POLYMERIC NANOCOMPOSITES: MOLECULAR MODELLING ASSESSMENT OF ORGANOPHILIC MOIETIES IN LAYERED SILICATES

Graziella Ranghino, Giorgio Giannotta, Gianluigi Marra and Riccardo Po

Polimeri Europa, S.p.A., Istituto Guido Donegani, Via Fauser 4, 28100 Novara, Italia

Abstract. Important among nanoscale structural materials are *nanocomposites*, in which the constituents are mixed on a nanometer-length scale. They often have properties that are superior to conventional microscale composites. The study of nanocomposite materials requires a multidisciplinary approach, involving novel chemical techniques and an understanding of physics and surface science. The present study uses molecular modelling to predict the behaviour of compatibilizers intercalated in the silicate matrix. The structure of the adduct is modelled and compared with the available X-ray and chemical data. A relationship between molecular volume and weight and the observed swelling of the layered structure is presented.

1. INTRODUCTION

Polymeric nanocomposites are one of the most exciting and promising classes of materials discovered in the last years.

A number of physical properties are successfully enhanced when a polymer matrix is modified with small amount of layered silicate on condition that the filler it is dispersed to nanoscopic level. Optical clarity, stiffness, flame retardancy, barrier properties and thermal stability are mainly influenced, but in some cases also the mechanical strength increases.

These composites are obtained by dispersion in a polymer matrix of small amounts (1-5%) of filler, having at least one of the three dimensions of nanometric scale. The most popular class of nanofillers is that of organofilicized layered silicates (i.e. lamellar clays exchanged with organic cations), able to form nanometric platelets when dispersed in a polymer [1]. The effective exfoliation – tactoids splitting in single layers – may be attained by surfaces and interlayer organo-modification.

Nanocomposites exhibit some distinctive advantages over conventional composites. First of all, they require a much smaller loading of filler, i.e. only few percent by weight vs. 20-60%. As a consequence these materials are much lighter than, for instance, glass-filled composites. They have better mechanical properties, like modulus and tensile strength, higher distortion temperatures and dimensional stability. Flame retardancy characteristics and thermal stability are generally greatly increased. Another important improvement is the gas-barrier property. Finally, the material recyclability is enhanced (because of the lower amount of filler) and nanocomposites based on amorphous polymers are transparent.

Flame retardancy is perhaps the most relevant field where nanocomposites may find applications, some of them being already commercially consolidated. Pioneering studies on these subjects have been carried out since 1961 [2], but the first effective autoestinguishing nanocomposite was obtained in 1976 [3] and developed by Toyota (Aichi, Japan), who launched the first commercial product (Nylon-6/montmorillonite) in the mid-1980s.

Corresponding author: Graziella Ranghino, e-mail: graziella.ranghino@polimerieuropa.com

Due to the increasing concerns for the health and environmental hazards of the halogenated flame retardants (HFR) used in everyday applications [4-7], several governments are strongly encouraging their substitution with other substances.

A recent European Community Directive (2003/11/CE 6 Feb. 2003) banned two brominated flame retardant, penta- and octabromodiphenylether, widely used for electric applications. In this frame, any potential substitute for HFR has to be carefully considered. From this point of view, nanocomposites could represent excellent candidates for the development of novel and safe flame retardant materials. As hinted above, organofilicized layered silicates (i.e. montmorillonites) are possibly the most widely studied nanofillers up to now. To improve dispersion the polymer matrix needs to be somewhat polar, in the more common case of non-polar material, the compatibilizing agent is carefully designed to facilitate the interaction with the polymer. This is especially true, for instance, in the case of polyolefins and polystyrene: these are materials where the improvement of flame retardancy would be a primary issue for many applications (wire & cables and electric/electronic appliances, respectively). Due to their hydrophobicity, they hardly interact with inorganics. As nanoscopic dispersion depends upon the layer separation of the clays, the knowledge and prediction of the *d*-spacing at equilibrium can offer a key index to evaluate the modifier or (co) polymer effectiveness.

In order to improve the interaction between filler and polymer and hence the dispersion of the inorganic in the organic matrix, atomistic and mesophase simulations are widely used and have contributed to both the understanding and the rationalisation of experimental data. The most recent examples of these studies are given in references [8-12] and in the references therein. The focus of the present study is on the same line of the above referred papers: we aim to correlate the swelling of the inorganic matrix with the type of organic cation that is exchanged with the natural metal cation. In a second step we aim to predict the swelling induced by the polymer, taking into account two different polymers interacting with the same layered silicate.

2. EXPERIMENTAL

Materials

- Cloisite 15A (Southern Clay) – montmorillonite modified with dimethyl dihydrogenated-tallow quaternary ammonium salt – CEC = 115 meq/100g.

- Cloisite 20A (Southern Clay) - montmorillonite modified with dimethyl dihydrogenatedtallow quaternary ammonium salt – CEC = 95 meq/100g.
- Dellite 72T (Laviosa) – montmorillonite modified with dimethyl dihydrogenatedtallow quaternary ammonium salt.
- Polystyrene (Edistir N1280, Polimeri Europa) – Mw 280000 – $MFI_{(280°, 5kg)}$: 1.4g/10'.
- Linear low density polyethylene (Flexirene CL10, Polimeri Europa) – density: 0.917 g/cm^3 – $MFI_{(190°, 2.16kg)}$: 2.6 g/10'.
- Maleated polyethylene (Fusabond MB226D, Du Pont Italia S.r.l.) – 0.9% maleic anhydride – $MFI_{(190°, 2.16kg)}$: 1.5 g/10'.

Compounding and Molding

The nanofiller dispersion in the matrices was carried out through a laboratory mixer Haake Rheomix 600 equipped with roller type rotors at 200 °C, rotational speed of 60 rpm and residence time ranging from 1 to 12 min. The mixing chamber occupied volume was 52 cm^3 and the polymer was recovered with the aid of air jet. The samples were cryo-milled, dried again and compression molded in the shape of 1mm tick disks 2.5 mm in diameter.

X-Ray Diffraction Analysis

XRD spectra were collected step-wise using Cu Kα radiation (λ=1.5416 Å) on a computer controlled Philips X'Pert PRO $\theta/2\theta$ diffractometer, equipped with a secondary curved pyrolytic graphite monochromator, in the 0.5-60° 2θ angular range, with 0.03° steps and 10 s counting time; to reduce the level of background radiation at low angle, programmable divergent and anti-scatter slits and a receiving slit of 0.04 mm are used. Both the programmable slits are sized to set a constant observed sample length of 18 mm. With this optic setting *d*-spacing up to 100-120 Å can be observed.

Modelling and theory

The structural data of Montmorillonite are taken from Cerius^2 [13] inorganic structure database. The structure of the organic compatibilizers molecules is built and optimized with Cerius^2 Builder and OFF modules. When a molecule is very flexible, as in the case of octadecyl-dimethyl-ammonium, a conformational study is performed by means of Molecular Dynamics with Quenching. In this way a large number of conformations, are detected: among these, a limited set is chosen (namely 4 to 7 different conformations), which represent different minima on the potential energy hypersurface. These conformers differs by 1 Å in the gyration radia, i.e the longest arm of the molecule spinning about its cen-

Table 1. *d*-spacing value (Å) of polymer nanocomposites (mixing time: 6 minutes).

	STARTING FILLER	POLYSTYRENE	POLYETHYLENE	MALEATEDPOLY-ETHYLENE
DELLITE 72T	28.1	33.0	N.D.	N.D.
CLOISITE 15A	32.8	33.0	29.7	EXFOLIATION
CLOISITE 20A	25.0	33.7	25.3	N.D.

ter of gravity: in other words, the both globular and elongated shapes are considered .

The loading of compatibilizer between the lamella is simulated by means of Sorption module of Cerius[2]. In order to hold the bulkier compatibilizer, not the native crystal cell is considered , but a multiple of it, namely a cell with has $A= N*a$, $B=N*b$, where N is an integer multiplier of the original a and b axis. In most cases N is equal to 5. The C axis of the solid is taken as a parameter and is elongated in steps. The starting value is 15 Å in the first Sorption run that counts 1 million moves . Other runs of the same length and same temperature follow, with c increasing of 2 Å in each run. The end of the simulation is reached when all the potassium ions are substitued by the organic ionic moiety. The resulting c value is compared with experimental values, when available.

The final configuration of the intercalated silicate is then energy minimized, i.e. the loaded molecules are free to move, rotate, relax their covalent geometry.

The intercalation of the polymer starts from the final swelled cell of the inorganic again empty, in which both the polymer and the compatibilizer can

intercalate: Sorption is used in one run of 3 million moves. The polymer is simulated with 3 to 5 different conformers of oligomers of 10 to 40 units: this choice allows to simulate the intercalation of polymer-stretch like model or a 'globular' polymer. Short branches are present in the longer models: one example is given in Fig. 1. Again the output is energy minimized with OFF modules, releasing the geometries of the intercalates and the *c* axis.

3. RESULTS

Three different organofilicized montmorillonites have been used to prepare nanocomposites with either polystyrene or polyethylene. Blends have been prepared by using a mixer for different mixing times ranging from 1 to 12 minutes. XRD analysis on compression molded specimen results are reported in Figs. 2-3 and Table 1.

The level of cationic exchange of MMT-org does not affect the final result for the polymer intercalation. Cloisite 15A and Cloisite 20A whose original *d*-spacing differs substantially, when compounded are readily intercalated at the same grade. The above mentioned result confirms that the intercalation of organosilicate by the polymer chains take place in

model for polyethylene   PE-maleate
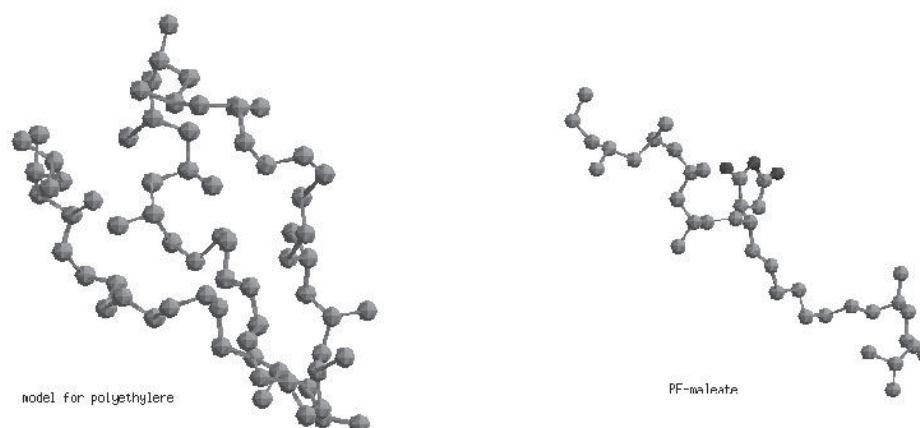
Fig. 1. Two structures of oligomers used to model PE (left) and Maleated-PE (right).
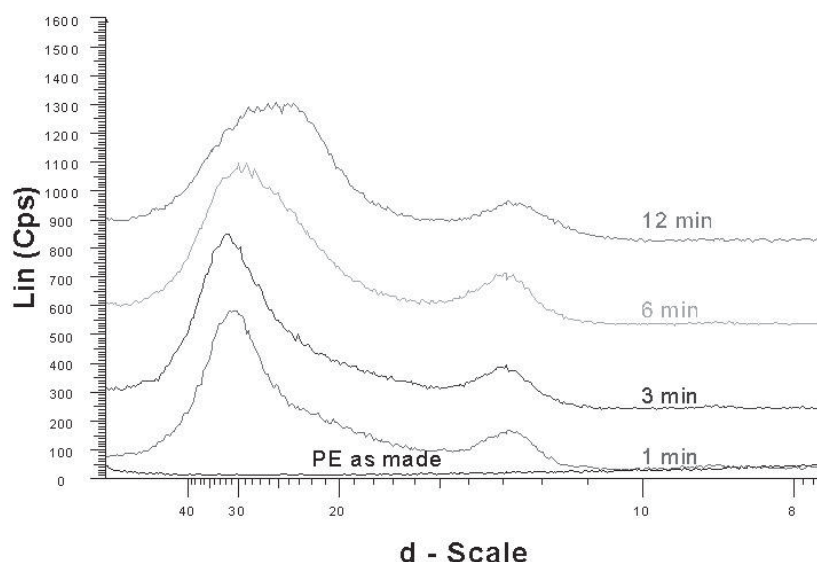
Fig. 2. XRD spectra on compression molded PE specimen obtained with different mixing time. The *d*-scale is in Å.

a very short time according previous reports [14-16].

As can be seen, the *d*-spacing for the polystyrene nanocomposites is not sensitive to the mixing time, a value of 33-34 Å being reached after 1 minute of mixing and maintained for longer mixing times. On the other hand, the *d*-spacing for polyethylene nanocomposites has a maximum value after 1 minute, whereas a decrease is observed for longer times, suggesting a progressive thinning of the galleries and a slight lack of crystal order.

Yoon *et al.* [14] observed this collapsing of the layers and correspondingly XRD basal reflections approaching that of pristine mineral in the prepara-

tion of nanocomposites. The cause of this behaviour was attributed to thermal degradation of the intercalated species. Recently the role of excess of organo-modifier in the thermal stability was also investigated [17-19] and same authors recognise in the so-called 'local bilayer' critical zones for premature degradation [17].

The classical way to attain a good dispersion/exfoliation inside a polyolefin matrix, consists in a mixing with a maleated-resin [1] which promote particles-matrix interaction and facilitate the lamellar stacks separation. Therefore a polyethylene nanocomposite has been prepared starting from a commercially available maleated-PE. The XRD spec-
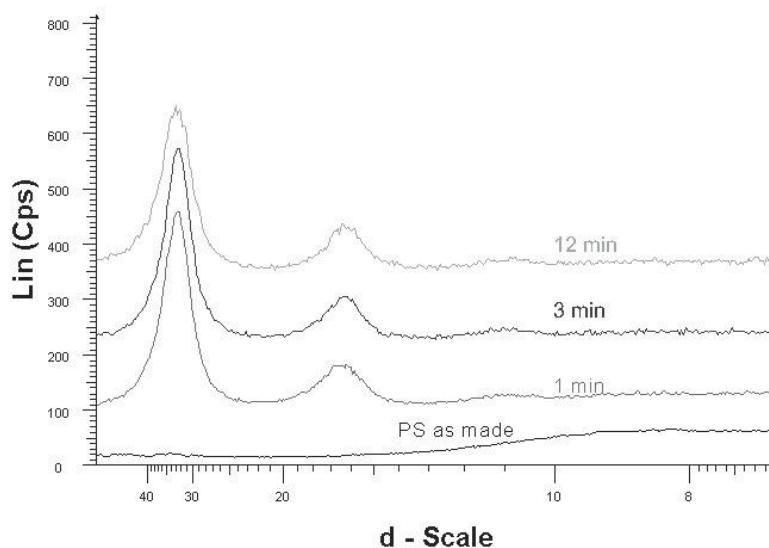

Fig. 3. XRD spectra on compression molded PS specimen obtained with different mixing time. The *d*-scale is in Å.
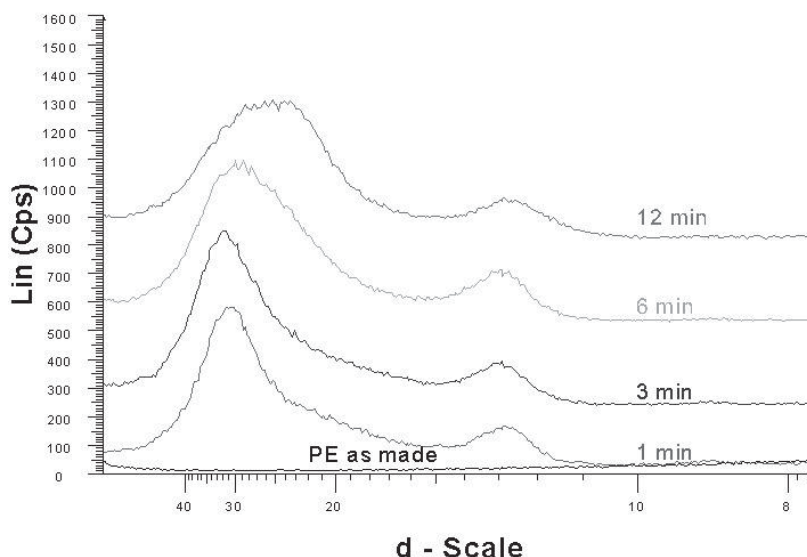
Fig. 4. XRD spectra of pure Cloisite 15 A, intercalated PE and swelled PE maleate. The *d*-scale is in Å.

trum of the material is reported in Fig. 4. As can be seen, an almost total exfoliation was achieved, even if some enduring reflection testifies for a residual presence of intercalated domains (very small, broad peak centred at around 33 Å).

4. MODELLING RESULTS

Structure and *d* spacing of compatibilized montmorillonite

In order to understand and predict the *d* spacing of an intercalated montmorillonite, a number of simulations are run on the lamellar silicate with SORPTION: four different compatibilizers are considered, namely: [18-crown-6]K^+; octadecyldimethylammonium; hexadecyldiphenyl phosphonium; protonated melamine. The same computational procedure has been applied to all of them and the final structure obtained has been compared with the available X-ray data.

The results are given in the Fig. 5 that also reports the computed *d* spacing. The agreement with X-ray data is acceptable when the organic cations completely substitute the K^+ cations: the final d-spacing is equal to 29.9 Å for the ammonium derivative (the experimental data are ranging between 24 and 32 Å, according to the montmorillonite type [20,21] and to 37 Å for the phosphonium one (the experimental data is in this case 37.2 [22]). The 18-crown-6 case is a different case: the crown ether is strongly selective for K^+ that is not exchanged but just kept inside the cage. The *d*-spacing (13.5 Å) compares well with the X-ray data (14. Å [23]) that

correspond to the chelation of the 20% of the potassium.

The fourth case, the melamine, has no experimental data available: the simulation shows that the d spacing corresponding to the 100% substitution is 20 Å, i.e. much smaller than the other two organic cations.

The correlation is observed between *d*-spacing and compatibilizer structure: an increase in swelling is correlated with the increase of molecular weight and polarity of the intercalate.

Simulation of polymer intercalation in the compatibilized lamellar silicate

The modelling consider one compatibiliser, namely the octadecyl dimethylammonium and the montmorillonite framework and two different polymers, namely the PE (polyethylene) and the PE-Maleate. The intercalation starts in both cases with the *c* axis equal to 30 Å. The results show that the d-spacing in the relaxed final structure is equal to 37 Å in the case of PE and 46 Å in the case of PE-maleated. The loading is different, namely the solid hosts the PE-maleate in higher density that in the PE case. Table 2 reports the final structural data.

It is evident that in presence of the maleated-PE, this is selected as more favourable intercalant so that the pure PE has very low load (2 molecules per cell) and the loading of PE-maleate is larger even of the ammonium salt.

On the contrary, when no maleate group are present, the PE content is higher, but also the ammonium salt is high as its presence is determinant to the stability of the complex.
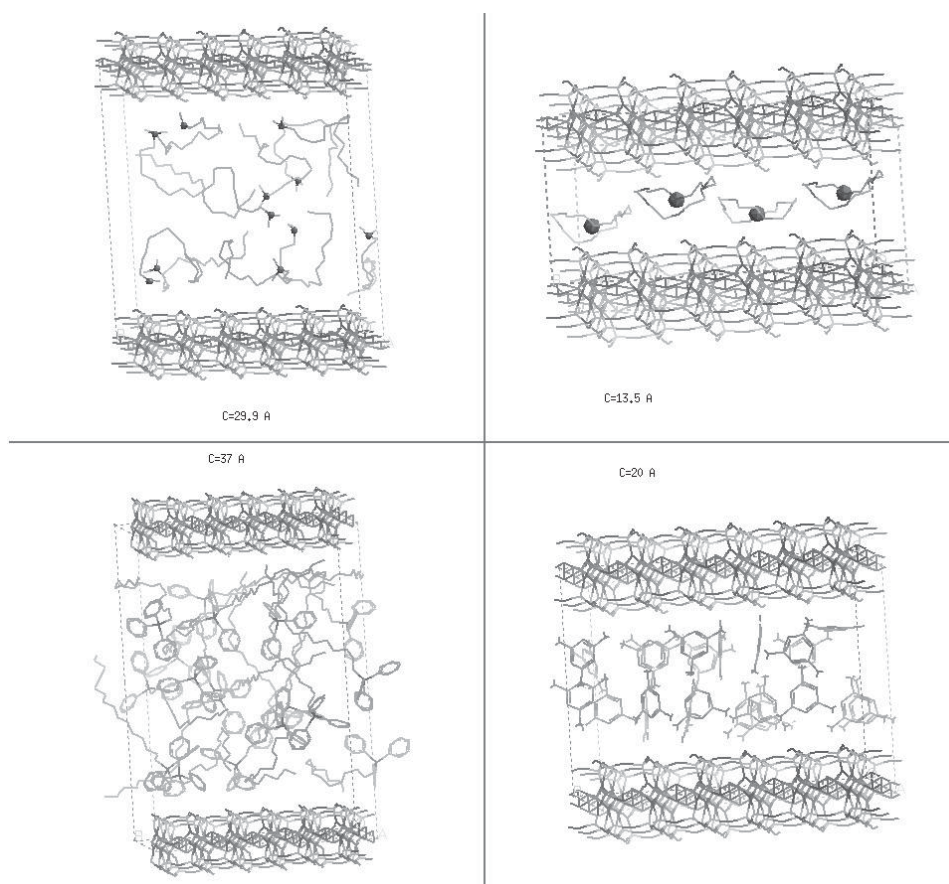
Fig. 5. Final structures of the modelled montmorillonite with compatibilizers. Top left: octadecyldimethylammonium; *d*-spacing 29.9 Å; 100% substitution of K⁺. Top right: 18-crown6, *d*-spacing 13.6 Å; 20% of K⁺ substitution. Bottom left: esadecyltriphenylphosphonium; *d*-spacing 37 E; 100% substitution of K⁺. Bottom right: melamine; *d*-spacing 20 Å; 100% substitution of K⁺.

The comparison of the computed *d* spacing with the experimentally observed is only partially in agreement. The *d* value of compatibilized montmorillonite is smaller than the observed one (30 Å versus 32.8 Å), but the final composite resulted swelled to 37 Å, while in the X-ray analysis the composite after 6 minutes of mixing with PE has a decreased d spacing of roughly 29.7Å. The simulated structure of the composite with maleated-PE-shows a very pronounced increase in *d* value. The tendency to increase the swelling is inferred also from the experimental data. There is a hardly visible peak ranging from 32 to 36 Å, which is smaller than the predicted one. However, the final exfoliation that is inferred from X-ray analysis, correlates well with the predicted trend and the computed value of 46 Å.

These preliminary data are sufficient to draw some conclusions: the chemical modifications of polymers and/or compatibilizers can lead to composites with the requested features; moreover, these

Table 2. Polymer nanocomposites: average number of loaded molecules of filler and of polymer and *d*-spacing values (Å).

	FILLER	POLYETHYLENE chains	Maleated-POLYETHYLENE-chains	*d*-spacing
POLYETHYLENE nanocomposites	8.5	8		37
Maleated PE nanocomposites	6	2	10	EXFOLIATION

features can be simulated and, hopefully, predicted by modelling; the successful results need the interplay of chemical, physical and micromechanical techniques.

ACKNOWLEDGEMENT

REFERENCES

[1] M.Alexandre and P.Dubois // *Mat.Sci. Eng.* **28** (2000) 1.

[2] A. Blumstein // *Bull. Chim. Soc.* (1961) 899.

[3] S. Fujiwara and T. Sakamoto // *JP-A 511976-109998* (1976), Unitika.

[4] *Selected Brominated Flame Retardants Background and National Experience with Reducing Risk*, OECD Environment Monograph Series No. 102 (Paris, 1995).

[5] *Brominated Flame Retardants* (Danish Environmental Protection Agency, June 1999).

[6] *Modern Plastics*, Apr. 2002, p. 50.

[7] www.defra.gov.uk/environment/consult/pentabde/pdfs/annexa.pdf.

[8] F. Dabrowsky, M. LeBras, R. Delobel, J. Gilma and T. Kashiwagi // *Macromol. Symp.* **194** (2003) 201.

[9] K. Anderson, A. Sinsawa, R. Vaia and B. Farmer, In: *Proc. 225th ACS Nat.Meet.* (Abstracts of Paper, New Orleans, 2003, COMP-042).

[10] V. Kuppa and E. Manias // *Chem. Mat.* **14** (2002) 2171.

[11] E. Hackett, E. Manias and E. Giannelis // *Chem. Mat.* **12** (2000) 2161.

[12] J. Bujdak, E. Hackett and E. Giannelis // *Chem. Mat.* **12** (2000) 2168.

[13] Cerius$^{2\,4.2}$, Accelrys Inc., San Diego (CA) 2002.

[14] J.T.Yoon, W.H.Jo, M.S.Lee and M.B.Ko // *Polymer* **42** (2001) 329.

[15] M. Sikka, L.N. Cerini, S.S. Ghosh and K.L.Winey // J.*Polym.Sci.: Part B: Polym. Phys.* **34** (1996) 1443.

[16] R.A. Vaia, K.D. Jandt, E.J. Kramer and E.P. Giannelis // *Macromolecules* **28** (1995) 8080.

[17] M.A. Osman, M. Ploetze and U.W.Suter // *J. Mater. Chem.* **13** (2003) 2359.

[18] A.B.Morgan and J.D.Harris // Polymer **44** (2003) 2313.

[19] W.Xie, Z.Gao, W.-P.Pan, D.Hunter, A.Singh and R.Vaia // *Chem.Mater.* **13** (2001) 2979.

[20] N.Hasegawa, H.Okamoto, M.Kawasumi and A.Usuki // *Polym. Mat. Sci.* **80** (1999) 253.

[21] Y.T.Lim and O.O.Park // *Macromol. Rapid Commun.* **21** (2000) 231.

[22] J.Zhu, A.B.Morgan, F.J.Lamelas and C.A.Wilkie // *Chem.Mater.* **13** (2000) 3774.

[23] H.Yao, J.Zhu, A.B.Morgan and C.H.Wilkie // *Polym. Eng. Sci.* **42** (2002) 1808.