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Polymer 47 (2006) 1649–1660

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Nanocomposites based on polyethylene and Mg–Al layered double hydroxide. Part II. Rheological characterization

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Received 15 August 2005; received in revised form 30 November 2005; accepted 2 December 2005
Available online 24 January 2006

Abstract

The rheological properties of Mg–Al based layered double hydroxide (LDH)/polyethylene nanocomposites have been presented in details. Both unmodified and maleic anhydride (MAH) grafted polyethylene based composites are characterised. The X-ray diffraction and electron microscopic investigations reveals the primary structures of the dispersed LDH particles exists as thin platelets. The rheological analysis carried out under different modes show behaviors typical of those reported extensively in literature for various cationic clay based polymer nanocomposites. The dispersed LDH particles show stronger interaction with maleic anhydride grafted matrix. The influence of LDH loading increases the shear thinning nature of the composite melt. The storage modulus vs. frequency plots of the composites show apparent plateau behaviors in low frequency region in a dynamic frequency sweep experiment. The appearance of stress overshoot peak in flow reversal experiment indicates that the dispersed LDH particles form structural aggregation, which are ruptured by shearing, but reform with time when shearing is stopped.

Keywords: Layered double hydroxide; Flow reversal experiment; Polymer nanocomposites

1. Introduction

The use of inorganic fillers as an alternative and environment friendly flame-retardant filler to the conventional halogen containing additives in polyolefin matrices is very common. For example, magnesium hydroxide, phosphorous and nitrogen containing chemicals, etc. are often used in various forms and dosages for this purpose. Metal hydroxides are most preferred candidates when environmental concerns are taken into account. However, the major difficulty associated with metal hydroxide filler is their large loading requirement to obtain satisfactory flammability of the final composites, which deteriorates other properties, especially the mechanical properties and processibilty. Poor dispersibility of these inorganic fillers in polyolefin matrix is often attributed as the main cause behind this. Therefore, improvement of the dispersibility of these inorganic fillers in polyolefin matrices has become a major issue in the flame-retardant industry. The concept used in synthesis of polymer/filler nanocomposites is certainly a noble idea in this regard. The improved flammability of polymer–clay nanocomposites with very low loading of filler is extensively reported in literature [1–4]. The increased melt viscosity and better dispersion of the clay particles in the matrix improves compactness of the char formed after burning and also reduce the dripping tendency during burning [2].

Layered double hydroxide (LDH) based on Mg and Al is usually used as heat stabilizer in polyvinyl chloride and flame retardant in polyolefins. Our special interest to this material is due to its layered structure and close similarity to $Mg(OH)_2$, which make it suitable to provide metal hydroxide type flame-retardant mechanism but with improved dispersion through polymer intercalation and or layer delamination. The non-toxic nature of this material also makes it suitable for addressing many environment related concerns associated with halogenated flame-retardants. In the previous article [5], we have reported the synthesis of LDPE/MgAl–LDH nanocomposites using melt-compounding process. The transmission electron micrographs of polyethylene–LDH nanocomposites synthesized by melt blending technique show signs of exfoliation of the LDH layers. However, more detail microscopic analysis of the composites, presented in the current article shows that the LDH particles are mostly present in form of thin platelets

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doi:10.1016/j.polymer.2005.12.011

and their aggregation. To understand the nature of particle dispersion in polymer nanocomposites more clearly, rheological analyses are extremely helpful. The melt rheological properties of polymer nanocomposites differ from those of conventional composites in various ways, which are related to the microscopic and mesoscopic structures of the clay particles and their interaction [6–8]. In our study, we conducted rheological experiments on polyethylene/LDH-based nanocomposites to investigate linear viscoelastic properties and the response to non-linear shearing. Rheological behaviors in the linear viscoelastic regime are very sensitive to any change in the microstructure of the composites as the shearing is carried under very low shear rate and frequency. They provide information that are directly related to the state of clay particle dispersion and possible particle–particle and particle–polymer interactions. The attractive interaction among the dispersed particles often leads to formation of localized domains of clay particles, where the structural units remain physically correlated [6]. The evolution of such filler-network structure could be investigated by non-linear shear experiments. Walker et al. [9] reported similar technique to study the structural evolution and relaxation process in textured solution of liquid crystalline polymer and later employed by Solomon et al. [6] in polypropylene/clay nanocomposites.

In the present paper, we report nanocomposites based on two different types of polyolefin matrices: one with unmodified polyethylene and the other with maleic anhydride (MAH) grafted polyethylene. The synthesis of unmodified polyethylene/LDH based nanocomposites was reported in details [5]. Here, we have presented comparison between the two systems showing how chemical compatibility of the polymer matrix influence their interaction with LDH particles and the rheological behaviors of the final composites.

2. Experimental section

2.1. Materials

LDPE (density 0.9225 g/cm^3, MFI 3.52 g/10 min) was purchased from Exxon Mobil, Belgium. Sodium dodecylbenzene sulfonate (SDBS) was purchased from Aldrich chemical company. Maleic anhydride grafted linear low-density polyethylene (density 0.926 g/cm^3, MFI 30.0 g/10 min, maleic anhydride level is 1.0 wt%) and maleic anhydride grafted high-density polyethylene (HDPE-*g*-MAH) (density 0.95 g/cm^3, MFI 5.0 g/10 min, maleic anhydride level is 1.0 wt%) were obtained from Crompton, USA.

Mg and Al based LDH used for preparation of composites was synthesized using the method described by Costantino et al. [10]. The modification of pristine LDH materials by anionic surfactant SDBS, has already been described in details [5].

2.2. Preparation of polyethylene–LDH composites

Polyethylene/LDH nanocomposites were prepared by melt mixing process in Brabender plasticorder. Two sets of composites were prepared, which are

1. HDPE-*g*-MAH (designated as PB) and LDH based ($\mathrm{PB}_{X\mathrm{LDH}}$ series, where X represents the weight parts of LDH per hundred parts of resin);
2. LDPE and LDH based ($\mathrm{PE}_{X\mathrm{LDH}}$ series in which maleic anhydride grafted LLDPE was used as compatibilizer and the weight ratio of LDH to compatibilizer was 1:2; X has the same meaning as before and the sum of the amounts of LDPE and compatibilizer is taken as the amount of resin).

The preparation of $\mathrm{PE}_{X\mathrm{LDH}}$ composites was described in the previous article [5]. The preparation of $\mathrm{PB}_{X\mathrm{LDH}}$ composites was carried out by adding modified LDH to molten HDPE-*g*-MAH in Brabender plasticorder. The screw speed and the temperature were maintained at 100 rpm and 200 °C, respectively, at all mixing steps.

2.3. Analysis of polyethylene/LDH nanocomposites

X-ray diffraction analysis (XRD) over $2\theta = 1.8–40°$, in steps of 0.02° was carried out using X-ray diffractometer P4 (Siemens AG Karlsruhe, now BRUKER axs Karlsruhe) with Cu K_α radiation ($\lambda = 0.154$ nm, monochromatization by primary graphite crystal) generated at 30 mA and 40 kV. XRD spectra were interpreted with respect to the position of the basal peak (003), which depends on the distance between two adjacent metal hydroxide sheets in the LDH crystal lattice. The higher order peaks of the same hkl series [(006), (009) and so on] were also reported as they indicate the presence of repeating crystal planes and symmetry in a specific crystallographic direction.

The state of aggregation of the LDH particles in polyethylene matrix was investigated by transmission electron microscope [TEM, which was carried out at room temperature using Zeiss EM 912 model with acceleration voltage: $U = 120$ kV and bright field illumination. The ultra thin sections of samples were prepared by ultramicrotomy at -130 °C using Reichert Ultracut S (Leica, Austria). The thickness of the section cut was in the range 100–130 nm] and scanning electron microscope (SEM, model: LEO 435 VP, Zeiss; scanning of the gold coated tensile fractured sample).

Rheological measurements were carried out on an ARES rheometer (Rheometrics Scientific, USA) with torque transducers having range of measurement from 0.02 to 2000 g cm. Two types of rheological measurements were carried out as follows:

1. Dynamic oscillatory shear measurements using parallel plates (diameter 25 mm) and sample thickness of 1–2 mm.
2. Non-linear shearing or so called flow reversal experiment using following shear cycle: first, the sample was sheared at shear rate $-0.3\ \mathrm{s}^{-1}$ for 300 s. Next, shearing is stop for a time period (called rest period) and finally, sheared again at shear rate $+0.3\ \mathrm{s}^{-1}$ for 300 s. This shear cycle was repeated several times with increasing rest period.

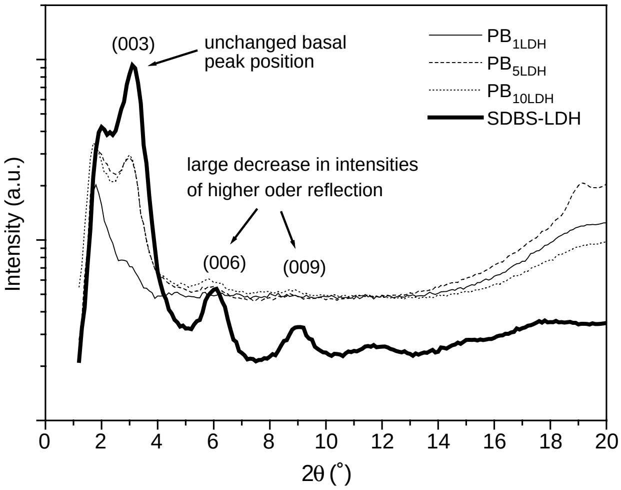

Fig. 1. XRD spectra of HDPE-*g*-MAH/LDH (PB_{XLDH}) nanocomposites.

3. Results and discussion

3.1. Morphology and XRD analysis

The morphological features as obtained from XRD and TEM for LDPE/LDH nanocomposites was discussed in the previous article [5]. The nanocomposites based on HDPE-*g*-MAH and LDH show the similar nature of the XRD spectra (Fig. 1). In the composites containing low concentration of LDH no peaks were detected. The reason may be either due to extremely low LDH concentration, which makes the region of interest in the scanned sample insensitive to XRD or due to high degree of exfoliation of the LDH crystallites. The TEM micrographs, as shown in Fig. 2, show the highly exfoliated nature of the dispersed particles. However, with increasing LDH concentration the dispersion state is changed. The XRD spectra are now characterized by the presence of basal peak and also sometimes extremely weak higher order peaks. The dispersed particles show a tendency to form structural association or clusters with increasing LDH loading. This is evident in the TEM micrographs in Fig. 2. The unchanged

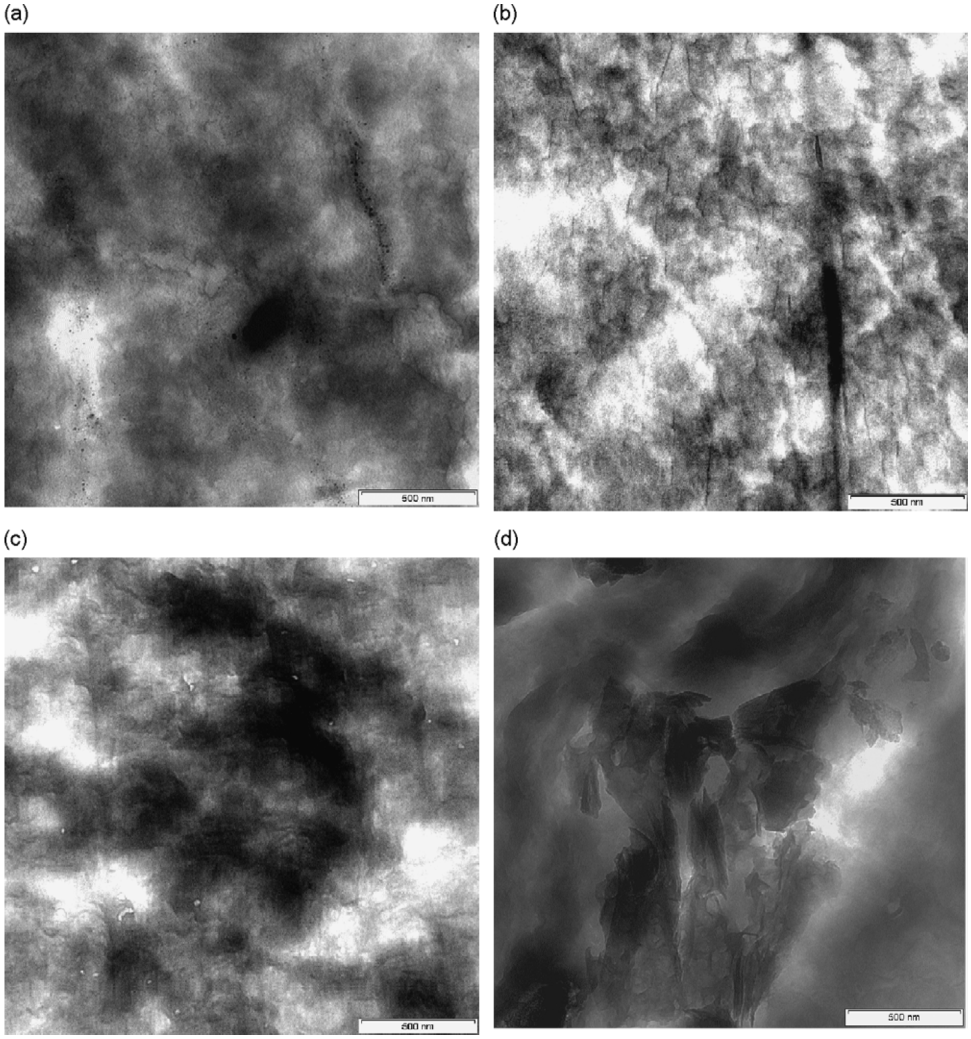

Fig. 2. TEM images of PB_{XLDH} nanocomposites at different LDH concentrations, a: 0.5 phr, b: 1.0 phr, c: 2.0 phr and d: 10.0 phr (scale shown is 500 nm).

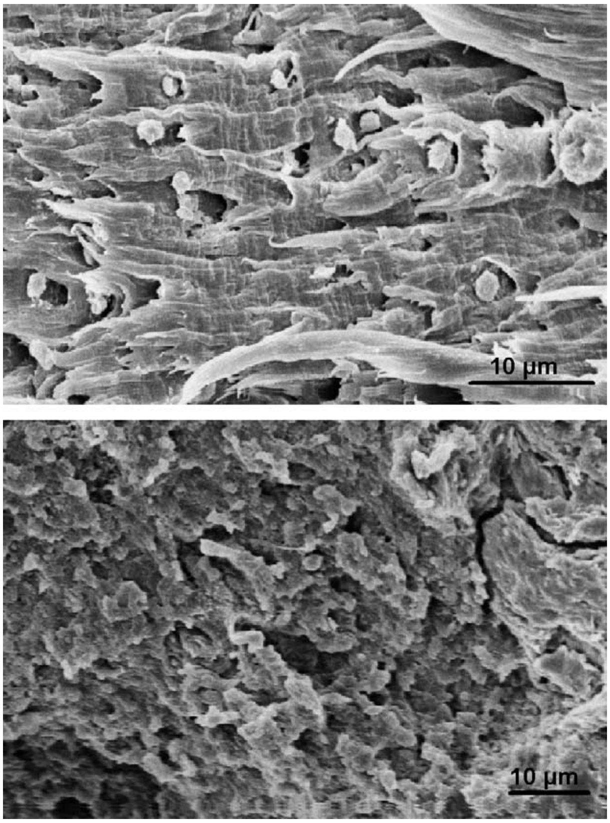

Fig. 3. SEM micrographs showing morphology and nature of LDH particles dispersion in PE_{10LDH} (upper) and PB_{10LDH} (lower). The surface scanned were the tensile fractured surface of the respective samples.

position of the basal peak (003) and the broadening or disappearance of the higher order reflection peaks indicates the preservation of the short range ordering of the stacked metal hydroxide layers (but with certainly lower symmetry as there occurs lowering of peak intensity) and the lowering of the average number of such layers in a single stacks [11]. However, neither XRD results nor the high magnification TEM images show the high degree of exfoliation of the LDH layers at high loading. Rather, they appear more likely of intercalated and flocculated type. The LDH particles in both the matrices are dispersed mainly in the form of single platelets, with occasional clustering and fragmentation of these platelets (Fig. 3) [5]. The single platelet seems coated more intensely with polymer chain in HDPE-*g*-MAH matrix. Fig. 4 shows the schematic illustration how the LDH particles undergo dispersion in polymer matrix. The SDBS modified LDH crystallites having expanded inter-gallery space undergo fragmentation during melt mixing giving thinner platelets of varying thickness with occasional delamination of individual layers. These thin platelets are composed of multiple numbers of metal hydroxide layers and are roughly hexagonal to circular in shapes. An approximate idea about the thickness (which ranges from below 50 nm to few hundred nanometers) and lateral dimensions (up to about 3 μm) of these platelets. This has been shown in Fig. 5. The presence of several layers in a single platelet is also apparent. The separation of LDH platelets from bigger LDH crystallites is possible due to the weakening of interaction force between the hydroxide layers by the inter-gallery SDBS anions.

3.2. Linear viscoelastic behaviors and effects of LDH loading

Linear viscoelastic properties of the composites were studied under dynamic oscillatory shearing using input strain function $\gamma(t) = \gamma_0 \sin(\omega t)$. The strain amplitude, γ_0 was maintained below 5% to ensure the linear viscoelastic regime of measurement. The frequency–temperature sweep was carried out within the frequency range 0.056–100 rad/s and the temperature range 180–260 °C. The changes in the rheological behaviors with temperature were more prominent in the low frequency region than that in the high frequency region. The effects of LDH loading on the temperature dependence of complex viscosity at low frequency are shown in Fig. 6. It is apparent that both pure LDPE and HDPE-*g*-MAH melts behave like liquids with steady decrease in viscosity with increasing temperature. But, in the composites,

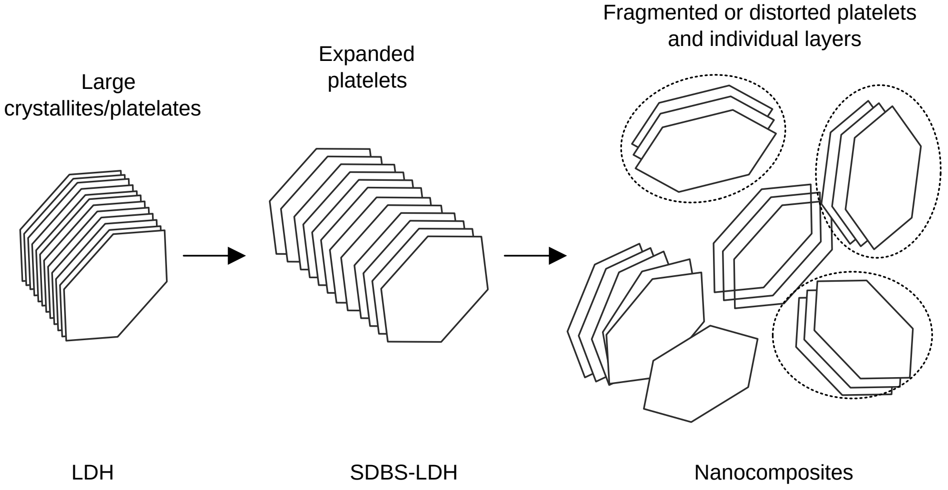

Fig. 4. Schematic illustration showing the nature of dispersion of LDH particles in nanocomposites (platelets of containing multiple number of hydroxide layers are shown in dotted circles).

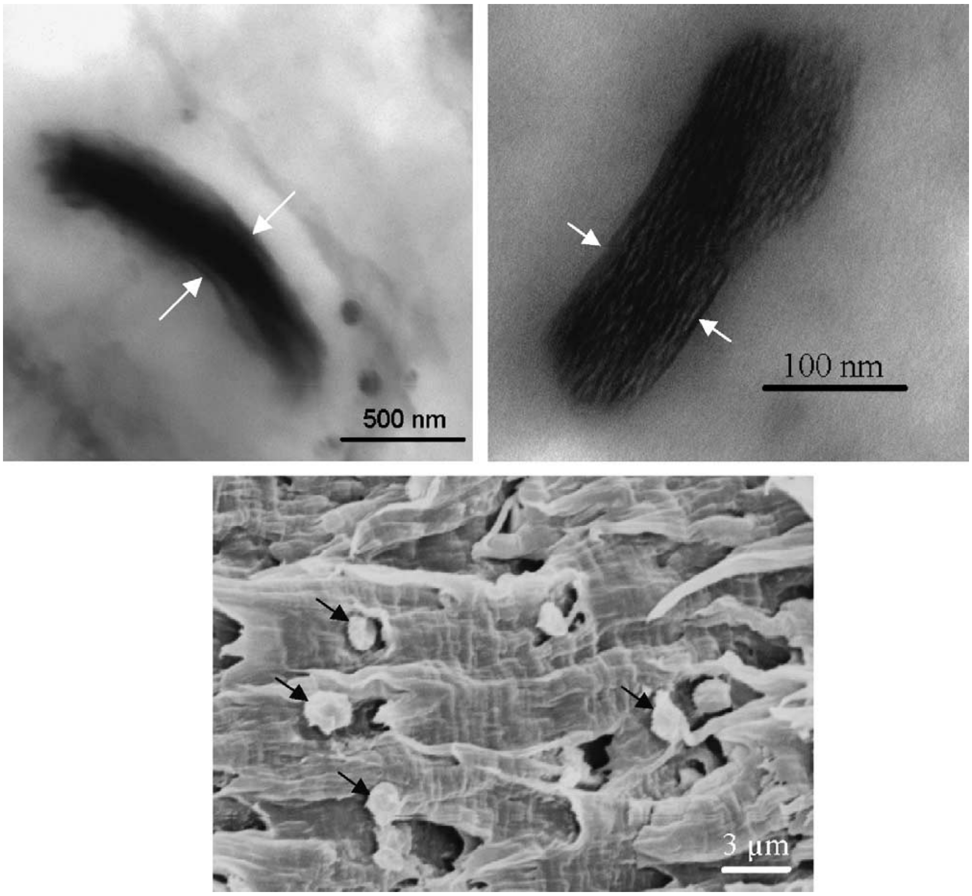

Fig. 5. Electron micrographs showing the possible geometrical nature of the dispersed LDH particles: the thickness and layered structure (top: TEM micrograph) and the size of LDH tactoids or platelets (below: SEM micrograph, arrow heads indicate LDH platelets) in the composites PE_{XLDH}.

especially beyond certain concentration of LDH, the temperature dependency of the rheological parameters is reduced significantly. This indicates the increasing deviation of the composite melts from the typical liquid-like-low-frequency flow behaviors and the appearance of pseudo-solid like behaviors. It is also interesting to note that in HDPE-*g*-MAH based nanocomposites (PB_{XLDH}) temperature independency of the complex viscosity is achieved at much lower LDH concentration (around 5 phr). Whereas in LDPE/compatibilizer based nanocomposites (PE_{XLDH}) the complex viscosity shows noticeable change even at 10 phr LDH concentration. This obviously demonstrates the difference in the nature of matrix strongly influence the effect of increasing LDH concentration on rheological behavior of the nanocomposites. This will be discussed in details in subsequent sections.

The linear viscoelastic response of the nanocomposite melts is reported in terms of storage modulus (G') (Fig. 7) and complex viscosity ($|\eta^*|$) (Fig. 8). The response in the low frequency region reveals that the nanocomposites show marked deviation in their behavior from that of the unfilled matrices. Though the general trend in both the systems (PB_{XLDH} and PE_{XLDH}) is that storage modulus monotonically increases with increasing LDH concentration, the difference in the extent of change in storage modulus in two systems is noticeable. The much larger increase in storage modulus in PB_{XLDH} system compared to PE_{XLDH} system shows that the matrix polarity favors the better dispersion of LDH particles. The tendency to G' vs. frequency (ω) plots to attain plateau shape in the low frequency region (as shown in Fig. 7) indicates the increasing hindrance to the relaxation process of the system with increasing LDH concentration. It is apparent that in a more polar matrix the plateau region is achieved at lower LDH concentration compared to a less polar one. In compatibilized system (PE_{XLDH}), the effect of low molecular weight compatibilizer is an important factor that influences the absolute change in the rheological parameter like G' and complex viscosity. Similar behavior has also been observed in case of polypropylene/montmorillinite-based nanocomposites [6]. The complex viscosity verses frequency plot (Fig. 8) for unfilled matrix show classical viscoelastic behavior characterized by transition from low frequency Newtonian flow behavior to high frequency shear thinning nature. In presence of LDH, however, the response in low frequency region gradually changes to strong shear thinning nature with increasing LDH concentration. This effect, once again, is similar in both types of nanocomposites with only difference observed in their extent. We believe two factors plays major roles: first, the polarity difference of the two matrices and second, presence of low molecular weight compatibilizer in one composite. The SEM micrographs of the fractured surface

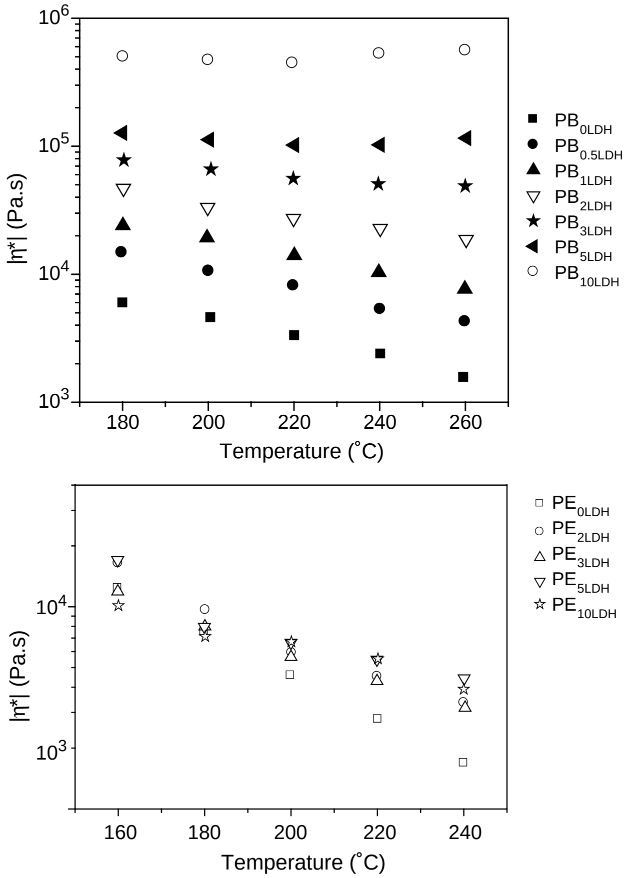

Fig. 6. Effects of LDH loading on the temperature dependence of complex viscosity at low frequency (0.177 rad/s) of polyethylene/LDH nanocomposites (top: PB_{XLDH} system, bottom: PE_{XLDH} system).

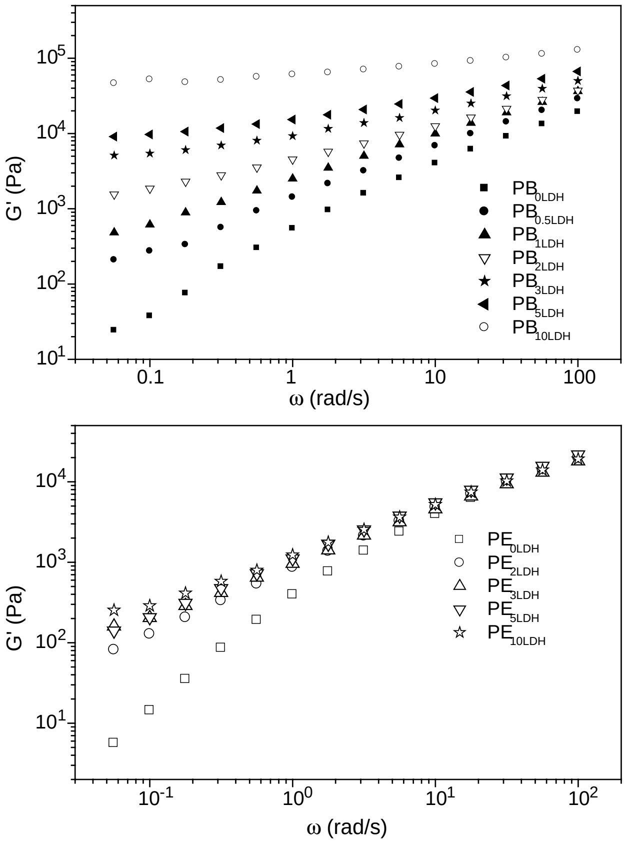

Fig. 7. Storage modulus (G') vs. frequency plots of HDPE-*g*-MAH/LDH (PB_{XLDH}, top) and LDPE/LDH (PE_{XLDH}, bottom) nanocomposites. Again trends in the low frequency region shows strong influence of LDH concentration on flow behavior. The plateau region in the flow curve indicates practically no change in the relaxation behaviors of the system occurs with frequency (the lower figure is reproduced from Ref. [5]).

show that the dispersed LDH platelets remain more intensely coated by polymer in more polar matrix and the fracture of the composites takes place in less ductile manner (Fig. 3). The LDH platelets also show higher tendency to form agglomerates in LDPE matrix even in presence of compatibilizer. May be the formation of compatibilizer-particles rich regions restricts the homogenous distribution of LDH particles in the whole matrix. The primary purpose of adding a low molecular weight compatibilizer is to facilitate the fragmentation/delamination of LDH platelet clusters and improve their compatibility with main matrix. But, being of low molecular weight, it reduces the average molecular weight of the matrix and hence the viscosity. The effects of lowering of average molecular weight is distinctly visible in the high frequency region of $|\eta^*|$ vs. ω plot, where composites show lower viscosity than unfilled matrix. Therefore, to understand the actual effect of particle loading, the change in the slope of the $|\eta^*|$ vs. ω plot rather than change in the absolute value of viscosity is more helpful.

The extent of deviation from Newtonian flow behavior in low frequency regime with LDH loading can be semi-qualitatively related to the terminal slopes of the flow curves, commonly called shear thinning exponent (in complex viscosity vs. frequency plot) and relaxation exponent (in storage modulus vs. frequency plot). An ideal Newtonian liquid should have shear-thinning exponent equal to zero, as its viscosity is independent of shear rate or frequency. Many polymeric melts show such behaviors at low frequency, where log $|\eta^*|$ vs. log ω attains a plateau region, like unfilled polymers in Fig. 8. In case of conventional composites this low frequency Newtonian behavior is also observable even at high concentration of filler. For example, we have observed similar behavior in case of LDPE/$Mg(OH)_2$ composites containing 50 wt% of $Mg(OH)_2$ loading. However, in nanocomposites, as the shear thinning behaviors develops, the shear thinning exponent increases with increasing filler loading. Fig. 9 shows the variation of these exponents (determined by fitting the low frequency data to power law equations: $|\eta^*| \sim \omega^n$ and $G' \sim \omega^n$) with LDH concentration in HDPE-*g*-MAH/LDH and LDPE/LDH composites. Both the exponents change significantly with concentration of LDH at the beginning and then become nearly independent of LDH loading. Wagener et al. [12] have described shear-thinning exponent as a semi-quantitative measure of the degree of exfoliation/delamination of the clay layers in polymer nanocomposites. The higher the negative value of n, higher is the degree of exfoliation of the clay crystallites. The XRD and TEM results of LDH based nanocomposites show no enhancement of degree of exfoliation of LDH layers in composites with increasing LDH concentration. Therefore, the change in the shear-thinning exponent

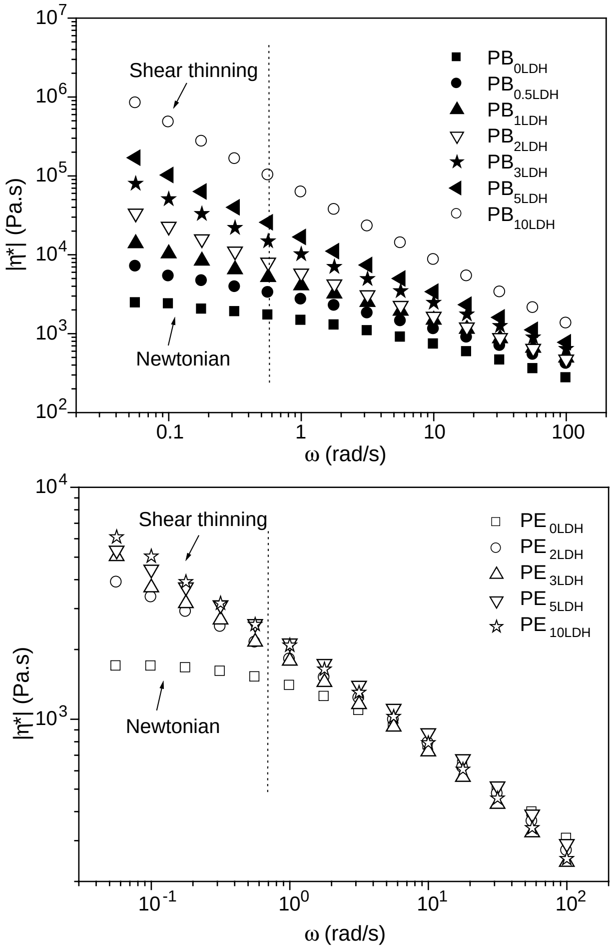

Fig. 8. Complex viscosity ($|\eta^*|$) vs. frequency (ω) curves (at 240 °C) for different nanocomposite samples showing the effects of LDH loading on flow behaviors in the low frequency regime.

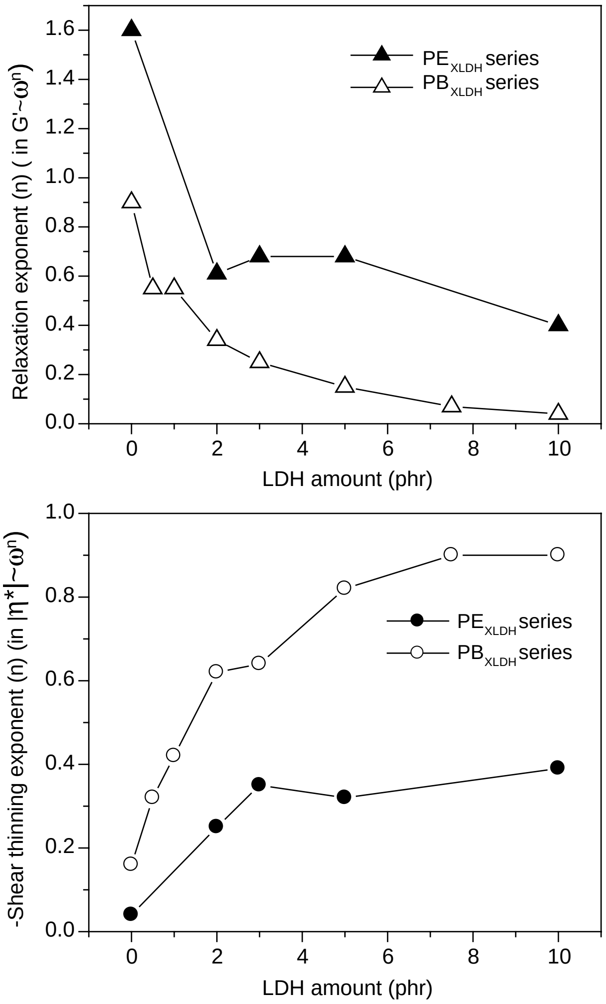

Fig. 9. Variation in the terminal slopes of the flow curves ($|\eta^*|$ vs. ω top and G' vs. ω, bottom) with LDH loading in nanocomposites. Trends in the slopes are clear indication of the deviation from Newtonian flow behavior to strong shear thinning flow behavior of the composites (slopes were calculated by fitting the low frequency data to power law model).

with LDH concentration as shown in Fig. 9 is not due to enhancement of degree of exfoliation. Rather, the increasing LDH concentration brings about two changes in the system, firstly, more number of polymer chains/segments get tethered on the LDH platelets surface or in the inter gallery space and secondly, the average distance between the dispersed platelets is decreased. These two factors contribute though different mechanisms to the final properties of the composites. The tethering of polymer chains on LDH platelets certainly restricts their mobility and hence delays their relaxation process. This effect is enhanced with increasing LDH loading. As a results G' increases and shows less dependency on frequency [13]. On the other hand, lowering of mean distance among the dispersed particles increases their tendency towards physical jamming or inter locking, which acts as an energy barrier against the relaxation of particle phase [6]. In the previous article, we have mentioned the tendency of the dispersed particles to form localised domains of oriented or physically correlated particles. Fig. 10 shows schematic presentation and practical examples of how LDH tactoids/platelets could interact with each other under application of oscillatory shear. With increasing LDH concentrations the tendency to form such localized network structure among the particles increases due to closer proximity of the particles augmented by their attractive interaction. The neat results of all these effects is the transition of the composite melt from liquid-like state to a pseudo solid-like state, which is reflected in the significant changes in the value of shear thinning exponent and relaxation exponent.

3.3. Response to non-linear shearing

Shearing in the linear viscoelastic regime (at low deformation) though exhibit time dependent behaviors of the melt, does not necessarily generate enough force to destroy the structural association among the dispersed particles. Whereas, during shearing in the non-linear flow regime (high deformation) not only does the microstructures of the dispersed phase take time to respond to the flow, but they also undergo time dependent changes by the action of shear force [14]. In polymer nanocomposites, the unusual rheological behaviors are often attributed to formation of physically interconnected network structure among the dispersed clay particles [6]. For the present system, though the continuous network structure

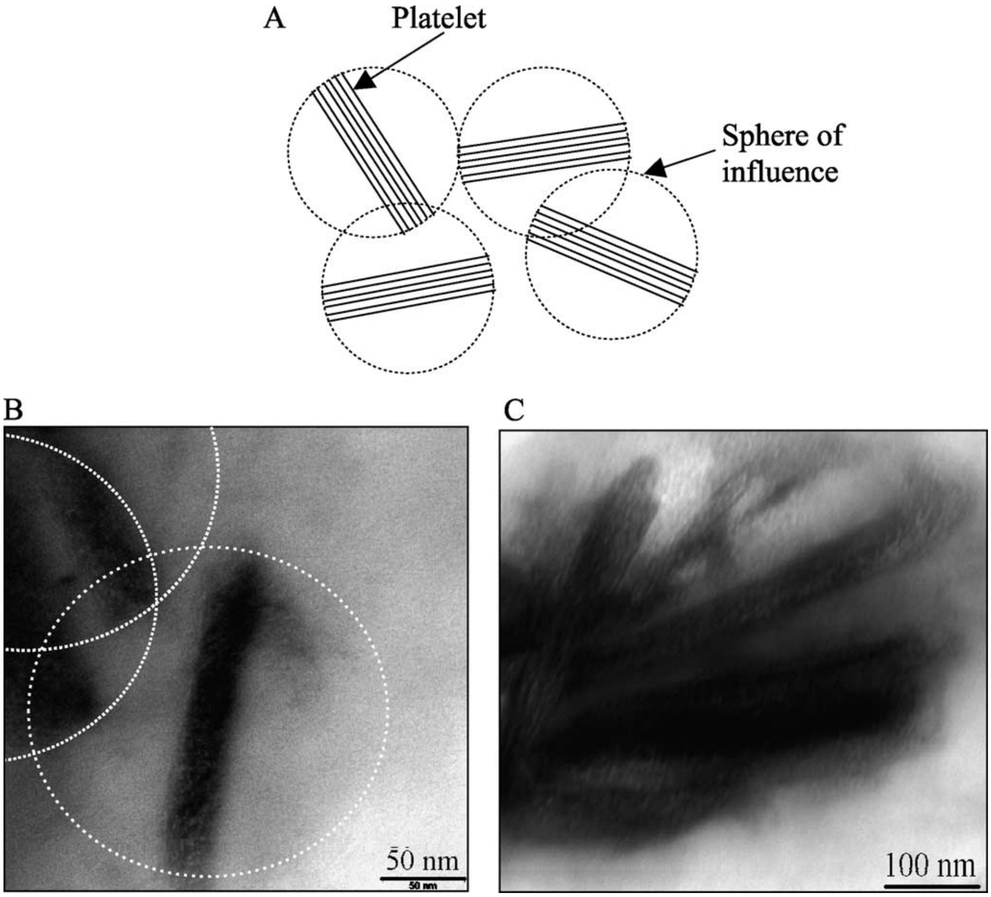

Fig. 10. Schematic representation (A) showing probable interaction of the closely associated LDH platelets. The TEM micrographs (B) and (C), respectively, of PE_{5LDH} and PE_{10LDH} showing localized orientation of the LDH platelets, which under oscillatory shear force may undergo frictional interactions.

among the dispersed LDH particles was not detected in the TEM micrographs, the presence of localized domains of agglomerated network structures formed by the dispersed particle fragments has been proposed [5] and is evident in Fig. 10. Understanding the kinetics of evolution of such structural associations under quiescent condition and their break down under steady shear could be very helpful in controlling the dispersion state of the clay particles during processing of polymer nanocomposites. To study this break down and regeneration processes associated with dispersed LDH phase in the present systems, the nanocomposite melts were first subjected to shearing at constant shear rate till steady state is reached and then the shearing was stopped for some time followed by reshearing (at the same shear rate, but in opposite direction). This type of step shearing has previously been employed to study similar effects in solutions of liquid crystalline polymers by Walker and co-workers [15] and later applied by others in case of polymer/layered silicate nanocomposites [6,16]. During the reshearing step, stress developed in the materials was monitored against time and the response of the two types of LDH based nanocomposites are shown in Fig. 11. It is apparent that a stress overshoot is observed at the start-up flow in all the composites when sufficient rest period is allowed. The height and the time of appearance of the stress overshoot peak depend on several factors, like duration of the rest period, concentration of LDH and perhaps the nature of interaction operating at phase interfaces. The appearance of this stress overshoot at the inception of flow is attributed to the presence of weakly agglomerated network structures among the dispersed particles [6], which are ruptured during first shearing step and reforms in the rest period followed after that. The subsequent decay of stress from the overshoot peak with time occurs due to breakdown of the aggregates till the ruptured particles are aligned in the direction flow to give steady viscosity of the melt. This cannot be explained by only in terms of viscoelastic nature of the filled composites. Rather a time dependent structural breakdown under constant shearing and regeneration at rest indicate the presence of thixotropic effect. Therefore, this behavior is interpreted as combined effect of viscoelastic nature of the matrix phase and the thixotropic break down and regeneration of microstructure associated with the dispersed phase and also with the macromolecules [14]. Though the unfilled polymer matrix under similar shearing did not show any significant stress overshoot, the influence of the molecular entanglement (more precisely entanglement density) cannot be neglected, especially in high molecular weight polymers. Such microstructure could also be the origin of thixotropic effects even in unfilled polymer melt under suitable shearing condition and time scale of measurements [14].

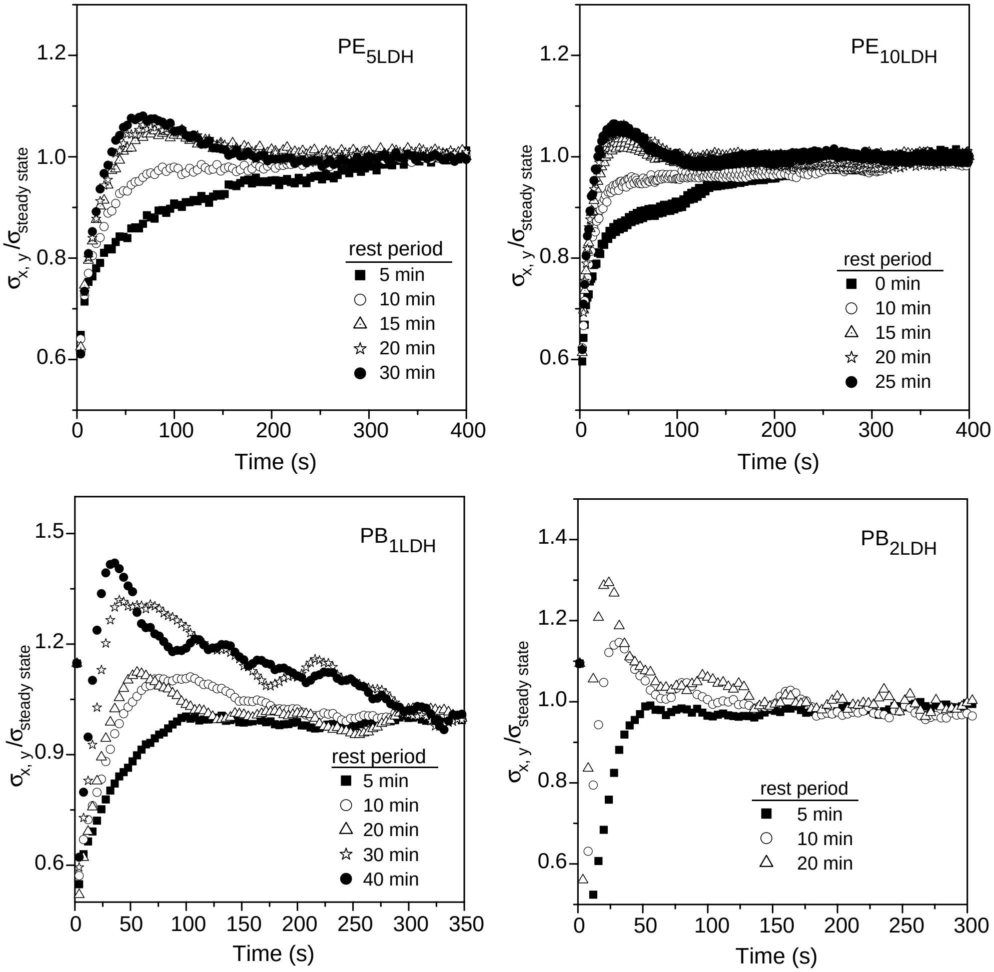

Fig. 11. Response to non-linear shearing of the LDH based nanocomposites showing the effects of particle–particle interaction and its kinetics.

The dependence of the height of the stress overshoot peak on the duration of the rest period gives us a notion that regeneration of structure is a time dependent process and longer this rest period greater is the extent of structure regeneration. The driving force behind this regeneration process is more likely the strong inter-particle attractive interaction coupled with thermodynamic incompatibility of the dispersed phase and the matrix polymer [6]. Since, these weakly agglomerated network structures are not destroyed during shearing in the linear viscoelastic regime, the regeneration of structure among the LDH particles could be monitored by observing the change in the storage modulus of the melt with time under the conditions of small frequency and strain amplitude. This is because the value of G' is very sensitive to the structure development in the dispersed phase [14]. Fig. 12 shows changes in the storage modulus with time over a 40-min rest period and subsequent response against steady shearing. It is apparent that G' increases steadily with time and does not reach steady state even after allowed time length. The effect of LDH loading is also very prominent. At higher loading, lower average distance among the dispersed particles makes regeneration process faster and more intensive. As a result, the rate of increase in G' is higher at higher LDH loading. The height of the stress shoot up peak depends on the net extent of the regenerated structure, i.e. the point in Fig. 12 (left column) where the rest condition is stopped and reshearing is started. Both the systems showed similar type of structure recovery during the rest period. However, as observed in case of oscillatory shear experiments within linear viscoelastic regime, the effects of low molecular weight compatibilizer in the compatibilized system are also visible here. When the particle network structure is destroyed by shearing and the polymer chain are aligned in the direction of flow, the low molecular weight fragments in the system deteriorates the elasticity of the matrix, i.e. G' falls. However, the influence of low molecular weight compatibilizer could be overcome at higher LDH concentration and after long rest period, which allows sufficient structural recovery. This is the situation with PE_{XLDH} system observed in Fig. 12.

The kinetics of breakdown and regeneration of structural agglomerates among a dispersed particles and also the stress over shoot behaviors in filled polymer system have been studied in details by many researchers in past [17–20]. In Leonov's model [17], it is stated that when stress is applied to such a system the particle aggregates accumulate energy till their critical strain energy is reached after which they undergo rupturing. This is manifested as stress overshoot at the start-up flows during a steady shear experiment. Lapasin and co-workers [21] have

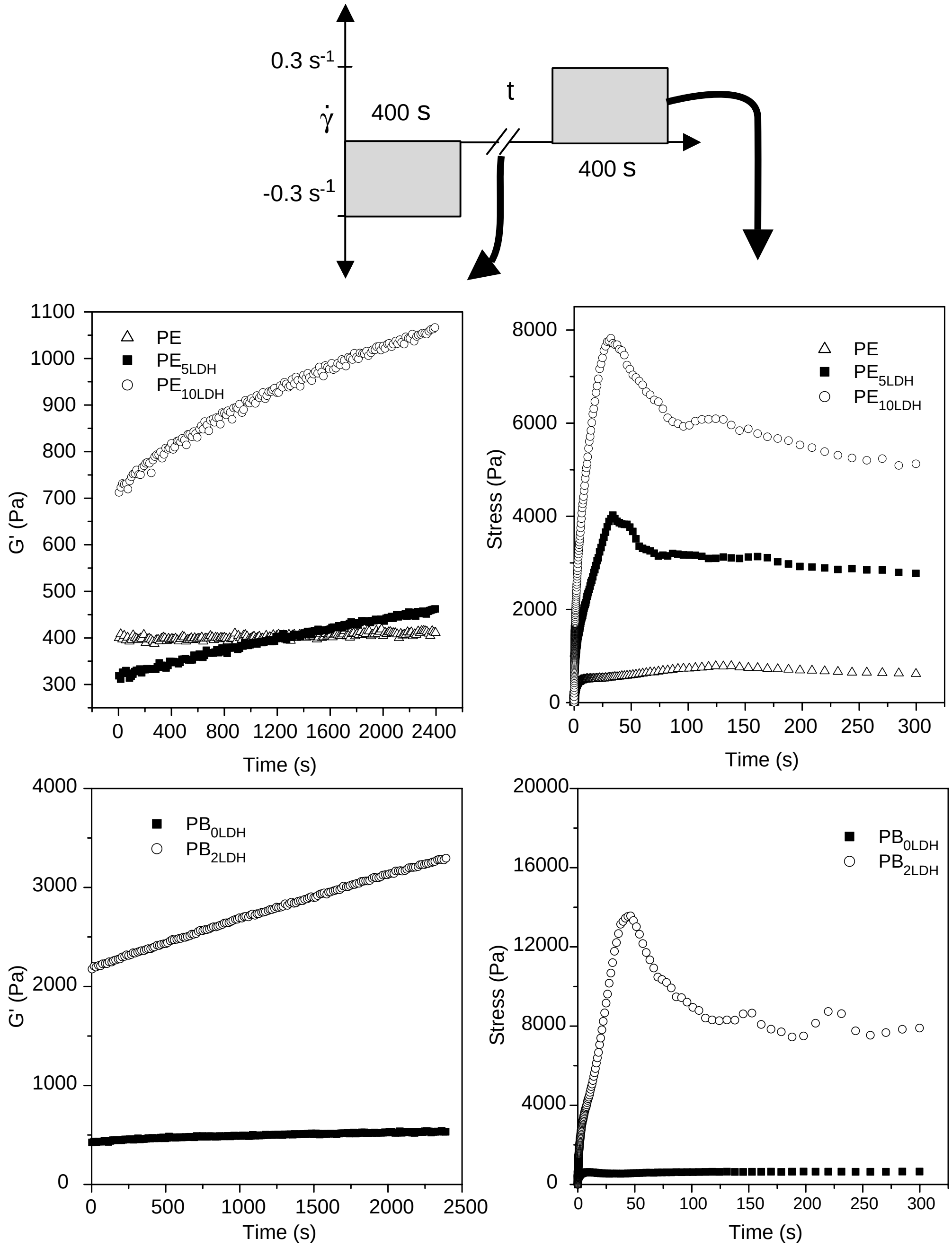

Fig. 12. The effect of structural regeneration of the dispersed LDH particles on the storage modulus (G') of the melt during the 'rest period' in the non-linear shearing experiment (left column: frequency 1 rad/s and strain 1%). Also shown (right column) is the subsequent response to the steady shearing applied after a rest period of 40 min (shear cycle has been shown top with $t=40$ min).

studied structural recovery in flocculated suspension of TiO_2 during rest period after initial phase of structure break down through steady shearing. They used oscillatory time sweep at low strain and low frequency to monitor the development of storage modulus during rest phase and observed the storage modulus of the suspension increased steadily with time. Recently, Lion and co-workers have introduced 'structure variable' concept in explaining the thixotropic recovery behavior observed in filled elastomers [18,20]. This so-called structure variable indicates phenomenological measure of current state of materials' microstructures and depends on deformation history of the material. They explained in terms of this 'structure variable' the strain induced breakage and recovery of weak physical bonds existing among the carbon black or silica clusters during deformation of filled elastomer. Originally, Lion et al. introduced the 'structure variable' concept for a quantitative physical explanation of the Payne effect that describes the strain amplitude dependence of the dynamic modulus of filled rubbers under periodical loads (for a review, see Refs. [22,23]).

We believe that the main reason for the stress overshoot shown by polyethylene/LDH based composites is the physical association of the dispersed LDH crystallites of various dimensions; more precisely, the interaction force present at the particle–particle interface. Such weak physical associations or the network-like structure act as the site for energy accumulation till the network rupture starts and hence a stress maximum is observed at the start-up flow during steady shear experiments. Therefore, it seems more logical, while describing stress overshoot phenomena in terms of model equations, to consider a physical parameter that gives a measure of current state of dispersed phase micro structures and is dependent on the shear history of the concerned material.

We finally note that we discussed very recently common features of structural filler reorganization in thermoplastic polymer nanocomposites and in filled elastomers using simple kinetic models of autonomous (but forced by restrictions) saturation in an aggregated growth process, which reflects the role of complexity and cooperative aggregation within the considered system [24].

4. Conclusion

Mg–Al based layered double hydroxides have properties that are typical of magnesium hydroxide and layered clay materials. Unlike conventional cationic clays, such as montmorilinite, the surface charge density of the hydroxide layers are very high, which makes large degree of exfoliation of the clay layers by polymer chains very difficult, if not practically impossible in thermodynamic sense. Suitable treatments of the pristine materials make them useful for nanocomposite synthesis with various polymer matrices. Also the method applied for such synthesis plays vital role in deciding the final state of particle dispersion in the matrix. Layered double hydroxide based polymer nanocomposites prepared by solution method show exfoliated nature of the dispersed particles [25–27]. The melt mixing method as we have employed to synthesis polyolefin–LDH based nanocomposites gives mostly intercalated or flocculated composites where LDH particles are dispersed mostly in the form of thin platelets. These platelets remains more intimately coated by the MAH grafted polyethylene matrix compared the unmodified polyethylene.

The rheological behaviors of LDH–polyethylene nanocomposites show marked influence of the nature of the polyethylene matrix, i.e. unmodified or MAH grafted. Though in unmodified polyethylene based composites a compatibilizer (low molecular weight MAH grafted polyethylene) was used, the effects of LDH loading on rheological properties were not as prominent as in case of MAH grafted polyethylene matrix based composites. From the XRD and SEM analysis, it is apparent that the primary particle structure in both the composites is thin platelets of LDH. But, polymer chains containing hanging polar groups, i.e. MAH grafted polyethylene, adhere to LDH particle surface more frequently and strongly than pure hydrocarbon chains. The possibility of chemical interaction between acidic MAH (also free some acid groups) and the basic LDH particles surface could also be a potential reason for such marked difference in rheological behaviors. However, to understand the exact nature of interaction with MAH grafted polyethylene and LDH particles more detail investigations are needed. The low frequency behaviors of the polyethylene/LDH nanocomposites are typical of polymer/layered silicate nanocomposites extensively reported in literatures. The rheological behaviors indicate the pseudo-solid like nature of the composite melt, which intensify with increasing LDH loading. The low frequency Newtonian flow behaviors of the unfilled polymers completely disappear when LDH loading is increased to 10 phr. Such characteristics are not observed in conventional polymer composites at similar loading of inorganic fillers. The differences in behaviors of the composites based on two chemically different matrices originate from the differences in the polymer–particle and particle interactions. Both these interactions influence the relaxation process that are operative in matrix phase as well as in particle phase during the oscillatory shear experiments. The low frequency plateau regions in the storage modulus vs. frequency plot means the incomplete polymer chain relaxation and this become more distinct with increasing LDH loading. In MAH grafted polyethylene based composites, the stronger interaction between the polymer and particles causes deviation from low frequency Newtonian behaviors at much lower LDH loading.

The non-linear shearing experiments show how the microstructures formed by the dispersed LDH particles respond to large deformation. This could be helpful, particularly in understanding how processing conditions influences the final properties of the composites. The breakdown and the recovery of these microstructures are the main processes that decide the stress developed in the melt during steady shearing. A thermodynamically more stable state of particle dispersion is achieved when the melt is allowed to stay at quiescent state for longer duration after shearing. This provides sufficient time for the self-reorganization of the ruptured and oriented LDH particles, which ultimately leads to the formation of network like structure, preferably in localized domains for the present systems. The attractive interaction among the LDH platelets possibly plays the major role for such particle phase reorganization and cause for the thixotropic behaviors of the composite melt. Krishnamoorti et al. [13] have suggested that the existence of such localized orientation among the primary structures of the dispersed particle are obvious in polymer/layered silicate nanocomposites showing apparent low frequency plateau regions in storage modulus vs. frequency plot.

In the case of nanocomposites of hybrid material of a thermoplastic melt and nanofillers our investigations lead to an improved understanding of the rheological and, hence, processing influences on the properties of the final composites. We demonstrated how results of measurements in the so-called non-linear viscoelastic domain are essential for understanding and predicting morphological changes during processing.

Acknowledgements

The authors thank Herr Andreas Janke for TEM experiments.

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