



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Investigation of Mechanical, Thermal and Chemical Properties of HDPE/PEG/OMT Nanocomposites

¹A. Mohaddespour, ²S.J. Ahmadi, ¹H. Abolghasemi and ¹Sh. Jafarinejad

¹Department of Chemical Engineering, Faculty of Engineering, Tehran University,
P.O. Box 11365/4563, Tehran, Iran

²Jaber Ibn Hayan Research Laboratories, Nuclear Science and Technology Research Institute,
End of North Karegar Ave., P.O. Box 1439951113, Tehran, Iran

Abstract: The combination of the high density polyethylene (HDPE) with variable amounts of the organoclay for investigating the mechanical, thermal and chemical properties of the synthesized nanocomposites were prepared. The effects of the addition of polyethylene glycol (PEG) as a compatibilizer into the polymer matrix on these properties were regarded. X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM) for estimating the morphology study of the nanocomposites were provided. Tensile strength, Young's modulus, surface hardness, Thermogravimetric analysis and adsorption resistant tests of all compounds for mechanical, thermal and chemical investigation were prepared. The morphology studies indicate that the addition of PEG has remarkably improved the dispersion of clay into the matrix. The most efficient amount of organoclay into the resin for enhancing the mechanical properties was obtained at about 5 wt. %. The results reveal that the thermal stability of nanocomposites enhanced with adding the organoclay and this property has been deteriorated without any compatibilizer. The adsorption resistant of samples decreased against the rising of the clay content into the polymer matrix.

Key words: HDPE, compatibilizer, organoclay, nanocomposite

INTRODUCTION

Recently, polymer nanocomposites reinforced with low volume content of 2:1 layered silicates have received considerable attention due to their substantial properties such as mechanical and thermal properties over their pristine polymers (Zhang *et al.*, 2006; Zhang and Wilkie, 2006; Zhao *et al.*, 2005; Wang *et al.*, 2003; Celini *et al.*, 2007; Drozdov and Christiansen, 2007; Lu *et al.*, 2006; Cho and Paul, 2001; Zanetti and Costa, 2004). The weak interaction between organic and inorganic phases in many conventional polymer composites causes unsatisfied mechanical and thermal properties. From the other point of view, using of organically modified clay (organoclay) instead of pure clay leads to better dispersion of inorganic phase into the polymer matrix (Wang *et al.*, 2001; Su *et al.*, 2004; Gopakumar *et al.*, 2002; Lee *et al.*, 2004). So, these inorganic fillers improve dramatically the physical and mechanical macroscopic properties of polymer even the amount of them is small. The enhanced properties are seemingly due to the synergistic effects of nanoscale structure and interaction of fillers with polymer. Many

advantages of the nanocomposites are the principle factors for investigating of these polymer/clay nanocomposites extremely. They are based on the use of a low concentration of expandable smectite clays, such as Montmorillonite Layered Silicates (MLS), in the matrix (Fu and Qutubuddin, 2001; Foresta *et al.*, 2001; Okamoto *et al.*, 2001). The addition of MLS in a polymeric matrix results in different clay distributions that do not always provide an improvement in performance. When MLS is added to a polymer, it remains an immiscible system (Alexandre and Dubois, 2000). The different clay distributions are the immiscible, intercalated, partially exfoliated and exfoliated dispersions.

Polyethylene is one of the most widely used polyolefin polymers. Since it does not include any polar group in its backbone, it is deliberated that the homogeneous dispersion of the clay minerals in polyethylene is not realized. In general, clay is modified with variable materials to increase the degree of reinforcement between the polymer layers and clay surface. Hexadecyl trimethyl ammonium bromide (C16) (Zhang *et al.*, 2006; Hongdian *et al.*, 2005) and

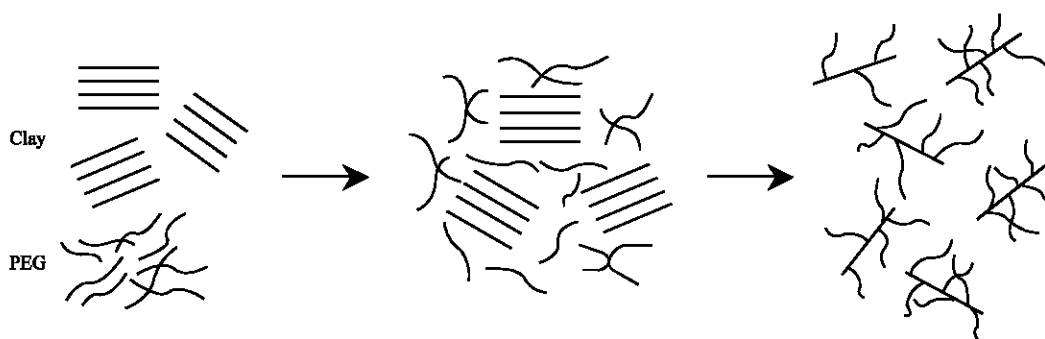


Fig. 1: The effect of PEG as a compatibilizer on the dispersion of clay into the polymer matrix and the structure of nanocomposite

Diocetadecyl Dimethyl ammonium chloride (DM) (Zhao *et al.*, 2005) and similar structures are used for modifying clay. In fact, clay is modified with alkylammonium to promote its interaction with a polymer because the alkylammonium makes the hydrophilic clay surface organophilic. The length and number of alkyl groups of cationic modifier also effect on intercalation behavior (Mravěáková *et al.*, 2006). The dispersion of clay into the polymer matrix can be promoted by using the appropriate method. The procedures that are widely used for this purpose are melt/solution blending or *in situ* polymerization (Ahmadi *et al.*, 2004). When registry between the layers is maintained, the material is described as an intercalated. When this registry is lost and the clay layers are accidentally distributed into the matrix the system is depicted as an exfoliated or delaminated nanocomposites. Lastly, if the clay is not dispersed, it is just filler and a nanocomposite is not constituted (Gilman *et al.*, 1998). For easier dispersion of clay into the polymer matrix, Instead of modifying clay we can use some oligomers as a compatibilizer for easier dispersion of clay into the polymer matrix and promoting the intercalation process is another way. In recent studies, effect of compatibilizer on polymer/clay nanocomposites has been investigated (Preston *et al.*, 2004; Zanetti *et al.*, 2004). The results revealed that compatibilizer plays the role of incorporator into the mixture of clay and polymer. In fact, these materials are a bridge from polymer matrix to mineral clay and cause the combination of polymer/clay approaches to intercalated or even exfoliated system. Some nanocomposite literatures (Ray and Okamoto, 2003; Hasegawa *et al.*, 2000; Manias *et al.*, 2001) indicate that increased strength, or elastic modulus, considerably decreases strain to failure and ductility. In PE, this is further complicated by the non-polar nature of PE, requiring the use of bridge molecules between the PE and the MLS. The reasoning being that the polar compatibilizer would solubilize the

MLS surfactant. This should increase the degree of reinforcement between polymer chains and layered silicate structures. The reality is that the low molecular weight compatibilizer reduces the stiffness and toughness of the material. In this study, we employed polyethylene glycol (PEG) as a compatibilizer for easier dispersion of clay into the polymer matrix. Figure 1 shows the effect of compatibilizer on the synthesized structure after adding clay into the matrix.

The purpose of this study is to investigate the effects of adding the nanoscale organically-modified montmorillonite (OMT) into the high density polyethylene (HDPE) matrix on thermal, mechanical and chemical properties. Usage of polyethylene glycol (PEG) as a compatibilizer and estimating of these properties also were regarded.

MATERIALS AND METHODS

Materials: The high density polyethylene (HDPE 5818, density 0.93 g cm^{-3}) was purchased from Imam petrochemical Co. and used as a composite matrix resin. As well as poly ethylene glycol (density 0.91 g cm^{-3} , melting flow index: 1-1.5 g/10 min at 230°C , maleic anhydride 0.7 wt. %) was provided as a compatibilizer. Natural montmorillonite modified with a quaternary ammonium salt (2 M2HT dimethyl, dihydrogenatedtallow, quaternary ammonium) and cation exchange capacity (CEC) of $\approx 125 \text{ meq/100 g}$ was provided by southern clay products, Inc.

Nanocomposite formation: For estimating the properties of HDPE/Clay nanocomposite, 5 sheets were prepared. The investigation of the effects of adding clay and the addition of polyethylene glycol as a compatibilizer was realized by these samples given in Table 1. For synthesizing of nanocomposites, first The polymer and compatibilizer were charged into the brabender chamber

Table 1: Composition and Mechanical properties of HDPE/PEG/Clay nanocomposites

Samples	HDPE (wt. %)	PEG (wt. %)	OMT (wt. %)	Young's modulus (MPa)	Tensile strength (MPa)	Hardness (shore A)
PE1	85	15	0	1017	27.45	62
PE2	82	15	3	1024	23.88	63
PE3	80	15	5	1129	24.90	64
PE4	78	15	7	1025	24.39	63
PE5	95	0	5	1153	25.99	61

simultaneously and then the OMT was charged in 5 min into the chamber. The mixtures were mixed for 5 min and then were discharged and were adapted for further estimation. Process temperature was at 160°C using a twin-roll mill with 70 rpm to yield composites.

Evaluation of dispersibility of clay into the polymer matrix: Morphology studies have been fulfilled on all composites. X-ray diffraction experiments were performed at room temperature by a Philips X'Pert X-ray diffractometer (40 kV, 40 mA) with Cu ($k = 0.154$ nm). The morphology of HDPE nanocomposites was studied by SEM also with a Philips XL30 scanning electron microscope. All specimens were coated with gold prior to imaging.

Mechanical properties: Nanocomposites were prepared by specimen preparation instrument, puncher model ZCP 020 ZWICK Germany, for mechanical tests. Tensile tests and Young modulus estimation were conducted at room temperature according to ISO 527-1, ASTM D638 m using an INSRTON model 4411 machine equipped with digital data acquisition capabilities. In addition, Measuring of surface hardness of nanocomposite specimens was investigated by using shore-A hardness instrument model ZWICK according to ASTM D2240.

Chemical properties: Comparison between polymer/clay nanocomposites and primitive polymer on chemical properties has been regarded in recent studies (Wang *et al.*, 2004; Ragosta *et al.*, 2005; Mravěáková *et al.*, 2006; Berta *et al.*, 2006). Since clay dispersion into the polymer matrix causes a growth of distance between clay layers, the chemical properties such as liquid adsorption ability as if thermal and mechanical properties can change. Xylene and Toluene are liquids which have been used to estimate the adsorption ability of the nanocomposite samples. Samples were prepared in $20 \times 10 \times 2$ mm³ sheets. All sheets individually were put in 20 mL of both liquids for 40 h and then weighted. The percentage of mass increase was also measured.

Thermal properties: Thermogravimetric analyses (TGA) was carried out on an STA 1500 unit, under

30-35 mL min⁻¹ argon flow at a scan rate of 20°C min⁻¹ from room temperature to 600°C at 10 mg scale for estimating thermal stability.

RESULTS AND DISCUSSION

X-ray diffraction (XRD) measurement and SEM results on the clay and its nanocomposites: The OMT displays a diffraction peak at 7.19° (Fig. 2). As that seen in curve (c) for HDPE/PEG/Clay nanocomposite, the diffraction peak has been approximately become extinct that reveals an exfoliated system has been formed. There is a flat feature nearly from 4-8 value of 2θ regions which causes the formation of exfoliation system in comparison of value from curve (a). Another result for the combination of HDPE and OMT without compatibilizer is shown in curve (b). Since the compatibilizer makes the easier dispersion of clay into the polymer matrix, so as we expected, the lack of PEG as a compatibilizer caused the lower expansion of the clay layers in comparison with the distance between the clay layers after incorporation of PEG into the nanocomposite that can deduced from peak value in curve (a). In fact, the organoclay improves the dispersibility of the clay and polymer. The corresponding peak in curve (b) for HDPE/OMT compound at 6.99° indicate that the distance between the clay layers has not been increased fairly. But another diffraction peak in this curve occurs at 4.33° that shows some layers expanded and the structure approached to intercalated system. This realities exhibit that the partially intercalation structure has been formed because of the effect of Alkylammonium chains on the mineral clay surface. The addition of PEG into the compound directs the mixture to the exfoliation system. The flat area in curve (c) reveals this fact. So, usage of compatibilizer has a favorable effect on morphology properties of HDPE/Clay nanocomposite. SEM images also show that the presence of compatibilizer in the polymer matrix has facilitated the dispersion of clay layers and has made a homogeneous structure (Fig. 3a). When there is no PEG, the distance between clay layers has not been expanded and the polymer has not been injected into this space (Fig. 3b). These results show that the PEG is compatible with the HDPE matrix and has made an exfoliated structure. The lack of PEG into the matrix has made a composite instead of nanocomposite structure that is because of the not appropriate dispersion of clay and the aggregation of its layers.

Mechanical properties: The Young's modulus and tensile strength of nanocomposites could, in principle, be improved when the content of the inorganic clay increases, but this would also lead to deficient in clay

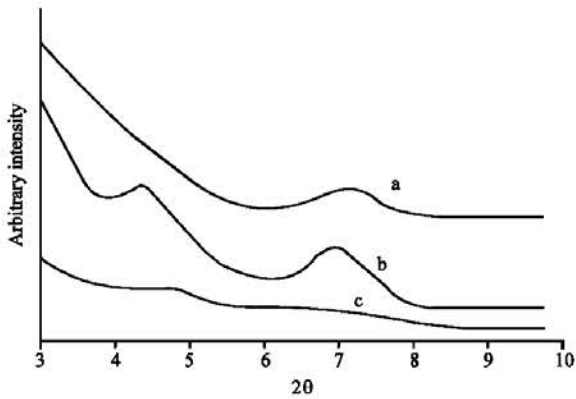


Fig. 2: The XRD pattern for (a) OMT, (b) HDPE/OMT and (c) HDPE/PEG/ OMT nanocomposite

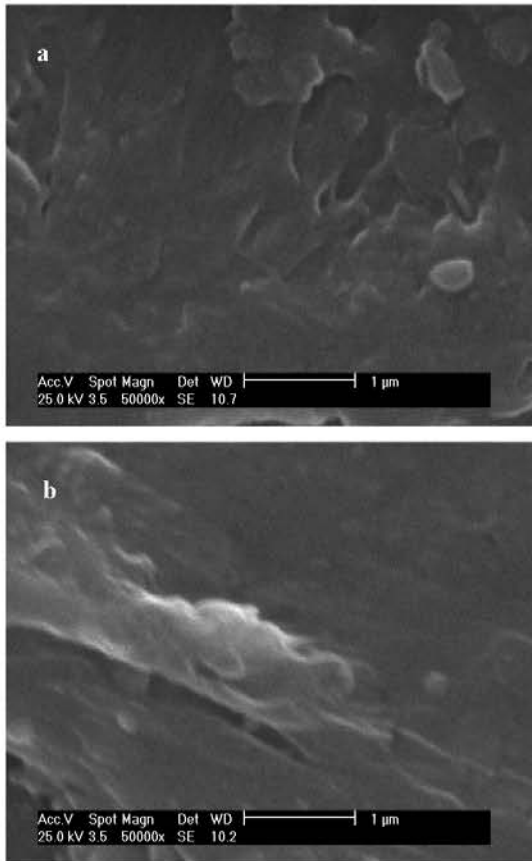


Fig. 3: SEM micrographs of (a) HDPE/PEG 15%/OMT 5% and (b) HDPE/OMT 5% nanocomposites

dispersion (Table 1). In fact, because of the interaction between the clay layers and the polymer matrix whatever clay content increases, the addition of clay could enhance those properties. But, while the clay content increases to

higher load, assembly of clay stacks can alter the nanocomposite structure and the clay will be a simply filler that leads to reduction in mechanical properties. From experimental data, Young' modulus improves till the OMT content increases to 5 wt. % and when the OMT content reaches to 7 wt. % this mechanical property is descended. Tensile strength after incorporation of the OMT into the polymer matrix also has decreased, but it is worth noting that we have an increase at 5 wt. % of clay content after reduction in this property at 3 wt. % of OMT. The addition of OMT into the polymer matrix can also enhance the surface hardness characteristic. The optimum of OMT content is 5 wt. % for enhancing hardness property of nanocomposites. As a consequence, Young's value has increased at 5 wt. % of OMT and tensile strength has overall reduced whatever clay content increases. The results show that increase of PEG as a compatibilizer has not had a fair effect on tensile and Young's tests but has improved the surface hardness of the nanocomposite in comparison of other samples. In fact, the compatibilizer has a plasticizing effect on polymer.

Thermogravimetric analysis: For estimating the thermal stability of organoclay nanocomposites we need to balance three parameters. Clay layers have good barrier action, which can improve the thermal stability of polymer/clay nanocomposites. On the other hand, the alkylammonium cations in the organoclay could suffer decomposition following the Hofmann elimination reaction and its product would catalyse the degradation of polymer matrixes. Thirdly, the clay itself can also catalyse the degradation of polymer matrixes. The latter two actions would reduce the thermal stability of polymer/clay nanocomposites.

The thermal stability of HDPE/PEG, HDPE/OMT and HDPE/PEG/OMT nanocomposites have been tested by TGA that TGA curves as in Fig. 4 and the corresponding data have been shown in Table 2. At the initial stage of the degradation (before 400°C), due to the Hofmann elimination reaction and the clay catalysed degradation, the PE/PEG/clay nanocomposites degrade faster than HDPE/PEG (the residual of HDPE/PEG and HDPE/PEG/OMT 3 wt. % at 400°C are 99.17 and 98.13%, respectively). Whatever clay content increases, the HDPE/PEG/OMT nanocomposites show higher thermal stability. The onset temperatures of HDPE/PEG/OMT nanocomposites are all higher than HDPE/PEG that has not any organoclay. As results reveal, thermal stability of nanocomposites after adding clay into the polymer matrix has been enhanced. Clay content played the role of barrier action before catalysing the degradation of polymer

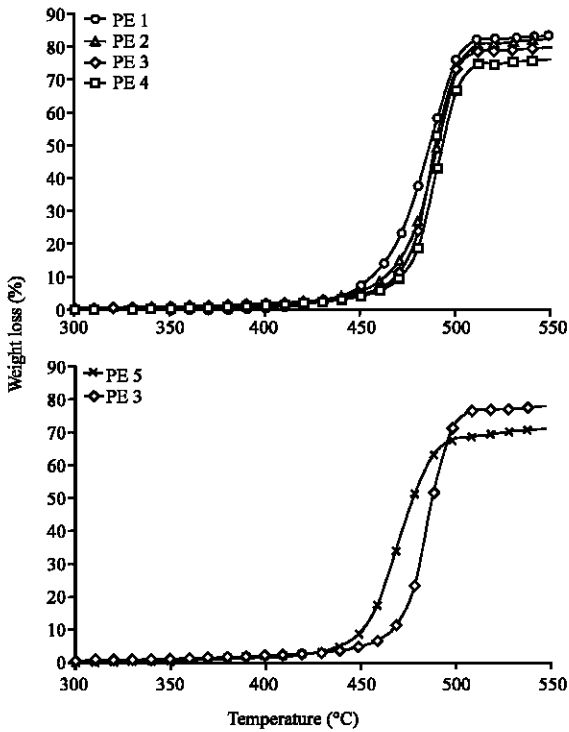


Fig. 4: TGA curves for HDPE/PEG, HDPE/PEG/OMT and HDPE/OMT nanocomposites in argon atmosphere

matrixes. Finally, the effect of using PEG as a compatibilizer is shown in Fig. 4 that exhibits the thermal stability of nanocomposite has been reduced. The residual of HDPE/OMT 5 wt. % nanocomposite before 400°C is less than HDPE/PEG/OMT 5% nanocomposite. But in higher temperatures the sample with compatibilizer is shown considerable improvement in thermal stability in comparison with the sample without polyethylene glycol.

Adsorption resistance: Table 3 shows the results of the adsorption measurement of HDPE/PEG/OMT nanocomposites in pure Xylene and Toluene for 40 h at room temperature. The nanocomposites exhibited the superior mechanical and thermal properties but not in adsorption resistant. Both of Xylene and Toluene can not solve the high density polyethylene. So, the decrease of weight for this substance can not be seen when placed in these liquids. But clay has high tendency for adsorbing of liquids. When this clay is added to the HDPE matrix, it can increase the adsorption of these liquids into the polymer chains that this fact is the principle reason of the sudden growth in amount of weight increase in Table 3 after adding 3 wt. % of OMT into the HDPE/PEG matrix.

Table 2: TGA data in argon atmosphere for HDPE/PEG, HDPE/OMT and HDPE/PEG/OMT nanocomposites

Samples	T ₀₁ (°C)	T ₀₅ (°C)
PE1	457	486
PE2	462	490
PE3	468	489
PE4	470	493
PE5	452	479

Table 3: The percent of weight increase for HDPE/PEG/OMT nanocomposites with different OMT content in pure Xylene and Toluene after 40 h at 25°C

Samples	Solvent	
	Xylene	Toluene
PE1	1.48	5.76
PE2	1.83	7.06
PE3	1.85	7.20
PE4	2.20	7.83

Whatever clay content increases, after adding 5 wt. % of OMT, the growth of the liquid adsorption amount for the nanocomposite can be attributed to aggregations of some layers in large silica layer volume that cause to further growth in weight increase amounts.

CONCLUSIONS

High density polyethylene and polyethylene glycol as a compatibilizer were prepared for synthesizing of HDPE/PEG/clay nanocomposite by adding of the organically modified clay in nanometer scale. The nanocomposite was prepared by melt blended in a Brabender mixer and mechanical, thermal and chemical properties of nanocomposites investigated. The clay content for improving Tensile strength and Young's modulus obtained. When the clay content reaches to 5 wt. %, Young's modulus of nanocomposites rises. On the other hand, the addition of OMT into the polymer matrix has overall decreased the tensile strength in comparison with pure blend. The effects of the addition of compatibilizer on nanocomposite properties also investigated. The usage of PEG enhanced the thermal stability of the nanocomposites. The addition of PEG as a compatibilizer on mechanical properties caused an improvement in hardness value. Morphology studies by XRD and SEM results revealed that PEG has improved the dispersion of clay into the polymer matrix.

REFERENCES

Ahmadi, S.J., Y.D. Huang and W. Li, 2004. Synthetic routs, properties and future application of polymer-layered silicate nanocomposites. *J. Mater. Sci.*, 39: 1919-1925.

- Alexandre, M. and P. Dubois, 2000. Polymer-layered silicate nanocomposites: Preparation, properties and uses of a new class of materials. *Mater. Sci. Eng. R.*, 28: 1-63.
- Berta, M., C. Lindsay, G. Pans and G. Camino, 2006. Effect of chemical structure on combustion and thermal behaviour of polyurethane elastomer layered silicate nanocomposites. *Polym. Degrad. Stab.*, 91: 1179-1191.
- Celini, N., F. Bergaya and F. Poncin-Epaillard, 2007. Grafting of hydrocarbon moieties on smectites by cold acetylene plasma and characterization of plasma-treated clay mineral polyethylene nanocomposites. *Polymer*, 48: 58-67.
- Cho, J.W. and D.R. Paul, 2001. Nylon 6 nanocomposites by melt compounding. *Polymer*, 42: 1083-1094.
- Drozhdov, A.D. and J.C. de Christiansen, 2007. Cyclic viscoplasticity of high-density polyethylene/montmorillonite clay nanocomposite. *Eur. Polymer*, 43: 10-25.
- Foresta, T., S. Piccarolo and G. Goldbeck-Wood, 2001. Competition between α and γ phases in isotactic polypropylene: Effects of ethylene content and nucleating agents at different cooling rates. *Polymer*, 42: 1167-1176.
- Fu, X. and S. Qutubuddin, 2001. Polymer-clay nanocomposites: Exfoliation of organophilic montmorillonite nanolayers in polystyrene. *Polymer*, 42: 807-813.
- Gilman, J.W., T. Kashiwagi, M. Nyden, J.E.T. Brown, C.L. Jackson and S. Lomakin, 1998. *Chemistry and Technology of Polymer Additives*. Al-Malaika, S., A. Golovoy and C.A. Wilkie (Eds.), Blackwell Sci. Oxford, pp: 249.
- Gopakumar, T.G., J.A. Lee, M. Kontopoulou and J.S. Parent, 2002. Influence of clay exfoliation on the physical properties of montmorillonite/polyethylene composites. *Polymer*, 43: 5483-5491.
- Hasegawa, N., H. Okamoto and M. Kawasumi, 2000. Polyolefin-clay hybrids based on modified polyolefins and organophilic clay. *Macromol. Mater. Eng.*, 280: 76-79.
- Hongdian, L., H. Yuan, X. Junfeng, K. Qinghong, C. Zuyao and F. Weicheng, 2005. The influence of irradiation on morphology evolution and flammability properties of maleated polyethylene/clay nanocomposite. *Mater. Lett.*, 59: 648-651.
- Lee, J.A., M. Kontopoulou and J.S. Parent, 2004. Time and shear dependent rheology of maleated polyethylene and its nanocomposites. *Polymer*, 45: 6595-6600.
- Lu, H., Y. Hu, M. Li, Z. Chen and W. Fan, 2006. Structure characteristics and thermal properties of silane-grafted-polyethylene/clay nanocomposite prepared by reactive extrusion. *J. Compos. Sci. Technol.*, 66: 3035-3039.
- Manias, E., A. Touny, L. Wu, K. Strawhecker, B. Lu and T.C. Chung, 2001. Polypropylene/Montmorillonite nanocomposites. Review of the synthetic routes and materials properties. *Chem. Mater.*, 13: 3516-3523.
- Mravěáková, M., K. Boukerma, M. Omastová, M. Mohamed and M.M. Chehimi, 2006. Montmorillonite/polypyrrole nanocomposites. The effect of organic modification of clay on the chemical and electrical properties. *Mater. Sci. Eng. C.*, 26: 306-313.
- Okamoto, M., P.H. Nam, P. Maiti, T. Kotaka, T. Nkayama and M. Takada, 2001. Biaxial flow-induced lignment of silicate layers in polypropylene/clay nanocomposite foam. *Nano. Lett.*, 1: 503-505.
- Preston, C.M.L., G. Amarasinghe, J.L. Hopewell, R.A. Shanksa and Z. Mathys, 2004. Evaluation of polar ethylene copolymers as fire retardant nanocomposite matrices. *Polym. Degrad. Stab.*, 84: 533-544.
- Ragosta, G., M. Abbate, P. Musto, G. Scarinzi and L. Mascia, 2005. Epoxy-silica particulate nanocomposites: Chemical interactions, reinforcement and fracture toughness. *Polymer*, 46: 10506-10516.
- Ray, S.S. and M. Okamoto, 2003. Polymer/layered silicate nanocomposites: A review from preparation to processing. *Prog. Polym. Sci.*, 28: 1539-1641.
- Su, S., D.D. Jiang and C.A. Wilkie, 2004. Poly (methyl methacrylate), polypropylene and polyethylene nanocomposite formation by melt blending using novel polymerically-modified clays. *Polym. Degrad. Stab.*, 83: 321-331.
- Wang, K.H., M.H. Choi, C.M. Koo, Y.S. Choi and I.J. Chung, 2001. Synthesis and characterization of maleated polyethylene/clay nanocomposites. *Polymer*, 42: 9818-9826.
- Wang, S., Y. Hu, Q. Zhongkai, Z. Wang, Z. Chen and W. Fan, 2003. Preparation and flammability properties of polyethylene/clay nanocomposites by melt intercalation method from Na⁺ montmorillonite. *Mater. Lett.*, 57: 2675-2678.
- Wang, L., R. Nemoto and M. Senna, 2004. Changes in microstructure and physico-chemical properties of hydroxyapatite-silk fibroin nanocomposite with varying silk fibroin content. *Eur. Ceramic Soc.*, 24: 2707-2715.

- Zanetti, M. and L. Costa, 2004. Preparation and combustion behaviour of polymer/layered silicate nanocomposites based upon PE and EVA. *Polymer*, 45: 4367-4373.
- Zanetti, M., P. Bracco and L. Costa, 2004. Thermal degradation behaviour of PE/clay nanocomposites. *Polym. Degrad. Stab.*, 85: 657-665.
- Zhang, J. and C.A. Wilkie, 2006. Polyethylene and polypropylene nanocomposites based on polymerically-modified clay containing alkylstyrene units. *Polymer*, 47: 5736-5743.
- Zhang, J., D.D. Jiang and C.A. Wilkie, 2006. Polyethylene and polypropylene nanocomposites based on a three component oligomerically-modified clay. *Polym. Degrad. Stab.*, 91: 641-648.
- Zhao, C., H. Qin, F. Gong, M. Feng, S. Zhang and M. Yang, 2005. Mechanical, thermal and flammability properties of polyethylene/clay nanocomposites. *Polym. Degrad. Stab.*, 87: 183-189.