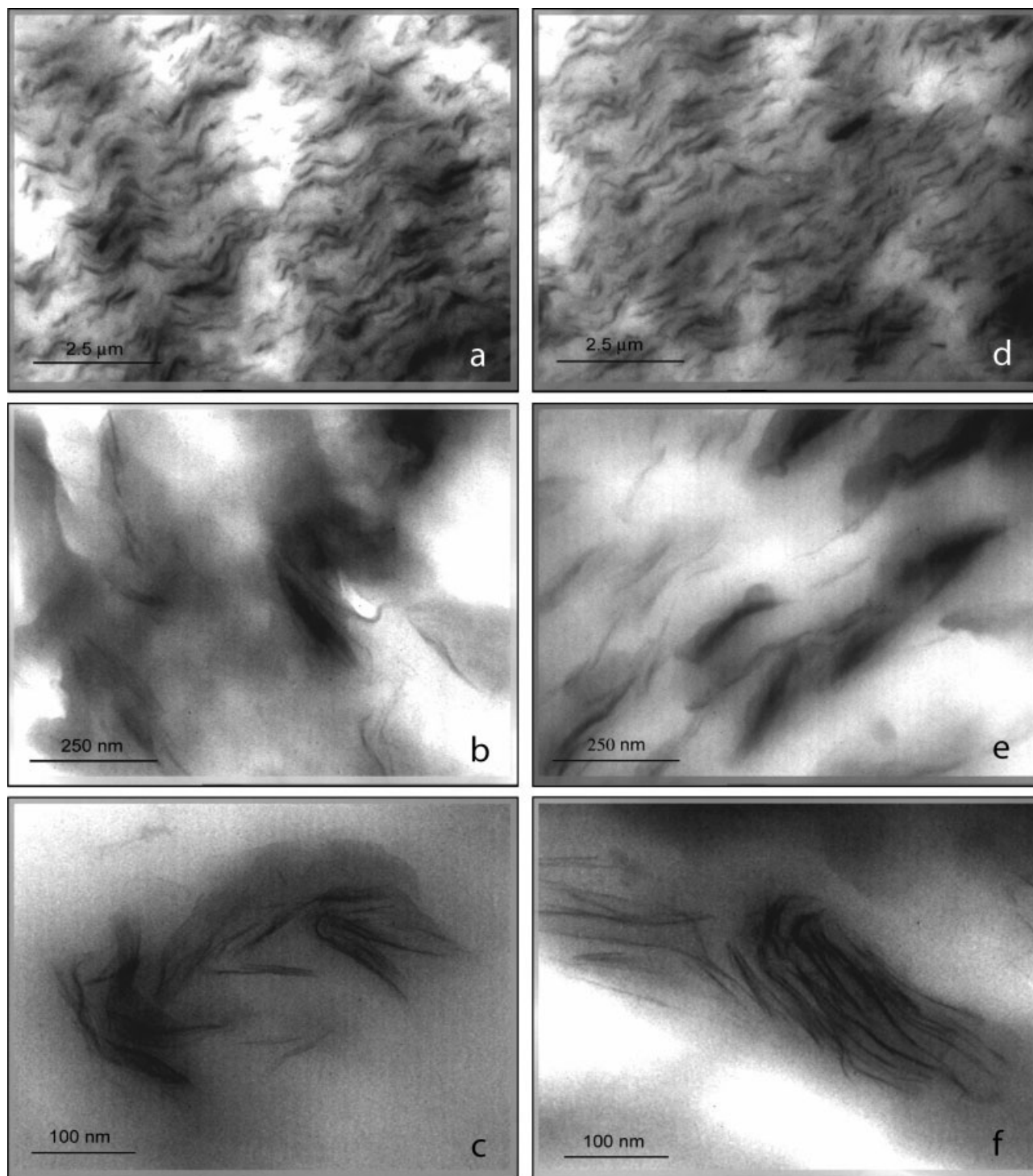

Figure 1 TEM micrographs of LLDPE (a, b, c) and LDPE (d, e, f) based hybrids at 8 wt % for various magnifications.
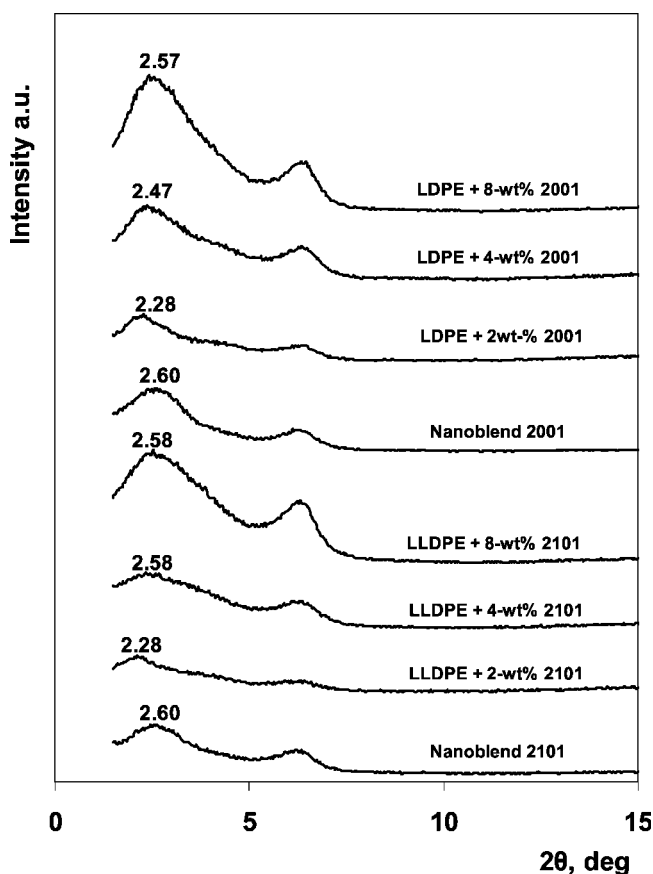
Figure 2 X-ray traces of the two masters and of all the nanocomposites.

Then, the specimens were cryo-fractured and SEM observations were carried out on the samples, previously coated with gold to generate electric current on their surfaces.

RESULTS AND DISCUSSION

Composite morphology

The internal structure of hybrids was examined via the transmission electron microscopy (TEM), allowing to the direct visualization of the hybrid structure in and the dispersion quality for silicate layers into the polymer matrix. A typical morphology of polymer-layered silicate hybrids, characterized by well distributed and partially exfoliated (dispersed as individual platelets) clay platelets, emerges from the analysis of Figure 1, in which the TEM micrographs of 8 wt % hybrids are shown for various magnifications. Similar pictures have been detected for the other compositions. Independently from the polymer matrix and the clay loading, it is important to note that the presence of clay layers in the form of flexible delaminated platelets have been always identified, together with intercalated zones plus some agglomerated tactoid.

In addition to TEM investigations, WAXD analyses were performed to better inspect the hybrid structure, and the X-rays traces obtained are reported in Figure 2 for all the samples, together with those of two nano-clay concentrates. A slight increase of the interlayer distances respect to the masterbatches can be noticed only for two samples at the lower nanoclay content, but in its complex, the effect of the compounding appears rather negligible. A peak in the range of $2\theta = 2.3$–$2.6°$ (corresponding to d-spacing of 3.8 and 3.4 nm, respectively) and a second peak around $2\theta = 6.4°$ have been detected for all the samples just like the values obtained for the two masters Nanoblend 2001[®] and 2101[®]. Moreover, the compounding does not causes any broadening of the X-ray traces, indicating small effects also on interlayer distance distribution.

Though the lack of information about the clays does not allow inferring direct indications concerning the effective increase of interlayer d-spacing respect to the virgin clays, in agreement with TEM results, WAXD analyses indicate again that different concentrations and polymer matrices do not significantly modify the structure of the hybrids. The degree of intercalation/exfoliation is similar to that of commercial masterbatches and in its complex, the structure of the hybrid blown films is characterized by the simultaneous presence of intercalated and delaminated layers, in addition to coexisting agglomerated tactoids.

Rheological behavior

The steady shear flow curves of the 4 and 8 wt % LLDPE-based hybrids are shown in Figure 3 in comparison with that of pure polyolefin. The viscosity of composites in the low shear rate region depends on the amount of filler, and the addition of nanoclay
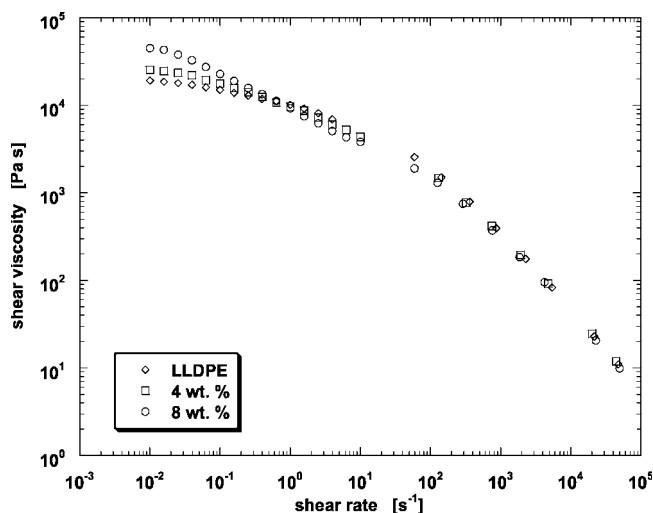

Figure 3 Effect of the clay content on the shear viscosity of LLDPE-based nanocomposites at 160°C.
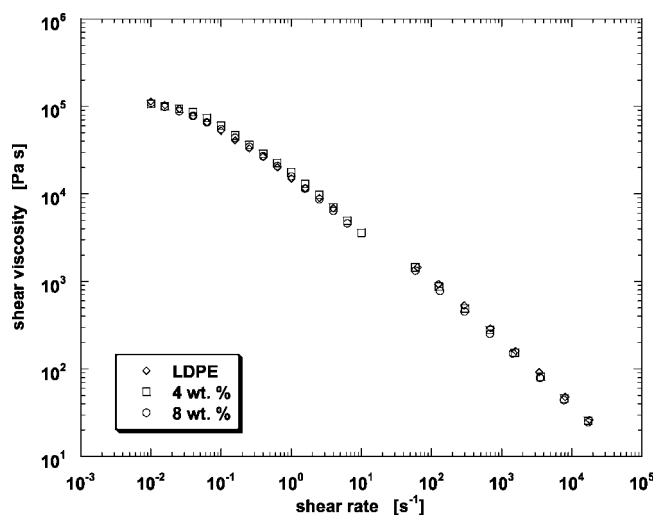
Figure 4 Effect of the clay content on the shear viscosity of LDPE-based nanocomposites at 160°C.

causes the progressive increase of the zero-shear-rate viscosity with filler loading and the shift toward lower shear rate of the Newtonian plateau. Wagener et al.[10] used a power law expression to fit the low shear rate viscosity data of polymer-clay nanocomposites, proposing the shear-thinning exponent n as a semiquantitative measure of nanodispersion of the samples. The rationale for fitting only the low shear rate data is that, in this range, the rheological response is most representative for the unperturbed platelet structure in the composite.

As shear rate increases, the matrix becomes shear-thinning and its chains start to align with the flow. This accelerates the clay orientation, causing a shear-thinning behavior for filled systems more pronounced than that of the matrix, and the crossing of the viscosity curves occurs at shear rate ~ 1 s^{-1}, independently from the filler loading. Different from what generally reported in literature for polymer-based nanocomposites,[5,6,11] exhibiting viscosities progressively similar to that of the matrices with increasing the shear rate, the curves of nanocomposites become lower than that of the unfilled LLDPE, and an overlapping only occurs at very high shear rates. Generally, a reduction of shear viscosity of a polymer layered silicate nanocomposite is attributed to a slipping between polymer and silicate layers or their tactoids.[12] This phenomenon, enhanced by clay flow-induced orientation, becomes more pronounced with increasing the shear rate. The steady shear viscosity curves of the 4 and 8 wt % LDPE-based nanocomposites are reported in Figure 4 together with that of the neat LDPE. In spite of the identical chemical nature of polymer matrices, only differing in the molecular architecture, and the similar microstructure emerged from TEM and WAXD investigations, the improvement of viscosity detected for LLDPE-based hybrids at low shear rates

is absent for LDPE-based hybrids. Several authors observed a small effect of clays for nanohybrids with polymer matrix characterized by a markedly shear-thinning behavior.[2,13] They concluded that the low shear rate viscosity of nanocomposites is mainly dominated by the clay loading, instead of by the matrix viscosity. The negligible effect of nanoparticles observed for the LDPE-based nanocomposite could be related to the long relaxation time of polymer matrix, as will be discussed in the following.

The comparison of dynamic moduli of nanohybrids and neat LLDPE is reported in Figure 5. Consistent with the addition of solid particles into a polymer matrix, the dynamic moduli of LLDPE-based nanohybrids increase at all frequencies with increasing the filler loading.[14] Nevertheless, alterations in the low-frequency behavior emerge, and the low frequency storage modulus exhibits the development of a plateau. Furthermore, the frequency dependence of the high-frequency relaxation behavior of the LLDPE-based hybrids is essentially unaffected by the addition of the filler, suggesting that the faster polymer chain relaxation modes are unaltered by the presence of silicate.

To explain this pseudosolid-like feature, generally detected for several other intercalated polymer-based layered-silicate nanocomposites, two different hypotheses are generally proposed.[7,15–17] The first arises from frictional interactions between clay particles, causing a physical jamming of the dispersed silicate layers because of their highly anisotropic nature and simple geometric constraints. The local correlation between silica layers (filler-filler networks) causes the presence of domains, and this would cause the enhanced low-frequency modulus and the related low power-law dependence. The second mechanism arises from the confinement of polymer chains between the silicate
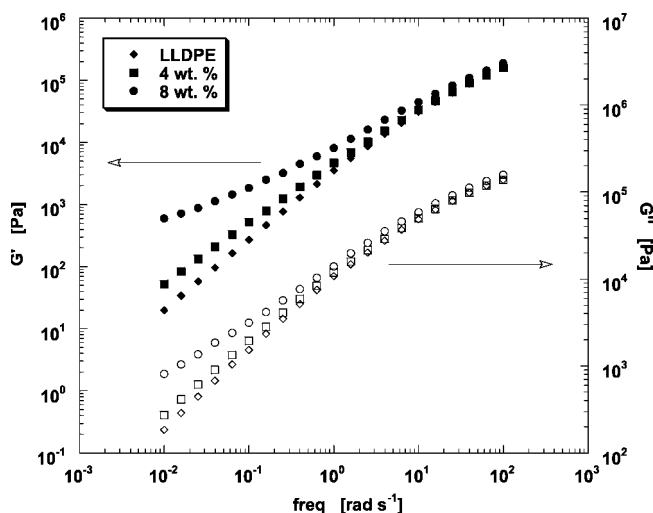

Figure 5 Linear storage (full symbols) and loss (empty symbols) moduli for the LLDPE-based nanocomposites and unfilled polymer at 160°C.

layers or tactoids and from the physical interactions between these two species. A sort of polymer-filler network form, characterized by different relaxation times respect to the bulk, and it would be responsible for the alterations in low-frequency rheology of the nanocomposites.

The dynamic moduli of LDPE-based hybrids shown in Figure 6 confirm the negligible effect of the clay emerged in steady shear flow, at least within the frequency range investigated. Independently from the clay loading, the frequency dependencies of both storage and loss moduli are, within the experimental error, identical to that of unfilled LDPE, indicating that the relaxation modes are unaltered by the presence of the silicate.

The SEM images of 8 wt % nanocomposites are reported in Figure 7. The samples obtained by superposition of blown films were cryo-fractured perpendicularly to the flow direction, indicated by the arrows. The images of the fractured surfaces show the existence of a preferential orientation along with the film biaxial drawing direction, at least for clay tactoids singled out by EDS analysis. Okamoto et al. observed biaxial flow-induced clay alignment in polypropylene/clay nanocomposite foams.[18] Several authors have investigated the effect of clay orientation on viscoelasticity of polymer layered-silicate nanocomposites over a wide range of matrices, layered silicates, flow, and techniques. A decrease of linear viscoelastic moduli is generally expected following the usage of large amplitude shear flow able to induce the orientation of filler.[7,11,19] The differences detectable between aligned and unaligned polymer layered-silicate nanocomposites have been explained in terms of a filler-filler networking mechanism. The high anisotropy of either layers or their tactoids leads to the
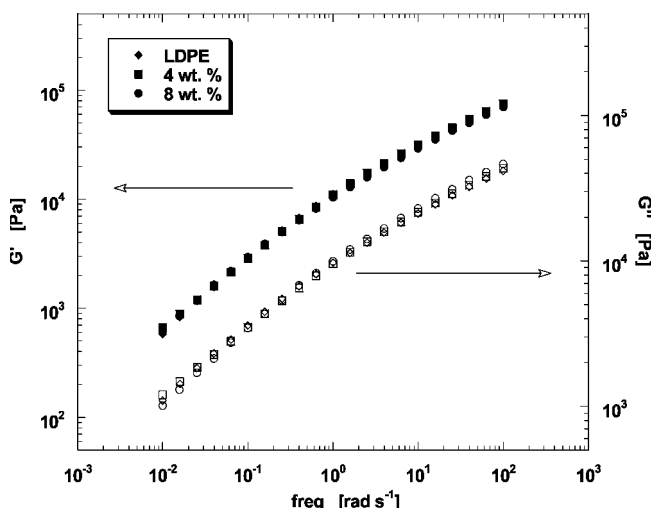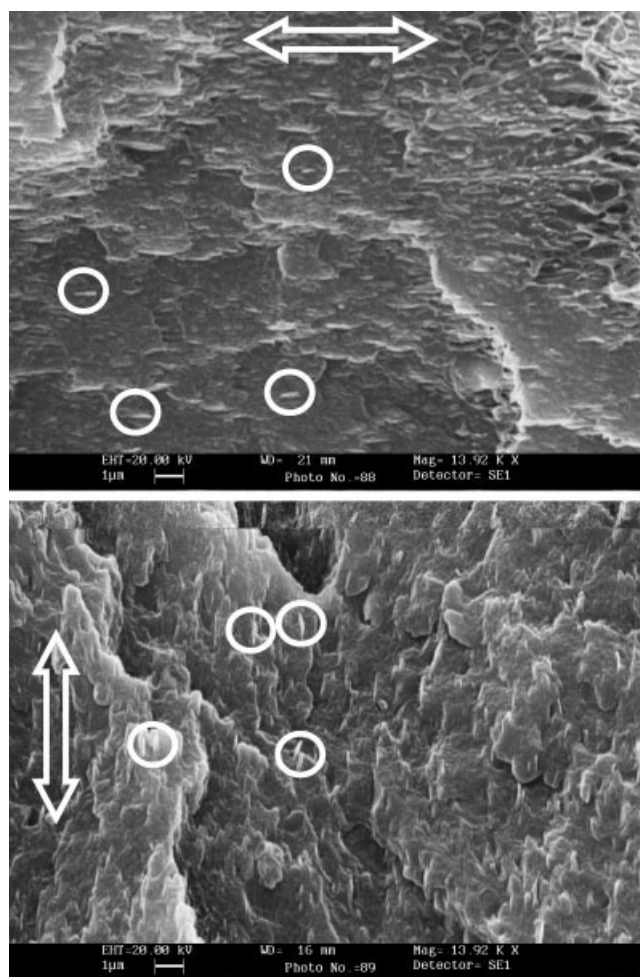

Figure 7 SEM images of 8 wt % LLDPE (above) and LDPE (below) based nanocomposites. Circles indicate silicate tactoids, as emerged through EDS analysis. The arrows indicate the film drawing direction.

Figure 6 Linear storage (full symbols) and loss (empty symbols) moduli for the LDPE-based nanocomposites and unfilled polymer at 160°C.

observation of pseudosolid-like phenomena for extremely low silicate loading, while considerably high filler loading are expected for some filler network that would form when nanoparticles are preferentially oriented in the shear direction.[7]

The comparisons of storage and loss moduli for films and mixed (unoriented) 8 wt % hybrids are shown in Figures 8 and 9. Dynamic oscillatory tests were also performed on mixed samples previously subjected to a prolonged preshear (600 s at 1 s^{-1}). Independently from the polymer matrix, the overlay of dynamic moduli of shear-aligned and filmed samples, besides confirming the clay alignment in blown films, indicates the reversibility of the flow-induced orientation of layered silicates in both the nanohybrid films. The effect of clay orientation appears more pronounced for the LLDPE-based nanohybrids, wherein the unoriented sample shows a significant enhancement of the pseudosolid-like feature. Nevertheless, a slight increase of dynamic moduli can be observed also
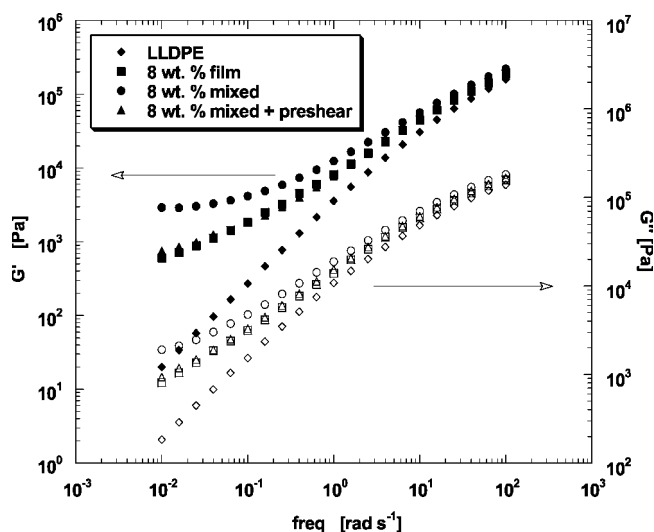
Figure 8 Effect of clay alignment on linear storage (full symbols) and loss (empty symbols) moduli for the 8 wt % LLDPE-based nanocomposites and unfilled polymer at 160°C.

Figure 10 Linear stress relaxation moduli for 8 wt % LLDPE-based nanocomposites and unfilled polymer at 160°C.

for the LDPE-based unoriented hybrid in the whole range of frequencies investigated. Moreover, the frequency dependence of mixed LDPE hybrids is different from that of homopolymer, indicating an effect of filler on composite rheology, which is undetectable when the clays are aligned in the flow direction.

To probe into the unusual viscoelastic behavior observed in the dynamic measurements for the hybrids, linear stress relaxation tests have been carried out upon films and mixed (presheared or not) 8 wt % composites, and the results are shown in Figures 10 and 11. First of all, as expected on the basis of the differences in molecular architecture, we observe that the homopolymers show different relaxation kinetics.
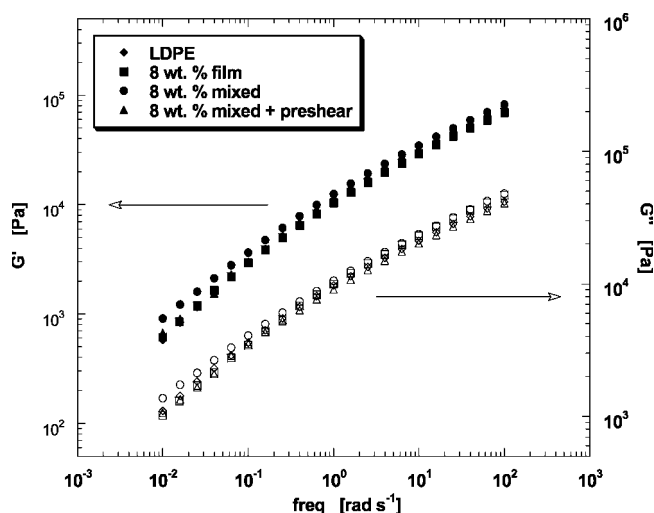
The LLDPE relaxes quickly than the LDPE in which more branched chains employ longer times to recover their relaxed configuration after the imposing of the strain. For the hybrid systems, the moduli of both the composites are higher than those of corresponding unfilled polymer at any fixed time. Moreover, according to the results of dynamic viscoelastic measurements, the hybrid moduli are higher when layered silicates are unoriented. We further observe that the relaxation kinetic of the LLDPE-based hybrids is similar to that of the homopolymer at short time (i.e., for $t < 0.1$ s). At longer time, however, the modulus $G(t)$ of the unfilled polymer drop down ~ 30 s after the imposition of strain, while the hybrids behave like a pseudosolid-like material for times as long as ~ 2000 s,

Figure 9 Effect of clay alignment on linear storage (full symbols) and loss (empty symbols) moduli for the 8 wt % LDPE-based nanocomposites and unfilled polymer at 160°C.
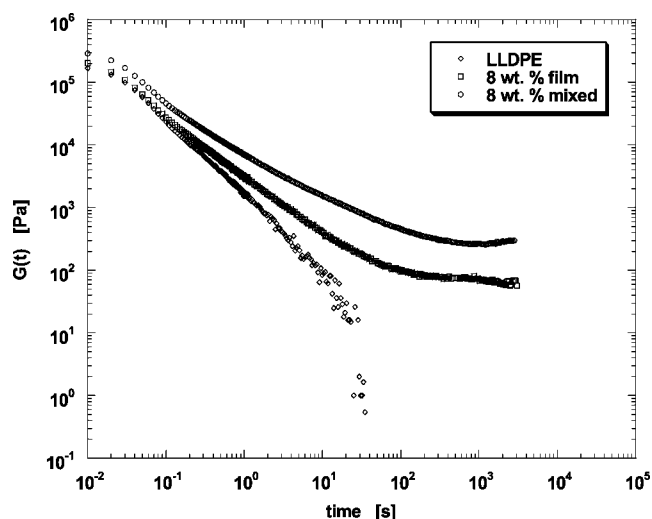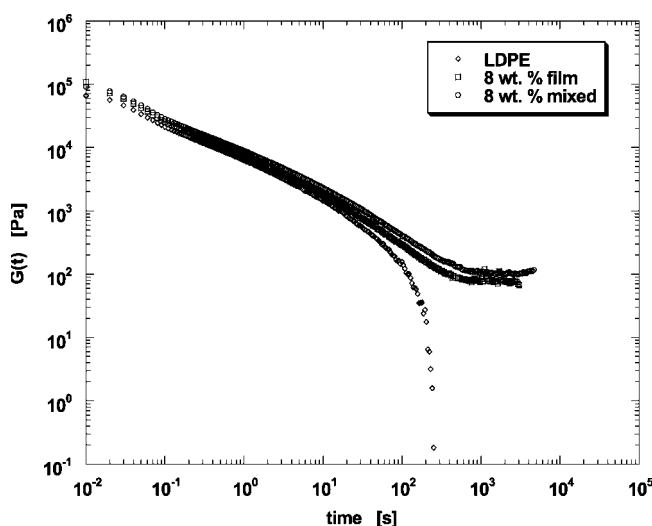

Figure 11 Linear stress relaxation moduli for 8 wt % LDPE-based nanocomposites and unfilled polymer at 160°C.
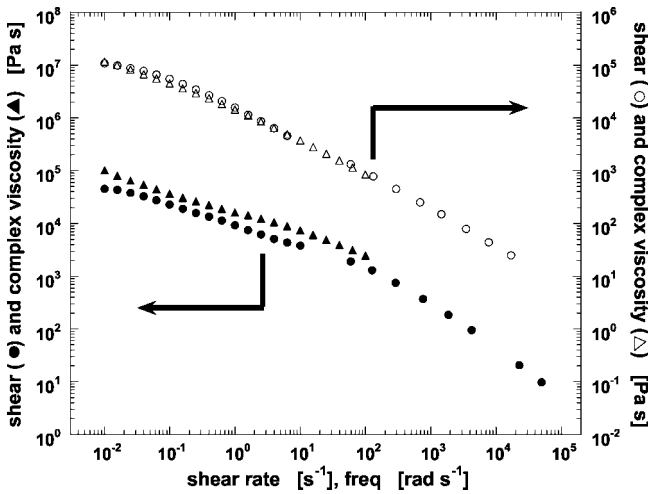
Figure 12 Complex and shear viscosity curves for 8 wt % LLDPE (full symbols) and LDPE (empty symbols) based hybrids at 160°C.

the particle orientation only affecting the plateau value of $G_{(t)}$. The relaxation behavior of LDPE-based hybrids is similar to that of unfilled polymer up to ~ 100 s. For higher times, the homopolymer relaxes like a liquid at $t = 200$ s, while the addition of filler has a profound influence only on the long time relaxation of the hybrids.

The linear viscoelastic behavior of the hybrids detected through dynamic and stress relaxation measurements could be roughly explained with the notion of two distinct populations of dynamic species within the hybrids, consistent with the hypotheses proposed by Ren et al.:[7] a matrix portion, substantially unaffected by the presence of layered silicate, whose relaxation process are homopolymer-like, governs the hybrid rheology at short times or, alternatively, at high frequencies. The second dynamical class, whose behavior is instead governed by the filler network dynamics, is characterized by slower relaxation kinetic, responsible for the pseudosolid-like feature observed at long times. Therefore, the presence of filler emerges when the homopolymer-like fraction relaxes faster than pseudosolid-like one. Alternatively, the homopolymer-like fraction governs the rheology of the hybrid, and the filler network dynamics could be hindered within the time scale of experiments.

The relaxation modulus is related to the dynamic oscillatory shear G' and G'' via the relaxation spectrum $H(\tau)$ as in Ref. 20.

$$G'(\omega) - G(t)\big|_{t=1/\omega} = \int_{-\infty}^{+\infty} \left[\frac{\omega^2 t^2}{1 + \omega^2 t^2} - e^{-(1/\omega t)} \right] H d(\ln \tau) \tag{1}$$

Therefore, the frequencies investigated during dynamic measurements correspond to the range from

10^{-2} up to 10^2 s of stress relaxation experiments. In this experimental frequency window, the rheology of LDPE-based nanocomposites is governed by the homopolymer-like fraction, because of the slow relaxation kinetic of unfilled polymer. This explain the absence of alterations in the low-frequency behavior of the hybrids, while pseudosolid-like feature is emerged for the LLDPE-based nanocomposites, characterized by a faster relaxation kinetic of polymer matrix.

The overlay of shear and complex viscosities for 8 wt % hybrids are shown in Figure 12. Similar results have been observed for 4 wt % hybrids. The empirical Cox-Merz rule requires that

$$\eta^*(\omega) = \eta(\dot\gamma) \quad \text{for} \quad \omega = \dot\gamma \tag{2}$$

The eq. (2), generally found to be applicable for homopolymers, fails for filled polymer systems and meso-structured materials.[21] Ren and Krishnamoorti found that the quiescent state linear dynamic oscillatory $\eta^*(\omega)$ always exceeds $\eta(\dot\gamma)$, the discrepancy being largest at low ω and $\dot\gamma$, and they attributed the failure of Cox–Merz rule for polymer layered-silicate nanocomposites to the ability of steady shear flow to alter the quiescent random arrangement of the silicate layers or their tactoids probed during small amplitude oscillatory tests.[11] Nevertheless, the Cox–Merz rule works quite well for LDPE-based nanocomposite, as demonstrated in Figure 12. We think that, because of the long relaxation time of LDPE matrix causing a homopolymer-like behavior of LDPE-based hybrids within the experimental frequency range, the alterations of silicate layers/tactoids network produced by the steady shear flow are hidden and, as a consequence of this, the Cox–Merz rule keep working despite of the meso-structured nature of the nanocomposite.

The ability of the melt to form film when subjected to a nonisothermal biaxial elongational flow can be characterized by the value of the melt strength (MS) and breaking stretching ratio (BSR), reported for all the samples in Table I. For both systems, the increase of MS values with increasing the nanofiller content is noticed, coupled with slight reductions in BSR (less than 10%). However, once again the increase of MS

TABLE I
Melt Strength and Breaking Stretching Ratio (BSR) of Homopolymers and Hybrids

	MS (cN)	BSR
LLDPE	2.4	180
LLDPE + 2 wt %	2.9	175
LLDPE + 4 wt %	3.1	167
LLDPE + 8 wt %	4.2	151
LDPE	11.9	21
LDPE + 2 wt %	12.3	21
LDPE + 4 wt %	12.6	19
LDPE + 8 wt %	13.1	17

TABLE II
Main Mechanical Properties (E, TS, EB, and BD) of the Two Homopolymers and Their Relative Increases for Nanohybrid Blown films With Respect to the Matrices in the Two Drawn Directions

	Machine direction			Transverse direction			
	E (MPa)	TS (MPa)	EB (%)	E (MPa)	TS (MPa)	EB (%)	BD (g mm^{-1})
LLDPE	109	34.3	688	151	28.6	604	3.9
LDPE	96	33.5	665	133	24.2	485	3.2
Increases of mechanical properties respect to the homopolymers (%)							
LLDPE + 2 wt %	+23.8	+2.3	−0.44	+20.5	+1.75	+0.16	+5.13
LLDPE + 4 wt %	+40.4	+3.5	+1.74	+47.7	+5.60	+1.82	+10.2
LLDPE + 8 wt %	+75.2	+18.6	+0.58	+64.2	+20.6	+10.1	+28.2
LDPE + 2 wt %	+26.0	+0.60	−0.75	+18.8	+2.10	−1.03	+6.25
LDPE + 4 wt %	+44.8	+3.00	−0.75	+37.6	+3.72	+1.03	+9.37
LDPE + 8 wt %	+64.6	+15.2	−3.76	+69.2	+14.9	+5.15	+15.6

E, elastic modulus; TS, tensile strength; EB, elongation break; BD, ball drop.

results significant only for the LLDPE-based samples (increase up to 75%), while negligible effects (not more than 10%) can be noticed for the samples having LDPE as matrix. Several authors suggested that the effects upon draw properties of nanohybrids were related to flow-induced clay alignment along with the stretching direction,[5,19] although the existence of at least some fraction of the silicate layers exhibiting drawing flow-perpendicular orientation has also been reported.[18]

The trend of the results summarized in Table I, in agreement with the shear flow results, clearly suggest that the presence of oriented clay particles strongly improves the values of the melt strength and the consequent scarce ability to produce film of LLDPE. However, despite of the similarity in the hybrid meso-strutures emerged from morphological analyses (TEM, WAXD, and SEM), the effect of clay on the elongational rheology of LDPE-based nanohybrids probably cannot be observed because of the homopolymer-like behavior of hybrids in the melt state, so that negligible effects on the shear and elongation rheology of LDPE-based nanocomposites can be noticed.

Mechanical properties

The percentage increase of mechanical properties (elastic modulus, E, tensile strength, TS, elongation at break, EB, and ball drop, BD) of the polyolefin/clay hybrid systems respect to the homopolymers are summarized in Table II. The hybrids are more rigid then homopolymers without remarkable loss of ductility. In particular, elastic modulus and tensile strength increase with increasing the nanoblend concentration for all the samples, while negligible variations of the elongation at break are detected. A slight increase of the EB emerges in the transverse direction, probably due to a better orientation in this direction. The ball drop values, representing a measure of the impact strength of the film, increase too for the hybrid sys-

tems. The increase of elastic modulus and tensile strength is roughly monotonic with filler content, while negligible effects are detectable upon the values of elongation at break within the experimental error.

It is important to observe that the effect of filler does not show a clear trend with respect to the nature of the matrix, and the relative enhancement of mechanical properties respect to the neat matrices are comparable for both the LLDPE- and LDPE-based hybrids. Though this could appear in disagreement with rheological results, this is not surprising considering that both WAXD and TEM analyses have indicated comparable mesostructure for the hybrids, independent from the nature of polymer matrix. The slight discrepancies of the dimensionless mechanical properties of LLDPE- and LDPE- based hybrids could be probably attributed to some difference in the clay orientation of tested samples rather than to the effect of either the adhesion between the matrix and the clays or the different degree of intercalation/exfoliation state. The results shown suggest that the increase of mechanical properties of the films as a consequence of adding the clay has to be mainly related to the reinforcement effect promoted by the filler, the polymer host playing a minor role in determining of the solid state properties of the hybrids. Conversely, the influence of matrix is resulted relevant in the melt state, the relaxation kinetics of homopolymer being able to shield the effect of clays within the investigated experimental range.

SUMMARY

The rheology, the ability to produce films and the mechanical properties of two different layered-silicate-based polyethylene hybrids for film manufacturing have been investigated. Despite the identical chemical nature of two polymer matrices, only differing in the molecular architecture, and the similar degrees of exfoliation/intercalation deduced from morphologi-

cal analyses, the presence of filler clearly affects only the rheological behavior of LLDPE-based nanocomposites, while the LDPE-based hybrid rheology appears comparable to that of unfilled LDPE. SEM observations and linear dynamic measurements indicate an effect of layered silicate or tactoids orientation upon flow behavior of both the hybrids. The results of dynamic tests carried out on mixed samples, and stress relaxation measurements are consistent with the existence of a roughly bimodal population of dynamical species: a matrix component behaving like the homopolymer matrix, and a fraction interacting with the filler, whose rheological behavior is controlled by the clays and their interactions with the polymer. The rheology of the hybrids depend on the whole of relaxation kinetics of these two dynamical species. The long relaxation times of LDPE produces that the flow behavior of the hybrids within the time scale of the experiments is governed by the homopolymer. Conversely, the presence of filler standout for LLDPE-based hybrids at low frequencies and shear rates, and a pseudosolid-like feature related to the filler become noticeable. Moreover, the Cox–Merz rule, generally inapplicable to mesostructured materials like those investigated in this study, still works for the LDPE-based hybrids because of its homopolymer-like rheological behavior. Even in elongational flow, the effect of layered silicate strongly improves the ability to make LLDPE-based films without significantly modifying the draw properties of LDPE-based hybrids.

The picture is different for the mechanical properties in the solid state. The increase of the elastic moduli and tensile strengths have been observed for all the filled films, together with a slight reduction of the elongation at break, but no significant difference between LDPE- and LLDPE-based films has been detected. The similarities of hybrid microstructures resulted from morphological analyses suggest that the increases of mechanical properties of the hybrids respect to the neat polymers is a consequence of their microstructure. Different from what happened in the melt state, the polymer host seems to play a minor role in the determining of the solid state properties of materials.

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