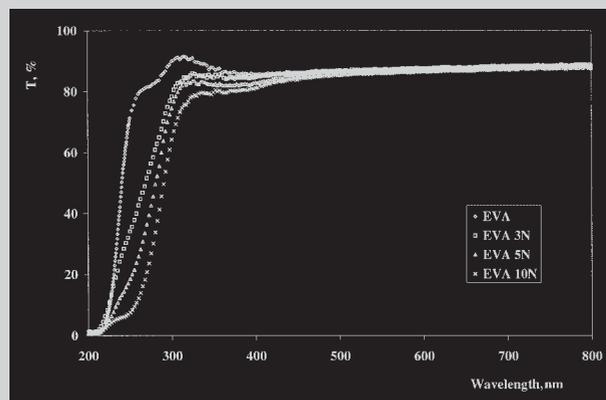**Full Paper:** Nanocomposites are a new class of polymer material with an ultrafine phase dispersion of the order of a few nanometers that shows very interesting properties often very different from those of conventional filled polymers. In this work the mechanical and optical properties of Poly-[ethylene-*co*-(vinyl acetate)] (EVA copolymer) based nanocomposites have been investigated to evaluate its possible use in several applications. For example, films for covering greenhouses made by EVA copolymer are appealing because of their interesting optical properties and for the so-called greenhouse effect. Mechanical properties, and the rigidity in particular, are, on the contrary, quite low. Nanocomposites should avoid this shortcoming if optical properties and processability are not unfavorably effected. EVA copolymer based nanocomposites have been prepared by compounding polymer matrix and two different functionalized silicates (0–10 wt.-%) in molten state. X-Ray diffractograms show that the in the adopted experimental conditions no exfoliation of the filler is obtained, but an intercalated morphology is observed. Rheological behavior both in shear and in non-isothermal elongational flow is only slightly influenced by the presence of the filler. As for the mechanical properties, the elastic modulus strongly increases without any worsening of the elongation at break. The permeability in the UV region is not influenced by adding even relatively high contents of the silicates. The improved mechanical and optical properties and the unmodified processability suggest then the use of these new polymeric systems in many applications and in particular as films for covering greenhouses.

UV spectra of the EVA/Nanofil system.

EVA Copolymer Based Nanocomposites

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Introduction

Nanocomposites are a new class of polymer materials with an ultrafine phase dispersion of the order of a few nanometers that shows very interesting properties often very different from those of conventional filled polymers.[1–4] The presence of these nanoparticles improves the elastic modulus without decreasing the elongation at break and does not worse the rheological and processing behavior and the optical properties of the polymer matrix. The main problem in the preparation of nanocomposites in the molten state[5–10] is to intercalate the single polymer chains between the layers of the particles or at least to exfoliate the filler particles. This condition is achieved by optimizing the processing parameters but, when the matrix is an apolar polymer, the exfoliation or even the intercalation is very difficult because of the polar nature of the filler. In this case additional compatibilizers could be necessary.[10] Poly-[ethylene-*co*-(vinyl acetate)], EVA, has been proved to form intercalated and/or exfoliated hybrids[11,12] without any additional compatibiliser. The formation of intercalated or exfoliated morphologies depend on the type of silicates, on the amount of vinyl acetate and on the processing conditions.

Aim of this work is to investigate the properties of a poly[ethylene-*co*-(vinyl acetate)] (EVA copolymer) based nanocomposites as a function of the amount of two different organoclays. All properties have been measured considering a possible use of this new materials for several different applications. In particular, films for covering greenhouses made by EVA copolymer are appealing because of their interesting optical properties and for the so-called greenhouse effect. Mechanical properties, and the rigidity in particular, are, on the contrary, quite low. EVA based nanocomposites should avoid this shortcoming provided that optical properties and processability are not unfavorably effected.

Experimental Part

Materials

The materials used in this work were a sample of film grade (melt index 0.3 dg/min) poly[ethylene-*co*-(vinyl acetate)] (Grenflex FC45 from Polimeri Europa, Italy), and two silicate samples (Cloisite 15A from Southern Clay Products and Nanofil 15 from Sud Chemie). Cloisite 15A, (CL), is a montmorillonite modified with ditallowdimethylammonium with an average diameter of 8 μm, whereas Nanofil 15 (N) is a bentonite modified having an average diameter of 3 μm.

EVA has been compounded with the two silicates at different concentrations, namely 3, 5 and 10 wt.-%. Polymer and filler have been compounded in a Brabender mixer at two temperatures and two mixing speeds for about 5 min, time enough to reach a constant value of the torque in all the investigated processing conditions. Pure polymer was subjected to the same treatments.

X-Ray diffractograms were recorded by using a Siemens D500 diffractometer with Cu K_α radiation. The polymer systems were analyzed in film obtained by compression molding and the silicates in powder.

Rheological tests in shear flow were performed with a Rheometrics RDA II in a plate-plate mode at a test temperature of 160 °C.

The rheological behavior in non-isothermal elongational flow has been tested by using a capillary viscometer, Rheoscope 1000, (CEAST, Italy) equipped with a drawing system.[13,14] The capillary diameter was 1 mm, the length-to-diameter ratio was 40 and the test temperature 180 °C. The extruded filament passes through a pulley system and is then drawn by two counter-rotating rolls. The run is carried out by pulling the filament, extruded at a given flow rate, at a rotational speed which increases with a linear acceleration of 100 rpm $\times$ min^{-1} $\times$ s^{-1}. The test ends with the breaking of the filament. The force in the molten filament at breaking is read directly and is known as melt strength (MS). The breaking stretching ratio (BSR) was calculated as the ratio between the drawing speed at breaking and the extrusion velocity at the die. The data were collected at the same temperature and with the same die of the viscosity measurements and at two apparent shear rates, 60 and 600 s^{-1}.

Mechanical tests were carried out with an universal Instron machine mod 4443 according to ASTM D882.

UV spectra were measured with a Shimadzu UV-2401 instrument.

The samples for all the tests were prepared by compression molding at 160 °C. The thickness of the samples was about 50 μm.

Results And Discussion

Compounding

The torque recorded during the compounding in the mixer is a measure of the shear viscosity of the melt and then of the processability of the polymer system. In Figure 1 the torque curves of the pure EVA and of the samples with 10% of the two organoclays (EVA10CL and EVA10N) are
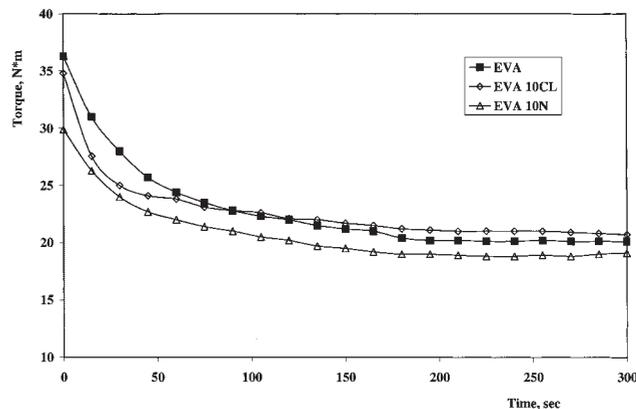

Figure 1. Torque curves of the pure EVA and of the samples with 10 wt.-% of the two organoclays.

shown. The data refers to materials compounded at 160 °C and 150 rpm. The curves of the system with 3 and 5% of solid particles, here not included for sake of simplicity, are intermediate between those at 0 and 10%.

The three curves run very near and the presence of the two fillers does not give any definite trend as for the effect of the dispersed particles on the processability. Indeed, Cloisite tends to slightly increase the value of the torque, while the opposite is observed for Nanofil. As a general comment, adding of relatively high amounts of these organoclays does not seem to influence the processability in shear flow of the EVA sample. This result can be considered quite unexpected considering the large increase of the viscosity of the polymer melt when compounded with inert fillers. This behavior can be considered as a test of a remarkable change of the size of the filler particles.

Morphology

The diffractograms of the two silicates and of the samples with 10% of Cloisite and Nanofil are reported in the Figure 2 and 3. The peaks of the two fillers do not disappear in the
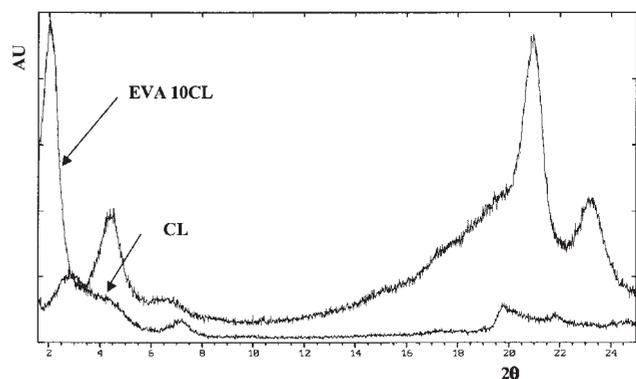

Figure 2. Diffractograms of the Cloisite sample and of EVA filled with 10 wt.-% of Cloisite.
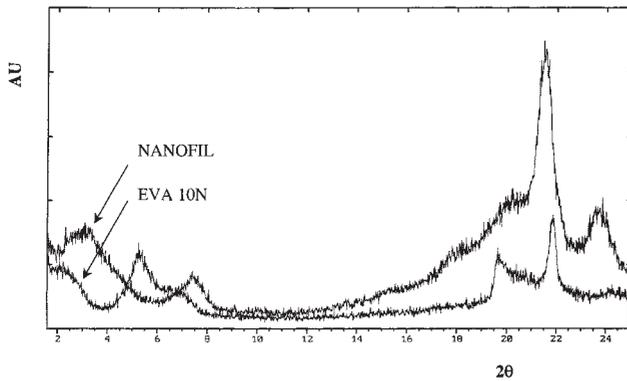
Figure 3. Diffractograms of the Nanofil sample and of EVA filled with 10 wt.-% of Nanofil.

Figure 5. Flow curves of the EVA/Nanofil system.

nanocomposites and this means that the exfoliation of the particles did not occur. However, the XRD traces clearly show the formation of an intercalated hybrid. Indeed, the compounding with Cloisite results in the disappearance of the peak at 2.8° 2θ angle and the appearance of a new peak at a lower 2θ angle. This means a greater distance between the silicate layers caused by insertion of the polymer chains. An intercalated hybrid has been then formed. Indeed, the peak of Cloisite at 2.8° 2θ angle corresponds to a 31.6 Å interlayer spacing, while the peak of the EVA/Cloisite system corresponds to a larger interlayer spacing of about 44 Å.

As for the nanocomposite with Nanofil, the interlayer spacing shifts from 27.5 to 39.3 Å showing also for this system a successful intercalation.

Rheological Properties

The flow curves of all the systems prepared at $T = 160\,°C$ and at a rotational speed of 150 rpm are reported in Figure 4 and 5. The flow curve of unfilled EVA sample has been measured on the processed material to take into account the effect of the thermomechanical treatment.

The flow curves of the filled samples are slightly higher than that of the unfilled polymer and increasing with the
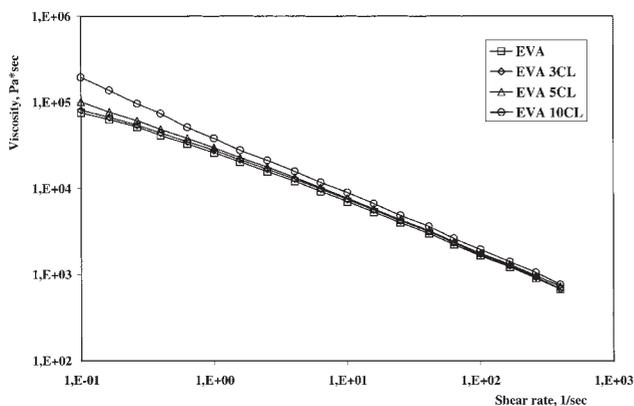

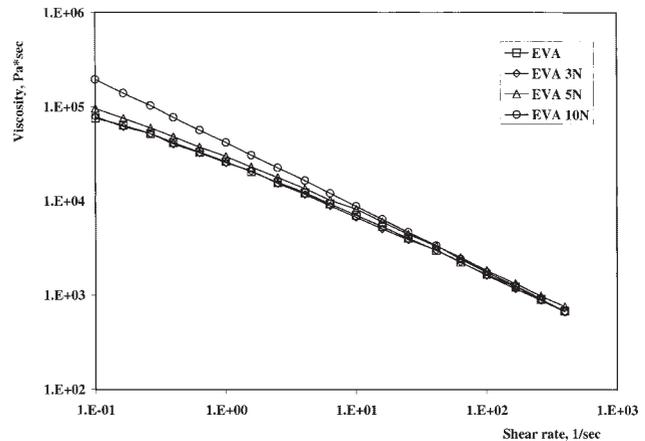Figure 4. Flow curves of the EVA/Cloisite system.

filler content. However, the rise of the viscosity is low and mostly only in the low shear rate region. By increasing the shear rate all the flow curves approach one another and that of the pure polymer. These data confirm the results and the comments previously done on the torque measurements. The flow curves, indeed, clearly show that the viscosity in shear flow at high shear rates – the shear rates involved in the compounding operation – is not significantly influenced by the presence of the nanoparticles. In particular, in the high shear rate region the EVA10N sample shows the lowest values of the viscosity, while the opposite is true for the EVA10CL sample confirming the torque data. The compounding is indeed done at high shear rate. The viscosity then rises in presence of the nanoparticles, but this increase is very small – in particular with respect to that observed for conventional filled polymers. The more pronounced non-Newtonian behavior, typical of all the filled systems, tends to reduce the viscosity to the values of the polymer matrix.

The non-isothermal elongational flow is involved in the film blowing operation and the measure of the melt strength, MS, and of the breaking stretching ratio, BSR, gives a very good indication of the filmability of the molten polymer system. The processability in this type of flow improves with increasing the values of MS and BSR.

In Figure 6 and 7 MS and BSR are reported as a function of the filler content for the two systems respectively. The BSR and the MS values are almost unaffected by the presence of the solid nanoparticles and small differences can be observed only at high concentrations of the filler. The presence of relatively high amounts of these fillers does not worse, then, the processability in elongational flow as occurs, on the contrary, in the conventional filled polymers.[15]

Mechanical Properties

In Table 1 the mechanical properties, elastic modulus E, tensile strength TS, and elongation at break EB, are reported for the pure EVA and for the compounds with 3 and 5% of Cloisite compounded in processing conditions. In all the
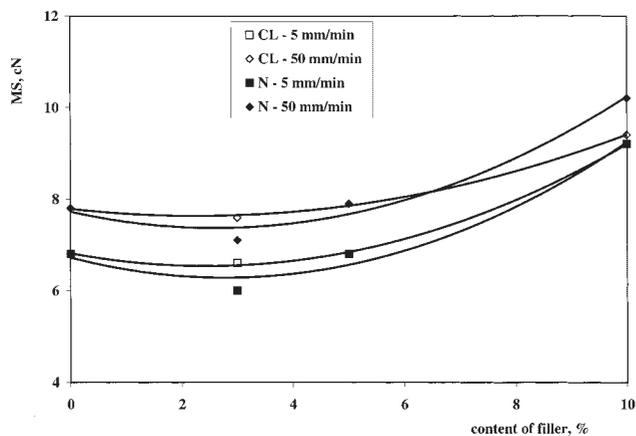
Figure 6.   Melt Strength as a function of the filler content for the two systems.

Table 1.   Elastic modulus E, tensile strength TS, and elongation at break EB, for the pure EVA and for the compounds with 3 and 5 wt.-% of Cloisite compounded in processing conditions.

Sample	Processing conditions	E	EB	TS
		MPa	%	MPa
EVA	$T = 110\,°C$; $n = 150$ rpm; $t = 5$ min	49	609	18.4
EVA3CL	$T = 110\,°C$; $n = 150$ rpm; $t = 5$ min	60	610	18.1
EVA5CL	$T = 110\,°C$; $n = 150$ rpm; $t = 5$ min	76	617	18.6
EVA	$T = 110\,°C$; $n = 250$ rpm; $t = 5$ min	47	598	18.3
EVA3CL	$T = 110\,°C$; $n = 250$ rpm; $t = 5$ min	62	598	18.5
EVA5CL	$T = 110\,°C$; $n = 250$ rpm; $t = 5$ min	74	574	17.5
EVA	$T = 160\,°C$; $n = 150$ rpm; $t = 5$ min	51	640	19.4
EVA3CL	$T = 160\,°C$; $n = 150$ rpm; $t = 5$ min	69	631	19.7
EVA5CL	$T = 160\,°C$; $n = 150$ rpm; $t = 5$ min	77	618	18.4
EVA	$T = 160\,°C$; $n = 250$ rpm; $t = 5$ min	45	519	17.1
EVA3CL	$T = 160\,°C$; $n = 250$ rpm; $t = 5$ min	54	538	18.4
EVA5CL	$T = 160\,°C$; $n = 250$ rpm; $t = 5$ min	61	537	17.5

processing conditions the elastic modulus strongly increases while tensile strength and elongation at break are almost uninfluenced by the presence of the nanoparticles. The behavior is better than that observed for conventional microcomposites and can be related to the large aspect ratio of the nanoparticles and with the larger matrix-particle interface allowing a better transmission of force between the two phases. Small differences are observed as a function of the processing conditions. Indeed, only at the higher temperature and rotational speed some decrease of all the investigated mechanical properties is observed. This behavior can be attributed to some thermomechanical degradation undergone by the molten polymer during the mixing.

In the Figure 8–10 elastic modulus E, tensile strength TS, and elongation at break EB, are plotted against the content of filler for the two systems. Both the two silicates give similar results. As already said, the elastic modulus strongly rises with increasing the amount of silicate and the composite with only 5% of filler shows a value about 50% higher
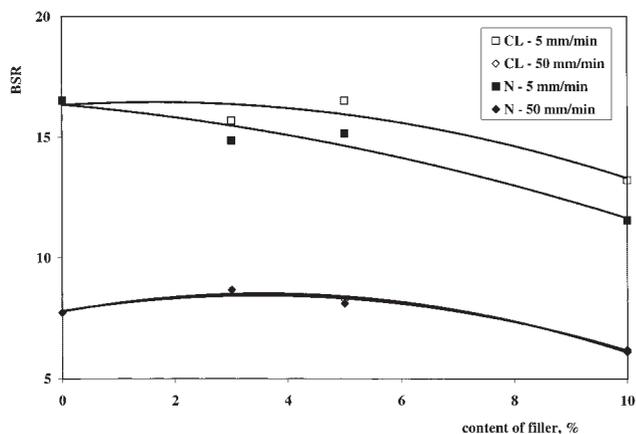
than that of the unfilled matrix. The tensile strength and the elongation at break are almost uninfluenced by the presence of the nanoparticles even at the higher silicate concentration. It is worth recalling that microcomposites with other inert filler show similar increase of the rigidity at larger content of filler when the elongation at break falls down dramatically.

Optical Properties

UV spectra of the two systems are plotted in the Figure 11–12. In the same figures the trace of the pure EVA, subjected to the same processing operations has been plotted. All the materials show the same optical permeability for wavelength larger than 500 nm. In the lower wavelength range the cut-off moves towards larger value of the wavelength with increasing the content of silicate. The high value of light transmitted through the compounds is a very interesting result because the microcomposite shows a

Figure 7.   Breaking Stretching Ratio as a function of the filler content for the two systems.
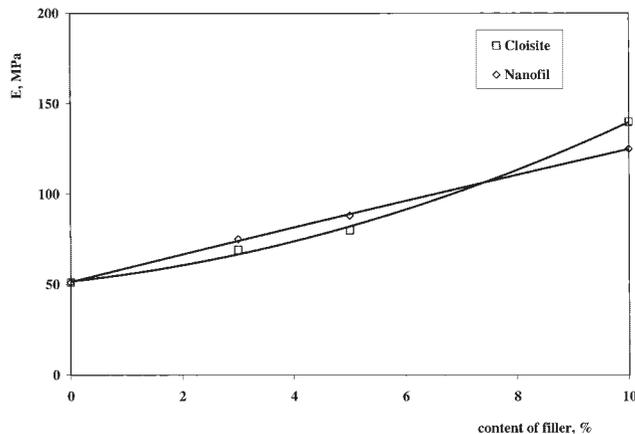

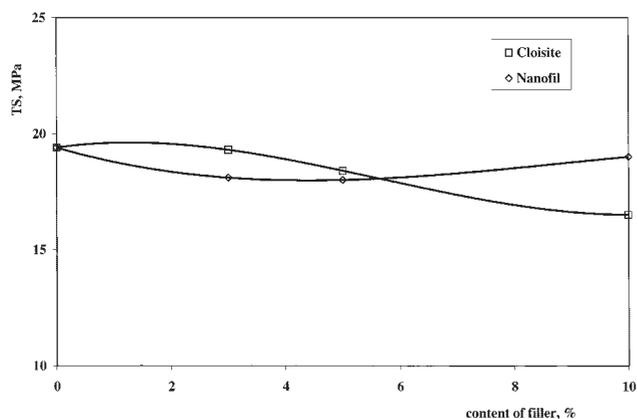Figure 8.   Elastic modulus against the content of filler for the two systems.

Figure 9. Tensile strength against the content of filler for the two systems.
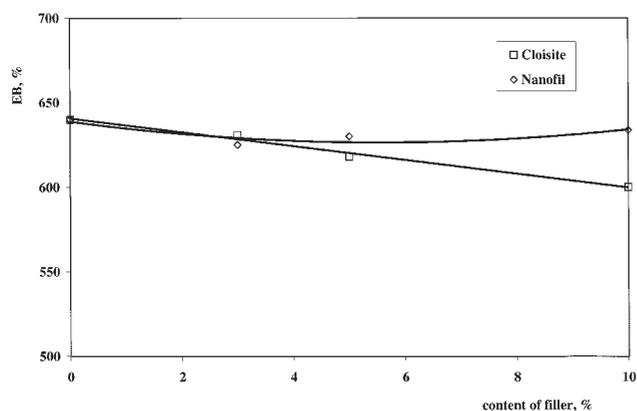

Figure 10. Elongation at break against the content of filler for the two systems.

dramatic decrease of the light transmittance in presence of solid particles. This result can be considered as an evidence of the presence of very small particles in the compound.
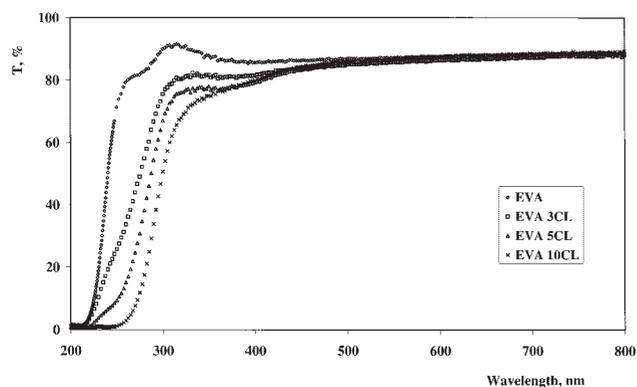

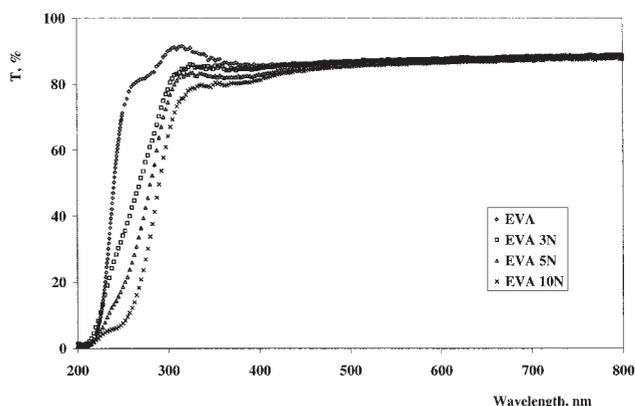Figure 11. UV spectra of the EVA/Cloisite system.

Figure 12. UV spectra of the EVA/Nanofil system.

Conclusions

EVA based nanocomposites present an intercalated morphology without any adding of compatibilizers. This morphology gives rise to a rheological behavior and to a processability very similar to that of the unfilled copolymer. In particular, the processability of the film grade EVA sample is almost uninfluenced by the presence of the nanoparticles both in shear flow and in non-isothermal elongational flow. This is very important if these nanocomposites are processed in a film blowing operation. A significant increase of the rigidity at very low content of silicate is observed while the elongation at break remains almost unchanged. Finally, the UV permeability does not change with respect to the unfilled EVA for silicate content up to 10 wt.-%.

[1] E. P. Giannellis, *Adv. Mater.* **1995**, *8*, 29.
[2] C. Zilg, F. Dietsche, B. Hoffmann, C. Dietrich, R. Mülhaupt, *Proceedings Eurofiller,* 1999.
[3] G. Lagaly, T. J. Pinnavaia, Eds, *Appl. Clay Sci.* **1999**, *15*.
[4] M. Zanetti, S. Lomakin, G. Camino, *Macromol. Mater. Eng.* **2000**, *279*, 1.
[5] R. A. Vaia. E. P. Giannellis, *Macromolecules* **1997**, *30*, 7990.
[6] L. M. Liu, Z. N. Qi, X. G. Zhu, *J. Appl. Polym. Sci.* **1999**, *71*, 1133.
[7] M. Kato, A. Usuki, A. Okada, *J. Appl. Polym. Sci.* **1997**, *66*, 1781.
[8] A. Oya, Y. Kurokawa, *J. Mater. Sci.* **2000**, *35*, 1045.

[9] M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki, A. Okada, *Macromolecules* **1997**, *30*, 6333.

[10] N. Hasegawa, M. Kawasumi, M. Kato, A. Usuki, A. Okada, *J. Appl. Polym. Sci.* **1998**, *67*, 87.

[11] M. Alexandre, G. Beyer, C. Henrist, R. Cloots, A. Ruhmont, P. Dubois, *Macromol. Rapid Commun.* **2001**, *22*, 643.

[12] M. Zanetti, G. Camino, R. Thomann, R. Mülhaupt, *Polymer* **2001**, *42*, 4501.

[13] F. P. La Mantia, D. Acierno, *Polym. Eng. Sci.* **1985**, *25*, 279.

[14] F. P. La Mantia, D. Acierno, *Plast. Rubber Process. Appl.* **1985**, *5*, 183.

[15] S. Ottani, A. Valenza, F. P. La Mantia, *Rheol. Acta* **1988**, *27*, 172.