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Recyclability of Polystyrene/Clay Nanocomposites

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PS/organo-modified clay (5% w/w) nanocomposite has been subjected to a series of eight processing cycles in a twin screw extruder. The influence of multiple recycling on the properties of the nanocomposite was studied by following the changes in the morphology, the molecular structure, the melt flow index (MFI) and the thermal properties. The WAXS results indicate a strong intercalation of PS chains between silicate layers of the organoclay and the extent of intercalation appears to increase with increasing the number of cycles. The main effects of recycling are a reduction in molecular weight due to chain scission, although the occurrence of a crosslinking fraction is probable after 8 cycles. The thermal properties remain almost stable during reprocessing.

Keywords Degradation; nanocomposites; organo-modified clay; polystyrene; recycling

Introduction

During the last decade, polymer/layered silicate nanocomposites (PLS), especially those containing organo-modified clays, have attracted a great academic and industrial interest [1]. They often exhibit remarkable improvement of mechanical, thermal, and physico-chemical properties when compared with pure polymer and their conventional microcomposites even at very low filler concentration due to the nano-level interactions with the polymer matrix [2–4]. It is projected that PLS nanocomposites will play an increasingly role as new materials in automotive, packaging and aerospace applications [5]. An attractive approach for producing PLS nanocomposites is by melt mixing the polymer of interest with organically modified clay due to its easy processability, non-use of solvent and cost effectiveness [6]. However, during processing, the melted polymeric material is exposed to high temperatures, shear, impurities, like catalyst residues and the decomposition of surfactant that can cause degradation resulting in molar mass distribution changes in the matrix [7, 8]. Indeed, Vander Hart et al. [9] and Shah et al. [10] reported that a considerable portion of the quaternary alkyl ammonium component is depleted during melt processing of PLS nanocomposites due to thermal degradation.

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Therefore, the knowledge of structural and property changes arising from reprocessing of PLS nanocomposites is crucial in their usage process because it usually shortens the lifetime of the material and also important for evaluating the economical and potential environmental impact for this relatively new class of material. According to the literature [11, 12], reprocessing of polymer nanocomposites have been studied only in the case of polyamide 6, polyamide 12, a thermoplastic olefin elastomer and polypropylene matrices. Although a considerable research work has been carried out on the multiple recycling of both virgin and waste polystyrene, however, studies on the effects of reprocessing on nanodispersion and the functional properties of polystyrene based nanocomposites are rather scarce. The property changes during series of subsequent recycling still remain to be understood for better controlling the performances of the recycled polymers. Therefore, the aim of this paper was to study the effects of repeated processing cycles on the morphology and properties of polystyrene (PS)/Cloisite 15A (5% w/w) nanocomposite. The samples were prepared by direct melt intercalation in a Brabender Plasticorder, and further they were subjected to 8 reprocessing cycles in a twin screw extruder. For comparative purposes, neat PS was also recycled in the same experimental conditions. The structure of the nanocomposite samples as well as the rheology, the molecular weight and the thermal properties were determined for each processing cycle.

Experimental Part

Materials Used

The PS used is an atactic homopolymer free of additives supplied by BASF Company and commercialized under the trade name POLYSTYROL 143E. The polymer in form of pellets, has an average molecular weight (M_w) = 307900 g/mol associated to a polydispersity index of 2.28, as determined by gel permeation chromatography (GPC), and a melt flow index of 10.43 g/10 min.

The type of nanofiller used is organophilic clay available from Southern Clay Product Inc. It is commercialized under the trade name Cloisite 15 A. According to the manufacturer, the nanoclay was subjected to a surface treatment before mixing with polystyrene. The Cloisite 15 A is a modified montmorillonite (OMMT) by a quaternary ammonium salt, and dimethyl dihydrogenatedtallow (2M2HT) with ca. 65% C18, 30% C16, 5% C14 and C.E.C. = 125 meq/100 g. The Cloisite 15A was used at a loading concentration of 5% (w/w).

Preparation of the Nanocomposite Samples and their Recycling

Initially, the PS/Cloisite 15A (5% w/w) nanocomposites were prepared by melt mixing in a Brabender Plasticorder mixing chamber (model W 50 EHT) having the following characteristics: chamber volume = 55 cm³, sample weight = 40–70 g, maximum couple = 200 Nm and maximum temperature = 500°C. Prior to mixing, the nanofiller was dried at 80°C for 24 h. The major processing parameters were processing temperature, screw speed and mixing time; they were set at 180°C, 50 rpm and 10 min, respectively. The resulting material was granulated, and then compressed to produce thin films of an average thickness of ca. 150 μm with the aid of hydraulic press equipped with two heated plates at 200°C with a pressure of 20 bars. Neat PS was also processed under the same experimental conditions as a reference material. Further a set of 8 passes were completed through a co-rotating intermeshing twin-screw extruder under the same processing conditions. For each cycle, a

part of resulting material was compressed to produce thin films of an average thickness of 150 μm at temperature of 200°C and pressure of 20 bars.

Characterization techniques

Wide Angle X-ray Scattering (WAXS). WAXS was used to analyze the structure of the materials and to determine the interlayer spacing between stacked clay platelets, and subsequently to prove the widening of this distance as matrix polymer intercalates between the galleries [13]. Changes in the value of 2θ reflect changes in the gallery distance of the clay and allow distinguishing the intercalated and nonintercalated silicate fractions. WAXS experiments were performed by using a Philips diffractometer (PW 1050) operating at the $\text{CuK}\alpha$ radiation (wavelength, $\lambda = 0.154 \text{ nm}$), 40 kV and 20 mA. The diffraction spectra were recorded in the reflection mode over a 2θ range of 2–10° at room temperature and a scan rate of 0.017°/s.

Rheological Measurements

Rheological measurements were carried out in an oscillatory mode on a rheometer (Gemini Bohlin, C-VOR), equipped with a parallel plate geometry using 25 mm diameter plates at 180°C. The samples in form of pellets having approximately 1 mm of thickness and 25 mm of diameter were prepared by compression molding at 180°C. The storage and loss moduli, i.e. (G') and (G'') and the complex viscosity (η^*) were measured in the linear domain in a frequency range between 0.01 to 10 rad/s. The average time for scan measurement was 20 min.

Gel Permeation Chromatography (GPC)

In order to measure molecular weights, a Shimadzu LC 20AD system was used in combination with a Shimadzu RID10A differential refractometer and a Shimadzu SP 10Avp UV dual wavelength detector ($\lambda_1 = 254 \text{ nm}$ and $\lambda_2 = 280 \text{ nm}$). The column set consists of five 30 cm gel columns with a granulometry of 10 μm (from Polymer Laboratories). The solvent was analytical grade THF, dried on calcium hydride at a flow rate of 1 $\text{mL}\cdot\text{min}^{-1}$. The GPC analyzes were performed at room temperature. Polystyrene samples and its nanocomposite were previously dissolved in solvent for 24 h under stirring and then heated to 40°C for 1 h. Solutions were filtered through 0.45 μm stainless steel frits prior to injection in order to remove the clay structure.

Melt Flow Index (MFI)

Assessment of polymer degradation during recycling was accomplished through monitoring its rheological implications. Indeed, the melt flow index test is a simple and convenient method for characterizing both the type of degradation (chain scission or cross-linking) and the extent of degradation of a polymer since the melt flow index (MFI) is inversely related to the molar mass of the polymer and is indicative of the flow characteristics of the molten polymer [14]. The MFI measurement of the reprocessed neat PS and PS nanocomposite was carried out according to the ISO 1133:19997 standard. The flow rate measurement of the extrudates was performed by MVR/MFR tester machine (model 1267 C5, Germany) at 200°C and the nominal load was 5 kg. Five measurements were performed for every sample and the average was taken as the representative value.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) analysis of neat PS and PS/Cloisite 15A (5% w/w) nanocomposite was performed on weighted samples of almost 10 mg. This was performed using Mettler-Toledo DSC-882 equipment for each processing cycle. The samples were heated from 25 to 200°C in nitrogen atmosphere. To erase thermal history, the first cooling and the second heating thermograms were recorded with the following scanning rate: 10°C/min in the first cooling and 10°C/min in the second heating. The glass transition temperature (T_g) was determined as the mid point inflexion from the DSC thermograms.

Thermogravimetric Analysis (TGA)

TG experiments were carried out in a Setaram TG-DTA 92-10 thermal analyzer using a scanning rate of 10°C/min under nitrogen atmosphere in the temperature range starting from 20°C to 650°C.

Results and Discussion

Nanostructural Characterization of PS/C15A Nanocomposite

Figure 1 shows the XRD pattern of PS/C15A (5% w/w) nanocomposite recorded after 8 processing cycles taken as example in comparison with that of pristine OMMT (Cloisite 15A). Cloisite 15A has a characteristic WAXS pattern at 2.8° corresponding to a d_{100} -spacing of 31 Å based on Bragg's equation in concordance to the literature [14, 15]. The PS nanocomposite shows a well defined peak at 2.05° after 8 reprocessing cycles. And correspondingly, the d_{001} -spacing has an increase from 31 Å of Cloisite 15A to 43.04 Å. The existence of (001) diffraction peak with an increase of gallery spacing is indicative of

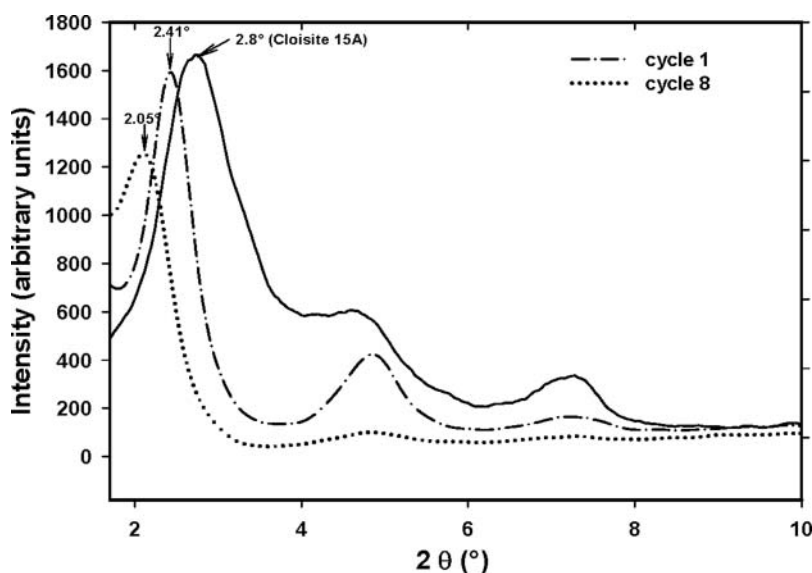


Figure 1. WAXS patterns of PS/Cloisite 15A (5% w/w) nanocomposite recorded after 8 reprocessing cycles compared to that of pristine Cloisite 15A.

the formation of intercalated layered silicate nanocomposite [16]. This is also proposed by Vaia et al. [17] who reported that an increase in the intergallery spacing, which is related to the intercalation of the polymer chains through the clay galleries, results in a new diffraction pattern that corresponds to the increased spacing of the clay galleries.

From Fig. 1, it appears clearly that a repeated reprocessing cycles in a twin screw extruder improves the intercalation of PS chains in the silicate galleries.

In order to investigate the effects of repetitive reprocessing cycles on the initial morphological structure of PS/C15A (5% w/w), rheological analyzes in oscillatory mode have been carried out on neat PS and PS nanocomposite samples. As well reported in literature [11, 18], rheology seems a powerful tool to discriminate the structural modifications occurring with reprocessing being very sensitive to the nanoscale arrangement of the silicate layers, as well as, to the viscoelastic characteristics of the neat polymer matrix. In Fig. 2(a) and (b), the complex viscosity is plotted as a function of frequency after 1 and 8 reprocessing cycles for neat PS and PS nanocomposite, respectively. From Fig. 2(a), it is observed that the complex viscosity of the neat PS decreases as the processing cycle increases from 1 to 8 cycles. This effect is more evident in the lower frequency region (0.01–0.1 Hz) and it is related to the decrease of the molecular weight (\bar{M}_w) of the neat PS after repetitive recycling caused by chain scission due to thermomechanical degradation [19]. Moreover, Fig. 2(a) shows the formation of a Newtonian plateau in the low frequency region (0.01–0.1 Hz), which is extended until frequencies of around 1 Hz for the sample which was subjected to 8 cycles. In Fig. 2(b), the complex viscosity of the nanocomposite is considerably higher than that of the polymer matrix. This is explained as a result of the strong interaction of organoclay and PS [20]. Moreover, the rheological curves of the nanocomposite samples show a regular decrease in the complex viscosity with increased frequency in the range of 0.01 to 10.0 Hz. Furthermore, it is clearly shown in Fig. 2(b) an increase in the complex viscosity of the nanocomposite sample at 0.01 Hz after 8 reprocessing cycles compared to the initial one, which can be attributed to an increase in the molecular weight suggesting the occurrence of crosslinking. With increased frequency, the flow curves of the nanocomposite are superposed. According to Incarnato et al. [19], both the crossover modulus, (G_c), which is defined as the point where the storage modulus (G') is equal to the loss modulus (G''), and the corresponding frequency (ω_c) can be used for an investigation on the structural modifications in the neat PS and PS/C15A nanocomposite. The cross-over coordinates are related to the average molecular weight \bar{M}_w and to the molecular weight distribution (MWD). In this respect, the dependence of G_c from the number of reprocessing cycles is shown in Fig. 3 for both neat PS and PS nanocomposite. It can be seen that G_c of neat PS increases gradually with reprocessing, according to reduction of \bar{M}_w . In addition, the fast increase of G_c after the fifth cycle indicates a narrowing in the molecular weight distribution [19]. Da Costa et al. [20] reported that an increase in the cross-over modulus (G_c) is associated to an abrupt degradation process. However, in the case of PS nanocomposite, it can be seen from Fig. 3 that the G_c values seem to be less affected by the number of reprocessing cycles within the experimental errors. However, after 8 cycles, a slight decrease in G_c is observed suggesting the probability of occurrence of some crosslinking in the nanocomposite, which is consistent with the result of the complex viscosity.

Molecular Weight Changes

Changes in molecular weight taking place during repeated reprocessing cycles provide a direct measurement of the degradation of the material and they have been estimated from the results of GPC measurements [21]. The effects of reprocessing on the molecular

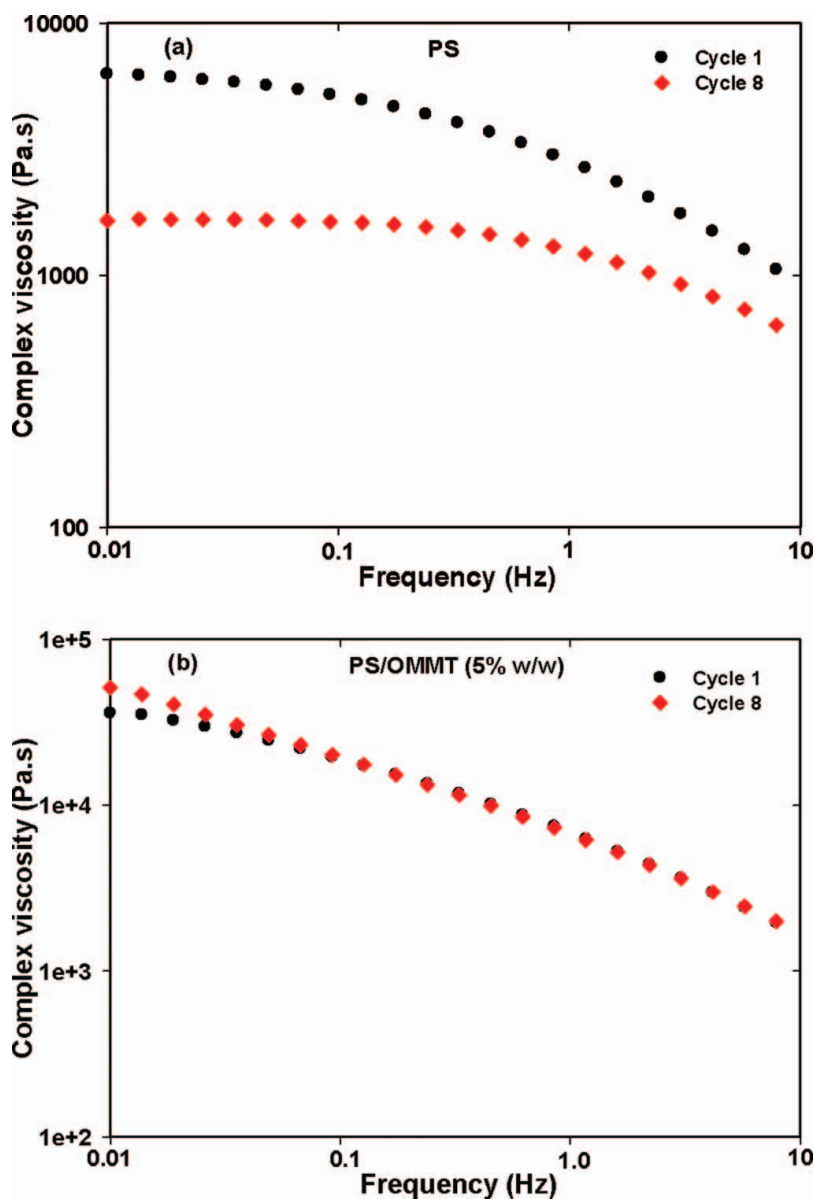


Figure 2. Complex viscosity curves versus frequency recorded after 1 and 8 reprocessing cycles. (a): neat PS and (b): PS/Cloisite 15A (5% w/w) nanocomposite.

weight distribution (MWD) of neat PS and PS nanocomposite is shown in Fig. 4 (a) and (b), respectively for 1, 4 and 8 reprocessing cycles. From Fig. 4(a), it is observed that the curves of MWD of neat PS shift progressively towards the lower molecular weight with increasing the number of reprocessing cycles, which is typical of processes dominated by chain scission phenomenon [22]. In Fig. 4(b), which is relative to the PS nanocomposite, the profile of the MWD curves for the reprocessed materials shows a slight shift to the left (smaller molecular size) after 4 cycles, but it is evident that a high molecular weight

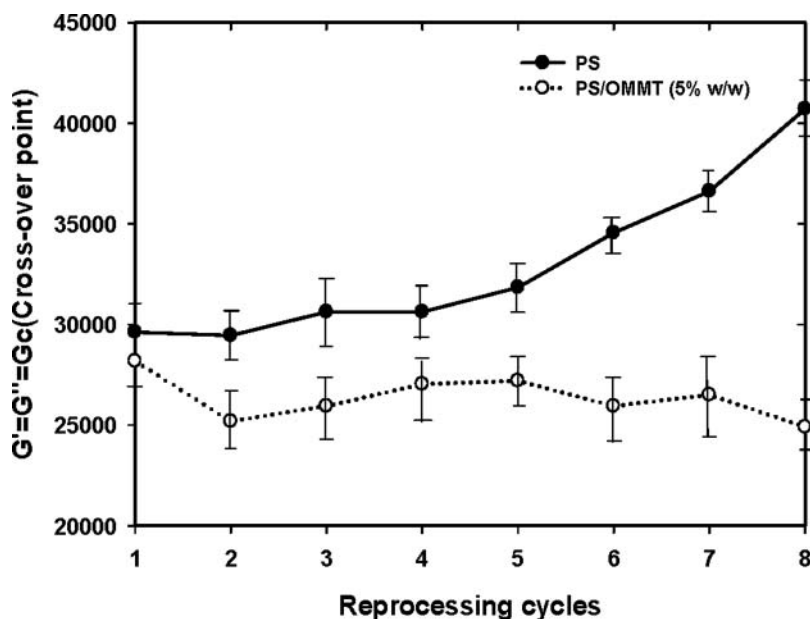


Figure 3. Cross-over point (G_c) versus reprocessing cycles for neat PS and PS/Cloisite 15A (5% w/w) nanocomposite.

tail has developed as well after 8 cycles, indicating that although chain scission must have taken place in the major part of recycling, crosslinking is however present in the last cycle. This is confirmed by the results shown in Fig. 5, which reports the scission index (SI) values calculated after 4 and 8 reprocessing cycles for both neat PS and PS nanocomposite. According to the literature [15], SI (or number of scissions per molecule is defined according to the following Eq. (1):

$$SI = [n(t) - n(t_0)]/n(t_0) = [\bar{M}_n(t_0)/\bar{M}_n(t)] - 1 \quad (1)$$

in which $n(t)$ represents the number of polymer chains at a given processing cycle and $n(t_0)$, the initial number of chains, while $\bar{M}_n(t_0)$ and $\bar{M}_n(t)$ are the number average molecular weight of samples after the initial cycle and a given processing cycle.

From Fig. 5, it is observed that there is a very large increase in the SI value from 4 to 8 reprocessing cycles which indicates clearly that further repetitive recycling increases the chain scission rate in the PS matrix. On the contrary, the SI value of the PS nanocomposite is negative after 8 cycles confirming the occurrence of crosslinking at this processing stage. In the intermediate cycle, a slight increase in the SI value of the nanocomposite sample is noticed which indicates a reduction in the molecular weight.

Melt Flow Index (MFI)

The effects of the number of reprocessing cycles on MFI for both neat PS and PS nanocomposite samples are shown in Fig. 6. MFI is an easy and quick measurement, normally used industrially for raw materials quality control before processing. MFI is strongly influenced by the molar mass of the molten polymer [23]. From Fig. 6, it is observed that a repetitive recycling of the neat PS causes a rapid increase of MFI passing from the initial value of

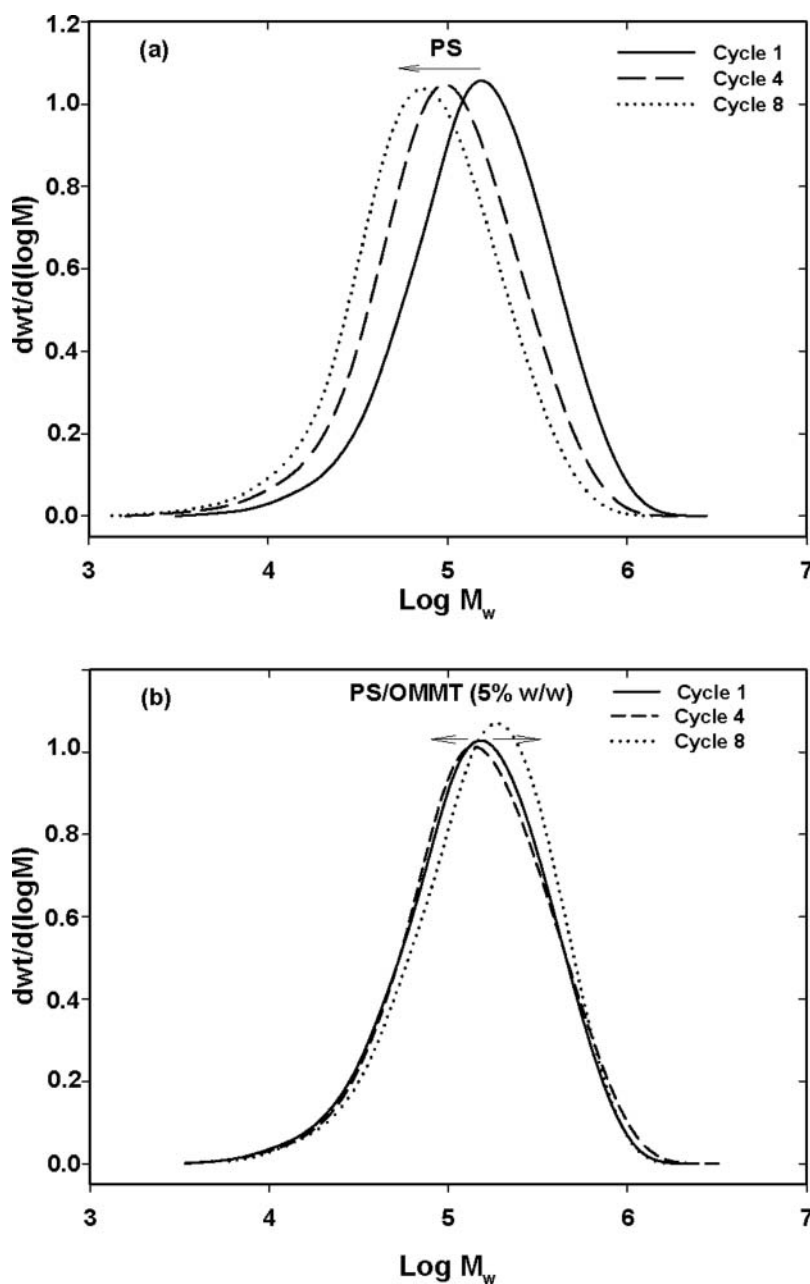


Figure 4. Molecular weight distribution (MWD) curves from GPC after 1, 4 and 8 reprocessing cycles. (a): neat PS and (b): PS/Cloisite 15A (5% w/w) nanocomposite.

almost 17.2 to 53 g/10 min, representing approximately 300% increase due to the formation of low molecular weight species as a result of a chain scission [24], which is in agreement with the data obtained by GPC analysis and rheological measurements. Moreover, the reduced melt viscosity, the lower molecular weight, and the increased scission index; all these

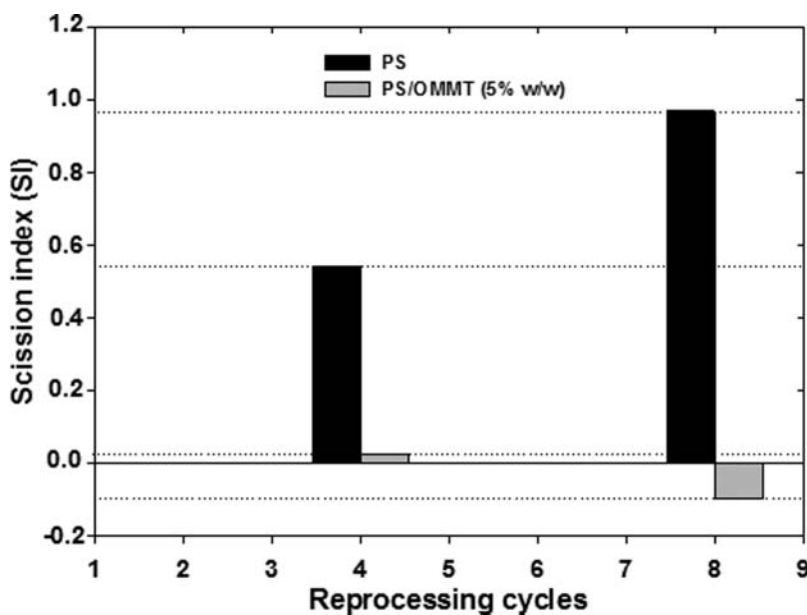


Figure 5. Scission index (SI) of neat PS and PS/Cloisite 15A (5% w/w) nanocomposite determined after 4 and 8 reprocessing cycles.

observations indicate further degradation [25]. However, it is observed that after the first cycle, there is a significant decrease ($\sim 53\%$) of the melt flow index for the nanocomposite compared with that of neat PS, which is a result of the increase in the system viscosity (see Fig. 3). Similar results were reported in the literature [26] and they were attributed to the

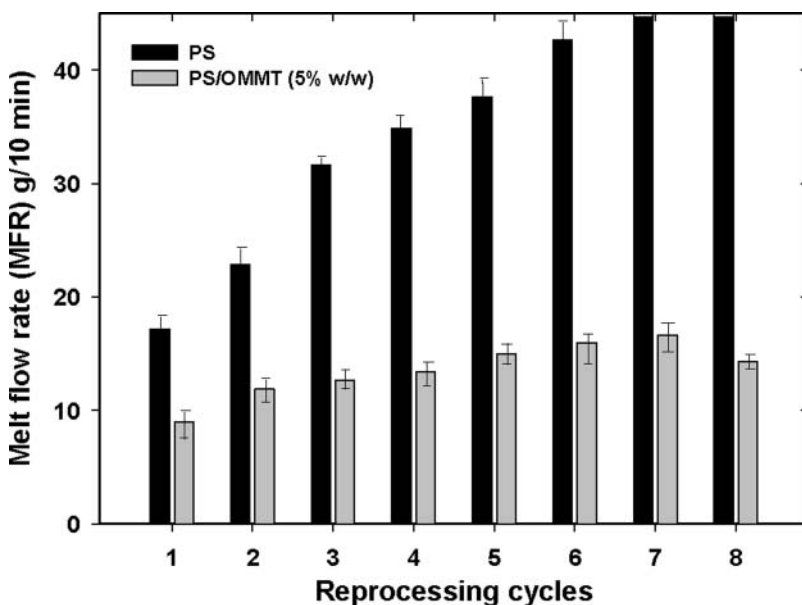


Figure 6. Melt flow index (MFI) as a function of reprocessing cycles for neat PS and PS/Cloisite 15A (5% w/w) nanocomposite.

confinement of polymer chain motion caused by organoclay platelets and tactoids in the polymer matrix. With increasing the number of reprocessing cycles, a slight, but progressive increase in the MFI values is observed during reprocessing passing from the value of 9.1 g/10 min after the first cycle to 16.6 g/10 min after 7 cycles. However, after 8 cycles, there is a decrease in the MFI value to almost 14 g/10 min, as clearly observed in Fig. 4. From processing point of view, the decrease in MFI implies an increase in molecular weight due probably to the formation of crosslinking. This result is consistent with rheological and GPC data. Thus, it is concluded that the thermal degradation of PS nanocomposite proceeds via two mechanisms. In the first series of reprocessing cycles, chain scission is the dominant one, whereas in the eighth cycle, the probability of crosslinking formation is higher over chain scission.

Thermal Stability

The thermal degradation behaviour under N_2 atmosphere of neat PS and PS/C15A (5% w/w) nanocomposite is given in Fig. 7 for the first and the last reprocessing cycles, i.e. 1 and 8 cycles. Further, the temperature corresponding to the initial 10 and 50% of weight loss, i.e. T_{10} and T_{50} , respectively and the final residue obtained at 600°C , determined by TGA and DTG experimental curves are presented in Table 1. As shown in Fig. 7, during the thermal degradation of neat PS in N_2 atmosphere, the samples show a single step of degradation and no evolution of the shape of TGA curve is observed after 8 cycles. The mechanism of thermal degradation of PS is well documented in literature [27, 28]. It is based on random chain scission at elevated temperature followed by β -scission (depolymerization), producing styrene monomer, dimer and trimer through an intra-chain reaction. The TGA results in Table 1 reveal that for neat PS, the initial values of T_{10} and T_{50} are about 403 and 433°C , respectively. After 8 cycles, the values remain almost unchanged. As is

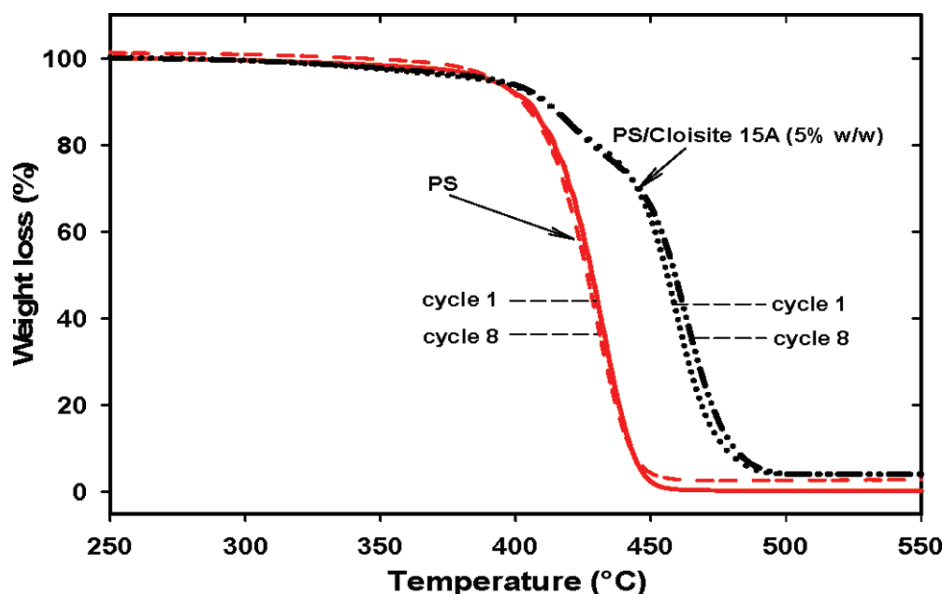


Figure 7. TGA thermograms under nitrogen atmosphere for neat PS and PS/Cloisite 15A (5% w/w) nanocomposite recorded after 1 and 8 reprocessing cycles.

Table 1. TGA data under nitrogen atmosphere for neat PS and PS/Cloisite 15A (5% w/w) nanocomposite as a function of number of reprocessing cycles

Samples	Cycles	T _{10%} (°C)	T _{50%} (°C)	Residue at 600°C (wt%)
PS	1	403 ± 1.0	433 ± 0.5	<0.5
	4	402 ± 0.5	432 ± 0.5	0.95 ± 0.5
	8	402 ± 1.0	432 ± 0.5	1.98 ± 0.6
PS/Cloisite 15A (5% w/w)	1	411 ± 0.5	452 ± 0.5	3.51 ± 0.5
	4	410 ± 1.0	455 ± 1.0	3.51 ± 0.5
	8	411 ± 1.0	455 ± 1.0	3.51 ± 0.5

obvious from Table 1 and Fig. 7, repeated reprocessing cycles do not have any noticeable effect on the degradation temperatures of neat PS. The addition of 5% w/w of the organic montmorillonite to the polymer matrix causes a shift of the initial 10 and 50% of weight loss to higher temperatures reaching, 411 and 452°C, respectively. The thermal degradation results also in a small residue (~3 wt.%) at 600°C, which is assigned to the mineral content of Cloisite 15A in the PS nanocomposite. From Fig. 7, it is also noticed that there is slight second-stage decomposition for the PS nanocomposite at approximately 428°C, which is probably due to the loss of the surfactant anchored on the clay layers [29]. The improvement in thermal stability may be resulted from interaction between organic and inorganic phases. The detailed mechanism of improvement of nanocomposite thermal stability has not been well established yet, but for some authors [28], this is due to the formation of char on the nanocomposite surface that is enhanced by impermeable montmorillonite layers. This char reduces the diffusion of volatile products of polymer degradation out of polymer bulk; therefore, the reduction in the rate of mass loss is observed. For Kim et al. [30], the enhancement of the thermal stability can be regarded as additional evidence of the intercalations between PS and organic montmorillonite. After 8 cycles, it can be seen from Table 1 that the value of T₁₀ remains almost constant with increasing the number of reprocessing cycles, while a very slight increase (~3°C) is observed for T₅₀ passing from 452°C to 455°C. This agrees with the results obtained by GPC analysis indicating a slight increase in \bar{M}_w of the PS nanocomposite after 8 cycles. Recombination through crosslinking could be responsible for the slight enhancement of T₅₀. Moreover, there is no noticeable change in the amount of residue at 600°C after 8 cycles.

Differential Scanning Calorimetry Analysis

The detailed DSC data are summarized in Table 2. The DSC measurements indicate that after the first cycle, the neat PS exhibits an endothermic process centered at the temperature of approximately 88°C corresponding to the T_g of PS [15]. After 8 reprocessing cycles, the value of T_g is almost the same within the estimated maximum error range of ±0.5°C. The results show clearly that T_g of PS is not so affected by reprocessing up to 8 cycles. The addition of 5% w/w of Cloisite 15A to the PS matrix does not induce any noticeable change in the T_g value, which is estimated roughly at 88°C. However, after the second cycle, a slight shift of T_g toward 91°C is observed for the PS nanocomposite remaining constant up to 8 cycles. The small increase of T_g (~3°C) obtained after the second cycle may be due to the restricted segmental motions of the polymer chains at the organic-inorganic interface,

Table 2. Glass transition temperature (T_g) versus reprocessing cycles for neat PS and PS/Cloisite 15A (5% w/w) nanocomposite determined by DSC

Reprocessing cycles	T_g ($^{\circ}\text{C}$)	
	PS	PS nanocomposite
1	87.7 ± 0.5	88 ± 0.5
2	87.9 ± 0.5	90 ± 0.5
3	88.3 ± 0.5	91 ± 0.5
4	88.1 ± 0.5	91 ± 0.5
5	87.6 ± 0.5	91 ± 0.5
6	87.1 ± 0.5	91 ± 0.5
7	86.9 ± 0.5	91 ± 0.5
8	86.7 ± 0.5	92 ± 0.5

as a result of the confinement of the PS chains between the silicate layers, as well as the silicate surface polymer interaction in the nanocomposite [15].

Conclusion

The effects of repetitive recycling on the structure and properties of polystyrene/Cloisite 15A incorporated at 5% (w/w) have been investigated through melt processing in a twin screw extruder up to 8 cycles. We have shown that during reprocessing the complementary processes of intercalation improvement and chain scission can balance and yield a stabilization of the mechanical performances of the PS nanocomposites over 8 cycles. It was found that reprocessing enhances the intercalation of the polymer chains inside the clay gallery. Indeed, the higher basal spacing of clay in the nanocomposite is obtained after 8 reprocessing cycles in comparison to those of the first pass and the pristine Cloisite 15A, which suggests that further reprocessing promotes higher intercalation, and subsequently higher dispersion of organoclay inside the polymer matrix. Moreover, from rheological measurements, GPC analysis and melt flow rate, changes in the microstructure of neat PS and PS nanocomposite have occurred during repetitive recycling due to thermal degradation. In neat PS, chain scission is the dominant mechanism of degradation. Whereas, in PS nanocomposite, the degradation involves however two mechanisms: in the first series of reprocessing up to 7 cycles, chain scission is the dominant one, but after 8 cycles, the probability of occurrence of some crosslinking reactions is higher over chain scission. Furthermore, both TGA and DSC data indicate well that the thermal properties of PS nanocomposite remain almost unchanged during the multiple recycling.

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