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Effect of the Organoclay Structure on Morphology and Rheological Response of PBT Nanocomposites

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Summary: In this paper the effect of different organoclays on the structure and the rheological properties of poly(butyleneterephtalate)–clay nanocomposites produced by melt compounding was investigated. The study was carried out using as nanometric fillers four commercial montmorillonites, treated with different organic modifiers and having similar interlayer spacing and organo-modifier concentration. Each organoclay was melt compounded with PBT (at 3%, 6% and 9% by weight of clay) using a twin screw extruder. Using the same processing conditions, hybrid samples containing the unmodified silicate were also prepared for comparison purposes. All the obtained nanocomposite samples were submitted to physico-chemical (XRD, TEM and FT-IR), and rheological measurements in order to evidence the role of polymer-clay affinity on the morphology and on the viscoelastic response of the materials. The results have pointed out that, with the used processing conditions, all nanocomposites exhibit a mixed intercalated/exfoliated structure; nevertheless, the clay dispersion homogeneity and the exfoliation level reached in the samples are higher for Nanofil 919 and Dellite 43B fillers, the organic modifiers of which may favorably interact with PBT matrix.

Keywords: chemical affinity; melt compounding; PBT/clay nanocomposites; rheology; TEM

Introduction

The dispersion of inorganic nanoscale fillers (such as silicates and aluminosilicates, metal nanoparticles, layered chalcogenides, etc.) in polymeric matrices was proved useful for achieving materials with enhanced performances.[1-10] These polymer nanocomposites are expected to have in the near future widespread potential applications in many fields, such as automotive, packaging, electronics, biotechnology, etc., motivating numerous research efforts both in industry and academy.

Of particular technological interest are the polymer/layered silicate nanocomposites (PLSNs), prepared by melt compounding using several thermoplastic polymeric matrices, such as polyamides, polyolefines and polyesthers.[11-22] Due to the incompatibility of the polymer

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matrix (hydrophobic) with the inorganic filler (hydrophilic), the nanolayer surfaces have to be treated to promote the lamellae exfoliation and increase the polymer adhesion on the mineral filler. Several organic compounds are continually proposed to increase the silicate surface hydrophobicity, but at present in the industrial practice modifications are generally achieved by surfactant cation exchange of alkyl-ammonium derivatives.[1, 12]

Since the chemical affinity between the organoclay and the polymer macromolecules plays a major role in determining the nano-scale morphology (clay dispersion, degree of exfoliation) of a polymer-layered silicate nanocomposite system, the property enhancements of melt compounded PLSN systems depend not only on the processing conditions and technology used for their preparation, but also, to a large degree, on the polymer-silicate interactions.[1-2, 10, 12] However, the experimental data up to now available are not sufficient to draw systematic relationships.

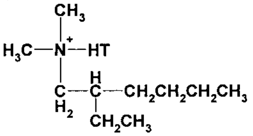
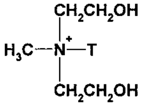
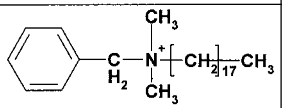
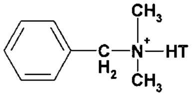
The main focus of this paper is to investigate the effects of different organo-treated montmorillonites on the structure and the rheological properties of poly(butyleneterephtalate)–clay nanocomposites produced by melt compounding. To this aim, four commercial organo-treated montmorillonites, having similar interlayer spacing and organo-modifier concentration, were selected for the study and melt compounded with PBT. Nanocomposite samples at three different weight percentages (3%, 6% and 9%) of each organoclay were prepared using a twin screw extruder with counter-rotating intermeshing conical screws. The role of polymer-clay affinity on the morphology (i.e. clay dispersion and exfoliation level) and viscoelastic response of the produced PBT/organo-silicate nanocomposites was experimentally investigated by means of physico-chemical (XRD, TEM and FT-IR) and rheological measurements. The same analyses were also performed, for comparison purpose, on hybrid samples containing the unmodified sodium-montmorillonite, prepared using the same processing conditions.

Experimental

Materials

The polymeric matrix used in this study was a poly(butyleneterephtalate) (PBT, M_n=28000) supplied by Montefibre (Italy). Several commercial organo-treated montmorillonites were selected as nanometric fillers: Cloisite 25A, Cloisite 30B (Southern Clay Products), Dellite 43B (Laviosa Chimica) and Nanofil 919 (Süd Chemie). The untreated sodium montmorillonite Cloisite Na^+ (Southern Clay Products) was also used for comparative purposes. All silicates were supplied as a powder of particles nominally < 8μm in size, excepted Nanofil 919 organoclay, which particles have medium size of 35μm. The fundamental organoclay characteristics are summarized in Table 1.

Table 1. Fundamental characteristics of the used organoclays.

Trade name	**Organo-modifier structure(1)**	**Organo-modifier concentration**	**Interstratic gap**	**Average medium size of particles**
Cloisite Na+	---	---	d_{001}= 11.7Å	< 8 μm
Cloisite 25A		95 meq/100g clay	d_{001}= 18.6Å	< 8 μm
Cloisite 30B		90 meq/100g clay	d_{001} =18.5Å	< 8 μm
Nanofil 919		90 meq/100g clay	d_{001} =19.5Å	35 μm
Dellite 43B		95 meq/100g clay	d_{001} =18.6Å	< 8 μm

(1)HT is Hydrogenated Tallow (~65% C18; ~30% C16; ~5% C14) and T is Tallow (~65% C18; ~30% C16; ~5% C14)

Processing

Mechanical polymer-silicate blends at three different weight percentages of each clay (3%, 6% and 9%) were prepared and dried in a vacuum oven at 90°C for 18 hrs to avoid moisture induced degradation reactions. The melt compounding of the blends was performed using a Haake twin screw extruder having counter-rotating intermeshing conical screws (L=300mm); this screw design allows to have varying degrees of mixing along the length of the screws. A temperature profile of 210-230-230-228°C from hopper to die was imposed and a rectangular die (1 mm x 40 mm) was used. Nanocomposite ribbons at different organoclay contents were extruded at screw speed of 90 rpm, corresponding to an average residence time in the extruder of about 3.0 min.

The sample nomenclature used for the discussion of results is reported in Table 2.

Table 2. Sample nomenclature.

Organoclay		Sample nomenclature
Trade name	**Weight percentage**	
---	---	PBT
Cloisite Na$^+$	3	3-Na$^+$
	6	6-Na$^+$
	9	9-Na$^+$
Cloisite 25A	3	3-25A
	6	6-25A
	9	9-25A
Cloisite 30B	3	3-30B
	6	6-30B
	9	9-30B
Nanofil 919	3	3-N919
	6	6-N919
	9	9-N919
Dellite 43B	3	3-D43B
	6	6-D43B
	9	9-D43B

Analyses

X-ray diffraction spectra were recorded by a flat camera using a sample-to-film distance of 140 mm (Ni-filtered Cu-Kα radiation). The incident X-ray beam was set normal to the extrusion direction (Figure 1). The Fujifilm MS 2025 imaging plate and a Fuji Bio-imaging Analyzer System, mod. BAS-1800, were used for digitizing the diffraction patterns.

Transmission electron microscopy (TEM) analyses were conducted using a Zeiss EM 900 operating at 80kV. Images with different magnification levels were captured on ultra-thin specimens cryogenically microtomed, on ribbon sections located normal to the extrusion direction (Figure 1).

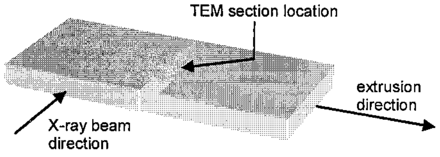


Figure 1. Schematic representation of incident X-ray path and TEM sampling location.

FT-IR spectra were recorded on a Nexus spectrometer (ThermoNicolet) in the frequency range of 4000-400 cm^{-1}. A total of 32 scans taken at 2 cm^{-1} of resolution were averaged.

The flow properties of the molten materials were measured with an ARES rheometer (Rheometrics, Inc.), using a parallel plates geometry (plate radius=12.5 mm, gap=0.1 mm). Dynamic frequency sweep tests were performed in the frequency range ω=0.01÷15 Hz, with a strain amplitude of 1% (proven to be in the linear viscoelasticity range). All samples were tested at 230°C after drying at 90°C in a vacuum oven for 18 hrs, under a nitrogen gas purge in order to minimize thermo-oxidative degradation phenomena.

Results and Discussion

In order to verify that the organoclays were dispersed on a nanometric scale in melt compounded samples, preliminary XRD analyses were carried out on all hybrid systems and pristine silicates. As example, Figure 2 reports the X-ray diffractograms of 9-25A and 9-N919 hybrids and compares them with the XRD patterns of the original 25A and N919 organoclays. All spectra were taken on a ribbon section oriented normal to the extrusion direction.

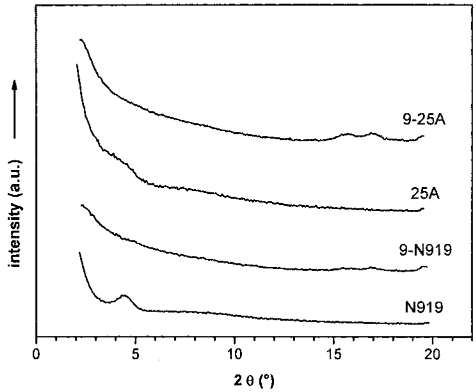


Figure 2. XRD patterns of N919, 9-N919, 25A and 9-25A samples.

The figure shows that the characteristic basal reflection of the organoclays is no more present in the pattern of the hybrids and only a broad halo can be detected at decreasing angles, thus pointing out that the silicate interstratic gap is increased and the clay is dispersed on a nano-scale in the PBT.

Similar results were obtained for all hybrids, irrespectively of clay concentration, indicating that a nano-scale dispersion of silicate layers have occurred in PBT matrix in our experimental conditions. Nevertheless, due to the differences in the molecular structure of the four organic modifiers selected for the study, a different polymer/silicate affinity degree is expected for each organoclay. In an effort to look for evidence that may support this postulation, FT-IR spectroscopy experiments were conducted on neat PBT matrix and on all hybrid ribbon samples containing 9wt% of each clay. Since the spectra show complicated regions at both high and low frequencies due to superposition of many molecular vibration modes within the samples, only the adequately resolved absorption bands will be discussed and reported in Figure 3. In the high-frequency range C-H stretching vibrations occur (olefinic, 3120-3000 cm^{-1}; aromatic, 3000-2800 cm^{-1}). In particular, the aromatic C-H vibrations appear as a complex multiple band, which maxima at ca. 2960 cm^{-1}, 2920 cm^{-1} and 2850 cm^{-1} have decreasing relative intensity in all samples except for the 9-N919 and 9-D43B systems, where the most intense peak is at ca. 2920 cm^{-1}. This change may be explained hypothesizing specific interactions between the aromatic rings of PBT and the phenyl groups of N919 and D43B organoclays, that increases the aromatic C-H bond length and reduces its frequency of absorption.[23] The aromatic out-of-plane C-H bend, instead, appears as a characteristic band at ca. 724 cm^{-1} in all cases. The ester C=O stretch results as a strong absorption band at ca. 1710 cm^{-1} and does not shows dependence from the organoclay type, revealing that no intermolecular hydrogen-bonding take place between the PBT carbonyl groups and the silicates, neither in the case of Cloisite 30B having O-H groups in the structure. In the FT-IR spectra of all the nanocomposite samples containing the organomodified clays, multiple combination bands of medium intensity occur in the 2680-2420 cm^{-1} region because of N-R stretching vibrations. The spectra show also a strong, broad absorption of ammonium ion in the range between 3300-3030 cm^{-1}. As expected, these bands are absent in the spectra corresponding to neat PBT and PBT added with natural Cloisite Na^{+}.

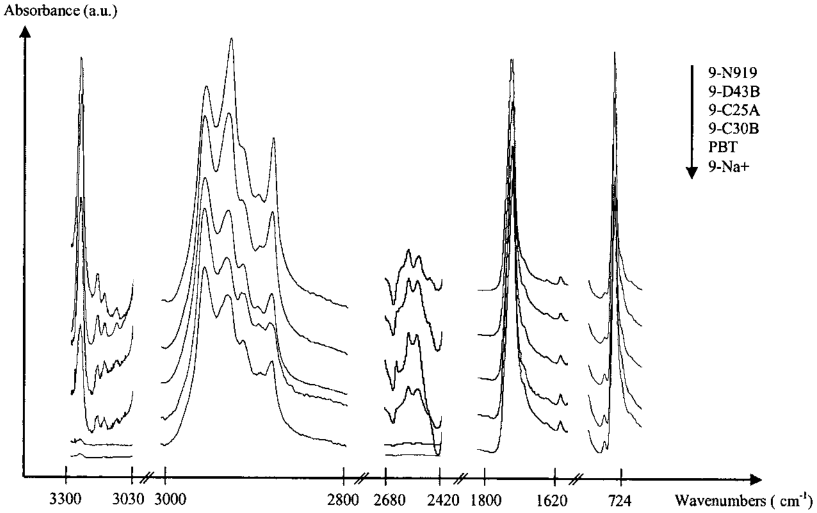


Figure 3. FT-IR spectra of neat PBT and its nanocomposites with 9wt% of organoclay.

The differences evidenced by FT-IR results are expected to affect the state of dispersion and exfoliation of the clay in the PBT matrix. So, transmission electron microscopy measurements and rheological analyses were performed to investigate the nanocomposite materials morphology. The viscoelastic response, in fact, was actually proven to be highly sensitive to the meso and nano-scale structure of polymer systems, although only qualitative correspondences can be deduced.[24-28]

Since FT-IR spectra have suggested that an higher interaction degree may exist between PBT and N919 organoclay, the rheological data corresponding to the hybrids containing such silicate will be discussed first. Figure 4 shows the complex viscosity curves and the corresponding TEM images of N919-based nanocomposite systems at 3%, 6% and 9% by wt of silicate. The complex viscosity curve of neat PBT matrix is also reported for comparison.

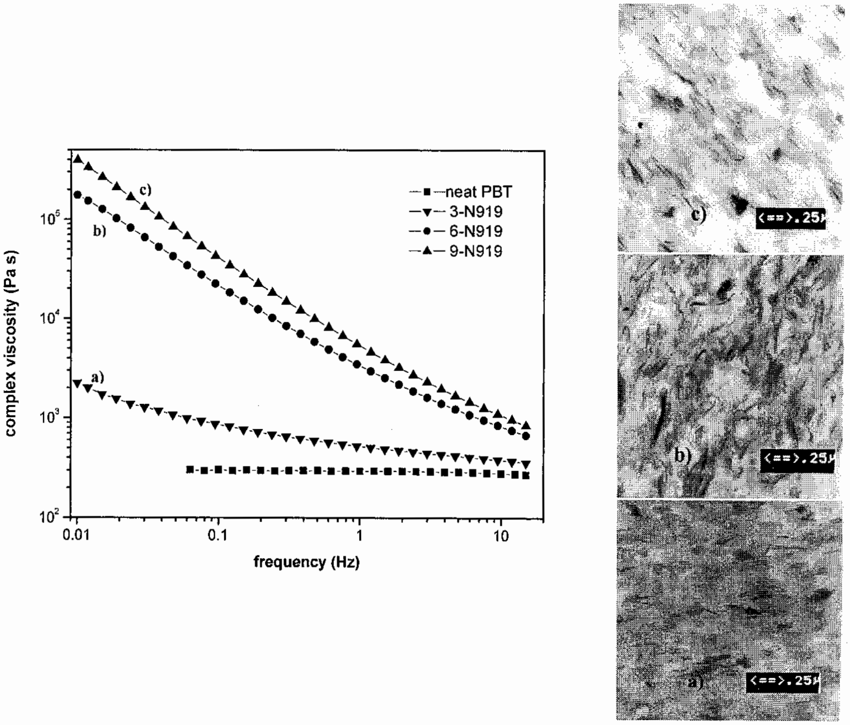


Figure 4. Effect of clay percentage on complex viscosity curves and TEM morphology of nanocomposites based on N919 organoclay.

As expected, the neat PBT matrix has a pseudo-Newtonian behavior in all the frequency range investigated, whereas all nanocomposites show an increasing deviation from the pseudo-Newtonian response and a significant enhancement in the complex viscosity even with the addition of the lowest clay amount. In particular, the flow curves of 6-N919 and 9-N919 samples exhibit a strong frequency dependence, with low frequency η^* values of about three orders of magnitude higher compared to the neat PBT and a pronounced pseudo-*shear thinning* behavior at high frequencies. These results are consistent with a pseudo-solid-like behavior of the samples at higher silicate loading (6 and 9 wt%). Related to each complex viscosity curve, Figure 4 shows also a TEM image of the corresponding specimen. The micrographs evidence that all nanocomposite systems have a mixed intercalated/exfoliated morphology, even if the dispersion degree and the orientation level of the N919 clay platelets increase with the silicate content, so that the more shear thinning trends correspond to the more homogeneous and aligned clay platelets distribution in PBT matrix. Similar results, already reported in literature for other end-tethered exfoliated and intercalated nanocomposite systems,[1, 14, 29-30] were also described in a previous work on PBT-based nanocomposites[21] and related to the meso-scale domain structure with long-range correlations defined by the highly anisotropic layered silicate.

The above discussed effect of silicate amount on the complex viscosity curves of N919-based nanocomposites was also found in systems containing Cloisite 25A, Cloisite 30B e Dellite 43B as organomodified clay, as shown in Figures 5a-c, respectively.

The graphs point out that, increasing the clay content, the rheological response of each nanocomposite systems was qualitatively altered in the same way, independently from the organoclay nature. However, compared to the neat PBT matrix, the percentage increase in the low frequency η^* values is of about two orders of magnitude for the systems based on 25A and 30B organoclays and of about three orders of magnitude, for the systems based on D43B organoclay. To better evidence the relationships between organoclay type, complex viscosity and morphology of the nanocomposite systems, Figure 6 compares the η^* curves for samples containing 9 wt% of each silicate and some corresponding TEM images. The figure clearly evidences that N919 and D43B-based nanocomposites, where specific polymer-organoclay interactions may exist, exhibit a more marked shear thinning trend with higher low frequency η^* values and a more exfoliated morphology respect the other systems, at same silicate content. The 9-Na+ system does not show significant differences in terms of complex viscosity response respect to the neat PBT matrix.

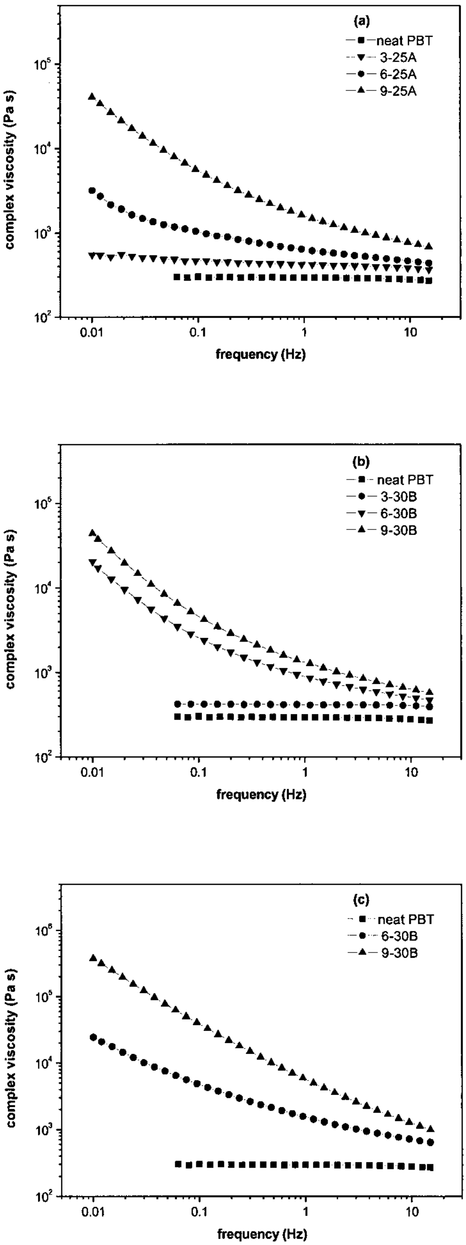


Figure 5. Effect of clay percentage on complex viscosity curves of nanocomposites based on (a) 25A, (b) 30B and (c) D43B organoclay, respectively.

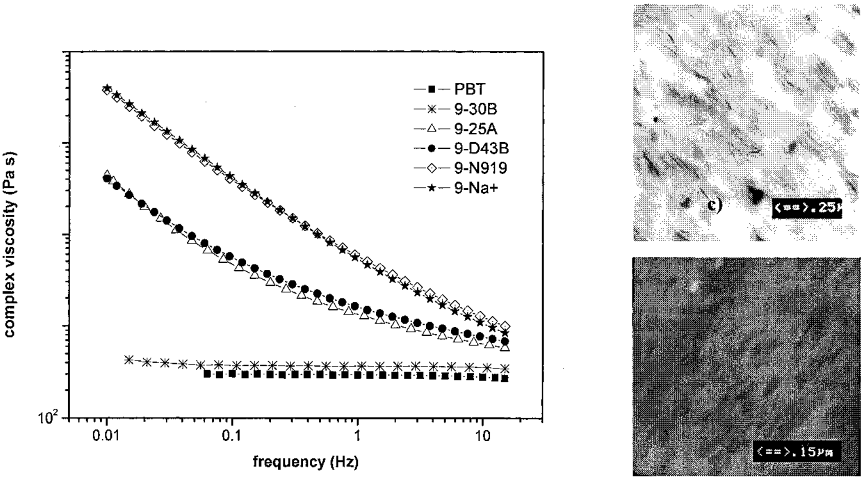


Figure 6. Effect of clay type on complex viscosity curves and TEM morphology of nanocomposites at 9 wt% of filler.

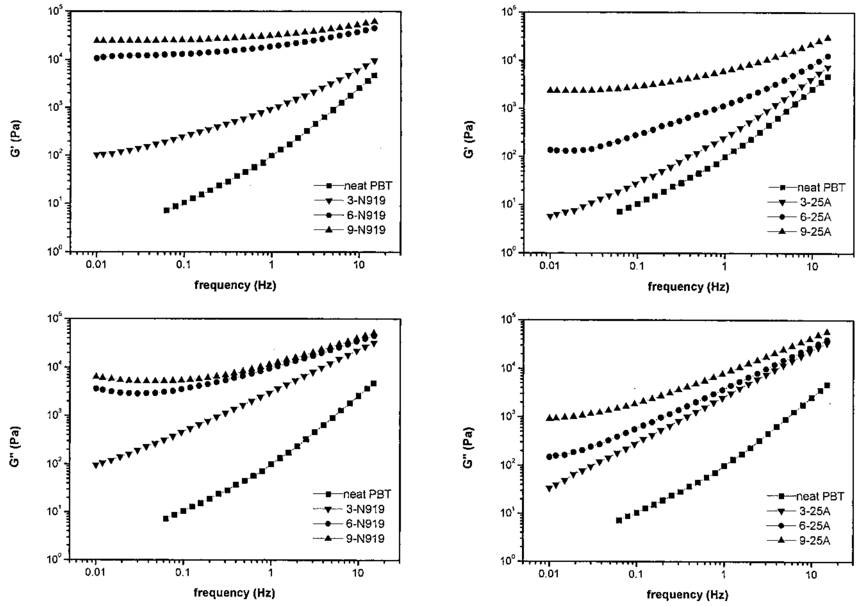


Figure 7. Storage (G') and loss (G'') moduli curves the for neat PBT and its N919 and 25A-based nanocomposites at 3%, 6% and 9% by wt of organoclay.

The formation of an extended structural network in nanocomposite systems is also proved by the dynamic spectra, reporting the linear viscoelastic storage (*G'*) and loss (*G''*) moduli *vs.* frequency, that are extremely sensitive to morphological state of the samples. Figure 7 shows the storage and loss moduli curves (at 3%, 6% and 9% by wt of silicate) the for neat PBT and its N919 and 25A-based nanocomposites, chosen as examples for their different polymer/clay affinity. As expected, in both systems G' and G'' curves monotonically increase with the frequency, exhibiting also a reduced frequency dependence with increasing the silicate loadings. The phenomenon is especially marked for samples at 6wt% and 9wt% of N919 clay, dynamic spectra of which display an "inverse cross-over", with G' higher than G'' in the whole frequency range investigated.

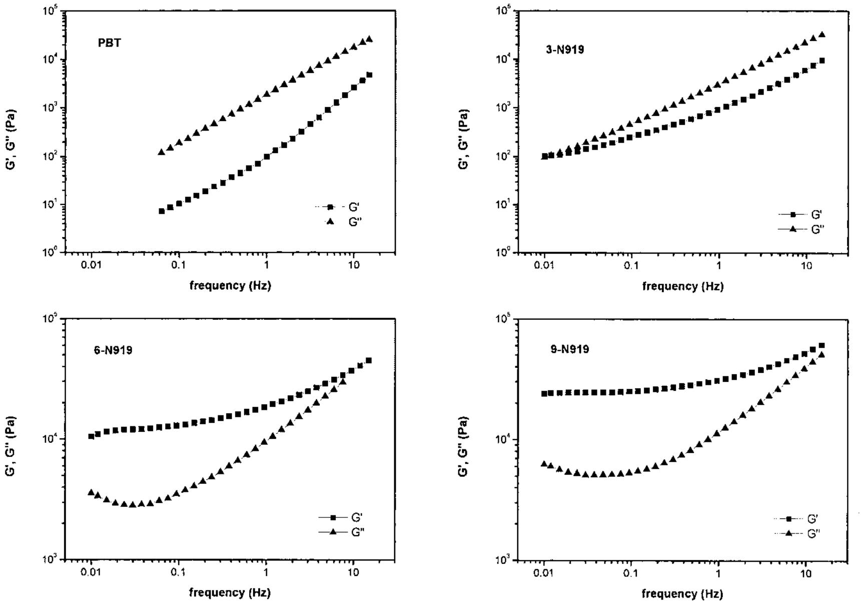


Figure 8. Dynamic spectra (G', G'' *vs.* frequency) for neat PBT and its N919-based nanocomposites at 3%, 6% and 9% by wt of organoclay.

To help in representing this behavior, Figure 8 plots in a same graph both G' and G'' curves for N919-based nanocomposites. Also these results may be interpreted as the effect of a pseudo-solid-like behavior at long times, due to occurrence of strong polymer-silicate interactions that slow the relaxation times of the PBT chains.[1, 10]

Conclusions

In this paper the effect of different commercial organoclay type on exfoliation and rheological response of PBT/organo-silicate nanocomposites was investigated. The study was performed on hybrids at three silicate loadings (3, 6 and 9 wt%), prepared by means of a laboratory-scale twin screw extruder. All samples were tested in order to analyze the relationships between composition (in terms of organoclay type and amount), morphology and rheological response of nanocomposite systems. X-ray diffraction experiments have demonstrated that all samples have a nanoscale dispersion of the silicate in the PBT matrix, however different morphologies were observed by TEM depending on both silicate type and loading. The more exfoliated clay dispersions were obtained with the Nanofil 919 and Dellite 43B organoclays, whose organic modifiers have a phenyl group that may determine favorable specific interactions with the aromatic ring of PBT chains, as suggested by FT-IR spectra. However, increasing the silicate loadings, the clay platelets become more aligned and uniformly distributed in the PBT matrix, for all analyzed systems. The study has also put in evidence that, correspondingly to the more exfoliated morphologies, the viscoelastic response is characterized by markedly shear thinning complex viscosity curves, with a pseudo-solid-like flow behavior at long times, due to the occurrence of strong polymer-silicate interactions that slow the relaxation times of the polymer chains. However, it has to be specified that the correspondence between rheology and morphology is qualitative only and no quantification on the exfoliation level of a nanocomposite system can be inferred by viscosity data.

All these results well remark the critical role of chemical affinity between the polymer matrix and the organic modifier of the silicate in determining an adequate exfoliation level of clay platelets during the melt compounding process and show that viscoelastic measurements, highly sensitive to the nanoscale structure of nanocomposite systems, can be a powerful method to probe the developed structure of such materials.

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[1] T.J. Pinnavaia, G.W. Beall, Eds, "*Polymer-Layered Silicate Nanocomposites*", J. Wiley & Sons, New York 2001.
[2] M. Alexandre, P. Dubois, *Mater. Sci. Eng.* **2000**, *28*, 1.
[3] P.C. LeBaron, Z. Wang, T.J. Pinnavaia. *Appl. Clay Sci.* **1999**,*15*, 11.
[4] M. Holmes, *Plast. Add. Comp.* **2000**, *7/8*, 34.
[5] P.B. Messersmith, E.P. Giannelis, *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 1047.
[6] S.D. Burnside, E.P. Giannelis, *Chem. Mater.* **1994**, *6*, 2216.
[7] J.S. Shelley, P.T. Mather, K.L. DeVries, *Polymer* **2001**, *42*, 5849.
[8] R.A. Vaia, K.D. Jandt, E.J. Kramer, E.P. Giannelis, *Macromolecules* **1995**, *28*, 8080.
[9] R.A. Vaia, K.D. Jandt, E.J. Kramer, E.P. Giannelis, *Chem. Mater.* **1996**, *8*, 2628.
[10] S. Sinha Ray, M. Okamoto, *Prog. Polym. Sci.*, **2003**, *28*, 1539.
[11] D. Schmidt, D. Shah, E.P. Giannelis, *Current Opinion in Solid State & Materials Science*, **2002**, *6*, 205.
[12] R. Krishnamoorti, R.A. Vaia, Eds, "*Polymer Nanocomposites. Synthesis, Characterization and Modeling*". ACS Symposium Series No. 804. Washington, DC., 2002.
[13] J.W. Cho, D.R. Paul, *Polymer* **2001**, *42*, 1083.
[14] T.D. Fornes, P.J. Yoon, H. Keskkula, D.R. Paul, *Polymer*, **2001**, *42*, 9929.
[15] H.R. Dennis, D.L. Hunter, D. Chang, S. Kim, J.L. White, J.W. Cho, D.R. Paul, *Polymer*, **2001**, *42*, 9513.
[16] T.X. Liu, Z.H. Liu, K.X. Ma, L. Shen, K.Y. Zeng, C.B. He, *Composites Science and Technology*, **2003**, *63*, 331.
[17] T.G. Gopakumar, J.A. Lee, M. Kontopoulou, J.S. Parent, *Polymer*, **2003**, *43*, 5483.
[18] S. Lee, H. Park, H. Lim, X. Li, T. Kang, W. Cho, J. Lee, C. Ha, *Polymer*, **2002**, *43*, 2495.
[19] B. Lepoittevin, M. Devalckenaere, N. Pantoustier, M. Alexandre, D. Kubies, C. Calberg, R. Jerome, P. Dubois, *Polymer*, **2002**, *43*, 4017.
[20] L. Incarnato, P. Scarfato, G.M. Russo, L. Di Maio, P. Iannelli, D. Acierno, *Polymer*, **2003**, *44*, 4625.
[21] L. Scatteia, P. Scarfato, D. Acierno, *Journal of Plastics, Rubbers and Composites*, **2004**, *33(2/3)*, 85.
[22] D. Acierno, E. Amendola, G. Costa, P. Scarfato, G. Nocerino, *Polymer Engineering and Science*, **2004**, *44(6)*, 1012.
[23] R.M. Silverstein, G.C. Bassler, T.C. Morrill. "*Spectrometric Identification of Organic Compounds*", 4th ed., N.Y.: John Wiley & Sons Ltd., 1981.
[24] R. Krishnamoorti, K. Yurekli, *Current Opinion in Colloid & Interface Science*, **2001**, *6*, 464.
[25] F. Pignon, A. Magnin, J.M. Piau. *Phys. Rev. Lett.* **1997**, *79*, 4689.
[26] J.M. Dealy, K.F. Wissbrum, Eds, "*Melt Rheology and its Role in Plastics Processing*", Kluwer Academic Publishers, Dordrecht 1999.
[27] J.D. Ferry, "*Viscoelastic Properties of Polymers*", 3rd ed., J. Wiley & Sons, New York 1980.
[28] L. Incarnato, P. Scarfato, L. Scatteia, D. Acierno, *Polymer*, **2004**, *45(10)*, 3487.
[29] R. Krishnamoorti, E.P. Giannelis, *Macromolecules,* **1997**, *30*, 4097.
[30] E.P. Giannelis, R. Krishnamoorti, E. Manias, *Advances in Polymer Science,* **1999**, *138*, 107.