Elongational and Shear Flow Behavior of Calcium Carbonate Filled Low Density Polyethylene: Effect of Filler Particle Size, Content, and Surface Treatment

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ABSTRACT: In this article, calcium carbonate filled low density polyethylene (LDPE) was prepared and the influence of filler content, particle size, and surface treatment with stearic acid on the strain hardening and viscoelastic properties of the composites were investigated. Both elongational and shear rheological measurements were conducted on the different formulations and completed by microscopical observations and by differential scanning thermal analysis. The obtained results indicate that the effect of filler content and particle size are negligible on strain hardening behavior. Also the filler surface treatment has a less important effect on the nonlinear elongational tests in comparison with low frequency range measurements. However in shear rheology, we noted the absence of yield stress and network structure at different filler contents, and the presence of shear thinning behavior. Scanning electron microscopy (SEM) observations showed the enhancement of dispersion for surface treated samples, while differential scanning calorimetry (DSC) experiments have shown that the content of crystallinity of LDPE matrix is slightly affected by the presence of filler. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 257–266, 2012

Key words: filled polyethylene; particle size; surface treatment; elongational flow; shear flow

INTRODUCTION

Inorganic fillers are widely used in the thermoplastics industry to improve processing and/or mechanical properties and to reduce the production costs. Osman et al.[1,2] reported the enhancement of stiffness and yield stress in calcium carbonate filled low density polyethylene (LDPE), and as well as the increase of viscosity, moduli, and viscoelastic nonlinearity in calcium carbonate filled high density polyethylene (HDPE). In general mineral fillers, such as calcium carbonate can also lead to a loss in properties of polymer due to the nonhomogenous dispersion and to the poor interaction between the hydrophilic filler and the hydrophobic matrix. Thus, to improve the interfacial adhesion and to facilitate filler dispersion a variety of coupling agents, such as silane, titane and stearic acid are used in addition to maleic anhydride grafted polypropylene compatibilizer.[3–5]

However the inclusion of filler may also introduce rheological problems and increase the cost of processing. Fillers have strong impact on the compound viscosity depending on filler content, particle size distribution and surface treatment. Therefore, an understanding of the rheology of filled systems is necessary to optimize the processing conditions and to predict the material performance in many commercial applications.[6] It has been accepted that elongational rheology is as an excellent indicator for processability conditions including elongational flow, such as film or bottle blowing, thermoforming, melt spinning and sheet casting.[7,8] Nevertheless, due to the difficult measurements and to the inherently unsteady nature of the elongational flow, availability of information is limited, especially for filled materials.[9] Few investigators have considered the elongational flow as well as the shear flow behavior of filled compounds with yield values.[10] Some studies have reported the shear thinning behavior for melts of HDPE/CaCO$_3$ and LDPE/zeolite composites where the increase of viscosity in these systems is more marked for untreated fillers than for the treated ones.[11,12] Greener and Evans[13] compared the dependence of shear and elongational relative viscosities of filled polyisobutylene on volume fraction of powder ceramic. Li et al.[14] indicated that the extensional viscosity of filled polyethylene contributes considerably to the apparent strain hardening

and appears to be dependent on wood content in the HDPE/wood composites, while Haworth[15] showed that the incorporation of inorganic calcium carbonate increases the transient state extensional viscosity and the rupture stress of HDPE. The materials which show no strain hardening have shortcomings in attractive processes such as blow molding and foaming when elongational flow dominates. Thus it has been desired to control these elongational flow properties, especially at large strain.[16]

Furthermore a limited number of papers dealing with the quantitative comparison between the strain hardening and dynamic shear results were published up to the time present in terms of the influence of particle size, surface treatment and content of filler. In this study, the effects of particle size, particle content, and surface treatment of calcium carbonate filler on the elongational and shear flow behavior of LDPE were studied. The elongational flow was analyzed at equal strain rate conditions. Rheological properties were compared with the results obtained from the morphological and thermal properties measurements by scanning electron microscopy (SEM) and differential scanning calorimetry (DSC), respectively.

We therefore examine here the sensitivity of these parameters between dynamic and elongational viscosities.

EXPERIMENTAL

Materials

The commercial grade of low density polyethylene LDPE used in this study as the matrix is a product of Enip (Algeria), with a density of 0.923 g/cm^3, a melt flow index of 1.20 g/10min (MFI, ASTM D 1238-62T) and a melting temperature of 109°C (ASTM D 1238). Four types of calcium carbonate were used as fillers, the CaCO$_3$ (CC2.6T), with trademark Omya BSH supplied by Omya (France), The CaCO$_3$ (CC14.2) supplied by Enof (Algeria), The CaCO$_3$(CC5) obtained after humid grinding of the local calcium carbonate according to NFXD11-507 and the CaCO$_3$ (CC5T) which was treated by 1% of stearic acid supplied by Henkel (Germany). Particle characterizations of all CaCO$_3$ grades (all with a density of 2.7 g/cm^3) are listed in Table I.

For the treatment procedure, stearic acid was dissolved in carbon tetrachloride (CCl$_4$), and then the calcium carbonate was added into the solution. The treatment was carried out by mixing at room temperature and for 12 h the obtained solution via agitation until complete homogeneity is achieved. The treated calcium carbonate was then dried in a vacuum oven for 24 h at 60°C. All compounds were prepared on a two-roll mill (Polymix 80T) at 160°C

TABLE I
Characteristics of CaCO$_3$ Grade Used in This Study

Referred filler type	Particle size (μm)	Average particle size (μm)	Type of surface treatment
CC14.2	1–128	14.2	Untreated
CC5	1–5	<5	Untreated
CC CC 5T	1–5	<5	Stearic acid treatment
CC 2.6T	1–16	2.6	Stearic acid treatment

for 15 min. The samples for rheological testing were compressed molded at a temperature of 200°C and a pressure of 10 bars. The samples for DSC and microscopic analysis were injection molded at 200°C.

Elongational rheology

Measurements of the uniaxial elongational viscosity at constant strain rate of 0.1 s^{-1} were carried out using a Meissner type extensional rheometer RME at 150°C. Typical sample dimensions were 62 × 8 × 1.4 mm^3. A detail description and discussion of the reliability of the extensional rheometer are given by Meissner and Hostettler.[17] In the RME analysis, when the test begins, the force required to extend the sample has been measured as a function of time, the uniaxial elongational viscosity η$_E$ is calculated assuming an exponential decrease in the cross-sectional area of sample as follows[18]:

$$\eta_E = \frac{F(t)}{H_o W_o e^{(-\dot{\varepsilon}t)\dot{\varepsilon}}} \tag{1}$$

Where H_0 and W_0 are respectively, the thickness and width of the sample at $t = 0$ and $\dot{\varepsilon}$ is the strain rate. The product $H_0 W_0$ represents the cross-sectional area of the sample at the measured temperature prior to extension and can be determined from the dimensions of the sample at room temperature:

$$H_o W_o = (H_o W_o)_{RT} \left(\frac{\rho_{RT}}{\rho_{MT}}\right)^{2/3} \tag{2}$$

Where $(H_0 W_0)_{RT}$ is the cross-sectional area of the sample at room temperature and ρ_{RT} and ρ_{MT} are the densities of the material at room temperature and at the measured temperature respectively. For example for 23% (30 phr) of CaCO$_3$ at room temperature, ρ_{filler} is 2.7 g/cm^3, ρ_{LDPE} is 0.923 g/cm^3 and $\rho_{composite}$ is 1.088 g/cm^3. The product $\dot{\varepsilon}t$ in eq. (1) is defined as the Hencky strain ε_H which is given by: $\varepsilon_H = \ln (L/L_0)$, where L and L_0 are the deformed and the initial sample length, respectively.

Dynamic shear rheology

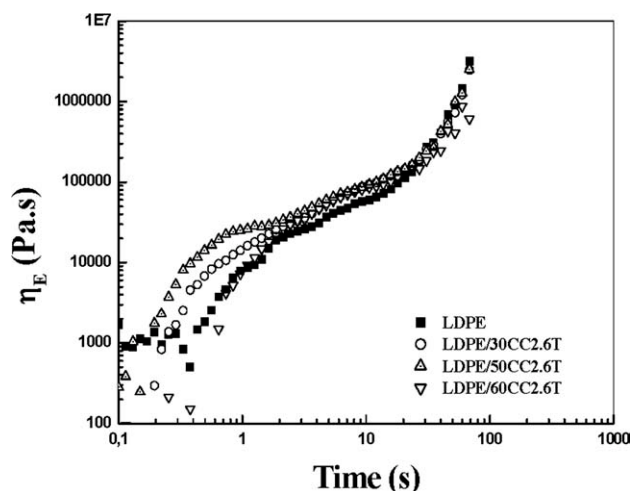Rheological measurements were made in dynamic mode on a Rheometer (Rubber Process Analyzer

Figure 1 Elongational viscosity as a function of time of LDPE and LDPE/CC2.6Tcomposites filled with 30, 50, and 60 phr treated CaCO₃ at 150°C under constant strain rate of 0.1 s⁻¹.

RPA 2000) equipped with parallel plate geometry at 150°C. The storage modulus (G'), loss modulus (G'') and the complex viscosity were measured as a function of angular frequency (ω) from 0.2 to 200 rad/s. Dynamic frequency tests were conducted for all samples at a strain rate of 0.56%.

Differential scanning calorimetry (DSC) measurements

Nonisothermal crystallization parameters were measured using a Mettler Toledo DSC 821e apparatus. The weight of all samples was approximately 10 mg and all measurements were carried out in nitrogen atmosphere. The samples of composites were heated for the first heating scan from −20 to 220°C at a rate of 10°C/min to eliminate previous thermal history and were held at this temperature for 2 min to ensure complete melting before starting the cooling. The second heating sweeps were carried out from 220°C to −20°C and from −20 to 220°C respectively, at the same constant rate. The crystallinity index (X_c) of LDPE and LDPE/CaCO₃ composites can be calculated from the following equation[11]:

$$x_c = \frac{\Delta H(\text{composite})}{\Delta H^0 \times W} \quad (3)$$

Where ΔH (composite) is the apparent enthalpy of fusion per gram of composite, ΔH^0 is the heat of fusion of 100% crystalline LDPE, taken as 290 J/g from[19] and W is the weight fraction of LDPE in the composite.

Morphological examination

Scanning Electron Microscopy SEM (ADSM982 Gemini Leo) was used to study the microstructure and the morphology of fractured surfaces; magnification was 500× and 2000× at a voltage of 1.00 kv. Samples were fractured in liquid nitrogen and covered with Gold before examination under microscopy.

RESULTS AND DISCUSSIONS

Elongational viscosities

Uniaxial elongational viscosities measurements are most often used to identify a material tendency to strain harden. Strain hardening is based on a comparison of the stress in start up flow with that predicted by the theory of linear viscoelasticity. If the stress increases faster than it is predicted by the linear theory, the material is said to be strain hardening.[20] Figures 1–3 show double-logarithmic plots of elongational viscosity η_E as a function of time observed for conventional composites at 150°C with a constant strain rate of 0.1 s⁻¹. For times less than one second (<1 s), the viscosity is found to diverge from a Trouton curve; this may be due to the creep effect that may occur after introducing the sample into the chamber at the relaxation phase. Indeed, during the relaxation phase, the sample does not retain its shape but tends to curb because the ends stick to the lower belts on which it is deposited and thus it tends to lengthen. The first tenths of a second will therefore serve to hold out the sample and also to give it a rectangular shape. The forces required to hold out the sample are considerably lower for the stretch state, since the viscosity is directly proportional to the force, therefore its apparent value will be lower. To avoid this underestimation, one can apply a pretension before the test; which is meant to
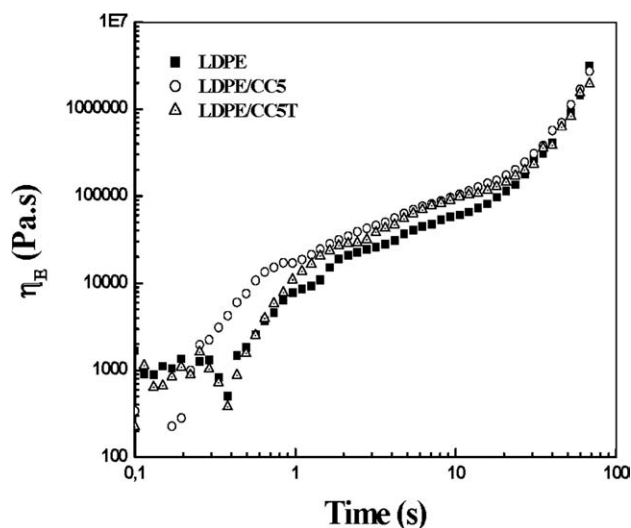

Figure 2 Elongational viscosity as a function of time of LDPE, LDPE/CC5, and LDPE/CC5T composites filled with 30 phr CaCO₃ at 150°C under constant strain rate of 0.1 s⁻¹.
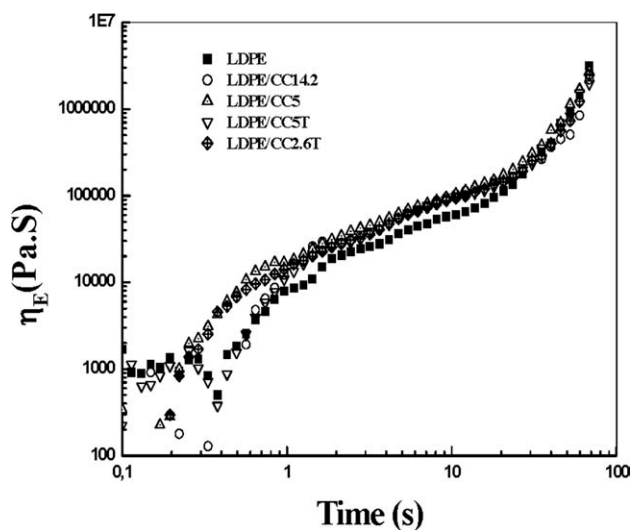
Figure 3 Elongational viscosity as a function of time of LDPE, LDPE/CC14.2, LDPE/CC5, LDPE/CC5T, and LDPE/CC2.6T composites filled with 30 phr CaCO₃ at 150°C under constant strain rate of 0.1 s⁻¹.

hold out manually the sample, after declining the upper belt, by moving successively two pairs of belts. At the end of this pretension, we let the sample again to relax to eliminate any stresses induced by the pretension. In the early stage ($t > 1$ s), the elongational viscosity gradually increases with the time but independent of strain rate, which we generally call the linear region of the elongational viscosity curve. After a certain time, which we call the up rising time, dependent on strain rate, a rapid upward deviation of elongational viscosity from the curves of the linear region is observed. The upward deviation in elongational viscosity is called strain hardening. In Figures 1–3 a very strong tendency to strain hardening is observed for the LDPE/CaCO₃ composites and also for the pure polymer. Thus it becomes clear that elongational viscosity measurements in molten polyethylene samples have a significant strain hardening.[21,22] Such behavior has been also reported for some composites in the literature.[14,15] Strain hardening or extensional thickening can be associated with long relaxation times that are caused by the presence of long molecules or by long chain branching.[22] The strong increase of the extensional viscosity in comparison to shear viscosity in the case of strain hardening leads to an additional shearing of the sample between the rotating belts so the flow is not purely extensional.

Figure 1 shows experimental results for the elongational viscosities of the pure polymer and LDPE/CaCO₃ composites containing treated particles with a diameter of 2.6 µm. One can notice that the elongational viscosities increase as the filler content is increased at lower times. However, the effect of particle content (30 and 50 phr) is not clearly observed

on the strain hardening behavior. Furthermore, the introduction of 60 phr of treated filler decreases slightly the strain hardening behavior. Similar results were reported by Prasad et al.[23] in ethylene vinyl acetate (EVA) nanocomposites in which the elongational viscosity eventually becomes independent of silicate content in the nonlinear region. Kabayashi et al.[24] showed also that the strain hardening did not appear if the filler content and the strain rate are sufficiently high in HDPE filled with glass beads system because the presence of the particles perturbates the deformation of matrix polymer chains around them and thus causes the suppression of strain hardening.

Figure 2 shows the effect of treatment of filler with stearic acid on the elongational viscosity. The elongational viscosity decreases at all measured times for the samples where calcium carbonate was treated stearic acid. The decrease is however less significant in strain hardening behavior. Generally, a reduction in viscosity is observed if the surface treatment wets and disperses the filler; but an increase in viscosity will occur if the surface treatment promotes adhesion between the filler and the polymer. In this case, strong interactions between the matrix and the filler tend to increase the viscosity as the polymer is strongly bonded to or adsorbed on the filler surface which subsequently restricts the mobility of the polymer matrix chains.

In Figure 3, the increase of viscosity related to particle size reduction is significant at low times in comparison to the nonlinear region, this behavior can be related to the fact that smaller particles with larger ones tend to increase packing fraction before elongational deformations take place and therefore result in an increase in viscosity. However, no size effect can be detected on strain hardening behavior, suggesting again that hydrodynamics effects dominate. Le Meins et al.[25] measured the elongational viscosity of monodisperse polystyrene spheres suspended in polyisobutene matrix. They argued that; when the particles are sufficiently large about 1.4 µm and 2.7 µm, the hydrodynamic effects dominate. The particle contribution then depends on the volume fraction but not on the particle size. For sufficiently small particles the amplitude of the strain hardening is reduced or even eliminated.

Measured elongational force and its analysis

Figures 4 and 5, show the force and the stress as a function of Hencky strain respectively, for a uniaxial elongational test at constant strain rate of 0.1 s⁻¹ for the untreated and the treated calcium carbonate polyethylene composite. Because of the dramatic decrease of the cross section of the sample during elongation, the force goes through a maximum and
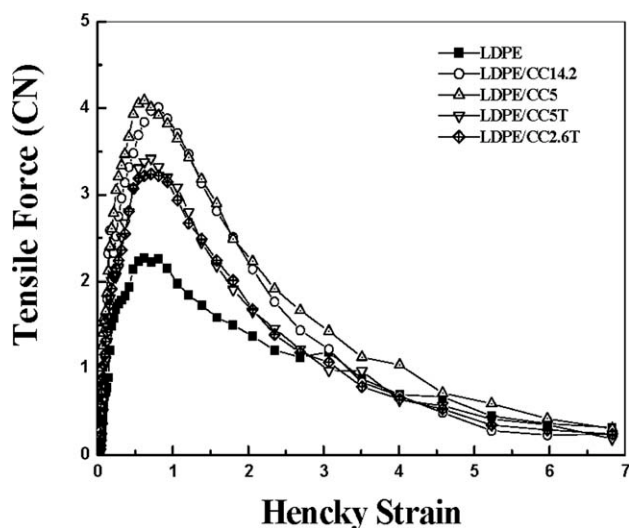
Figure 4 Measured elongational force as a function of time of LDPE, LDPE/CC14.2, LDPE/CC5, LDPE/CC5T, and LDPE/CC2.6T composites filled with 30 phr $CaCO_3$ at $150°C$ under constant rate strain of $0.1 \ s^{-1}$.

disappears at the end of the test for all samples. The stress defined as the force divided by the current cross section increases with Hencky strain for all samples. Moreover, from Figures 4 and 5, one can observe the measured elongational force and stress as a function of Hencky strain respectively, for all LDPE/$CaCO_3$ composites. When elongation Hencky was lower (<1), the tensile stress values for all of the samples were not much different because the loose chains of LDPE exhibited the same resistant force. However, at high elongation Hencky, the chains were stretched; also calcium carbonate particles could block the stretching of LDPE chains.
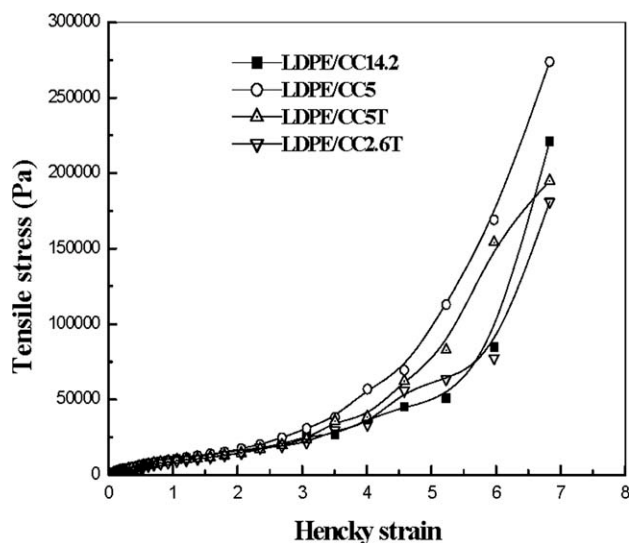

Figure 5 Measured elongational stress as a function of Hencky strain of LDPE/CC14.2, LDPE/CC5, LDPE/CC5T, and LDPE/CC2.6T composites filled with 30 phr $CaCO_3$ at $150°C$ under constant rate strain of $01 \ s^{-1}$.

Note that, it takes more force to pull the composites with untreated filler at a Hencky strain of 1. The tensile force maximum is always higher in the LDPE/CC14.2 and LDPE/CC5 composites of the untreated filler than in the LDPE/CC5T and LDPE/CC2.6T composites of the treated one. These results suggest the presence of filler agglomerates of different size. The number of agglomerates must be higher in the untreated composites than of the treated ones. Agglomerates of the untreated filler did not deform under stretching and hence exerted more resistance to the flow than those of the treated filler because the dipole-dipole interactions existing between the untreated filler are stronger than the Van der walls attractions forces between the alkyl chains of filler coating. On the other hand, it can be seen that all samples break at a sensibly same strain.

Shear rheology

The effects of different fillers in the dynamic shear rheological properties of conventional composites have been also studied. With regard to shear, the RPA rheometer was successfully used on polyolefins (pure and compounds) for shear elastic and viscous modulus, the wide strain range allows testing polymeric materials in both linear and nonlinear viscoelasticiy domains with excellent repeatability. In all case, this rheometer did not give any significant results than the reference data. In Figures 6 and 7, the complex viscosity (η^*) increases only slightly with the addition of 30 phr (23%) of different calcium carbonate fillers. This slight increase in complex viscosity and linear viscoelastic behavior at low frequencies is the expected result for a macrocomposites system containing low amount of filler.[26,27] However, no specific effect on the dynamic viscosity
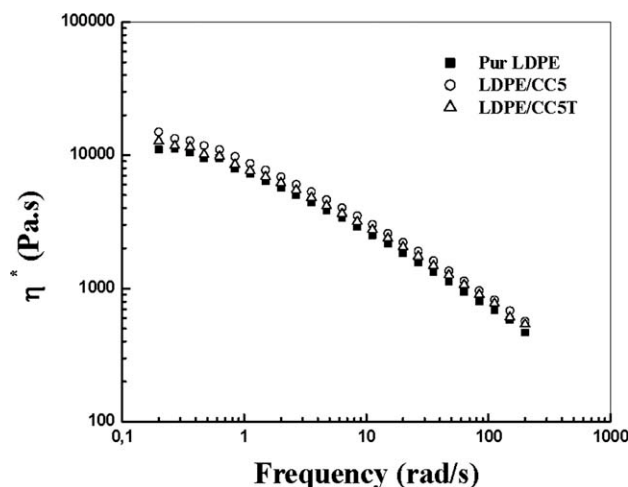

Figure 6 Shear viscosity as a function of frequency for LDPE, LDPE/CC5, and LDPE/CC5T composites filled with 30 phr $CaCO_3$ at $150°C$.
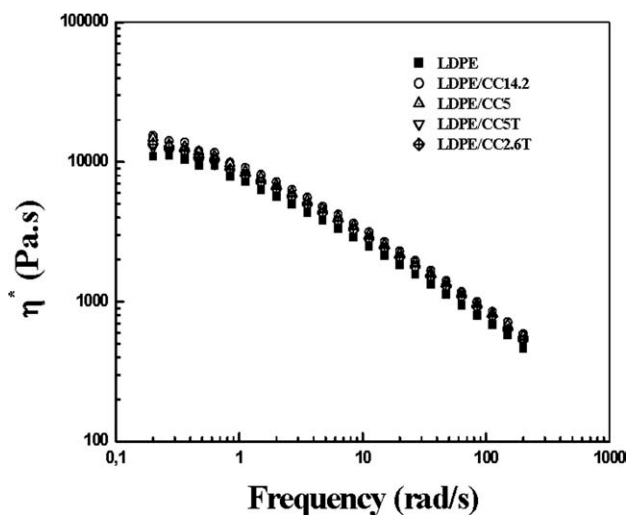
Figure 7 Shear viscosity as a function of frequency for LDPE, LDPE/CC14.2, LDPE/CC5, LDPE/CC5T, and LDPE/CC2.6T composites filled with 30 phr CaCO$_3$ at 150°C.

at low frequency is observed by the reduction of filler particle size (Fig. 7).

In Figure 6, the viscosity slightly decreases by surface treatment of filler. The effect is more pronounced at low frequency range, Similar behavior is observed in the extensional characteristics mentioned earlier and can be attributed to the difference in the state of dispersion. It is generally observed in such a system as LDPE/CaCO$_3$ thata reduction of particle sizes causes an increase in apparent viscosity and that the addition of stearic acid treatment induces a decrease in complex viscosity, with respect to the value of uncoated filled composite. This is probably due to the reduction of agglomerates. In this study, all materials showed a shear thinning behavior, the value of viscosity decreases with increasing shear rates. Thus the presence of the pronounced shear thinning should facilitate the processing of LDPE/CaCO$_3$ composites using conventional processing equipments.

Conversely, there is an increase in viscosity as the filler content is increased for the following formulations (CC14.2) and CaCO$_3$ (CC2.6T) as shown in Figure 8. Unlike extensional viscosities which appear to be independent of filler content in the nonlinear region when the filler content was 30 and 50 phr, the increase in dynamic viscosity is a result of increased filler–filler interaction due to its higher content. The extent of shear thinning increased with filler content due to the more extensive filler interaction. In Figure 9, the LDPE/CC2.6 treated composites with filler content of 30, 40, and 50 phr shows an increase in the storage modulus G′ at all frequencies. Also the loss modulus G″ of these materials follows a similar trend, which indicates a pronounced

interaction between the CaCO$_3$ filler particles. This indicates an inhibition of the polymer chain motions by the filler particles. Furthermore, at larger frequencies, the effect of filler concentration on the storage modulus becomes small, which suggests a probable breakdown of the agglomerates formed by Van der Walls and/or London forces.[28] The loss modulus G″ is larger than the storage modulus G′ indicating a viscous nature (liquid like behavior) of the composites. Similar results were obtained by Osman et al.[29] for untreated filler composites. Moreover, Lertwimolen et al.[30] reported that the increase in complex viscosity and storage modulus at low frequency can be compared to those materials exhibiting a yield stress and could be explained by the existence of a percolated network structure. Thus increasing the content beyond the test range may also produce materials which have yield stress.

When the particles are sufficiently large (≥ 2.6 μm), the hydrodynamic effects dominate the particle
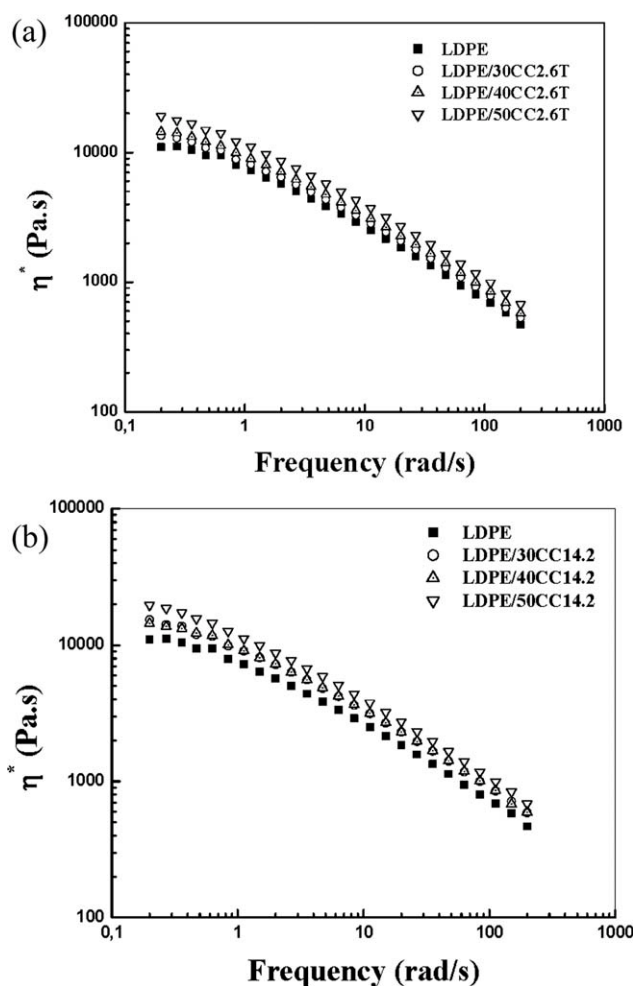

Figure 8 Shear viscosity as a function of frequency for (a) LDPE and LDPE/CC2.6T composites filled with 30phr, 40 phr and 50 phr treated CaCO$_3$, (b) LDPE and LDPE/CC14.2 composites filled with 30, 40, and 50 phr untreated CaCO$_3$ at 150°C.
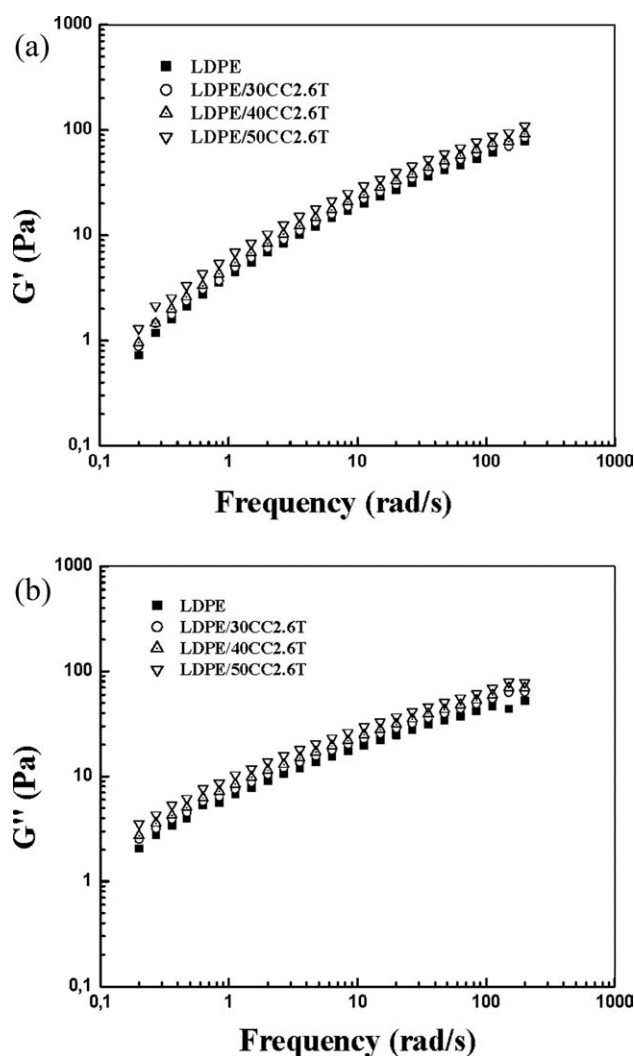
Figure 9 (a) Storage modulus, G′ as a function of frequency for LDPE and LDPE/CC2.6T composites filled with 30, 40, and 50 phr of treated $CaCO_3$, and (b) loss modulus, G″ as a function of frequency for LDPE and LDPE/CC2.6T composites filled with 30, 40, and 50 phr treated $CaCO_3$ at 150°C.

contribution which then depends on surface treatment, but not on particle size. For systems with such particles a good agreement is found between the viscosities and moduli in dynamic shear flow and the extensional viscosities at low stretching rate. The extent of the effect of filler content is not similar on the elongational and the shear viscosities. These

results imply also that flow induced internal structural change occurs in both shear and elongational flow, but the changes are quite different from each other.

Melting and crystallization behaviors

The crystallinity behavior of thermoplastic polymers during nonisothermal processing has a vital technological importance, because these conditions are closely related to the industrial processing parameters. However there have been little research related to the nonisothermal crystallization behaviors of $CaCO_3$ filled LDPE composites. DSC results in Table II show that the melting temperature (T_m) in neat polymer and LDPE/$CaCO_3$ composites are very similar. The addition of 23% $CaCO_3$ to the polymer matrix causes a decrease in the values of the heat of fusion. According to Table II, theses values change from 127 J/g for pure LDPE to 95 J/g for LDPE/CC14.2. The observed decrease in the heat fusion can be mainly attributed to substitution of LDPE by $CaCO_3$ particles in LDPE/$CaCO_3$ composites and to the fact that particles present in amorphous regions prevent the nucleation and the growth of crystal domains. Similar results are reported by Sahebian et al.[31] for HDPE/$CaCO_3$ nanocomposites. The crystallization temperature T_c during cooling is not affected by the presence of the different calcium carbonate fillers, suggesting that the crystal microstructure of LDPE has not been changed. The crystallinity content (X_c) of treated composites was slightly higher than that of pure LDPE and of untreated composites because of the better dispersion of treated filler in the matrix polymer. The addition of stearic acid has small effect on the crystallization process. This may be explained by the fact that when the surface of $CaCO_3$ is coated by stearic acid the outer layer plays a role of coupling agent at the interface thus shielding the $CaCO_3$ particles from direct contact with the polymer which is necessary for the its nucleation. This is in agreement with published results on PP/elastomer particle composites characterized by encapsulation core shell microstructure.[32,33] In a previous article,[4] we obtained similar results for a silica/polypropylene system

TABLE II
Thermal Properties of LDPE/CaCO₃ Composites

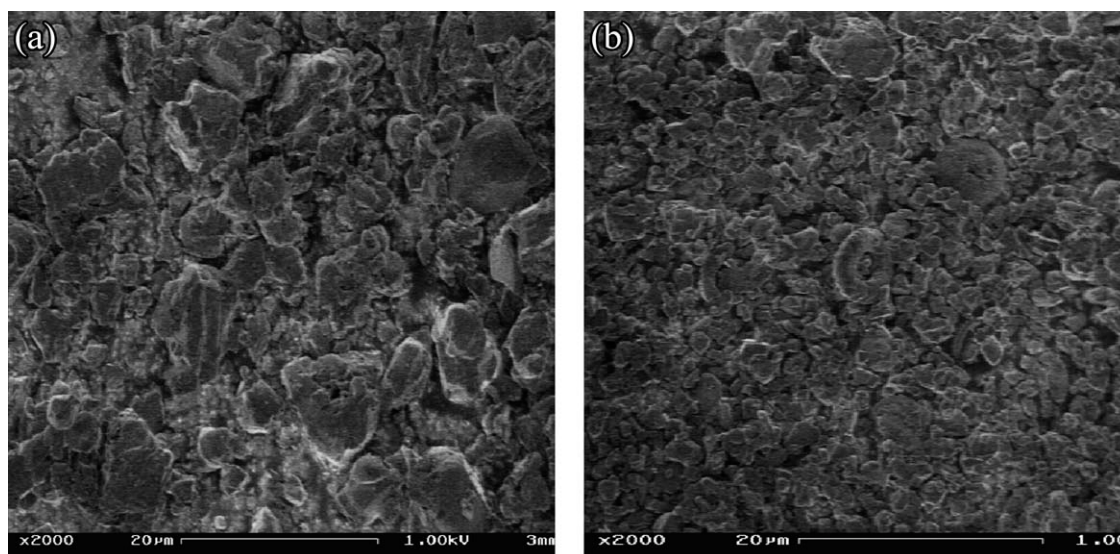| Materials	ΔH_c (J/g)	T_c (°C)	ΔH_m (J/g)	T_m (°C)	X_c (%)
LDPE	117.9	102.9	126.7	114.6	43.7
LDPE/CC14.2	89.2	102.4	94.6	114.6	42.4
LDPE/CC5	94.8	102.5	99.5	114.4	44.5
LDPE/CC5T	95.4	102.9	100.3	114.2	44.9
LDPE/CC2.6T	92.6	102.7	98.8	114.2	44.2

Figure 10 Scanning electron micrographs of (a) untreated CaCO₃ (CC14.2), and (b) treated CaCO₃ (CC2.6T).

compatibilized by glycerol monostearate (GMS) and ethylene acrylic acid ionomer. The X_c of LDPE/CC14.2 untreated composite was smaller than that of LDPE matrix, this can be referred to the low compatibility between untreated calcium carbonate with particle diameter of 14.2 μm and LDPE matrix, In fact, both low polarity and free energy of LDPE and high polarity of CaCO₃ cause that particles cannot induce suitable nucleation sites for the formation of spherulites.[34] Lazzeri et al.[11] reported that uncoated CaCO₃ has a very weak nucleating effect on the crystallization of HDPE, and stearic acidcoated CaCO₃ has no influence either on the crystallization process in CaCO₃/HDPE nanocomposites. The X_c of untreated LDPE/CC 5 composite was slightly higher than LDPE/CC14.2 composite and the pure LDPE, which can be related to the reduction of particle size. Pukanszky[35] reported that the nucleating effect of a filler may also depend on its particle characteristics, decreasing particle size of CaCO₃ leads first to the appearance of a second crystallization peak than a shift of the complete crystallization process to higher temperatures indicating a very strong nucleation effect of this filler and that the increase of nucleating effect with decreasing particle size is caused by the aggregation of CaCO₃.

Microstructural observation

Scanning electron microscopy (SEM) is widely applied to study the extent of interfacial adhesion in polymer composite, generally through examination of fracture surfaces. So to explain some results reported in a uniaxial elongational and dynamic shear flow and to verify the interfacial adhesion properties at the LDPE/CaCO₃ interface. And also to determine whether stearic acid treated CaCO₃ particles really help its dispersion in the low density polyethylene matrix. For this, SEM micrographs of the fillers particles CaCO₃(CC14.2) and CaCO₃ (CC2.6T) in Figure 10(a,b), show generally irregularly shaped filler particles especially for calcium carbonate CC2.6T. Since most mineral fillers do not fracture uniformly, there were no observable significant difference between the untreated samples and those treated with stearic acid. However, the particle size distribution of CaCO₃ (CC14.2) is larger than the treated ones. According to micrographs shown in Figure 11, the dispersion of untreated CaCO₃ particles appears to be rather uniform, it is observed that fibrils of LDPE surround calcium carbonate particles and are also seen on the clean surface of calcium carbonate particles in LDPE/CC14.2 composites. It means that polyethylene debonded completely from calcium carbonate large particles of CC14.2, It can also be seen clearly how the presence of irregular small filler particles in CC14.2 lead to a strong tendency for agglomeration. Similar results have been shown by some authors.[10] On the other hand, one can notice an improvement in the particle-particle interaction for LDPE/CC5 compound. Thus the simplest way to improve interactions consists of decreasing the particle size and thus increasing the specific surface area.[36] Calcium carbonate is well dispersed when its surface is treated with stearic acid Figure 11(c,d), it could be expected that this type of surface treatment reduce particle-particle interaction resulting in the decrease of particle agglomeration.[37] Also, very few surface defects are present; confirming the excellent levels of dispersion achieved with treated compounds. The treated system shows enhanced dispersion as compared to the
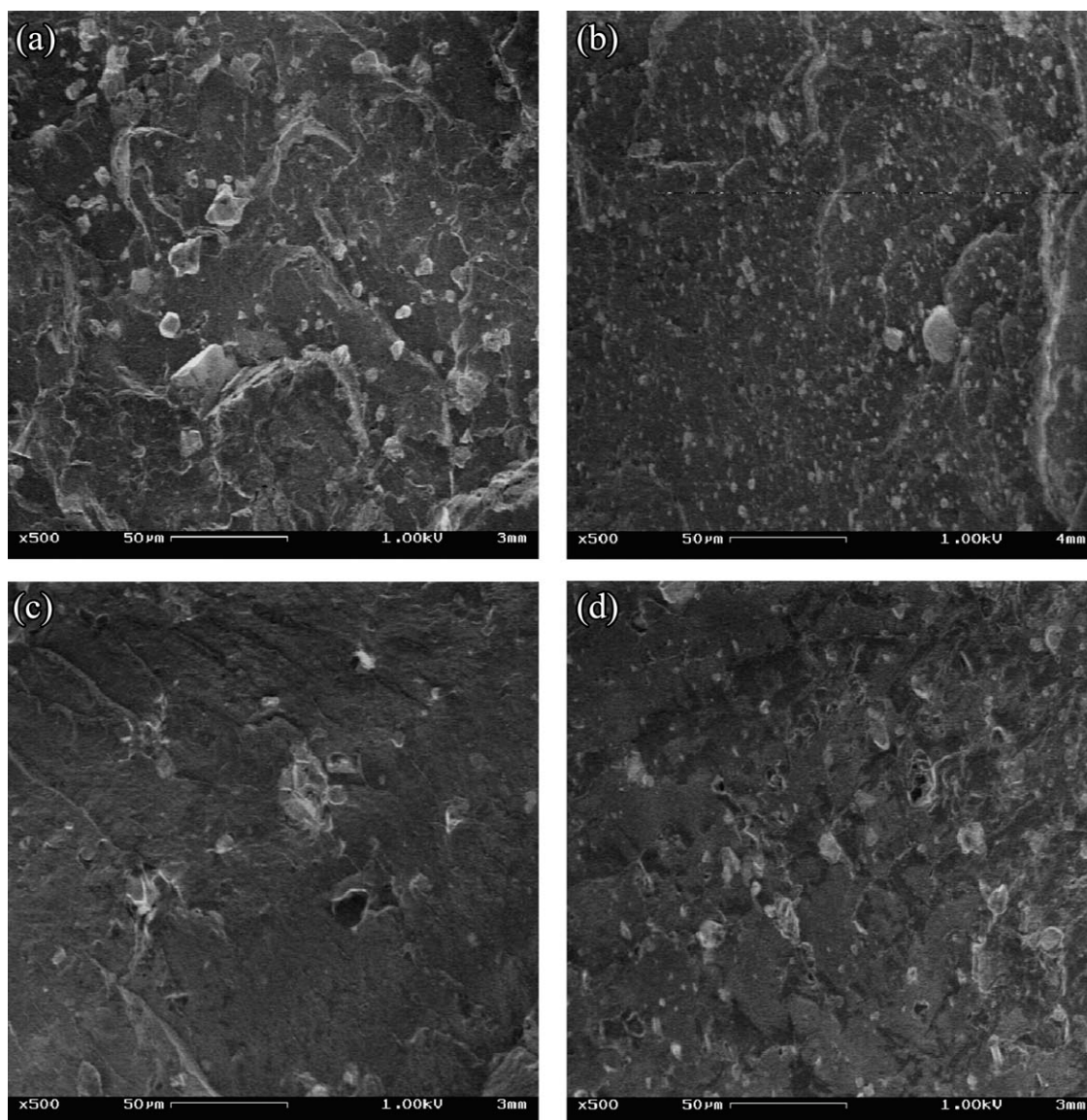
Figure 11 Scanning electron micrographs of fracture surface of composites containing 30 phr of untreated and treated CaCO$_3$, (a) LDPE/CC14.2, (b) LDPE/CC5, (c) LDPE/CC5T, and (d) LDPE/CC2.6T.

untreated system. It may be due to the coating of the filler by stearic acid.

CONCLUSIONS

From the results, it was found that unlike complex viscosity of LDPE filled with 30 phr (23%) CaCO$_3$, nonlinear elongational viscosity becomes independent of treated filler content. The storage and loss moduli increased with the content of treated calcium carbonate. Both viscosities (elongational and complex) decrease but do not change significantly as a result of stearic acid surface coating of the filler. The particle size has no effect on strain hardening behavior and shear rheology, all composites showed strain hardening and shear thinning behavior but no yield stress was noticeable. Microscopic analysis showed

that the dispersion is enhanced by stearic acid treatment and thermal analysis has shown that the melting temperature T_m and the crystallization temperature T_c are not influenced by the introduction of calcium carbonate. However the content of crystallinity X_c is slightly increased by the surface treatment and by the reduction of filler particles size.

References

1. Osman, M. A.; Atallah, A. Polymer 2005, 46, 9476.
2. Osman, M. A.; Atallah, A.; Suter, U.W. Polymer 2004, 45, 1177.
3. Chacko, V. P.; Farris, R. J.; Karasz, F. E. J Appl Polym Sci 1983, 28, 2701.
4. Zoukrami, F.; Haddaoui, N.; Vanzeveren, C.; Sclavons, M.; Devaux, J. Polym Int 2008, 57, 756.
5. Doufnoune, R.; Haddaoui, N.; Riahi, F. Int J Polym Mater 2006, 55, 815.

6. Agarwal, S.; Salovey, R. Polym Eng Sci 1995, 35, 1241.
7. Minegishi, A.; Nishioka, A.; Takahashi, T.; Masubuchi, Y.; Tachimoto, T.; Koyama, K. Rheol Acta 2001, 40, 329.
8. Sugimoto, M. Y.; Masubuchi, Y.; Takimoto, J.; Koyama, K. Macromolecules 2001, 34, 6056.
9. Gupta M. Adv Polym Technol 2002, 21, 98.
10. Wang, Y.; Wang, J. J. Polym Eng Sci 1999, 39, 190.
11. Lazzeri, A.; Zebarjad, S. M.; Pracella, M.; Cavalier, K.; Rosa, R. Polymer 2005, 46, 827.
12. Kim, H.; Biswas, J.; Choe, S. Polymer 2006, 47, 3981.
13. Greener, J.; Evans, J. R. G. J Rheol 1998, 42, 697.
14. Li, T. Q.; Wolcott, M. P. Compos Part A 2004, 35, 303.
15. Haworth, B.; Jumpa, S.; Miller, N. A. Polym Test 2000, 19, 459.
16. Minegishi, A.; Takahashi, T.; Nishioka, A.; Masubuchi, Y.; Takimoto, J.; Koyama, K. Nihon Reoroji Gakacishi 2001, 29, 61.
17. Meissner, J.; Hostettler, J. Rheol Acta 1994, 33, 1.
18. Schulze, J. S.; Lodge, T. P.; Macosko, C. W.; Hepperle, J.; Munstedt, H.; Bastian, H.; Ferri, D.; Groves, D. J.; Kim, Y. H.; Lyon, M.; Schweizer, T.; Virkler, T.; Wassner, E.; Zoetelief, W. Rheol Acta 2001, 40, 457.
19. Brady, J. M.; Thomas, E. L. J Polym Sci Part B Polym Phys 1988, 26, 2385.
20. Park, J. H.; Hyun, J. C.; Kim, W. N.; Kim, S. R.; Ryu, S. C. Macromol Res 2002, 10, 135.
21. Münstedt, H.; Kurzbeck, S.; Egersdörfer, L. Rheol Acta 1998, 37, 21.
22. Münstedt, H.; Laun, H. M. Rheol Acta 1981, 20, 211.
23. Prasad, R.; Zujo, V. P.; Gupta, R. K.; Cser, F.; Bhattacharya, S. N. Polym Eng Sci 2004, 44, 1221.
24. Kobayashi, M.; Takahashi, T.; Takimoto, J.; Koyama, K. Polymer 1996, 37, 3745.
25. Le Meins, J. F.; Moldenaers, P.; Mewis, J. Rheol Acta 2003, 42, 184.
26. Khan, S. A.; Prud'homme, R. K. Rev Chem Eng 1987, 4, 205.
27. Poslinski, A. J.; Ryan, M. E.; Gupta, R. K.; Seshadri, S. G.; Frechette, F. J. J Rheol 1988, 32, 703.
28. Kraus W, J. Appl Polym Sci Appl Polym Symp 1984, 39, 75.
29. Osman, M. A.; Atallah, A. Polymer 2006, 47, 2357.
30. Lertwimolnum, W.; Vergnes, B. Polymer 2005, 46, 3462.
31. Sahebian, S.; Zebarjad, S. M.; Vahdati Khaki, J.; Sajjadi, S. A. J Mater Proce Techn 2009, 209, 1310.
32. Liu, Y.; Kontopoulou, M. Polymer 2006, 47, 7731.
33. Long, Y.; Shanks, R. A. J Appl Polym Sci 1996, 62, 639.
34. Pukanszky, B.; Voros, G. Polym Compo 1996, 17, 384.
35. Pukánszky, B. In Polypropylene: Structure, Blends and Composites; Karger-. Kocsis, J., Ed., Chapman and Hall: London, 1995; Vol. 3, p 1–70.
36. Kovacevic, V.; Packham, D.; Lucic, S.; Hace, D.; Smit, I. Polym Eng Sci 1999, 39, 1433.
37. Supaphol, P.; Harnsiri, W.; Junkasem, J. J Appl Polym Sci 2004, 92, 201.