

Effects of Processing Conditions on Exfoliation and Rheological Behaviour of PBT-Clay Nanocomposites

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ABSTRACT

In this paper the effects of different processing conditions on exfoliation and rheological properties of melt compounded PBT–clay nanocomposites were investigated. Hybrids containing different kind of organo-clays were extruded at 2 extrusion rates using a twin screw extruder and a single screw extruders and then submitted to TEM analysis and rheological measurements.

The level of exfoliation, and, consequently, the flow behaviour of the nanocomposites was found to be markedly dependant upon the processing parameters employed in the production of the samples.

INTRODUCTION

Polymer-layered silicate nanocomposites gathered substantial academic and industrial interest in the past decade for the remarkable improvement in their functional and structural properties (barrier properties and flame resistance, stiffness, dimensional stability, impact strength) over the pristine polymer matrices^{1,2}.

Being the poly(butylene terephthalate) (PBT) an important semi-crystalline engineering thermoplastic polymer, there is a considerable effort in obtaining PBT-clay hybrids with increased key properties like impact strength and heat distortion temperature, therefore increasing the

industrial interest and widening the field of applicability of this polyester.

In this paper we report on the melt compounding and melt flow properties of PBT-clay systems, evaluating the effects of processing conditions on exfoliation and rheological behaviour of these hybrids. Melt rheology has already proven to be closely related to the material microstructure and therefore particularly useful to improve the processing of these hybrids^{3,4}.

The melt processing of nanocomposites samples was carried out using two different shear devices, a single-screw extruder and a twin-screw extruder, and two different extrusion rates in order to evaluate the effects of shear geometry and shear rate during the process on microstructure and melt flow behavior of melt compounded samples.

Four commercial organo-modified montmorillonites, differing by the organic treatment used in the modification, were employed as nanometric fillers and blended with the PBT at three weight percentages each (3, 6 and 9wt%). The nanocomposite samples were submitted to structural (XRD and TEM) and rheological measurements.

The obtained results were related to the role of chemical affinity between the polymer matrix and the clay in the exfoliation process, inferred in one of our previous works⁵.

EXPERIMENTAL

Materials

The polymeric matrix used in this study was a poly(butylene terephthalate) (PBT, Mn=28000) supplied by Montefibre (Italy). The commercial organoclays selected were Cloisite 25A, Cloisite 30B (produced by Southern Clay Products), Dellite 43B (Laviosa Chimica) and Nanofil 919 (Süd Chemie). All silicates were supplied as a powder of particles nominally < 8µm in size, except Nanofil 919 organoclay, whose particles have an average size of 35µm.

Melt 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 Brabender single screw extruder (L=300 mm, L/D=20) and a Haake twin screw extruder having counter-rotating intermeshing conical screws (L=300 mm). A temperature profile of 210-230-230-228°C from hopper to die was imposed in both the processing devices and a rectangular die (1 mm x 40 mm) was used. Nanocomposite tapes at 3 different organoclay contents were extruded at screw speed of 90 and 150rpm, corresponding to an average residence time in the extruder of about 3.0 min and 1.6 min.

To verify the correspondence between the nominal and the effective weight percentage of clay into the nanocomposite blends, all the extruded samples were submitted to thermogravimetric analysis under the conditions reported in the 'Methods' section below. Small differences (less than 6%) between the nominal and effective weight percentage of clay were found in all cases, consequently their effects were considered not relevant for the discussion of results.

The samples nomenclature is the following *X-CN-ER (M)*, where:

- *X* is the weight percentage of clay
- *CN* is the clay commercial initials
- *ER* is the extrusion rate expressed in screw rotation per minute
- while the optional *M* identify the samples extruded using the single screw extruder.

Methods

Thermogravimetric analyses (TGA) were carried out on neat PBT and all its blends extruded with different clay contents and extrusion rates. TGA tests were performed using a TA TGA 2950 apparatus in the temperature range 25–900°C with a heating rate of 20°C/min under a nitrogen atmosphere.

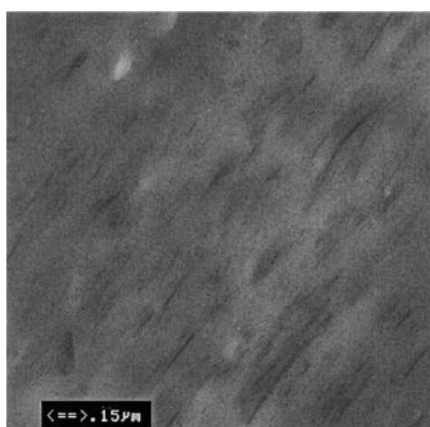
X-ray diffraction spectra were recorded with a flat camera using a sample-to-film distance of 140 mm (Ni-filtered Cu-Kα radiation). The Fujifilm MS 2025 imaging plate and a Fuji Bio-imaging Analyzer System, mod. BAS-1800, were used for digitising the diffraction patterns.

Transmission electron microscopy (TEM) analysis was conducted using a Zeiss EM 900 operating at 80 kV. The images were captured on sections located normal to the extrusion direction prepared by cryogenically microtoming ultra-thin specimens (50 nm thick) using a Leica Ultracut UCT microtome operating at -80°C.

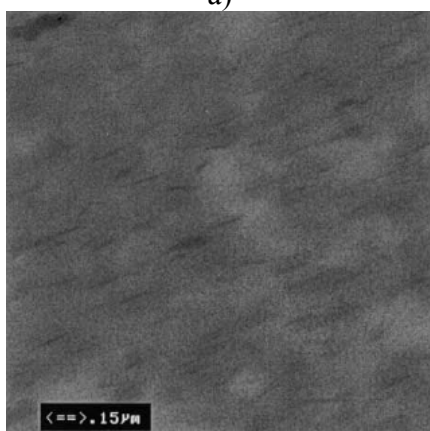
The flow properties of the molten materials were measured with an ARES rheometer (Rheometrics, Inc.), using a parallel plates geometry (plate radius=12.5 mm, gap=0.1 mm). The nanocomposite samples were tested at 230°C, after drying at 90°C in a vacuum oven for 18 h. Dynamic frequency sweep tests were performed in the frequency range $\omega=0.01-15$ Hz, with a strain amplitude of 1% (proven to be in the linear viscoelasticity range).

DISCUSSION

XRD analyses performed on pristine silicates and on nanocomposites showed that the characteristic basal reflection of the organoclays is no more present in the pattern of the hybrids, thus pointing out that the silicate interstratic gap is increased and the clay is dispersed at a nanoscale level in the PBT. More detailed morphological information were obtained from TEM measurements.



a)



b)

Figure 1. TEM images of a) 9-25A-100, b) 9-25A-150

As examples, TEM images of samples 9-25A-100 and 9-25-150 are shown in figure 2a–b, respectively. All samples exhibit a nanoscale dispersed morphology containing both individual silicate sheets and intercalated structures resulting from an extensive penetration of the PBT matrix by the organoclay galleries of Cloisite 25A.

The maximum thickness of the intercalated stacks does not exceed ~40 nm in all cases and the size of the dispersed phase appears nearly independent upon the extrusion rate.

Rheological analyses were performed to investigate the relationships between morphology and flow behaviour of the nanocomposite samples. Figure 2 shows a comparison between the complex viscosity curves of neat PBT and samples 6-25A-100, 6-30B-100, 6-43B-100 and 6-919-100. The characteristic dynamic flow behaviour of nanocomposite systems can be observed for each of the different compositions examined.

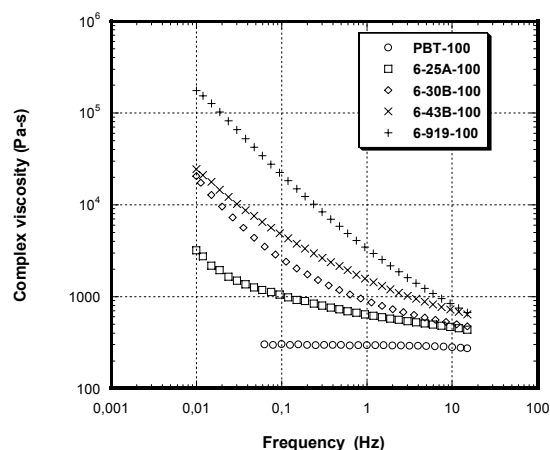


Figure 2. Complex viscosity curves comparison of neat PBT and hybrids 6-25A-100, 6-30B-100, 6-43B-100, 6-919-100.

Low frequency complex viscosity values of nanocomposites are much higher than that of the pure polymer; contextually, the pseudo-newtonian behaviour of the neat polymer matrix changes into a marked pseudo-shear thinning behaviour for all the examined systems. From the graph is indeed evident a marked difference between the flow behaviour of hybrids containing the same percentage of different kind of organoclays. The effect of clay loading is much more marked on hybrids containing Dellite 43B and Nanofil 919 organoclays. These results were related to the different chemical affinity of PBT with the organic modifiers of the filler used, as came out

from our previous work on the same systems⁵.

In order to point out the effect of processing condition like shear level and process residence time on the flow behaviour of these nanocomposite systems, we carried out dynamic rheological measurement on samples extruded at two different screw rotation speeds.

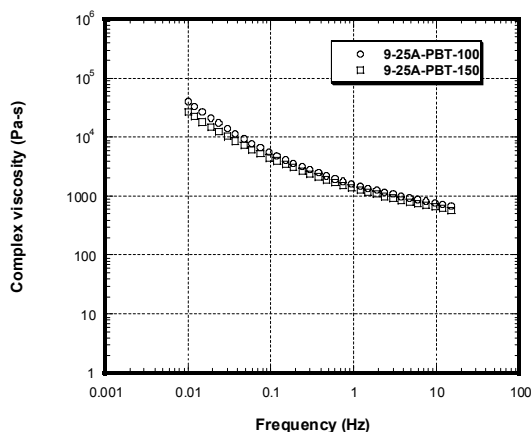
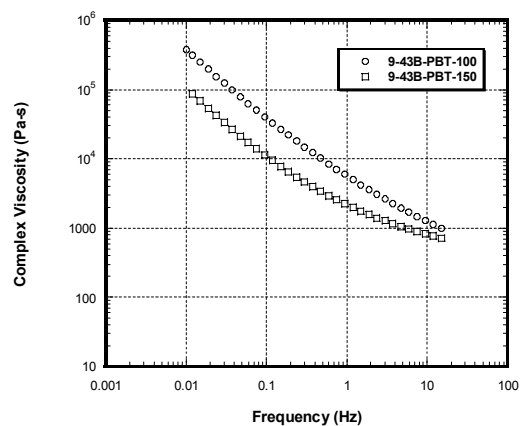


Figure 3. Comparison between the complex viscosity curves for samples 925A100 and 925A150. No significant difference can be detected in the dynamic flow behaviour of the hybrids extruded at different screw rotation rates.

Figure 3 shows a comparison between the complex viscosity curves for samples 9-25A-100 and 9-25A-150, i.e. for samples having the same composition processed using different extrusion rates (100 and 150 rpm). It is evident from the graph that, using our experimental plant, the change in the extrusion rate did not affect the flow behaviour in a significant way; the flow curves related to samples extruded at 100 and 150rpm are actually almost superimposed: at a closer analysis, complex viscosity values for samples extruded at 100rpm are slightly higher than the ones related to samples processed at higher rate. These results point out that, for the PBT hybrids containing the 25A filler, an increase in shear stress do not particularly help the exfoliation process.

Figure 4 shows the dynamic response for samples 943B100 and 943B150. In this case the graphs highlights that the samples extruded at lower extrusion rate have a more marked pseudo-shear thinning behaviour and higher complex viscosity values at all frequencies. This flow behaviour may be associated to a higher degree of exfoliation in the nanocomposite sample extruded at lower rate.



b)

Figure 4. Comparison between the dynamic responses of samples 943B100 and 943B150.

These last results indicate that a lower level of shear and an higher residence time, resulting from the lower extrusion rate, lead to higher degree of exfoliation in the final product with respect to the case of higher shear and lower residence time (condition associated with the higher extrusion rate). This phenomenon can be explained considering the good affinity between the silicate and the matrix, which particularly contributes to the intercalation of polymer chains via direct diffusion, and that benefit from the additional residence processing time⁵.

Figure 5 shows the complex viscosity curves of pure PBT and 625A100M and 625A100T samples. The rheological behaviour is essentially unchanged after the addition of clay, suggesting that the dispersion of the silicate platelets in the

polymer matrix is occurred on a microscopic scale. Morphological investigations (XRD and TEM) have confirmed this hypothesis, highlighting that an adequate level of shear is required in order to obtain nanoscale dispersion and that chemical affinity alone is not enough.

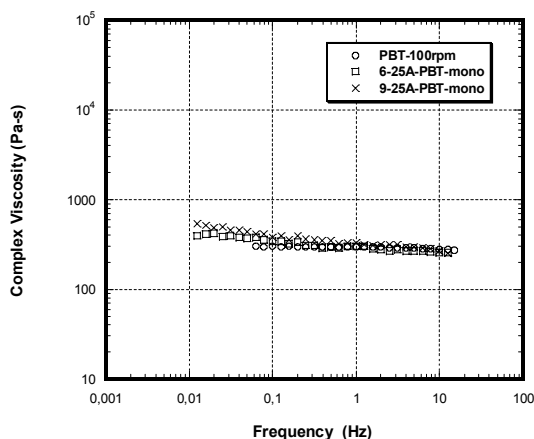


Figure 5. Complex viscosity curves related to pure PBT and to samples 6-25A-100M and 6-25A-100

CONCLUSIONS

In this paper the effects of preparation conditions on the exfoliation and rheological response of PBT/organo-silicate nanocomposites were evaluated. In particular, different processing parameters (extruder geometry, extrusion rate) and system compositions (organoclay kind and amount) were investigated.

In terms of morphology, all samples produced with the twin screw extruder showed a mixed intercalated-exfoliated structure, as evidenced from XRD and TEM measurements. The flow behavior exhibits a marked dependence upon the processing residence time and extrusion rate. The strength of this dependence was found connected to the chemical affinity between the clay and the matrix: the dispersion and exfoliation of the filler with the higher affinity benefits from higher residence times, and therefore slower extrusion rates.

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