

Nanocomposites based on polyethylene and Mg–Al layered double hydroxide. I. Synthesis and characterization

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Available online 11 March 2005

Abstract

Low density polyethylene (LDPE)/Mg–Al layered double hydroxide (LDH) nanocomposites have been synthesized with different compositions by melt-mixing technique using maleic anhydride grafted polyethylene as compatibilizer. LDH has been modified by sodium dodecylbenzene sulfonate using reconstruction method and characterized by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The nanocomposites are characterized by different techniques such as, transmission electron microscopy (TEM), XRD and rheology. The TEM analysis shows a complex nature of particle dispersion in the polymer matrix with wide distribution of particles sizes and shapes. The rheological analysis showed significant changes in linear viscoelastic responses of the composites, even at very low concentration (2 phr) of LDH materials, in comparison to the pure polymer in low frequency regime in dynamic frequency sweep experiments. These changes are related to the LDHs-polymer chains interactions resulting in network-like structure.
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Keywords: Layered double hydroxide; Low density polyethylene; Nanocomposites

1. Introduction

The concept of nanoscale dispersion of additives, especially fillers, into polymer matrix has already been established as an effective method to obtain improved properties of the composites using minimum amount of the additives. Polymer nanocomposite, prepared using the same concept, is now a very popular class of hybrid materials because of their various unique properties [1] such as improved mechanical properties [1,2], gas barrier properties [1,3] and reduced flammability [1,4,5]. The polymer nanocomposites could be obtained by using two different types of additives, one with particle size in the nanometer range [6,7] and other with layered crystalline geometry. The prerequisite condition for using layered crystalline materials as nanofiller is their ability to undergo intercalation or exfoliation by polymer chains, which could be facilitated by suitable treatment prior to their incorporation into polymer matrix. So far, the majority of research works on polymer

nanocomposites based on layered materials have been focused on the materials of natural origin such as natural clays of various kinds, which are mostly cationic clays. Reports on polymer nanocomposites based on polyolefins and layered double hydroxides (LDH), so called hydro-talcite-like materials or synthetic clays, are still very rare.

The LDHs have similar geometrical structures as the natural clay minerals such as montmorillinite, but with opposite charge of the hydroxide layers. They could be represented by a general chemical formula $[M_{1-x}^{II}M_x^{III}(\text{OH})_2]^{x+}A_{x/n}\cdot m\text{H}_2\text{O}$, where M^{II} is divalent metal ion (like, Mg^{+2} , Zn^{+2} , etc.), M^{III} is trivalent metal ion (like, Al^{+3} , Cr^{+3} , etc.) and A is an anion with valency n (like CO_3^{-2} , Cl^- , etc.). The hydroxide layers of LDH have close similarity to the mineral brucite or $\text{Mg}(\text{OH})_2$, where some M^{II} ions of brucite layers are substituted by a trivalent cation yielding positively charged $[M_{1-x}^{II}M_x^{III}(\text{OH})_2]^{x+}$ layers (Fig. 1). These positively charged layers remain stacked in z direction with anions and the water molecules in the interlayer space [8,9]. The characteristic that makes LDH materials suitable for polymer nanocomposite synthesis is the exchangeable nature of the inter layer anions by suitable oligomeric or polymeric anion.

There are various methods by which LDH based polymer nanocomposites could be synthesized [10]. But all these

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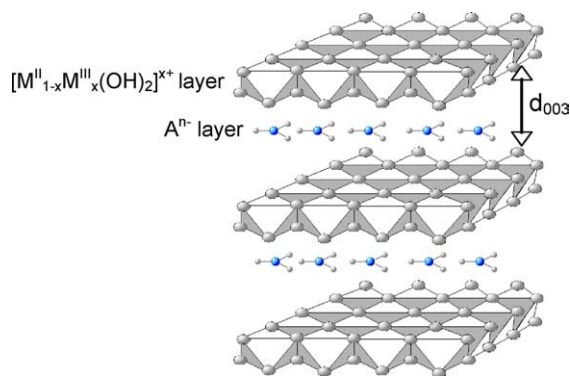


Fig. 1. Schematic representation of LDH crystal structure.

methods involve mostly solution intercalation process, for examples, in situ polymerization [10,11], direct intercalation in polymer solution [12,13] and so on. However, not much work has been reported yet on polymer-LDH nanocomposites synthesis using melt-intercalation technique. In the present paper, we report the synthesis and characterization of nanocomposites based on low-density polyethylene (LDPE) and Mg–Al layered double hydroxide prepared by melt-intercalation technique. The pristine LDH materials are not suitable for intercalation by large species like polymer chains because of the reasons that the inter gallery space is too short (about 7.6 Å) to allow polymer chains to penetrate in and the charged nature of the metal hydroxide layers makes them incompatible with non-polar species. In order to make such layered materials suitable for intercalation and ultimately exfoliation by polymer molecules, the inter layer regions should be made compatible and sufficiently large so that the polymer molecules either as a whole or its segments could penetrate there. Therefore, pristine LDH materials were treated with anionic surfactant sodium dodecylbenzene sulfonate (SDBS), which replaced the carbonate ion and water molecules in the interlayer regions [14]. There are several methods reported in literature for treatment of LDHs by anionic surfactants among which restacking or reconstruction method is the most common and effective one [15]. To improve the compatibility of LDPE within the inter layer space of LDH a compatibilizer, maleic anhydride grafted polyethylene was used.

The nanocomposites based on polymer interleaved LDH materials is a new emerging class of hybrid material and have been reported by researchers for their unique combination of properties [9,11]. The most remarkable of LDH materials in comparison to various natural clay minerals is their homogeneous composition, which allows compound designers to maintain the impurity level at minimum. Besides, the composition and hence the chemical nature of LDHs could be tailored during their synthesis by choosing suitable method and proper reactants ratio. The last, but not the least is their close similarity to magnesium hydroxide chemistry, which could project them as a

potential replacement of magnesium hydroxide in preparing environment friendly flame retardant composites with much reduced loading requirement and better dispersibility through polymer intercalation. In the present study, we report the synthesis of polyethylene/Mg–Al LDH based nanocomposites and their detail characterizations. A third component, maleic anhydride grafted polyethylene (MAH-g-PE) was used to facilitate the intercalation process of the layered inorganic material. The LDH to MAH-g-PE weight ratio was kept constant (1:2) in all the compositions. The rheological analysis is well known as a powerful tool to characterize polymer nanocomposite materials [16–20]. We studied rheological behaviors of our samples in the linear viscoelastic regime using oscillatory shear.

2. Experimental section

2.1. Materials

LDPE (density 0.9225 g/cm³, MFI 3.52 g/10 min) was purchased from Exxon Mobil, Belgium. Magnesium chloride (MgCl₂) (hexahydrated, 98% purity), urea (98% purity), sodium dodecylbenzene sulfonate (SDBS) and aluminum chloride (AlCl₃) (hexahydrated, 98% purity) were purchased from Aldrich chemical company. Maleic anhydride grafted polyethylene (MAH-g-PE) (density 0.926 g/cm³, MFI 32.0 g/10 min, maleic anhydride level is 1.0 wt%) was obtained from Crompton, USA.

2.2. Preparation of Mg–Al LDH

Mg–Al LDH was synthesized by urea hydrolysis method described by Costantino et al. [21]. An aqueous solution containing Al⁺³ and Mg⁺² with the molar fraction Al⁺³/(Al⁺³ + Mg⁺²) equal to 0.33 was prepared by dissolving AlCl₃ and MgCl₂ in distilled water. To this solution solid urea was added until the molar fraction urea/(Mg⁺² + Al⁺³) reached 3.3. The clear solution was refluxed for 36 h. The white precipitate was then filtered, washed until chloride free and dried in vacuum at 60 °C till constant weight.

2.3. Treatment of LDH by anionic surfactant

LDH was calcined in a muffle furnace at 450 °C for about 3 h to convert it into metal oxide (CLDH). The calcined product was dispersed in 0.1 M aqueous solution of SDBS with solid/solution ratio 1 g/50 cm³ and the dispersion was stirred by magnetic stirrer for 24 h at 25 °C. The regenerated SDBS intercalated LDH (SDBS-LDH) was then filtered out followed by drying in vacuum at 60 °C.

2.4. Preparation of LDPE–LDH composites

The LDPE–LDH composites we prepared in two steps

using a Haake lab mixer (50 cm³) at 200 °C and 100 rpm rotor speed.

Step 1. Preparation of master batch: SDBS intercalated LDH was mixed with MAH-g-PE in a weight proportion 1:2 for 6 min to prepare a master batch of filler in compatibilizer.

Step 2. Preparation of composites: master batch of MAH-g-PE and LDH was added to molten LDPE and mixed for 6 min.

This provided similar relative proportions of LDH and MAH-g-PE in all the compositions. The compositions of different composites prepared are given in details in Table 1.

2.5. Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectra for pristine LDH, its calcined and SDBS treated form were recorded over the wave number range 400–4000 cm⁻¹ using Bruker IFS 66v/s FTIR spectrometer. The powdered samples were mixed with KBR and pressed in the form of pellets for measurement.

2.6. X-ray diffraction (XRD) analysis

X-ray diffraction analysis (XRD) over $2\theta = 1.8\text{--}40^\circ$, 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.

2.7. Rheological analysis

The melt rheological properties of the material were determined using an ARES-rheometer (Rheometrics Scientific, USA). In this work the measurements were performed

Table 1
Formulations of the LDPE–LDH composites

Sample designation	LDPE (phr)	MAH-g-PE ^a (phr)	SDBS-LDH ^b (phr)
PE ₂ LDH	96	4	2
PE ₃ LDH	94	6	3
PE ₅ LDH	90	10	5
PE ₁₀ LDH	80	20	10

^a Maleic anhydride grafted polyethylene.

^b Mg–Al LDH treated with SDBS phr: parts/100 rubber (same as used in elastomer compounding).

in the dynamic mode and 25 mm parallel plates geometry with gap settings about 2 mm under nitrogen atmosphere. The strain amplitude was kept 2% in the whole frequency range to ensure viscoelastic linearity. The temperature was varied from 160 to 240 °C as a function of the angular frequency, ω . The frequency is varied between 100 and 0.056 rad/s.

2.8. Transmission electron microscopy (TEM)

The state of aggregation of the LDH particles in polyethylene matrix was investigated by TEM, which was carried out at room temperature using transmission electron microscope Zeiss EM 912 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.

3. Results and discussion

3.1. Synthesis of Mg–Al LDH and its treatment

The XRD spectrum (Fig. 2) of synthesized Mg–Al LDH shows that the synthesized material has highly crystalline nature and layered geometry [21]. The position of the basal peak (003) indicates that the distance between two adjacent metal hydroxide sheets (d_{003} in Fig. 1) is about 0.76 nm. With such small interlayer distance, it becomes necessary to modify the pristine materials so that the crystal layers are moved apart and penetration of polymeric chains becomes less difficult. The rehydration method for intercalating LDH materials with large molecules was pioneered in late 1980s [22]. This method is based on the principle that the calcined LDH (which are mostly mixed metal oxides) regenerates the crystalline structure of the original materials when dispersed in an aqueous solution of suitable anion under ambient conditions. The synthesized Mg–Al LDH also forms

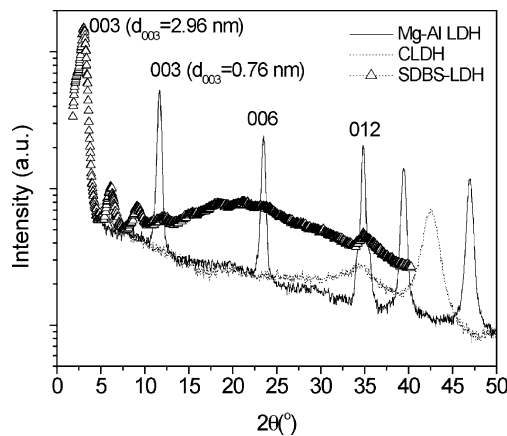


Fig. 2. XRD spectra of Mg–Al LDH, its calcined product (CLDH) and SDBS treated form (SDBS-LDH).

amorphous metal oxide on calcination (apparent from Fig. 2 [23]) at 450 °C for over 3 h. We confirmed that the calcined Mg–Al LDH (CLDH) regenerates the original structure by dispersing CLDH in to an aqueous solution of sodium bicarbonates. The XRD spectra of regenerated material virtually overlapped with that of Mg–Al LDH in Fig. 2. When such dispersion is made in a solution containing SDBS, it is entrapped between the $[M_{1-x}^{II}M_x^{III}(\text{OH})_2]^{x+}$ layers during regeneration process. As a result, the position of the basal peak in the XRD spectrum shifts to lower value of 2θ (Fig. 2). This results in an enlargement of interlayer distance from 0.76 to 2.96 nm. The analysis of the FTIR spectra (Fig. 3) of Mg–Al LDH reveals the presence of interlayer carbonate ions (1356 cm^{-1}) and water molecules (the broad band in the range $3150\text{--}3600\text{ cm}^{-1}$). The hydrogen bonding in the interlayer region between water molecules and the hydroxide sheet is evident from the shoulder at $3050\text{--}3100\text{ cm}^{-1}$ in Mg–Al LDH spectrum. In CLDH the loss of interlayer, carbonate anions and water molecules results disappearance or weakening of the corresponding peaks in FTIR spectrum of CLDH. The weak and broad peak around 3400 cm^{-1} in CLDH spectrum might be due to some adsorbed water molecules on the surface of CLDH. In the SDBS treated LDH, recovery of the O–H stretching vibration peak takes place without accompanying shoulder as in the original Mg–Al LDH. The recovery of the carbonate peak (1356 cm^{-1}) does not take place indicating the absence of carbonate ions in the interlayer region. In the spectrum of SDBS-LDH the CH_2 stretching peaks ($2850\text{--}3000\text{ cm}^{-1}$) and characteristic S–O stretching peaks ($1040\text{--}1198\text{ cm}^{-1}$) are distinctly visible. Therefore, from the analysis of Figs. 2 and 3 it can be concluded that the SDBS treatment of Mg–Al LDH materials through rehydration method provides SDBS intercalated layered materials with large interlayer separation.

3.2. XRD and TEM analysis of LDPE–LDH composites

The XRD analysis is used as a very useful method to describe the extent of intercalation and exfoliation of the nanofiller having layered structure. The complete or high degree of exfoliation of layered crystalline filler in polymer matrix certainly means disappearance of corresponding peaks from the XRD spectra of the composites. However, the reverse may not be true always, because the disappearance of peaks from the XRD spectrum could be caused by several reasons, for examples, extremely low concentration of the filler in the regions, where X-ray beams scan the materials or loss of symmetry in certain crystallographic direction. The XRD analysis of our LDPE–LDH composites shows no significant change in the position of the basal peak. But, all the peaks become broader and surprisingly the higher order peaks either disappear or become extremely weak (Fig. 4). Therefore, it is apparent that the short range ordering of the LDH crystals is preserved and the exfoliation process is not complete. The TEM analysis also supports this observation.

TEM analysis of the composites reveals a very complex nature of the morphology of the dispersed LDH particles, which vary widely in sizes and shapes. The distribution of the particles in the LDPE matrix appears inhomogeneous as shown in Fig. 5(a). However, the higher magnification TEM images show diffused nature of these particles (Fig. 5(b)). Though the XRD results do not give us any concrete information about the exfoliation the LDH particles in the LDPE/LDPE-g-MAH matrix, the TEM images, like Fig. 5(c) and (d), show that their occurs detachment of tiny clusters from the surface of the LDH particles and their dispersion into the neighboring polymer matrix. The detection of single LDH layers was not possible in these TEM images, may be because of the resolution limit of the instrument (the thickness of single metal hydroxide layers of LDH ranges from 4.8–4.9 Å) or the absence high degree of

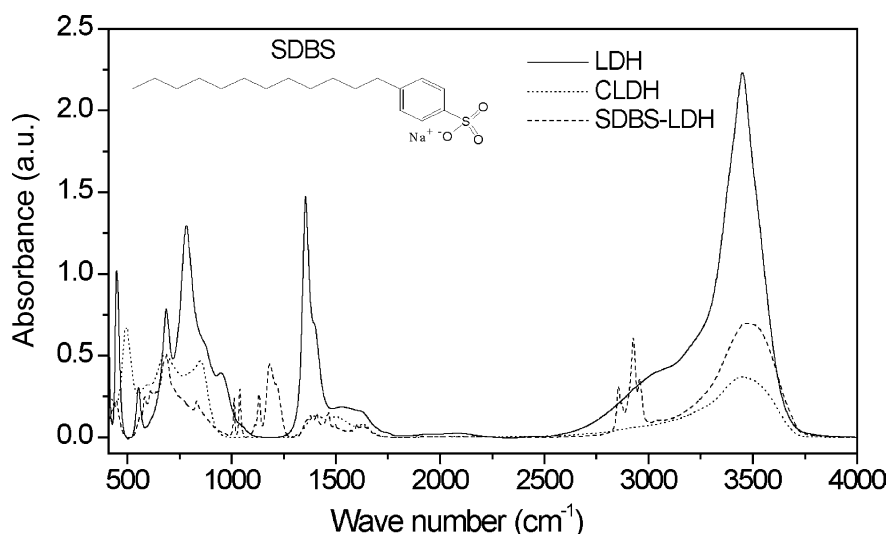


Fig. 3. FTIR spectra of Mg–Al LDH, its calcined form CLDH and SDBS-LDH.

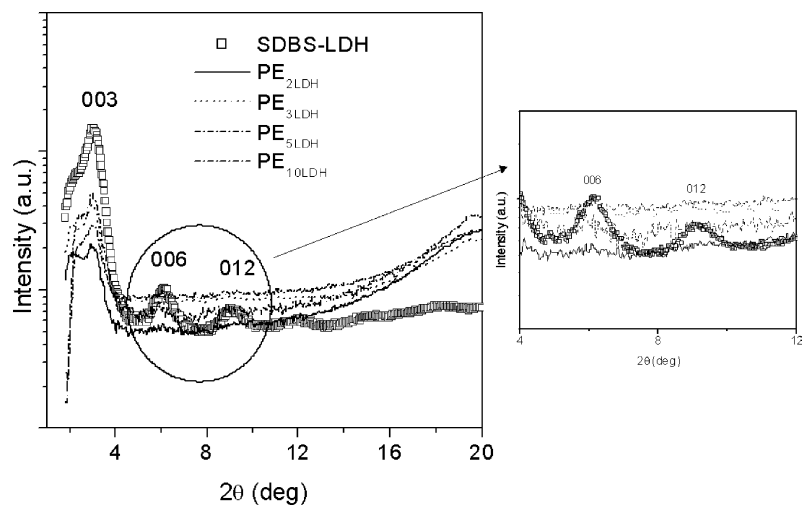


Fig. 4. XRD spectra of LDPE-LDH composites (higher order peaks either weakened or disappear in the composites).

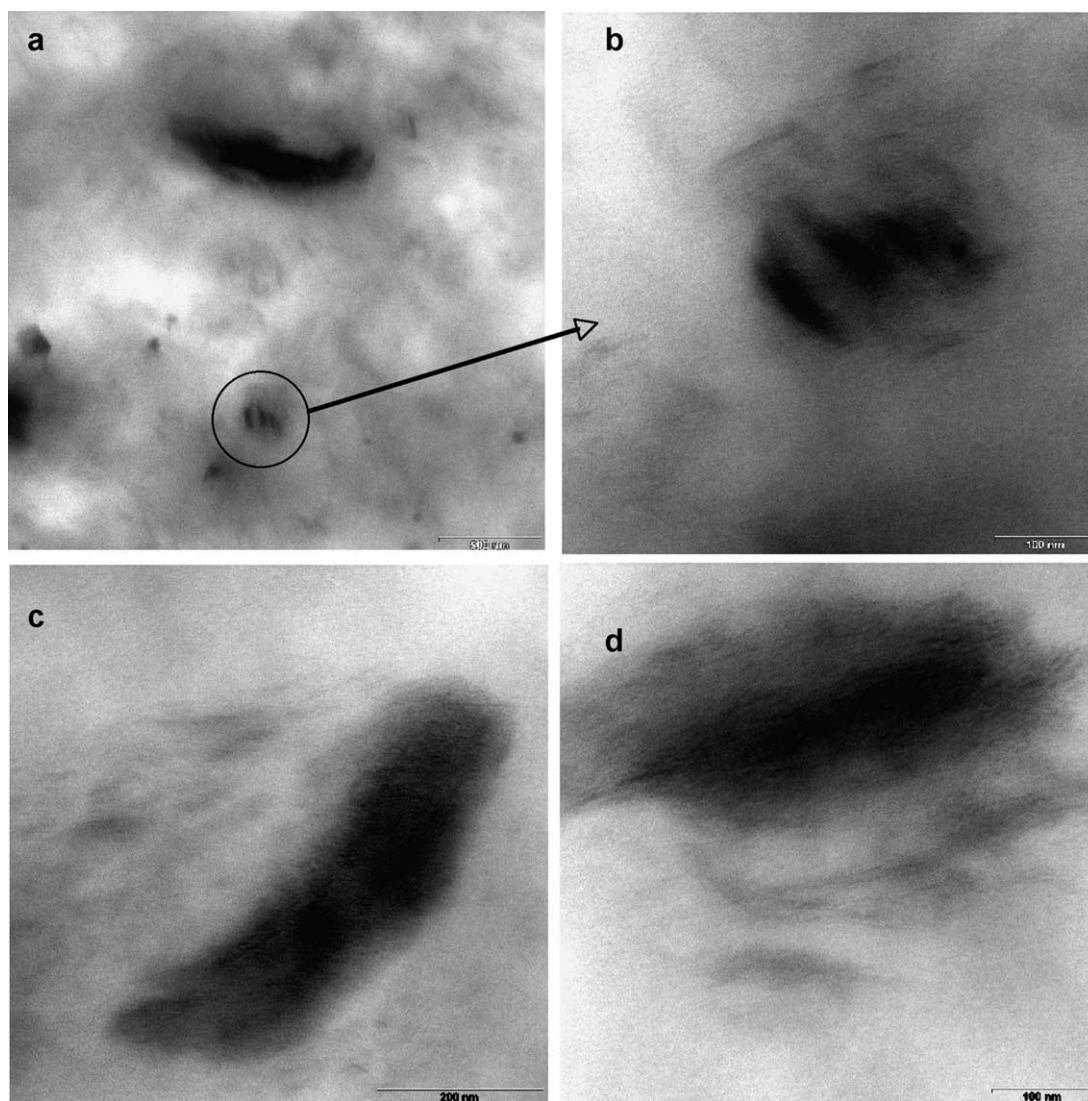


Fig. 5. TEM images of LDPE_{10LDH} showing nature of dispersion of LDH particles in LDPE/LDPE-g-MAH matrix (magnification bar: *a* = 500 nm, *b* = 100 nm, *c* = 200 nm and *d* = 100 nm). The white arrow heads indicate the different size of the particle clusters.

exfoliation that gives high concentration of exfoliated clay layers in the matrix. However, the dark regions in the vicinity of such diffused LDH particles is certainly caused by very fine dimensions of these detached particle segments. The intercalated nature of the big LDH particles is also apparent from the TEM images (Fig. 6). Such particles will always show poor long-range symmetry in crystallographic sense and hence explain the weakening or disappearance of higher order peaks in the XRD spectra. In summary, it could be said that the morphological features of the dispersed LDH particles is composed of hierarchy of particles geometry including the regions containing large agglomerates as well as nanoscale dispersion of particle segments. The uneven distribution of LDH particles between regions with higher and lower concentrations of compatibilizer molecules might be a cause of the coexistence of different natures of particle geometry in the composite matrix. The compatibilizer, MAH-g-PE, is chemically more compatible with LDH materials and more efficient than non-polar highly branched polyethylene chains to cause detachment of layers from the LDH particles surface.

3.3. Rheological studies of LDPE–LDH nanocomposites

The presented data were measured at 240 °C only as to display the effects of incorporation of LDH into LDPE. We found similar results for all the measured temperatures (160–240 °C).

Storage modulus, G' , of LDPE and the LDPE–LDH composites is logarithmically plotted as a function of angular frequency in Fig. 7. This figure shows that the values of G' of the composites are higher than those of the neat LDPE. In particular at low frequencies, the difference is significant and their values are found to increase—within the experiments range—with increasing the LDH loadings.

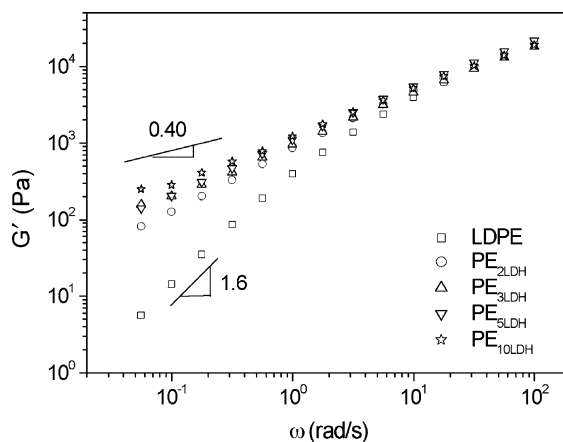


Fig. 7. Comparison of storage modulus of LDPE–LDH composites and pure LDPE at 240 °C.

The slopes of the $\log G'$ vs. $\log \omega$ plot in the low frequency regime were estimated for all the samples, and it was found that they decrease significantly with LDH loading, from 1.6 for neat LDPE to 0.4 for composite containing 10 phr LDH. These observations resemble typical polymer/clay nanocomposite systems extensively reported in literature [18,24] and are related to the formation of the network like structure via the interaction between the LDH layers and polymer chains.

The effects of LDH loading can be more clearly understood from the dependence of the complex viscosity, $|\eta^*|$, and loss factor, $(\tan \delta = G''/G')$, measured at low dynamic frequency on the level of LDH as shown in Fig. 8. It is evident that starting from 2 phr loading, significant differences in the melt rheological behaviors of the composite are observed and the complex viscosity of the melt increases by a factor of 2. The value of $\tan \delta$ above this level of LDH becomes nearly independent of the LDH amount due to the development of the elasticity.

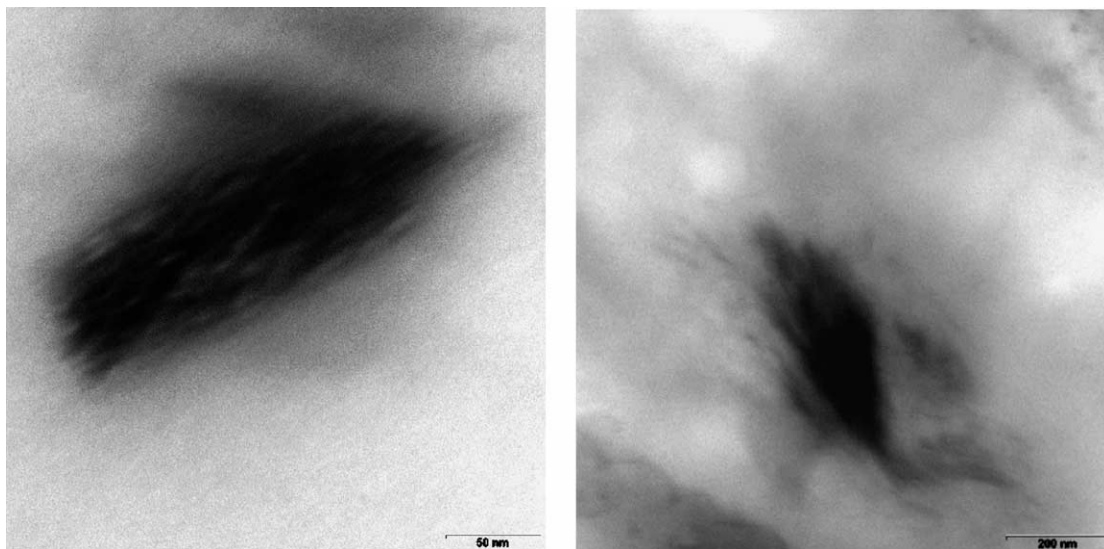


Fig. 6. TEM images of single LDH particles in LDPE–LDH composites showing their intercalated nature (magnification bar: left = 50 nm and right = 200 nm).

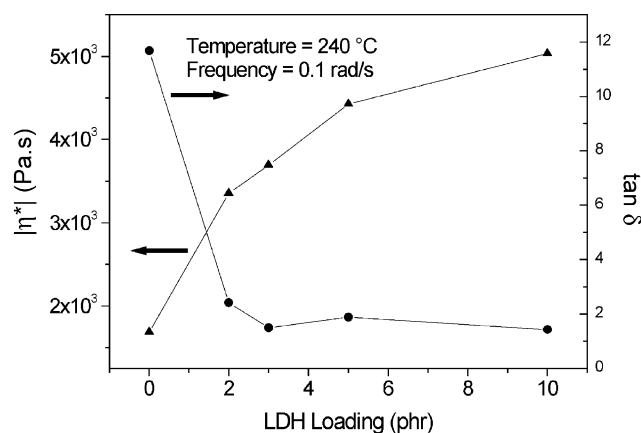


Fig. 8. Variation of complex viscosity and $\tan \delta$ at low frequency with LDH loading in LDPE-LDH composites.

4. Conclusion

The achievement of high degree of exfoliation of layered crystalline materials in non-polar polymer matrix, such as polyethylene, polypropylene, is a major issue to the material scientists. The chemical incompatibility between these two components hinders the separation and the dispersion of the individual clay layers. As a result, occurrence of particulate agglomerates, intercalated and swollen particles is often associated with the morphology of such composites. We have experienced the similar situation in LDPE-LDH composites. Though a good dispersion of the LDH particles is not evident from the TEM analysis of the composites, the highly diffused nature of large particles, especially in their surface regions, shows their ability to undergo layer separation process in a non-polar matrix. The rheological analysis showed significant changes in linear viscoelastic responses of the composites in comparison to the pure polymer in low frequency regime in dynamic frequency sweep experiments. These changes were observed even at very low concentration (2 phr) of LDH materials. The liquid–solid-like transition behaviors of these composites resemble the systems having gelation features or 3-D network like structures of the dispersed particles. But, the inhomogeneous distribution of the dispersed particles does not support the formation of a continuous or an infinite network structure among them. Rather, existence of localized domains of finely dispersed particles or particle segments could be the potential cause of pseudo- solid like viscoelastic behaviors of the composites in low frequency region [24]. Such structures should be considered rather as finite sub network structures of fillers (see, for example [25]) instead of an infinite network structure, which arises at the critical sol gel transition during polymer network formation.

The primary focus of the present investigation was to explore the potential of LDH materials as a nano filler and

improvement of dispersion of metal hydroxide type minerals in non-polar polymer. We have observed that it is indeed possible. In drawing a more vivid picture of composite morphology, microscopic analysis alone is not sufficient as it represents only an extremely small region of the whole system and should be coupled with other techniques, like rheological investigation of the system. The detail rheological characterizations and their relation with microstructure of the present system are the interests of the authors and will be the subject of the future communication.

Acknowledgements

The authors thank Mr Andreas Janke for carrying out TEM analysis of the samples.

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