

PREPARATION AND CHARACTERIZATION OF EXFOLIATED LDPE/ORGANOLAPONITE NANOCOMPOSITES

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ABSTRACT

LDPE based nanocomposites with organo-modified synthetic laponite, without any polymer modification, were prepared by melt compounding method. XRD analyses performed on composites obtained by dispersing the organolaponite in molten LDPE evidenced an exfoliated structure, in contrast to that prepared by solution blending method, where conventional composites were received. Some thermal and mechanical properties were evaluated and correlated to the obtained composite's structure.

1. INTRODUCTION

Polymer-layered silicate nanocomposites have generated great interest due to their improved thermal, mechanical and gas barrier properties compared to conventional composites or neat polymers. Since most polymers are usually hydrophobic and layered silicate nanoparticles are completely hydrophilic, interactions between them are not favourable. Thus, the first step in the direction of a nanocomposite synthesis is to convert the hydrophilic clay surface to organophilic, by ion-exchange of the metal cations in the interlayer region with alkylammonium ions [1]. However, the organically modified silicates do not disperse well in nonpolar polymer, such as polypropylene or polyethylene, due to their very high hydrophobicity [2]. Another approach for the synthesis of nanocomposites involves the use of modified polymers, in particular with grafting of pendant anhydride groups, to mediate the polarity between the silicate surface and polymer, and to achieve miscibility between the two phases [3,4].

Low density polyethylene (LDPE) is a widely used packaging material, and the preparation of nanocomposites is expected to improve its mechanical and barrier properties. However the achievement of nanocomposite structure is much more difficult than in HDPE because of the branched macromolecules (in LDPE) which hinder the penetration into the clay galleries [5].

Nanocomposites based on LDPE using organoclays and maleic anhydride-grafted PE [6] or ethylene vinyl acetate (EVA) [7,8] as compatibilizer were synthesized, obtaining intercalated or partially exfoliated structures. As far as we know there are no reports in open literature relative to preparation and characterization of unmodified LDPE based nanocomposites.

The objective of this study was to synthesize LDPE based nanocomposites with organo-modified synthetic laponite, without any polymer modification. The structure of the resulting composites was investigated by X-ray diffraction. Also the thermal and

mechanical properties of the obtained materials were evaluated and correlated to their structure.

2. EXPERIMENTAL

The clay used in this work was laponite (Lp), a synthetic hectorite composed of two tetrahedral silica sheets and a central octahedral magnesia sheet obtained from Southern Clay Products Inc., with cation exchange capacity (CEC) 50 meq/100g of clay.

The polyethylene used for the nanocomposites preparation, was LDPE supplied by Aldrich, with Melt Index=25g/10min (190°C/2.16kg) and density 0.915 g cm⁻³.

Surface modification of the synthetic clay was attained using the surfactant di(hydrogenated tallow) dimethylammonium Chloride (Fig.1) (Arquad[®] 2HT-75, Fluka), consists mainly of C₁₈ and C₁₆ carbon chains. A 1 wt % solution of surfactant in warm water was prepared and added dropwise to a 1 wt% laponite suspension in the same solvent. The obtained mixture was stirred vigorously for 24h at 70°C. The amount of the surfactant added was equivalent to 0.8, 1.5 or 3.0 times the CEC of laponite. The resulting samples were washed four times with deionized water and once with ethanol in order to remove the excess of surfactant and dried in a vacuum oven at 40 °C.

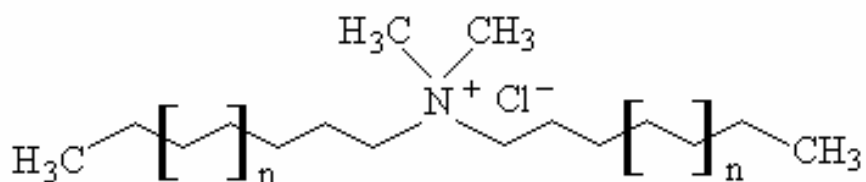


Fig. 1. Structure of the surfactant di(hydrogenated tallow) dimethylammonium Chloride.

LDPE-OLp nanocomposites with 2wt%, 5 wt % and 10wt% organosilicate loadings were prepared via *solution blend method* by diluting appropriate amount of LDPE in CCl₄ at 85°C and mixing the solution, under vigorous stirring, with the 1.5xCEC-OLp suspension in the same solvent, followed by solvent evaporation. A second series of nanocomposites with the same OLp loadings, were prepared by melting, in an oven, a part of the above obtained materials under periodical stirring, at 180°C.

The organic phase content, in the organomodified laponite (OLp) as well as the thermal stability of the obtained nanocomposites were estimated by thermogravimetric analysis (TGA) using a NETZSCH STA 449C apparatus. Samples of about 10 mg were heated in air from 25-900 °C at a rate of 10 K min⁻¹. DSC measurements were carried out at the same instrument. Samples of about 10 mg were heated from -15 to 170 °C, melt annealed for 5 min, cooled down and heated again at a rate of 5 K min⁻¹ in N₂.

Samples of OLp for XRD analysis were prepared by spreading about 1ml of suspension (10 mg/ml) of each sample on glass slides. The interlayer d-spacing of these sample films orientated along the (001) direction, was measured using a D8 Advanced Bruker diffractometer with CuK_α radiation (λ=1.5418 Å). XRD analyses of polymer nanocomposites took place on films prepared using a hydraulic press with heated platens, in the same diffractometer.

Tensile tests were performed on an Instron Tensile Testing Machine model 3344 according to ASTM D638 using dogbone-shaped specimens with dimensions 22 x 5 x

0.22mm at 5mm/min crosshead speed. Three specimens from each sample were tested to establish reproducibility of the measurements and average values of elastic modulus are given in Table 2.

3. RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of the parent laponite and the organoclays at various surfactants' loadings. An increase of the basal spacing (d_{001}) of the clay is observed after the insertion of the surfactant. More specifically, the pristine laponite (Lp) shows a d_{001} -spacing of 1.26 nm which correspond to an interlayer space $D=1.21-0.95=0.26$ nm, where 0.95 nm is the thickness of the individual clay sheet. In the case of the organosilicates, very broad diffraction beaks were obtained. This indicates a non uniform interlayer opening. The maxima of the peaks correspond to basal spacing $d_{001}=1.75$ nm for 0.8xCEC-OLp and 1.99 nm for both 1.5xCEC-OLp and 3.0xCEC-OLp, with corresponding interlayer space: $D_1=0.8$ nm, $D_2=D_3=1.04$ nm. Based on the size and shape of the alkylammonium ion (Fig. 1) a lateral bilayer and /or inclined monolayer configuration between the clay layers can be suggested.

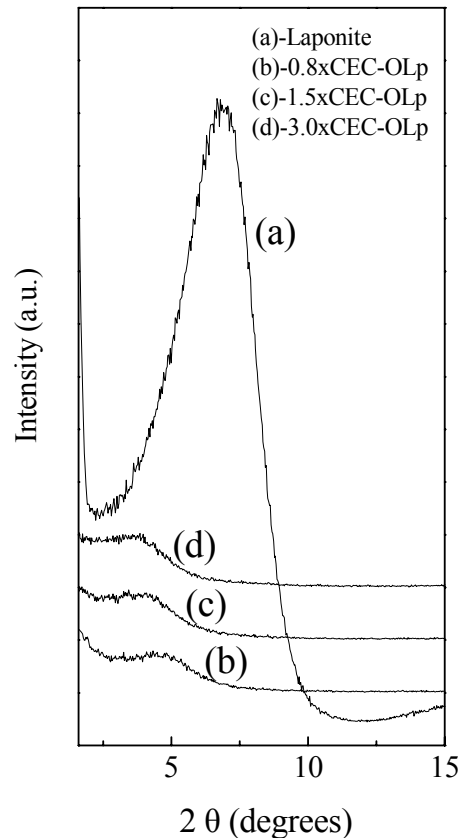


Fig. 2. XRD patterns of the pristine laponite (a) and the organolaponites at various organic phase loading: (b)-0.8xCEC; (c)-1.5xCEC and (d)-3.0xCEC.

The organic phase content, in the organosilicates, was estimated by thermogravimetric analysis assuming that the weight loss between 160 and 720 °C is due to the loss of organic matter. The obtained TG curves of the pristine Lp as well as the organolaponites are shown in Fig. 3. The corresponding weight losses (theoretical and experimental) are tabulated in Table 1.

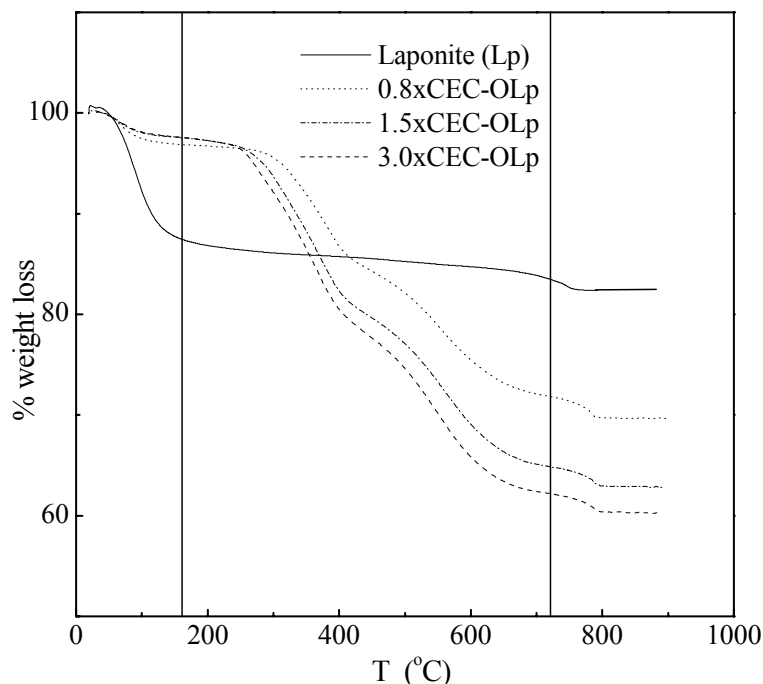


Fig. 3. TGA curves of the pristine laponite and the prepared organolaponites.

Table 1. Water content (% weight loss at the temperature range 30-160°C), % weight loss at the temperature range 160-720°C, theoretical organic content, (wt% of organic surfactant added on clay) and d-spacing values of pristine laponite and organolaponites.

Material	Water content (%weight loss at 30-160 °C)	% weight loss at 160-720 °C	Theoretical organic content (wt%)	d-spacing (d_{001}) (nm)
Laponite (Lp)	12.5	4.0	-	1.21
0.8xCEC-OLp	3.4	25.1	23.1	1.75
1.5xCEC-OLp	2.4	32.6	35.9	1.99
3.0xCEC-OLp	2.4	35.4	53.1	1.99

The weight losses (that correspond to the organic matter) 25.1% wt for 0.8xCEC-OLp and 32.6%wt for 1.5xCEC-OLp were very close to the theoretical amounts, that were expected for complete adsorption of the surfactant quantity added. For the 3.0xCEC-OLp the estimated organic content was 35.4 %wt. This value is by far lower compared

to the surfactant quantity added. As discussed above, the interlayer distance for 1.5x and 3.0xCEC-OLp is identical. Since the organic content of the latter sample is by 3.2 % higher, it can be suggested that more surfactant molecules have been adsorbed on the clay surface of 3.0xCEC-OLp and as a result the free lateral distance between the adsorbed molecules in the interlayer space becomes shorter compared to 1.5xCEC-OLp. This indicates that there is an upper limit above which the clay gallery cannot expand more by accommodating more alkylammonium ions.

XRD patterns of the prepared composites are shown in Fig. 4. Graphs on the left hand part of Fig. 4, correspond to materials prepared using the solution blend method, while on the right hand part to materials received after melting process. The estimated d-spacings from the XRD analysis are presented in Table 2.

Table 2. The crystallization and melting temperatures, the % residues at the end of weight loss, the d-spacing (d_{001}) as well as the elastic modulus values for the neat polymer and the prepared composites.

Material	$T_c/^\circ\text{C}$	$T_m/^\circ\text{C}$	Residue at the end of weight loss (%)	d_{001} (nm)	Elastic modulus MPa
LDPE (neat)	100.2	115.2	0.2	-	288
LDPE-2%OLp(Sol)	101.7	115.1	2.3	1.99	286
LDPE-5%OLp(Sol)	102.1	114.7	4.1	1.99	295
LDPE-10%OLp(Sol)	102.6	114.2	7.2	1.99	215
LDPE-2% OLp (Melt)	102.1	114.5	4.3	n.p.*	269
LDPE-5% OLp (Melt)	102.4	114.5	4.5	n.p.	305
LDPE-10% OLp (Melt)	102.6	114.7	7.9	n.p.	345

n.p.* = no peak

XRD-diagrams for materials prepared via solution blend method present a broad and low intensity peak at the same angle as OLp. This means that polymer chains were not incorporated effectively between the silicate layers. The peak in XRD is due to packages of silicate layers that keep their stacking, creating a conventional phase separated composite. Probably the strong affinity between solvent and polymer (both totally non polar substances) did not allow the dispersion of nanosilicate sheets into the polymer solution.

The absence of peaks in the XRD-patterns for the materials received using melt process, is indicative of exfoliated structure, in which the individual clay layers lose their ordered stacking and are exfoliated and dispersed in the continuous polymer matrix. This result is attributed to the absence of solvent due to its evaporation. Furthermore the use of laponite, a particularly low aspect ratio silicate (20-30), favors the formation of exfoliated nanocomposite structure while silicates with high aspect ratio (100-200) like montmorillonite prefer intercalated nanostructure formation [9].

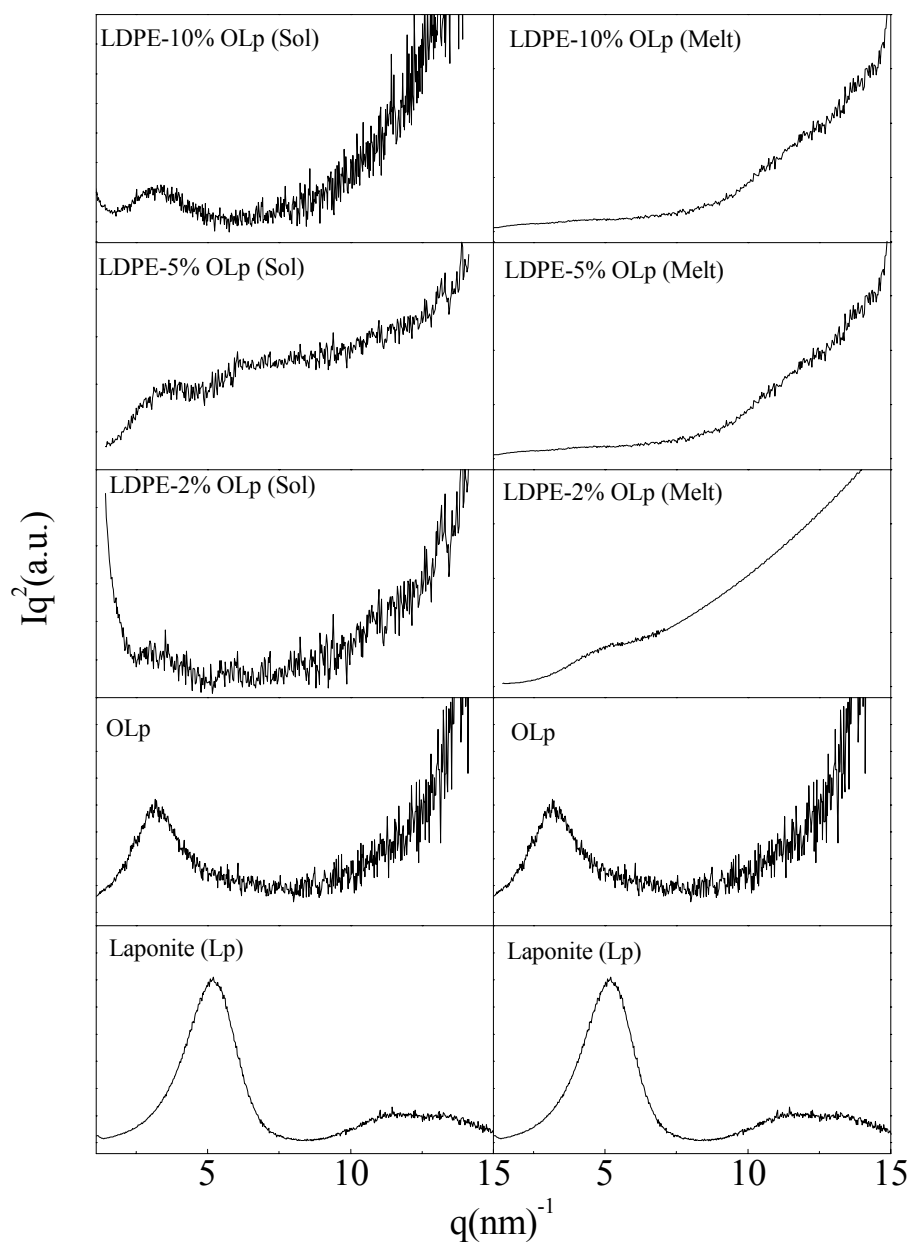


Fig. 4. XRD patterns of the pristine laponite, organolaponite and the prepared polymer-silicate composites in the form of $Iq^2=f(q)$ where I is the intensity and $q=4\pi \sin\theta/\lambda$, [10].

The TGA curves of pure LDPE and the prepared composites are shown in Fig.5. TGA results indicate an improvement of the thermal stability for LDPE-composites compared to neat polyethylene up to ~50 % weight loss. This increment in thermal stability was more prevalent for nanocomposites prepared by melt compounding compared to conventional composites prepared by solution blend method. Especially in the case of 10 wt% filler loading, the decomposition temperature for 10% weight loss increased from 285°C to 322°C and 349°C for pure polymer, conventional composite and

nanocomposite respectively. With further calcination, up to 600 °C, the examined nanocomposites or composites lost weight in a similar way as the pure polymer.

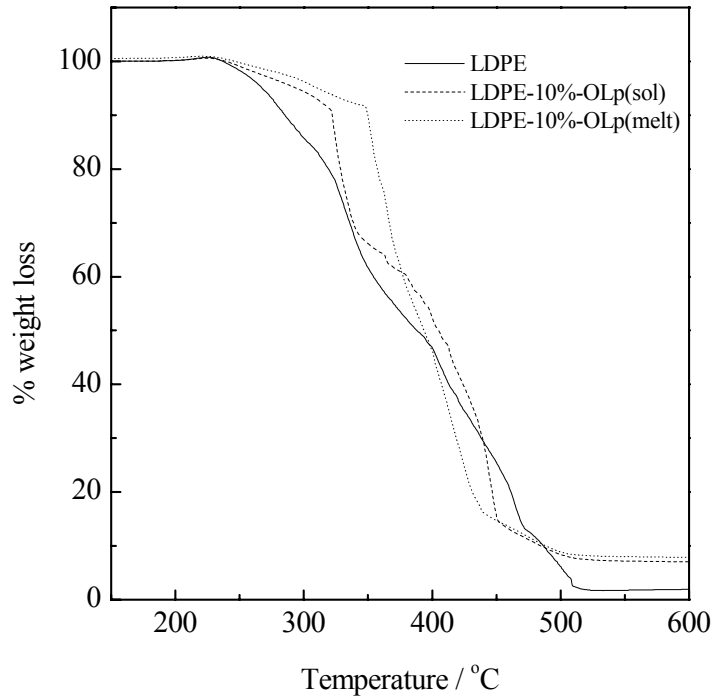


Fig. 5. Characteristic TGA curves of neat polymer and LDPE-laponite composites with 10 wt % organolaponite content.

DSC melting endotherms and crystallization exotherms for neat polymer and tested composites are plotted in Fig.6. The crystallization temperatures (T_c) as well as the melting temperatures (T_m) during the second heating are tabulated in Table 2. For all examined materials, the melting started early and achieved a peak at about 114.2-115.2 °C. Similar results have been published recently by Morawiec et.al. [6] for the LDPE-Organomontmorillonite system.

At the crystallization exotherms a gradual increase of T_c , with increasing inorganic phase content, from 100.2 °C (for pristine LDPE) to 102.6 °C (for LDPE-10 wt%OLp composites) was observed. Similar crystallization behaviour has been reported by Gopakumar et. al. [4], and Wang et. al [11] for PE or PE-g-MAN / organomontmorillonite composites. They observed that the peak crystallization temperature of all composites was much higher (~5 °C) than that of PE-g-MAN and PE. The observed increase of T_c with increasing clay content was attributed to the nucleation-controlled polymer crystallization. They also checked the effect of clay on the crystalline structure of PE by the analysis of the XRD diffraction patterns, where a substantial reduction in the intensity of the 110 reflection (at $2\theta=21.6^\circ$) of PE-g-MAN was observed in the presence of exfoliated clay.

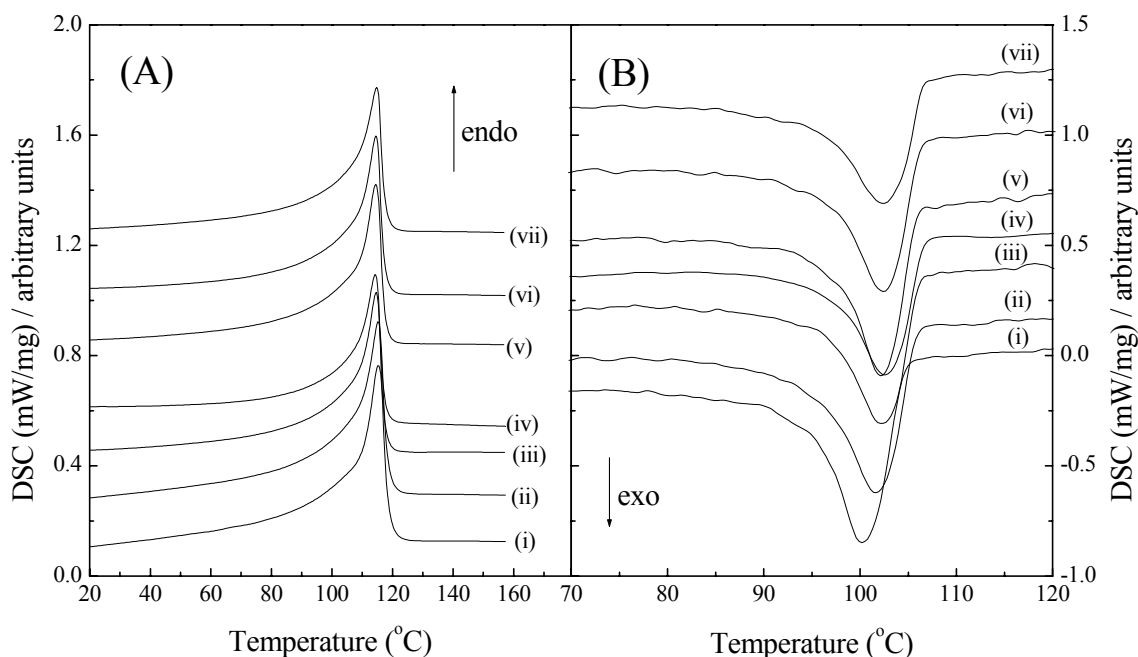


Fig. 6. DSC thermographs of (i) LDPE, (ii) LDPE-2%OLp(Solution), (iii) LDPE-5%OLp(Solution), (iv) LDPE-10%OLp(Solution), (v) LDPE-2% OLp (Melt), (vi) LDPE-5% OLp (Melt) and (vii) LDPE-10% OLp (Melt) : (A) heating and (B) cooling process.

Elastic modulus (E) of the samples was determined from the slope of the initial elastic region in stress-strain measurements. E was found as 288 MPa for LDPE and similar values was estimated for samples with 2 wt % organosilicate content irrespective of the preparation method, which means that the small addition of filler does not induce any reinforcing effects. As the organosilicate content increases the E values exhibit a significant differentiation. Particularly, in the case of 10 wt % filler content, E value was enhanced by 30% for exfoliated nanocomposites prepared by melt process while the conventional composite received by solution blending method possess an elastic modulus value that decreased by 25%, when compared with the pure polymer.

4. CONCLUSIONS

LDPE based nanocomposites with organo-modified synthetic laponite, without any polymer modification, were prepared by melt compounding method. XRD-patterns for the materials received using melt process, revealed an exfoliated structure, in contrast to that prepared by solution blending method, where conventional composites were received. Improvement of the thermal stability for LDPE-nanocomposites compared to neat polyethylene up to ~50 % weight loss was observed by TGA analysis. The crystallization temperature of LDPE was increased with the addition of laponite. Tensile measurements evidenced an increase in elastic modulus of polymer with the addition of organosilicate. This increment was more prevalent for nanocomposites prepared by melt

process and high organosilicate content (i.e. 10 wt %), compared to conventional composites prepared by solution blend method.

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REFERENCES

1. Pinnavaia, T.J. and Beall, G.W., in "Polymer/layered silicate nanocomposites", John Wiley & Sons, New York (2001).
2. Jeon, H.G., Jung, H.T., Lee, S.W., Hudson, S.D., "Morphology of polymer/silicate nanocomposites. High density polyethylene and a nitrile copolymer", *Polym. Bull.*, 1998; 41: 107-113.
3. Chrissopoulou K., Altintzi I., Anastasiadis S.H., Giannelis E.P., Pitsikalis M., Hadjichristidis N., Theophilou N., "Controlling the miscibility of polyethylene/layered silicate nanocomposites by altering the polymer/surface interactions" *Polymer*, 2005; 46: 12440-12451.
4. Gopakumar, T.G., Lee, J.A., Kontopoulou, M. Parent, J.S., "Influence of clay exfoliation on the physical properties of montmorillonite/polyethylene composites" *Polymer*, 2002; 43: 5483-5491.
5. Liang, G., Xu, J., Bao, S., and Xu, W., "Polyethylene/ maleic anhydride grafted polyethylene/organic montmorillonite nanocomposites. I. Preparation, microstructure, and mechanical properties". *J. Appl. Polym. Sci.*, 2004; 91:3974-3980.
6. Morawiec J., Pawlak, A., Slouf, M., Galeski, A., Piorkowska, E. and Krasnikowa, N., "Preparation and properties of compatibilized LDPE/organo-modified montmorillonite nanocomposites". *European Polymer Journal*, 2005; 41: 1115-1122.
7. Yang H., Song Y., Xu B., Zheng Q., "Preparation of exfoliated Low-density Polyethylene/Montmorillonite nanocomposites through melt extrusion" *Chem. Res. Chinese U.*, 2006; 22(3): 383-87.
8. Malucelli, G., Ronchetti, S., Lak, N., Priola, A., Dintcheva, N., Paolo La Mantia, F., "Intercalation effects in LDPE/o-montmorillonites nanocomposites." *European Polymer Journal*, 2007; 43: 328-335.
9. Giannakas A. and Ladavos A., *unpublished results*.
10. Billinge S.J.L. and Kanatzidis M.G., "Beyond crystallography: the study of disorder, nanocrystallinity and crystallographically challenged materials with pair distribution functions" *Chem. Comm.*, 2004; 749-760.
11. Wang K.H., Choi M.H., Koo C.M., Xu M., Chung I.J., Jang M.C., Choi S.W. Song H.H., "Morphology and physical properties of Polyethylene/Silicate nanocomposite prepared by melt intercalation", *J. Polym. Sci. : Part B: Polym. Phys.*, 2002; 40: 1454-1463.