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LDH as Nanofiller: Organic Modification and Dispersion in Polymers

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Summary: Layered double hydroxide (LDH) is a relatively new class of layered crystalline clay materials to be used as nanofiller in various polymer matrices. We report here the organic modification of LDH by anionic surfactants having different sizes and functionalities. Subsequently, their dispersion in polymer is discussed and finally the characteristics of the polymer/LDH nanocomposites are investigated. LDH has been modified using regeneration method, which shows that irrespective of size and functionality of the anionic surfactant, organic modification can be carried out efficiently. However, it has been observed that alkyl sulfonate are more efficiently intercalated within LDH layers than other surfactants giving well defined crystal structure of the modified LDH. These modified LDH, when dispersed in polymers like maleic anhydride grafted polyethylene shows that not only the size of the surfactant, but also the functionality of the surfactant influences their dispersion in a non polar polymer matrix.

Keywords: layered double hydroxide; nanoclay; nanocomposites; regeneration method

Introduction

In recent years, layered double hydroxide (LDH) has drawn a considerable attention as novel nanofiller in the area of polymer nanocomposites.[1–3] The major advantages of LDH in comparison to layered silicates as nanofiller are as follows: (i) its ability to intercalate large variety of anionic and inorganic anionic species, (ii) metal hydroxide (like $Mg(OH)_2$ and $Al(OH)_3$) type thermal decomposition behavior, (iii) simple synthesis procedure, (iv) homogenous composition, etc.[4,5] However, like layered silicates LDH also needs to be organically modified first to form suitable organo-clay precursor for the preparation of polymer nanocomposites, especially when melt-compounding technique is used. Though the main purposes of these organic modifiers are to enlarge the interlayer distance (d-value) of the pristine clay and to render the clay more organophillic, they also influence the thermal stability and also the total organic content of the modified clay, which in turn influences the final properties of the polymer/clay based nanocomposites.[4] A high degree of intercalation and large size of the organic modifier increase the organic content of the modified clay excessively. As it is the inorganic fraction of the modified clay that contributes to the reinforcement, barrier properties, flame-retardancy, etc of the nanocomposites, such high organic contents may often be deleterious to many final properties. Therefore, it is always desirable to obtain an optimum organic content and the optimum d-value in the modified clay that would be sufficient to provide nanoscale dispersion of the clay into a polymer matrix. The d-value of the organo clay depends on the size of the organic intercalant and how it is organized in the interlayer space. In the present study, we investigate the influence of different anionic surfactants (based on their size and the functionality) on the intercalation behavior of LDH and also the

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dispersion of the organically modified LDH (O-LDH) in polymer.

Materials and Method

Materials and Modification of LDH

The raw materials for the synthesis of Mg-Al LDH were magnesium chloride, aluminum chloride and urea, which were purchased from Sigma-Aldrich. The alkyl sulfonates containing various alkyl chain lengths (C6 to C18), sodium dodecylbenzene sulfonate, bis(2-ethylhexyl)phosphate (BEHP), lauric acid were also purchased from Sigma-Aldrich. All the chemicals were used without further purification.

The synthesis of LDH was carried out by urea hydrolysis method and the synthesized LDHs were modified by regeneration method, which is based on its 'memory effect'. Both these experimental steps are described in details in our previous publications.[4,5]

Synthesis of PE-g-MAH/O-LDH Nanocomposites

The nanocomposites based on organically modified LDH (O-LDH) and maleic anhydride grafted polyethylene (PE-g-MAH) were synthesized by melt compounding using a corotating twin-screw microextruder (15-mL microcompounder, DSM Xplore, Geleen, The Netherlands). The conditions used for melt-compounding steps were 190 °C with 200 rpm screw speed for 10 min. The concentrations of O-LDH in the nanocomposites were determined based on an approximate metal hydroxide content of the filler and kept 5.0 wt% for different O-LDH.

Characterization of O-LDH and the Nanocomposites

Wide angle X-ray scattering (WAXS) of the powdered LDH materials were carried out with a θ/θ instrument (XRD 3003 θ/θ) from Seifert-FPM Freiberg, Germany using Cu-Kα radiation ($\lambda \sim 0.154$ nm) and monochromatisation by primary multilayer system, with a step size of 0.05° and 15 s measuring time for each point. The d-value in the LDH materials was calculated using Bragg's equation and was averaged over the first four orders of diffraction.

The morphological analysis was carried out using transmission electron microscopy (TEM) with microscope LEO 912. The conditions used during analysis were room temperature, 120 kV acceleration voltage and bright field illumination. The ultra thin sections of the samples were prepared by ultramicrotomy at −120 °C with a thickness of a section 80 nm.

The rheological analysis was carried on an ARES rheometer (Rheometrics Scientific, USA) with torque transducers having range of measurement from 0.02 to 2000 g.cm and parallel plate geometry with 25 mm plate diameter and a sample thickness of 2 mm was used.

Results and Discussion

WAXS Analysis of the O-LDH

LDH containing Mg and Al as the metal ions was modified with wide range of anionic surfactants and the efficiency of the modification process and the crystallinity of the modified LDHs (O-LDH) were analyzed by WAXS method. Figure 1 show the WAXS patterns of three batches of organo-LDHs, the first batch being modified with alkyl sulfonates having different chain lengths (Figure 1a), the second one with carboxylic acid having different chain lengths (Figure 1b) and the third one with surfactant having different functionalities (Figure 1c).

Figure 1a and 1b shows the influence of the chain length of the anionic surfactant on the crystallinity of the organo-LDH and also the efficiency of organic modification. It is apparent that alkyl sulfonates are very efficient surfactants, which provides much more ordered structure (basal reflection up to several orders can be detected in the WAXS pattern) than the carboxylates. The interlayer distance increases with increasing alkyl chain length of the surfactants and corresponds to monolayer packing of the

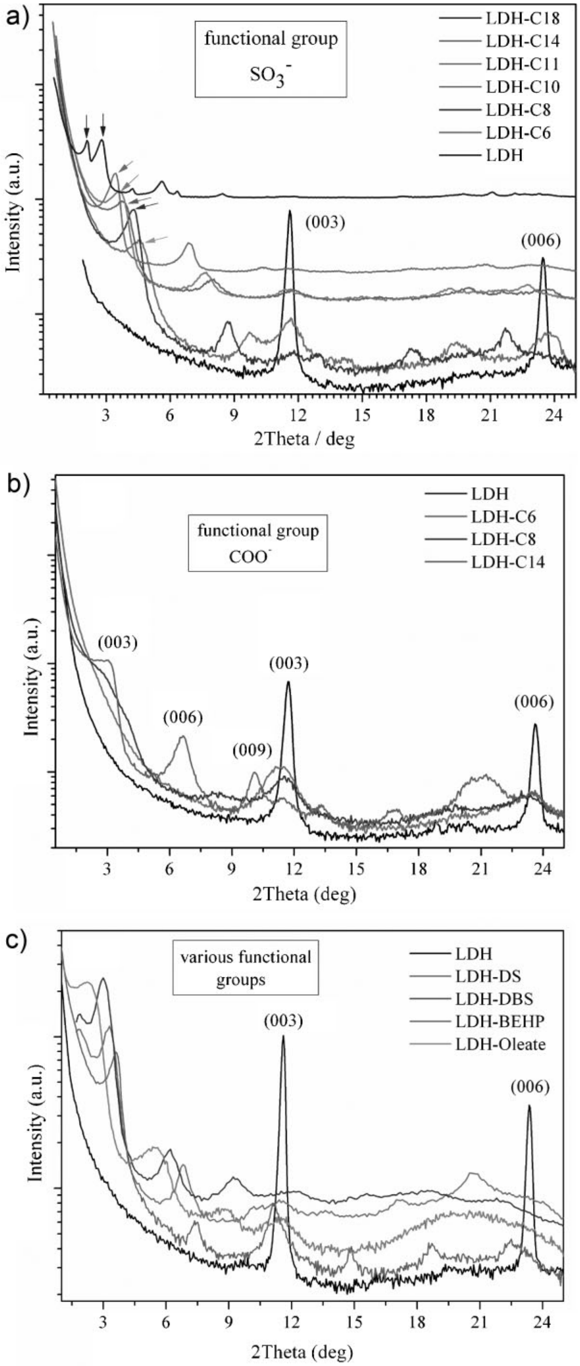

Figure 1.
WAXS analysis of the organically modified LDH by various surfactants: (a) surfactants are alkyl sulfonate with different chain length, (b) carboxylate with different chain length and (c) surfactant with different functionalities.

Table 1.
Interlayer spacing (d-value) averaged over first three order of reflection in the WAXS pattern of each LDH samples

No of C in RSO_3^-	d-value of O-LDH	No of C in RCO_2^-	d-value of O-LDH	Surfactant with different functional group	d-value of O-LDH
	nm		nm		nm
0	0.77	0	0.77	DS	2.63
6	1.85	6**	–	DBS	2.89
8	2.03	8**	–	BEHP	2.41
10	2.24	14	2.64	Oleate	3.39
11	2.35				
14	2.57				
18	3.15				
18*	4.16				

*The WAXS pattern of C-18 sulfonate modified LDH shows two-phase morphology with two distinct set of (00l) reflection.**These reflection were so broad that any approximation in calculating d-values is not possible.

anion in the interlayer space (Table 1). Only exception was observed in case of C-18 alkyl sulfonate modified LDH, where the WAXS pattern shows the presence of two-phase morphology characterized by their respective (00I) reflections and d-values. However, in case of carboxylates having smaller tail lengths, organic modification by regeneration method is not very efficient and not very well crystallized materials are obtained along with large fraction of the unmodified LDH. Figure 1c shows the influence of anionic functional group of the surfactants on the modification process. Once again, it is apparent that LDH can be effectively modified with different anionic surfactants, like sulfonates, sulphates, phosphates and carboxylates, while carboxylate being the most difficult among the surfactants used in this study. This means that LDH is highly flexible as nanofiller to be modified with organic species, which is its clear advantage over layered silicate based nanofillers. The regeneration method though very effective always produces a non homogeneous product containing a mixer of O-LDH and small fraction of unmodified LDH. This is also reflected in the WAXS patterns where the first basal reflection of the unmodified LDH can be detected in all the samples. Additionally, this method causes some irreversible changes in the crystal structure.[6] However, recently we have reported a new method called ‘single-step self assembling method’ to synthesize homogenous and more crystalline O-LDH.[7]

Morphological Analysis of PE-g-MAH/O-LDH Nanocomposites

The morphological analysis of PE-g-MAH/O-LDH nanocomposites shows strong influence of the organic modifier on the dispersion of the O-LDH in PE-g-MAH matrix. This influence can be classified into two categories: one is the influence of the size of the surfactants, which is somewhat indirect effect as explained later and the second is the influence of the functional group. For assessing the size of the surfactant O-LDH containing alkyl sulfonates were used as the nanofiller and the WAXS analysis of the nanocomposites are shown in Figure 2.

With the increasing size of the organic modifier, the d-value of the O-LDH also increases. For a given surfactant, the ease of exfoliation of the O-LDH increases with increasing d-value. This is what we have observed in case of PE-g-MAH/O-LDH nanocomposites. When the d-value is small in O-LDH (LDH modified with C6 alkyl sulfonate giving a d-value of 1.94 nm) most of the O-LDH particles are dispersed as micro particles and as aggregates. The WAXS patterns show no change in the position of the basal reflection of the O-LDH in the nanocomposites (Figure 2a).

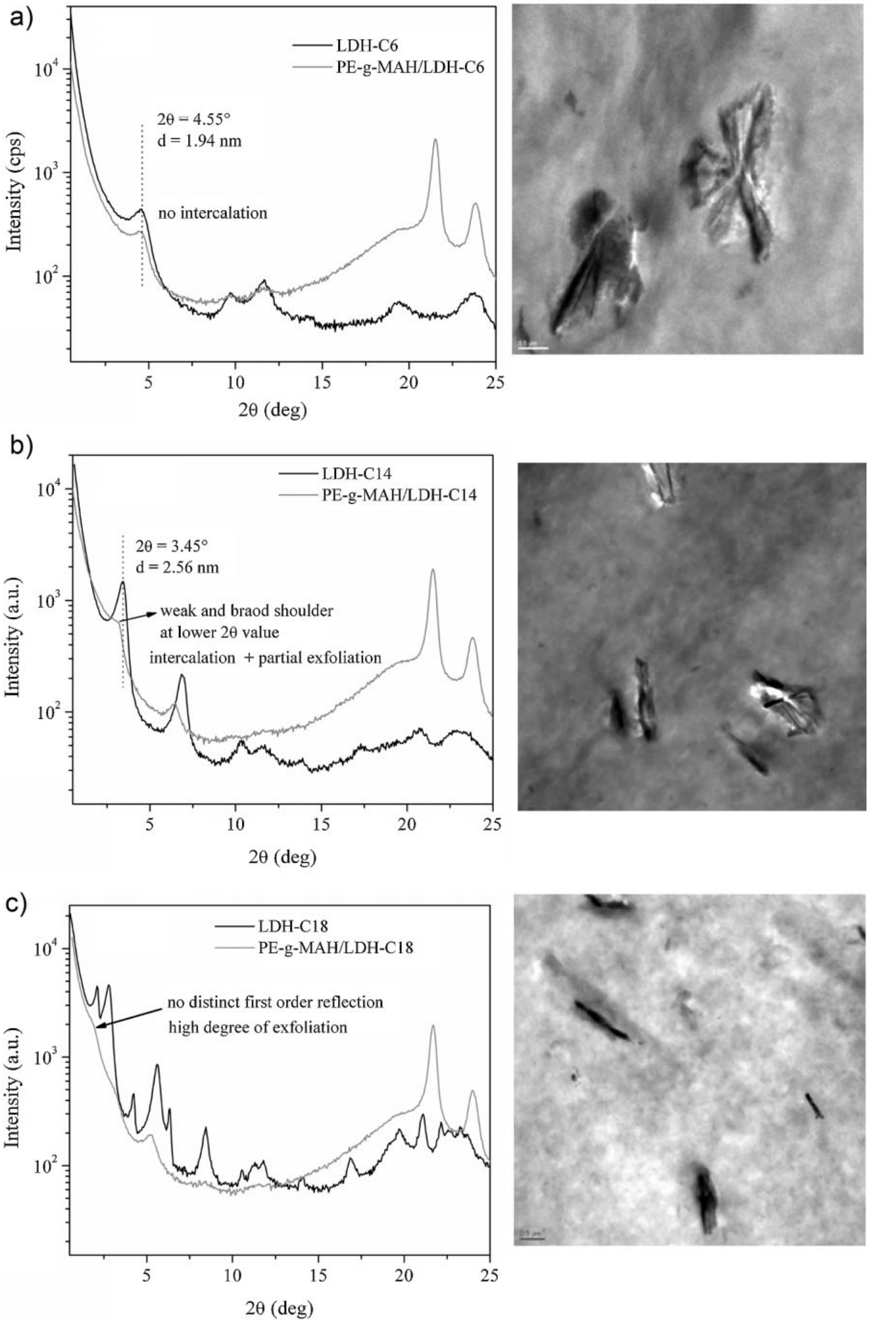

Figure 2.

Morphological analysis of PE-g-MAH/O-LDH nanocomposites containing 5.0 wt% O-LDH (left column: WAXS pattern of O-LDH and the corresponding nanocomposites, the right column: TEM micrographs of the nanocomposites, the scale is 0.5 μm): O-LDH modified with (a) C6 alkylsulfonate, (b) C14 alkyl sulfonate and (c) C18 alkyl sulfonate.

With increasing d-value, the O-LDH particles undergo more and more fragmentation during melt compounding and lose their ordered structures to a great extent. This is apparent in O-LDH containing C14 alkyl sulfonate as the intercalant, where in the nanocomposites (PE-g-MAH/LDH-C14) the first basal reflection becomes very broad and the maximum shifts to lower 2θ value as compared to neat O-LDH. The corresponding TEM image also shows that the dispersed O-LDH particles sizes are significantly reduced and also they appear more disordered and swollen due to possible intercalation of polymer chain segments (Figure 2b). At the extreme case when d-value is very high (as in the case with C18 alkyl sulfonate modified LDH), the WAXS pattern of the nanocomposites shows no distinct first order basal reflection of O-LDH indicating a high degree of exfoliation. This is also supported by the TEM micrograph, which show very few sub micron sized particles and large concentration of exfoliated fragments (Figure 2c).

Figure 3 shows the influence of functional group of the surfactant on the dispersion of O-LDH in PE-g-MAH matrix. The WAXS patterns show that with carboxylate modified LDH, no reflection corresponding to the O-LDH can be detected indicating either there is a high degree of exfoliation or the O-LDH particles undergo severe disordering in their crystal structure during melt compounding so that no significant symmetry exists in certain crystallographic direction. However, with alkyl sulfonate modified LDHs, the WAXS patterns reveal the presence of well defined basal reflection from the O-LDH indicating that the O-LDH particles remain largely unchanged in the matrix. In both cases, however, the reflection corresponding to the unmodified LDH fraction can be observed in the WAXS patterns of the nanocomposites.

The TEM analysis of the nanocomposites also shows a distinct difference in the nature of filler particle dispersion between O-LDH modified by C14 carboxalate (Figure 4 a-b) and O-LDH containing C14 alkyl sulfonate (Figure 4 c-d). The carboxalate containing O-LDHs are mainly dispersed in submicron sized particle fragments (low magnification image) and with a large concentration of the exfoliated layers homogenously dispersed throughout the matrix (high magnification image). On the contrary, the particles of O-LDH containing C14 alkyl sulfonate are very difficult to fragment or exfoliate under similar condition of processing and so they are mostly dispersed as large aggregates or micron sized particles with very limited sign of exfoliation. The comparison of the WAXS

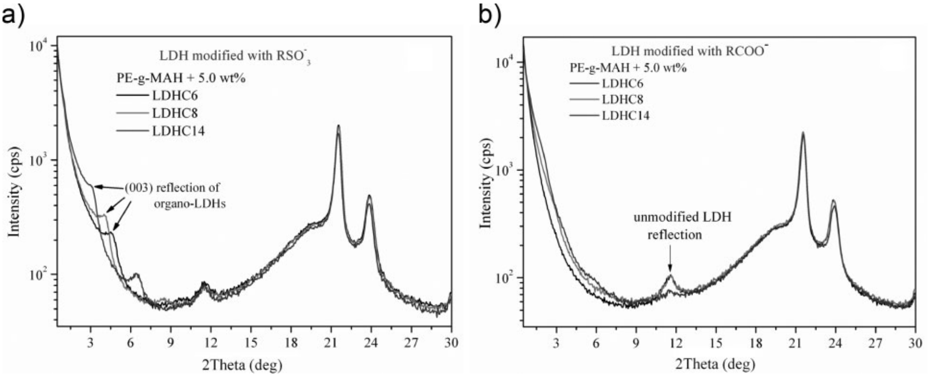

Figure 3.
WAXS patterns showing the difference in O-LDH particle morphology in the nanocomposites. O-LDH containing (a) alkyl sulfonates as modifier, (b) carboxalates as modifier.

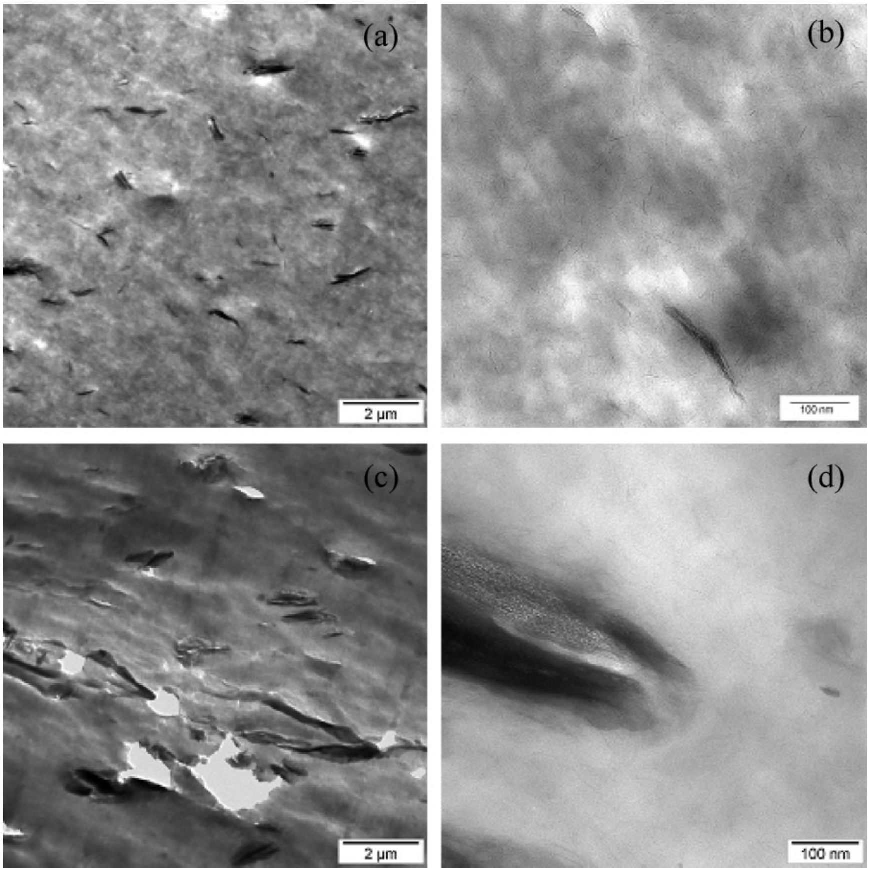

Figure 4.
TEM micrographs showing the influence of the functional group of the anionic surfactants used for the modification of LDH on the dispersion of O-LDH in PE-g-MAH matrix: (a-b) O-LDH containing C14 carboxylate and (c-d) O-LDH containing C14 alkyl sulfonate.

patterns in Figure 1 revealed that alkylsulfonates are more efficient than carboxylate as anionic surfactant for the modification LDH by regeneration method. But, as organo nanofiller carboxylete modified LDH are more easily dispersed and exfoliated in polyolefin matrix during melt compounding. We speculate that sulfonate and carboxalate groups have different affinities to the positively charged LDH layers. Carboxalates being more close to the maleic anhydride functional group, the chain segments in PE-g-MAH would be nearly equally compatible like carboxylate in the interlayer space of O-LDH giving a better chance of polymer intercalation in the clay structure.

Rheological Behviour of PE-g-MAH/O-LDH Nanocomposites

The dynamic oscillatory shear experiment has been used to investigate the influence of the d-value on the rheological behavior of the PE-g-MAH/O-LDH nanocomposites. The complex viscosity versus frequency plots as shown in Figure 5a indicates a strong shear-thinning behavior of the nanocomposites whereas pure PE-g-MAH shows Newtonian flow behavior, especially in the low frequency region. The O-LDH used in this study, always contains a significant amount of the surfactant as the organic fraction and as compared to the inorganic part, they can provide opposite effect on the melt rheology, like acting as

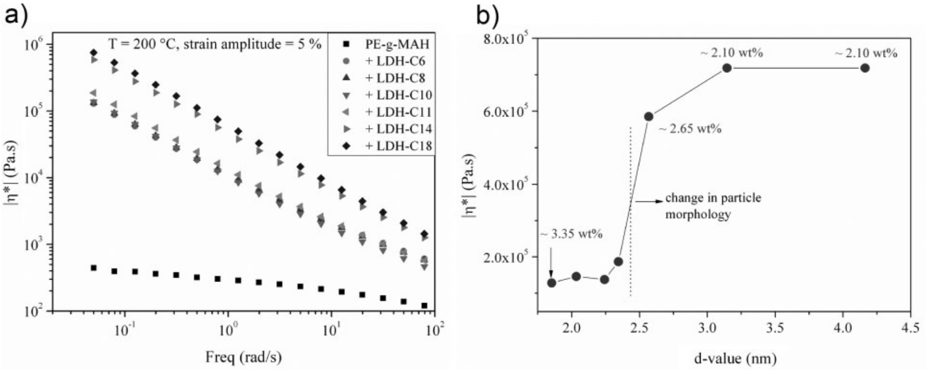

Figure 5.
Rheological behavior of PE-g-MAH nanocomposites: left – complex viscosity (|η*|) versus frequency plot for different nanocomposites composition containing 5.0 wt% of O-LDH (alkyl sulfonate as modifier), right – variation of |η*| with d-value of O-LDH.

plasticizers if freely dispersed in the polymer. The elemental analysis of the O-LDH shows that with increasing size of the surfactant (more specifically the size of the hydrocarbon tail) the inorganic fraction of the O-LDH decreases. This might in turn decrease reinforcing capability of the O-LDH as it is only the inorganic part of the organofiller that contributes most to mechanical reinforcement. But, in practice the opposite is observed in Figure 5, where increasing d-value (which means in the present case also decreasing inorganic content) results in increasing melt reinforcement. However, this observation can be explained if one considers that with increasing d-value degree of exfoliation of the O-LDH also increases, which in turn generates more number of exfoliated layer per unit amount of the O-LDH added in the compound. In Figure 5, as one relates the change in the complex viscosity (at very low frequency) with the d-value, a transition region can be observed where abrupt increase in complex viscosity occurs indicating a significant change in the dispersed phase morphology.

Conclusion

The modification of LDH with wide range of anionic surfactants has been investigated in this study. It has been observed that not only the size of the anionic surfactant, but also their functional group that influence the efficiency of the modification process carried out by regeneration method. In general, it has been found that alkyl sulfonates are the most efficient anionic surfactants for the modification of LDH by this method. The influence of the organic modifier on the morphology and rheological behavior polymer/O-LDH nanocomposites has also been reported. It is obvious that as the chain length of the modifier increases, the interlayer distance of the O-LDH is also increased. This in turn facilitates the easier intercalation of the polymer chains within the interlayer region of the O-LDH in the nanocomposites. From the WAXS and rheological analysis it was observed that there exists a critical chain length of the organic modifier and hence the d-value of the O-LDHs at which the particle morphology undergoes significant changes from a state containing non-intercalated and large tactoids of LDH particles to a state with highly exfoliated LDH particles in the nanocomposites. Besides, the carboxalate modified LDH are more easily dispersed and exfoliated in PP-g-MAH matrix giving more homogeneous dispersion of the nano structured LDH particles.

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