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Microstructure of Nanocomposites of Styrenic Polymers

*Danilo Justino Carastan, Nicole Raymonde Demarquette**

Summary: Nanocomposites of three different styrenic polymers (polystyrene – PS, styrene-butadiene-styrene triblock copolymer – SBS, and styrene-ethylene/butylene-styrene triblock copolymer – SEBS) containing organophilic silicates have been prepared using three different techniques. The materials were prepared by melt mixing, solution casting and a process in which a highly filled masterbatch prepared by solution is mixed in the melt with the pure polymer. These composites were characterized by X-ray diffraction (XRD), optical microscopy (OM), transmission electron microscopy (TEM) and small amplitude oscillatory shear analysis (SAOS). The results obtained showed that the nanocomposites of PS formed an intercalated microstructure, while those of SBS and especially SEBS are more easily exfoliated. To achieve this better silicate dispersion it was shown that it is necessary to use solution casting as one of the stages in the nanocomposite preparation. The masterbatch process showed to be an effective method to disperse the clay because it combines the advantages of the solution casting technique, which is good to dissolve coarse clay aggregates, and the shear provided by melt mixing.

Keywords: block copolymers; compounding; microstructure; nanocomposites; polystyrene (PS)

Introduction

During the last years, many research groups have been interested in studying a novel class of materials, the polymer nanocomposites (PNCs), which may present unusual, very improved properties in some cases. The most well known type of PNC is the one composed by a polymeric matrix filled with an organically modified layered silicate. These composites may exhibit improved mechanical properties, higher thermal and chemical stability and decreased gas permeability, among other properties that lead to promising industrial applications [1].

However, it is not that simple to obtain a material presenting such properties, as they usually depend on a good, uniform dispersion of the clay platelets within the polymer, becoming more significant when they are individually exfoliated. Achieving a complete exfoliation is a difficult task for most polymers, as it depends on many variables, such as physical chemical interactions between the components, rheological properties of the matrix and processing techniques. It is not yet possible to accurately predict the final morphology of a PNC, despite of some efforts to better understand the interactions between the polymer and the clay [2,3].

It is known that polystyrene (PS) has a rather good affinity with organosilicates, due to a weak polarity of its molecules [3]. Even so, exfoliation is not easily obtained, since the PS molecules tend to penetrate between the platelets to form an intercalated rather than an exfoliated morphology. PS nanocomposites have been prepared by many different routines, such as in situ

Metallurgical and Materials Engineering Department – Polytechnic School – University of São Paulo, Av. Prof. Mello Moraes, 2463, CEP:05508-900, Cidade Universitária, São Paulo, SP, Brazil
E-mail: danilo.carastan@poli.usp.br, nick@usp.br

polymerization [4], solution casting [5] and melt mixing [6]. In situ polymerization is a very versatile technique, as it makes it possible to adjust the chemistry to optimize the affinity between the clay and the polymer. Many different types of polymerization techniques have been used to prepare PS nanocomposites, such as bulk [7], solution [8], suspension [9] or emulsion [10] free radical polymerizations, and living anionic polymerization [11], among others. It is even possible to make the PS chains grow from the surface of the clay platelets using suitable surfactants, which also behave as initiators [12]. This flexibility in preparation of PNCs by in situ polymerization has led to some materials with very good clay dispersion. In fact, not only for PS, but for most polymers, the resulting nanocomposites with better exfoliation have been prepared by in situ polymerization, so far. However, this technique has some disadvantages. It is not always simple to synthesize the materials, so that the processes may be quite expensive, what makes them not very suitable for large scale production and industrial applications. Sometimes it is also difficult to control the molecular weight of the polymer being produced, as it may be sensitive to variables like clay concentration, type of surfactant present in the clay, etc; and this may be a problem [4,13].

The use of commercial polymers to prepare nanocomposites is much more desirable in a practical and economical point of view. These nanocomposites may be prepared basically by two techniques: melt mixing and solution casting. PS nanocomposites prepared by melt mixing have resulted mostly in intercalated materials [14], although there are some examples of exfoliated materials, more difficult to obtain [15]. PS molecules in the molten state tend to spontaneously intercalate organophilic clay through a diffusive process [3]. However, when preparing PS nanocomposites by melt mixing, less reactive clay surfactants must be used, because the most reactive ones are more thermally unstable and decompose during the preparation of the material [9]. When using the melt preparation technique, it is possible to use common polymer processing equipment to produce the material, such as extrusion and mixing in internal mixers, what makes this technique easier to use. The shear provided by processing may also help to increase the clay dispersion, although most times it is not enough to break big clay aggregates, and the resulting dispersion is poorer than in a material prepared by in situ polymerization.

An alternative is to prepare the material using a solvent that dissolves the polymer and disperses the clay at the same time. After the evaporation of the solvent the structure of the material is usually rearranged, so that the clay usually forms an intercalated morphology, rather than an exfoliated one [16]. However, the clay dispersion is usually better than in materials prepared by melt mixing, once that the solvent is able to disrupt large, coarse clay aggregates, and these coarse structures are not rearranged after the evaporation of the solvent, as it will be shown in this work. A disadvantage of this technique is the need to use an organic solvent, what is not very desirable, especially due to environmental issues.

An interesting possibility is to mix two different techniques to prepare a PNC, joining their advantages and trying to minimize their disadvantages. This is a new way to produce nanocomposites, where it is possible to prepare a masterbatch with high clay loading using one technique, like in situ polymerization [17] or solution casting (proposed in this work), and then melt blend it with pure polymer to lower the clay concentration to desired values. Through this technique it is possible to combine the advantages of in situ polymerization and melt mixing, or solution casting and melt mixing. Another advantage is that as melt mixing is a simpler technique, most of the volume of polymer may be added only in the last stage of preparation of the PNC. Less polymer needs to be prepared by in situ polymerization, or less solvent needs to be used in the masterbatch prepared by

solution casting. In this work the combination of solution casting and melt mixing was used to prepare the PNCs.

Besides pure PS, it is possible to prepare nanocomposites of styrene-containing copolymers. The tendency of styrene to intercalate the clay is still active in these materials. In particular it is possible to prepare nanocomposites of styrenic block copolymers. Many of these polymers are commercially available, being used as thermoplastic elastomers or as polymers with higher impact resistance than PS. Block copolymer nanocomposites have been prepared by solution casting [18] or melt mixing [19]. In situ polymerization is usually not possible, because most block copolymers are prepared by living polymerization, and the presence of clay would probably inhibit this kind of reaction.

In this work, PS and two styrene-containing block copolymers were mixed to organically-modified layered silicates using the techniques of solution casting, melt mixing and a masterbatch technique which combines both techniques, aiming the obtention of nanocomposites of styrenic polymers. They were then characterized by X-ray diffraction, optical microscopy, transmission electron microscopy and small amplitude oscillatory shear analysis.

Experimental

In this work, three different commercial styrene-based polymers were used: PS (N1841 from InNova), styrene-butadiene-styrene triblock copolymer (SBS – Styrolux 3G33 from BASF), and styrene-ethylene/butylene-styrene triblock copolymer (SEBS – Kraton G-1652 from Kraton Polymers). The organophilic clay used was Cloisite 15A, from Southern Clay Products Inc. It is a montmorillonite modified with a saturated quaternary ammonium cation (dimethyl, dihydrogenated tallow ammonium). The materials data are presented in Table 1.

The composites were prepared using three different techniques: melt mixing, solution casting and a hybrid masterbatch process, which is a combination of the former two. In the case of melt mixing, the materials were prepared in a mixing chamber attached to a torque rheometer (Thermo Haake's PolyLab 900/Rheomix 600p). Each polymer was mixed with the clay at 200 °C at a rotor speed of 50 rpm for 5 minutes. The clay fraction was fixed at 5 wt%. The samples obtained were frozen in liquid nitrogen and ground into a coarse powder to be pressed in a hydraulic press into the shape of small discs (25 mm in diameter and 1 mm in thickness). For the solution casting method, each polymer and 5 wt% of clay were dissolved in toluene (about 20 g of polymer in 600 mL of toluene). Toluene was very effective in dispersing the clay, as the solutions became completely transparent, having only a light coloration. Each solution was then cast into a bowl for the solvent to completely evaporate. The last method is a combination of solution casting and melt mixing. First, highly filled masterbatches were prepared by dissolving each polymer and 25 wt% of clay in toluene. After the evaporation of the solvent, each masterbatch was melt blended with pure polymer at the same conditions of the melt mixing process, so that the final clay concentration became 5 wt%.

The materials obtained were analyzed by X-ray diffraction (XRD), optical micro-

Table 1.
Materials used in this work.

Polymer	Supplier	Grade	MFI (g/10 min – 200 °C/5 kg)
PS	InNova	N1841	11
SBS	BASF	Styrolux 3G33	16
SEBS	Kraton Polymers	G-1652	5
Clay	Supplier	Grade	Organic Modifier
Montmorillonite	Southern Clay	Cloisite 15A	dimethyl, dihydrogenated tallow ammonium

scopy (OM), transmission electron microscopy (TEM) and small amplitude oscillatory shear analysis (SAOS). For the XRD, the samples were analyzed in a Phillips MPD diffractometer using CuKα radiation. The samples for OM observation were prepared by pressing a small piece of each PNC between two glass slides while being heated at 200 °C inside a hot stage (Mettler Toledo FP-82 HT). The thin PNC films sandwiched between the slides were then observed in an Olympus BX50 microscope at magnifications ranging from 50 to 200x. Pictures were taken using a CCD camera attached to the microscope. The samples for TEM were prepared by cutting ultrathin sections (around 70 nm) in an ultramicrotome and observed in a Jeol JEM-1010 transmission electron microscope at 90 kV. No staining was necessary, once the clay platelets have enough contrast to be observed. The rheological measurements were performed in a rheometer SR5000 from Rheometrics at 200 °C using stress levels within the range of linear viscoelasticity of each sample.

Results and Discussion

Figures 1 and 2 present some micrographs of the nanocomposites observed by OM. Figures 1a and 1b show the microstructure of PS and SEBS nanocomposites prepared by melt mixing, and Figures 2a and 2b show the nanocomposites of the same polymers prepared by solution casting. The morphologies of SBS samples were very similar to those of PS, and the samples prepared by the masterbatch technique had the same aspect of the ones prepared by solution casting, when observed by OM. Many clusters bigger than 20 μm could be observed in the samples prepared by melt mixing, while the materials prepared via solution or the masterbatch technique did not present any big cluster of clay. In the samples of PS and SBS prepared by these techniques only a very fine structure could be seen, like in the example of Figure 2a for the PS nanocomposite. The SEBS samples were almost completely clear, as seen in Figure 2b.

Figure 3 presents the X-ray diffratograms of the pristine clay and of each PNC prepared by the masterbatch technique. The peaks on the diffratograms correspond to the basal spacing between the clay layers. The original clay spacing was 3.08 nm, and after the addition of polymer it reached values of around 3.30 nm. Essentially all PNCs in this work presented similar interlayer spacing, no matter which type of polymer or preparation technique were used.

Figures 4 through 6 present typical TEM micrographs of the samples obtained in this work. Figure 4 shows the morphology of the PS nanocomposite prepared by the masterbatch technique; Figure 5 shows the morphology of the SBS nanocomposite prepared by melt mixing and Figure 6 shows the morphology of the SEBS nanocomposite prepared by solution casting. To exemplify the morphology obtained by the masterbatch technique PS was chosen, as it is the most difficult polymer to disperse the clay. It can be seen in Figure 4a some

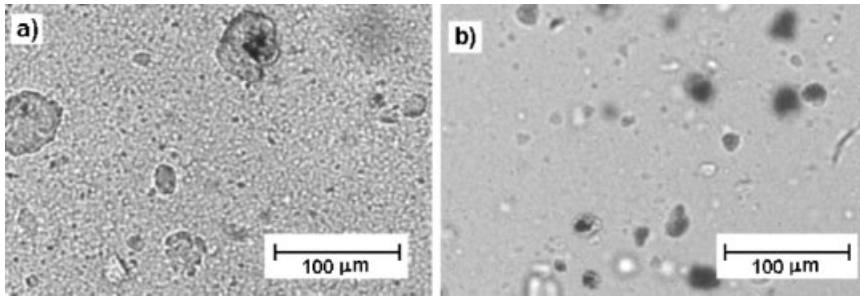

Figure 1.
OM images of PNCs containing 5 wt% clay prepared by melt mixing of a) PS, b) SEBS.

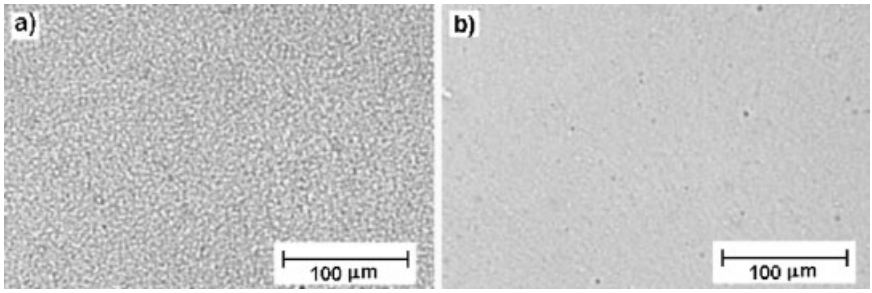

Figure 2.
OM images of PNCs containing 5 wt% clay prepared by solution casting of a) PS, b) SEBS.

tactoids larger than 1 μm, all aligned in one direction. An image of higher magnification of the same sample (Figure 4b) shows an intercalated structure of the clay. In the sample of SBS prepared by the melt mixing process (Figure 5), some rather large clay crystals can be observed (Figure 5a), as well as some almost individually separated platelets (Figure 5b, indicated by arrows). When the composites were prepared by solution casting a very good clay dispersion was obtained, especially in the case of the SEBS nanocomposite (Figure 6). In this sample small stacks of clay can be seen in a lower magnification micrograph (Figure 6a), and, at a higher magnification, it is possible to observe an intercalated tactoid with a very loose structure, and some exfoliated clay platelets as well, indicated by arrows on Figure 6b.

The OM observations revealed that for the composites prepared by melt mixing the clay wasn't very well dispersed in a micrometric scale. The big clay clusters seen in Figures 1a and 1b indicate that the shear provided by melt mixing was not effective to break these aggregates. The materials prepared via solution and the masterbatch technique presented a much better dispersed morphology, showing that the presence of a solution stage is effective to disperse the clay aggregates. The fine structure observed in the samples of PS and SBS nanocomposites suggested that the clay aggregates were broken down to individual clay tactoids, which have the size of around 1 μm, near the visual limit of the optical microscope. This was confirmed by the TEM observations, which revealed the structure of these tactoids.

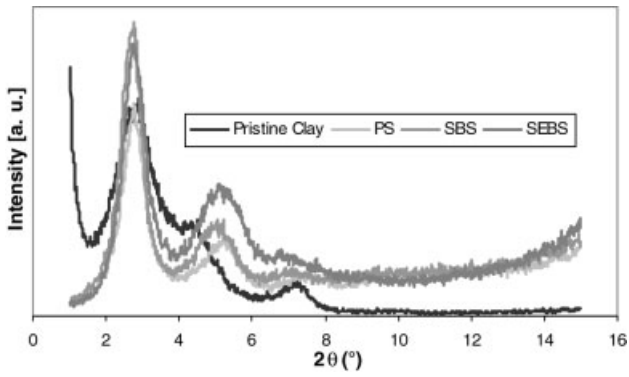

Figure 3.
X-ray diffratograms of pristine clay and of PNCs of PS, SBS and SEBS containing 5 wt% clay.

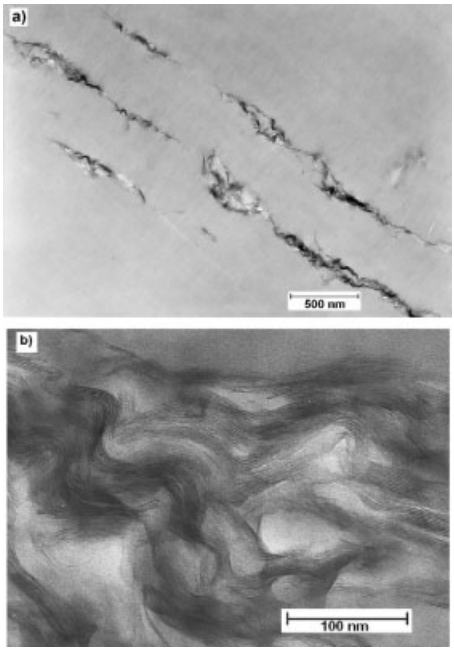

Figure 4.
TEM images of a PS nanocomposite prepared by the masterbatch process: a) low magnification, b) high magnification.

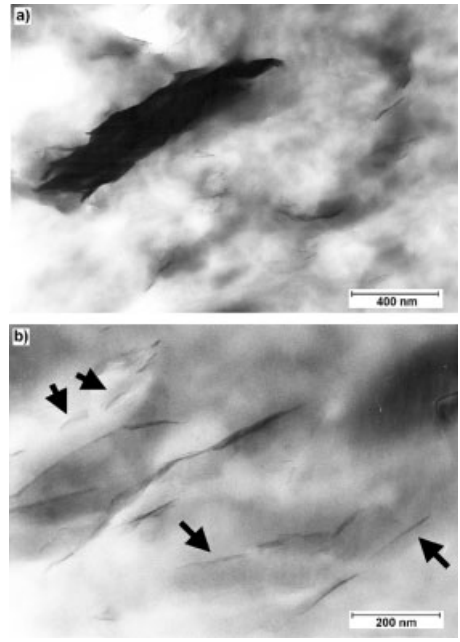

Figure 5.
TEM images of a SBS nanocomposite prepared by melt mixing: a) low magnification, b) high magnification.

It can be said that all nanocomposites in this work present intercalated nanostructures. XRD results show a small increase of interlayer spacing, probably indicating polymer intercalation. It is worth noting that Cloisite 15A has a rather large initial spacing in comparison to other organosilicates, and that the final spacings obtained for the composites are the typical values found in literature for intercalated PNCs [3]. The final clay spacing is usually related to the cross-sectional diameter of the polymer molecules that penetrate between the platelets via reptation diffusive processes. However, as the XRD method only gives an average value of clay spacing, it cannot be used conclusively to determine the PNC morphology. Therefore, only through TEM observations the nanostructure can be directly observed.

The observation of Figures 4 and 5 shows that indeed PS and SBS nanocomposites present mostly intercalated nanostructures, although in the SBS sample some individually exfoliated clay platelets can be seen. This shows that there can be the coexistence between intercalated and exfoliated clay morphologies in the same sample, yet in this case there is still the predomination of large clay crystals. The orientation of the clay tactoids in both samples is probably due to shear from the melt mixing stage. The SEBS sample, on the other hand, has a more dispersed structure. This was already suggested from OM observation, where almost no structure could be seen (Figure 2b), what would indicate that the clay structure was finer than the resolution limit of the OM, and even by observation by naked eye, as SEBS samples were optically clear, while the PS and SBS nanocomposites were translucent. Figure 6 shows that the clay is better dispersed for SEBS than in the case of PS and SBS samples, presenting only some very small clay tactoids. These tactoids are randomly oriented within the material, which was prepared by solution casting,

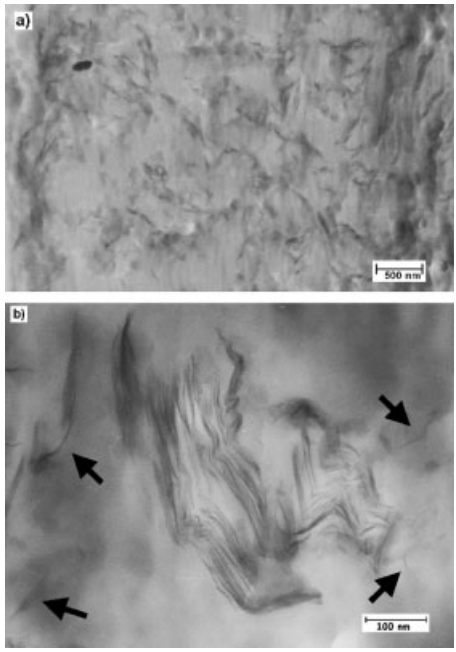

Figure 6.
TEM image of a SEBS nanocomposite prepared by solution casting: a) low magnification, b) high magnification.

while those in the samples prepared by melt mixing or the masterbatch technique (Figures 4 and 5) are more aligned in one direction. This can be explained by the differences between each preparation technique. In solution casting the sample is prepared by stirring the solution, and then the material is put to rest until all solvent has evaporated. During this process the clay tactoids rearrange themselves in a type of structure commonly called ''house of cards'', where the clay is piled up in a more loose, random fashion. But the final structure is not completely exfoliated, as it can be seen in Figure 6 that there are small intercalated clay tactoids together with exfoliated clay platelets. The melt mixing stage present in the other two techniques provides shearing of the samples, and this is probably the cause of the alignment of the clay tactoids seen in Figures 4 and 5. This shear may also improve clay exfoliation, but only a quantitative analysis of the morphology could confirm this statement.

To further analyse the effects of different processing techniques and different polymers, rheological measurements were carried out for the different materials. If the materials are studied within the linear viscoelastic regime, SAOS results show interesting morphology-related behaviour. The analyses were performed on samples of each pure polymer and their nanocomposites prepared by melt mixing and the masterbatch technique, and the results are presented on Figure 7.

Figure 7a presents the values of storage modulus (G') and complex viscosity ($|\eta^*|$) as a function of frequency for the PS samples. As expected by the TEM measurements, which did not present exfoliated platelets, the addition of clay in PS did not result in many significant changes in its rheological behaviour. When there is exfoliation, it has been reported that the low frequency region tends to a non-terminal behaviour, showing a plateau in the values of G' and the absence of a zero-shear viscosity value[20]. The results for PS did not present such behaviour. Instead, only a small increase in the values of G' and $|\eta^*|$ was observed for the nanocomposite samples throughout all frequency range, remaining parallel to the pure PS curves. Also, no difference was observed between the samples prepared by melt mixing and the masterbatch technique, indicating that even though the solution masterbatch was able to break most coarse clay aggregates, the final tactoid size was not small enough to significantly change the rheological behaviour of the nanocomposite. The rheological behaviour of SBS samples is presented in Figure 7b. Unlike the PS results, each sample behaves differently, and it can be seen that there is a decrease in the slope of G' at low frequencies for the nanocomposites, showing a tendency to form the non-terminal plateau. The sample prepared by the masterbatch technique shows the highest values of G' and $|\eta^*|$, indicating that it presents a better exfoliated morphology. These results confirm that the SBS samples present a higher tendency to disperse clay than pure PS,

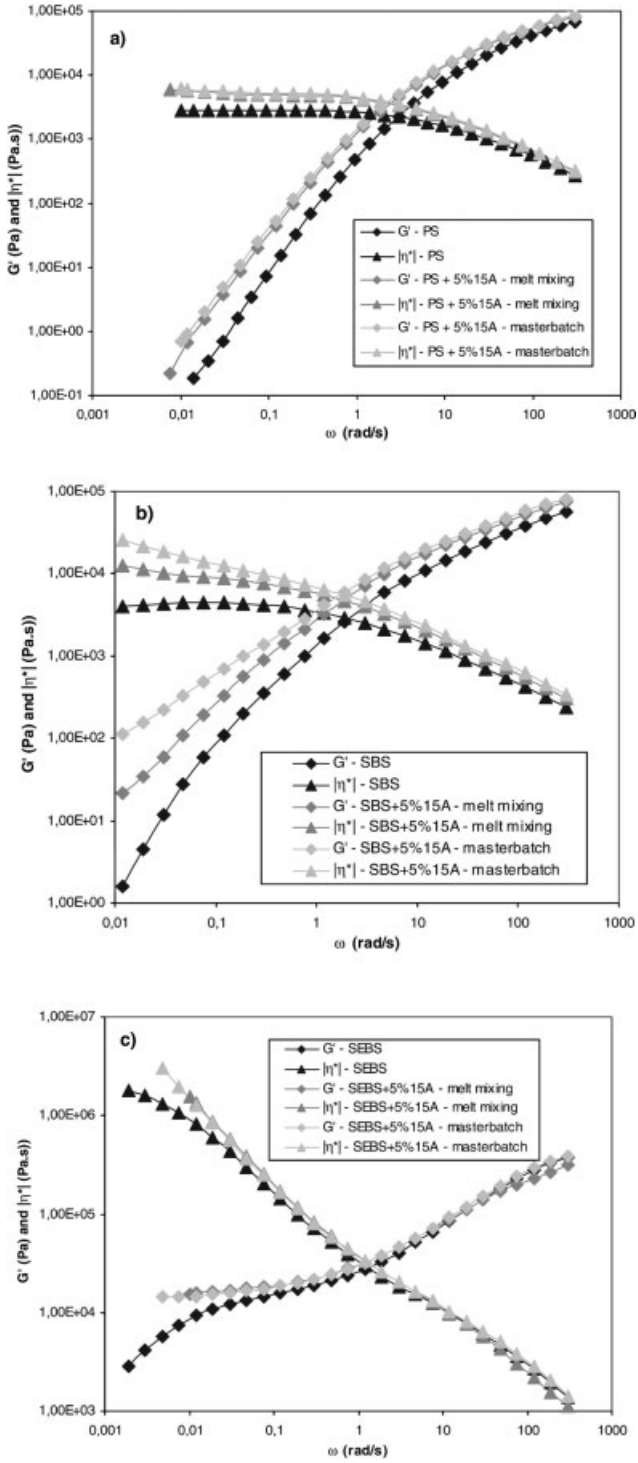

Figure 7.
SAOS results of the samples: a) PS, b) SBS and c) SEBS.

and that the masterbatch technique is more effective to delaminate than melt mixing alone. The final graph, Figure 7c, shows the results for the SEBS samples. It can clearly be seen that the nanocomposites present a non-terminal plateau for low frequencies, while the pure copolymer shows a decrease in the values of G′. The samples prepared by melt mixing and the masterbatch technique present the same behaviour, suggesting that even for the sample prepared by melt mixing there might be enough exfoliated platelets to form the plateau, despite the presence of some coarse clay aggregates. This could be expected, as in the OM observations shown in Figure 1b the clear background suggested the formation of a more dispersed structure in comparison to the PS sample (Figure 1a), which presented tactoids in the background structure.

Through these results it can be seen that the PS nanocomposites have the least dispersed microstructures, followed by the SBS and SEBS samples. The SBS and SEBS nanocomposites both present some intercalated clay tactoids as well as some individually exfoliated clay platelets. They can be then classified as partially exfoliated, but in different extents, as the SEBS samples have a better dispersed structure. These results indicate that the formation of a styrenic nanocomposite is improved by the presence of a different block in the structure of the polymer, however further studies are being done to better understand the differences between the behaviour of SBS and SEBS samples.

Conclusion

The results of OM, TEM and SAOS have shown that the PNCs prepared by solution casting or by the masterbatch process present better clay dispersion than those prepared by melt mixing. The masterbatch process is probably the best process because it requires less solvent than the conventional solution casting and its melt mixing stage may induce further clay exfoliation. The SEBS and, in smaller extent, SBS nanocomposites showed better exfoliation than pure PS, probably due to the presence of the non-styrenic blocks, which may help to push clay platelets apart, increasing their dispersion.

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