Macromol. Symp. **2006**, 245–246, 337–342 DOI: 10.1002/masy.200651346

Effect of Foster Swelling Degree in Polystyrene/Clay Nanocomposites Obtained by In Situ Incorporation

Rafael Arioli,[1] *Odinei H. Gonçalves,*[1] *Lizabeth G. Castellares,*[2] *João Manoel da Costa,*[2] *Pedro H. Araújo,**[1] *Ricardo Machado,*[1] *Ariovaldo Bolzan*[1]

Summary: During the in-situ incorporation of an organophilic clay into the polymer matrix in a free radical polymerization, the radical should penetrate the basal space between the layers of the clay increasing the distance between these layers and leading to a nanocomposite with an intercalated or exfoliated morphology. The final morphology depends on the affinity of the monomer for the cation used to change the organophilicity of the clay. In this work, Foster swelling is applied as a method to obtain a degree of affinity of the clay for the monomer. The objective of this work is to study the effect of the Foster swelling degree on the final polystyrene/clay composite obtained by free-radical polymerization of styrene containing organophilic clay. Some commercial organophilic clays with different Foster swelling degree were employed and the incorporation of the clays into polymer was carried out in bulk styrene polymerization reactions. The X-ray diffraction (*XRD*) reveals the basal spacing of the clays before and after in-situ incorporation indicating the morphology of the nanocomposite. The nanocomposites were also characterized by thermal gravimetric analysis (*TGA*). Results showed a correlation between Foster swelling degree and the morphology obtained. High values of Foster swelling degree lead to exfoliated polystyrene/clay nanocomposites, whereas decreasing this value intercalated, partially intercalated and only dispersed composites were obtained depending on the degree of affinity of the monomer for the clay.

Keywords: foster swelling; nanocomposite; organophilic clay; polymerization; polystyrene

Introduction

Research on polymer/clay nanocomposites has become an area of great academic and industrial interest because hybrid organic/layered inorganic composites such as clays show better properties when these inorganic layers are dispersed on a nanometer scale in the polymer matrix comparing to pure polymer or traditional microcomposities. These properties, such as better mechanical properties, thermal stability, gas barrier properties and flame resistance are achieved at very low filler level, usually inferior to 5 w/w %,[1,2] and can be obtained due to the high ratio of superficial area of the inorganic dispersed phase per volume of polymer.

The process to obtain polymer/clay nanocomposites presents two main steps: the first one is the clay modification of its native hydrophilicity. Natural occurring clays are hydrophilic and not compatible with organic compounds. Replacing Na^+ or K^+ cations of native montmorillonite by more hydrophobic cations changes the hydrophilic characteristic of the clay, transforming the clay in an ‘‘organoclay’’. The second step is the incorporation of the organoclay into the polymer matrix in order to obtain nanocomposites. The incorporation may be carried out by different ways, as

---

[1] Departamento de Eng. Química e Eng. de Alimentos, Universidade Federal de Santa Catarina, Centro Tecnológico, Florianópolis, 88010-970 SC, Brazil
E-mail: pedro@enq.ufsc.br

[2] CENPES/PETROBRAS, Rio de Janeiro, RJ, Brazil

in situ polymerization, melt intercalation or solution intercalation.[3] During the in-situ polymerization, the organophilic clay is swollen with monomer or dispersed in the reaction medium. Then the monomers are polymerized and the nanocomposite is formed with layered silicate dispersed in the polymer matrix. The melt intercalation occurs when the polymer matrix in the molten state is mixed with the layered silicates. The polymer chains insert into the interlayer space and form a nanocomposite. In the solution intercalation, the layered silicate is dispersed in a solvent mixture with the polymer. The polymer is adsorbed onto the exfoliated silicate layers and the solvent is evaporated forming a nanocomposite.

Three types of polymer-layered silicate composites may be obtained: phase separated, intercalated and exfoliated. Intercalated nanocomposites are obtained when polymer chains are intercalated between the silicate layers, resulting in a well ordered multilayer morphology with alternating polymeric and inorganic silicate layers. Another possible structure for the hybrid nanocomposite is the exfoliated or delaminated structure in which the layers are completely dispersed in a continuous polymer matrix as single layers.[2] The phase-separated structure corresponds to a traditional microcomposite and its not a nanocomposite. It is obtained when polymer cannot intercalate into the silicate layers and the clay is only dispersed in the polymer matrix.

The clay pre-treatment (e.g. to turn it from hydrophilic to organophilic) and the way the polymer is incorporated into the nanocomposites are the keys variables that can be controlled and that have an intense influence on the final properties of the nanocomposite. During the in-situ incorporation of an organophilic clay into the polymer matrix in a free radical polymerization, the radical should penetrate the basal space between the layers of the clay increasing the distance between these layers and leading to a nanocomposite with an intercalated or exfoliated morphology. The structure of the composite as a conventional microcomposite or nanocomposite depends on the affinity of the organophilic clay for the monomer and it is affected by the clay type and pre-treatment conditions including the kind of hydrophobic cation used to replace the hydrophilic cation.[3]

Several commercial organophilic clays can be employed in order to obtain nanocomposites by in situ polymerization. Nevertheless, very often, the kind of hydrophobic cation or cations used in the clay treatment is not informed as many companies consider it confidential. Therefore, using a simple method to obtain the degree of affinity of the clay for the monomer should be a very useful tool in order to predict the kind of nanocomposite to be obtained.

In this work, Foster swelling is applied as a method to obtain the degree of affinity of the clay for the monomer. The objective is to study the effect of the Foster swelling degree on the final polystyrene/clay composite obtained by free-radical polymerization of styrene containing organophilic clay. Some commercial organophilic clays with different Foster swelling degree were employed and the incorporation of the clays into polymer was carried out in bulk styrene polymerization reactions. The X-ray diffraction (*XRD*) reveals the basal spacing of the clays before and after in-situ incorporation indicating the morphology of the nanocomposite (exfoliated, intercalated or only dispersed). The nanocomposites were also characterized by thermal gravimetric analysis (*TGA*).

Experimental Procedure

The organophilic clays were obtained from SudChemie Company (Nanofil 15), Spectrochem Company (Spectrogel AD) and Bentec Company (Viscogel B7 and Viscogel ED). Industrial grade inhibited styrene (Innova S.A.) was used throughout the reactions. Benzoyl peroxide (BPO) with 75% of oxygen active (Elf Atochem

Chemicals) was used as initiator. All materials were used as received.

In all reactions, the organophilic clay was first dispersed in styrene (2.8% w/w clay/styrene). The dispersion was kept under stirring (1000 rpm) at 30 °C for two hours to allow the swelling of the clay with styrene. The initiator was added to the dispersion just before the ampoules (with the dispersion and initiator) were immersed in a thermal bath at 90 °C. The reactions were complete after 7 hours. The complete description about the bulk polymerization in ampoule can be found in many works.[4–6]

The affinity of the clays for styrene was analyzed by Foster swelling. This analysis consists in the immersion of 1 g of clay in 100 ml of styrene. After 24 h at 25°C it is observed the volume occupied by the clay swelled by styrene. X-ray diffraction (*XRD*) was used to get the direct evidence of the nano-structure of the PS/clay hybrid.[2,7,8] Thermogravimetric analyses (*TGA*) was used in order to evaluate the stability of the nanocomposite after thermal degradation.[9]

Results and Discussion

Table 1 shows the results of Foster swelling for the commercial clays. A high value of Foster swelling represents a high affinity of the clay for styrene. Therefore, clays Nanofil 15 and Viscogel B7 show high affinity for styrene. The clay Viscogel ED has an intermediate value and clay Spectrogel AD has a low affinity.

The clays and the polystyrene/clay hybrid obtained by *in situ* incorporation of these clays were analyzed by *XRD*. It is possible to find the basal spacing (*d*) from the results of *XRD*, as a function of the intensity changes in 2θ, where *d* is calculated by Braggs Law:

$$d = \lambda/2\,\mathrm{sen}\,2\theta \qquad (1)$$

Figure 1 shows the *XRD*'s curves for Nanofil 15 clay and PS/Nanofil 15 nanocomposite. It is possible to observe for Nanofil 15 clay a peak of intensity in 2θ equal to 2.91° that corresponds to a basal spacing of 3.03 nm. The PS/Nanofil 15 nanocomposite presents the displacement of this peak to 2.13°, corresponding to a basal spacing of 4.14 nm. The difference Δd is equal to 1.11 nm. It means that has occurred an increase of the interlayer distance by PS polymer chains polymerized in the interlayer and that an intercalated nanocomposite was obtained.

Figure 2 shows the *XRD*'s curves for Viscogel B7 clay and PS/Viscogel B7 nanocomposite. Here there is a peak of intensity for Viscogel B7 clay in 4.75° corresponding

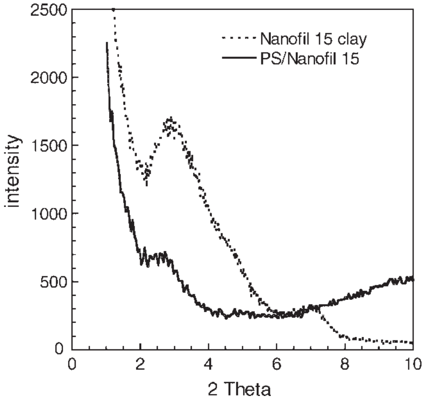

Figure 1.
XRD patterns of Nanofil 15 clay and its composite (PS/Nanofil 15).

Table 1.
Foster swelling results.

Organophilic clay	Foster swelling (mL/100 mL Sty)
Nanofil15 (SudChemie)	16
Viscogel B7 (Bentec)	20
Viscogel ED (Bentec)	13
Spectrogel AD (Spectrochem)	8

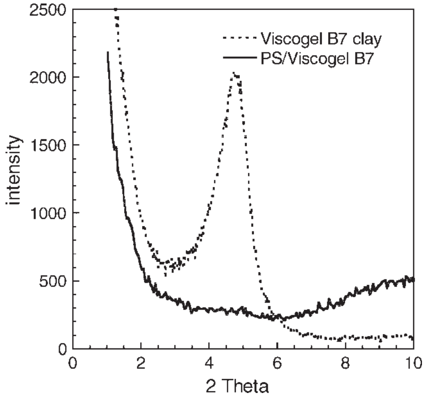

Figure 2.
XRD patterns of Viscogel B7 clay and its composite (PS/Viscogel B7).

to a basal spacing of 1.85 nm. It is not possible to detect precisely the peak of intensity in the *XRD* curve of PS/Viscogel B7. It may indicate a broad distribution of the interlayer distance or that the clay was delaminated instead of intercalated. *In situ* polymerization may lead to intercalated or delaminated nanocomposites,[2] the delaminated morphology would be obtained if the affinity of the clay for the monomer is so high that the monomer swell the layers breaking the weak force that stack the layers together.[1]

Figure 3 shows the *XRD*'s results for Viscogel ED clay and PS/Viscogel ED nanocomposite. Comparing the higher peaks of each diffraction, it is possible to notice that the basal spacing increases from 3.35 nm (2.63°) to 3.62 nm (2.43°). It means that some intercalated structure was obtained. It is also possible to notice a peak of lower intensity located in 4.6° for Viscogel ED clay and its composite and both peaks have a basal spacing of 1.9 nm. Thus, apparently the layers that showed a lower basal spacing were not intercalated only dispersed in the polymer matrix. It means that the clay presents some heterogeneity and, apparently, the cation exchange was not complete during the treatment to make the clay organophilic. This is observed by the different peaks showed in the *XRD* of the clay and in the different behavior of each peak after the *in situ* incorporation.

The *XRD*'s curves of Spectrogel AD clay and PS/Spectrogel AD nanocomposite are showed in Figure 4. No significant change is observed in the basal spacing for the higher intensity peaks, with 3.62 nm (2.43°) to the clay and 3,65 nm (2.41°) to the composite. Moreover, comparing the lower intensity peaks among 4.5 and 4.6 2θ of both materials, it is not possible to observe any significant change (both peaks correspond a basal spacing of 1.9 nm). Therefore, for this

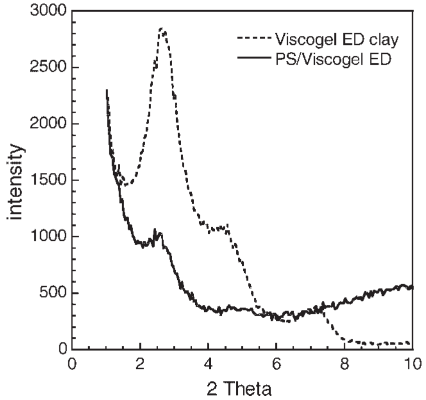

Figure 3.
XRD patterns of Viscogel ED clay and its composite (PS/Viscogel ED).

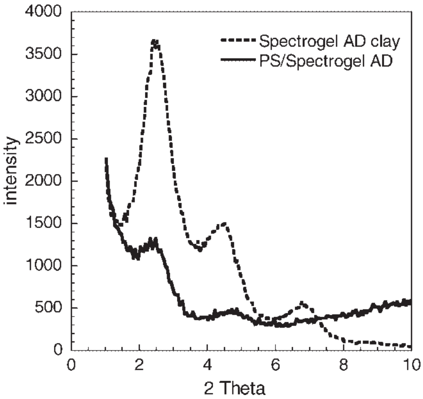

Figure 4.
XRD patterns of Spectrogel AD clay and its composite (PS/Spectrogel AD).

clay a nanocomposite was not obtained, as the clay was only dispersed in the polymer matrix.

Comparing Foster swelling results with *XRD* results it is possible to observe a correlation. The clay with higher swelling value (Viscogel B7) presented a *XRD* spectrum to its nanocomposite that can correspond to an exfoliated nanocomposite. The Nanofil 15 clay showed a swelling value slightly lower than Viscogel B7 and a high increase of the basal spacing of the clay was observed ($\Delta d = 1.11$ nm) demonstrating that an intercalated structure was obtained after polystyrene in-situ incorporation. The Viscogel ED clay presented an intermediate swelling value and observing the *XRD* curve, it is possible to notice some intercalated structure, but part of the clay layers were only dispersed. The Spectrogel AD clay showed a low swelling value by styrene and was only dispersed into the polymer matrix, this way, a nanocomposite was not formed. These results are in accordance to the fact that the high affinity of the clay for styrene is an indication that the styrene molecules are able to penetrate into the space between the clay's layers, swelling it and allowing the radicals formed in the continuous phase to enter in this space leading to an intercalated structure. If the increase in the basal space is very high, the forces that keep the layers together are not enough to keep an intercalated structure generating an exfoliated structure. Indeed, the clays that showed low swelling values, that indicates a low affinity of the clays by the monomer (styrene), showed that a nanocomposite was not formed due to this low affinity.

The nanocomposites obtained from the different clays were analyzed by thermogravimetric analysis (*TGA*) and compared to the pure polystyrene obtained under the same conditions of the nanocomposites, to allow a better comparison of the nanocomposites with the pure polystyrene (PS). The *TGA*'s curves of the nanocomposites and pure PS are presented in Figure 5. All the hybrids obtained show higher decomposition temperature when compared to PS. The higher decomposition temperature was obtained by the hybrid PS/Nanofil 15. This result shows that a nanocomposite with a well defined intercalated morphology presents a higher stability after thermal degradation as observed by other authors.[2,3,10] The other hybrids clay/polymer with different morphologies (exfoliated nanocomposite, partially intercalated and microcomposite) showed a similar higher degradation temperature.

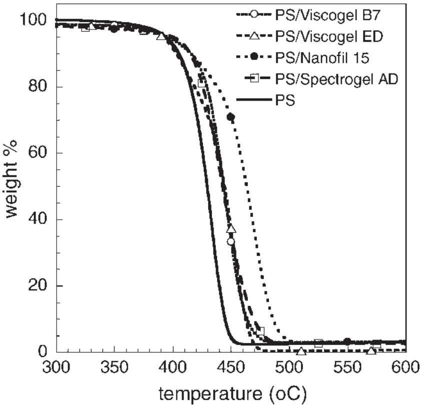

Figure 5.
TGA thermograms for PS and PS/clay hybrids.

Analyzing the higher degradation temperatures, XRD curves and Foster's swelling data, it could be expected that the clays that presented higher swelling values would provide nanocomposites with higher degradation temperatures. However, it is not possible to get a direct correlation, as the composite PS/Spectrogel AD showed a higher degradation temperature similar to PS/Viscogel B7 nanocomposite while Spectrogel AD clay presented a low swelling value and the clay was only dispersed in the polymer matrix, and Viscogel B7 clay presented a high Foster's swelling value and formed a exfoliated nanocomposite with polystyrene.

Conclusions

TGA thermograms showed that all PS/clay composites presented higher decomposition temperature then the pure polystyrene. Nevertheless, the affinity of the clay for styrene is not the unique parameter to be observed in obtaining a hybrid PS/clay with high stability after thermal degradation as clays with very different affinity for styrene (Viscogel B7 and Spectrogel AD) originated hybrids with very similar high decomposition temperature.

Results showed that there is a correlation between clay's Foster swelling degree and the morphology obtained for the PS/clay hybrid. High values of Foster swelling degree lead to exfoliated polystyrene/clay nanocomposites, whereas decreasing this value intercalated, partially intercalated and only dispersed composites, in this order, were obtained depending on the degree of affinity of the monomer for the clay.

Acknowledgements: The financial support from CNPq – Conselho Nacional de Desenvolvimento Científico e Tecnológico, MCT/FNDCT/FINEP (Ações Transversais: Nanocompósitos, grant number - 0.1.05.0547.00) and PETROBRÁS/CENPES (grant number: PD-01644) are gratefully appreciated.

[1] S. S. Ray, M. Okamoto, *Prog. Polym. Sci.*, **2003**, *28*, 1539.
[2] M. Alexandre, P. Dubois, *Materials Science and Engineering*, **2000**, *28*, 1.
[3] X. Fu, S. Qutubuddin, *Journal of Colloid and Interface Science*, **2005**, *283*, 373.
[4] M. A. Villalobos, *Master Thesis of Engineering*, McMaster University, Hamilton, Ontario, **1989**, 225.
[5] M. A. Dubé, A. Penlidis, K. F. O'Driscool, *Can. J. Chem. Engng.*, **1990**, *68*, 6, 974.
[6] R. Arioli, *Dissertação de Mestrado*, Universidade Federal de Santa Catarina, Florianópolis, SC, **2004**, 146.
[7] A. B. Morgan, J. D. Harris, *Polymer*, **2001**, *42*, 8695.
[8] B. Mailhot, S. Morlat, J. L. Gardette, S. Boucard, J. Duchet, J. F. Gerard, *Polymer Degradation and Stability*, **2003**, *82*, 163.
[9] J. Zhang, C. A. Wilkie, *Polymer Degradation and Stability*, **2004**, *83*, 301.
[10] X. Fu, S. Qutubuddin, *Polymer*, **2001**, *42*, 807.