European Polymer Journal 44 (2008) 3915–3921

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Preparation, characterization and water barrier properties of PS/organo-montmorillonite nanocomposites

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ARTICLE INFO

Article history:
Received 13 May 2008
Received in revised form 28 August 2008
Accepted 1 October 2008
Available online 10 October 2008

Keywords:
Nanocomposite
Polystyrene
Organoclay
Thermal stability
WVT

ABSTRACT

Polystyrene/organo-montmorillonite nanocomposites were prepared via solution blending method, using $CHCl_3$ and CCl_4 as solvents. The clay used was organically modified by hexadecyltrimethyl-ammonium bromide (CTAB) at various surfactant loadings. Intercalated nanocomposite structure was obtained using $CHCl_3$ as solvent while exfoliated or partially exfoliated was probably the predominated form in the case of CCl_4, as shown by X-ray diffraction measurements. Enhancement in thermal stability and in water barrier properties was observed for PS-nanocomposites compared to that of pristine polymer as indicated by thermogravimetric analysis and water vapor transmission measurements. This increment was more prevalent for nanocomposites prepared with carbon tetrachloride as solvent.

1. Introduction

Polymer/clay nanocomposites, two-phase materials with improved physical properties, have been developed over the last two decades. Introduction of low clay content (1–10 wt%) produces materials with dramatic improvement in mechanical, thermal, gas barrier properties, compared to conventional composites or pure polymers [1]. The extent of the improvement is directly related to the aspect ratio and the dispersion of the clay layers in the polymer matrix. Depending on the strength of interfacial interactions between the polymer matrix and the layered silicate (organically modified or not), three different types of composites are thermodynamically achievable: (i) conventional composites, where packages of silicate layers, keep their stacking, creating a conventional phase separated composite (microcomposite) (ii) intercalated nanocomposites, where the multi-layer structure of the silicates are retained, with alternating polymer/silicate layers and a repeat spacing larger than that of original clay or organically modified clay (organoclay) and (iii) exfoliated nanocomposites, where the primary particles of the organoclay are delaminated into individual nm-thick silicate layers [1,2].

Although complete compatibility between the long chain of organic modifier and the polymer matrix may be preferable for better dispersion of clay, it appears that the modification of clay by introducing surfactants to obtain better compatibility is less important than the modification of polymer matrix by introducing polar groups. The role of the surfactant is mainly to enlarge the interlayer-spacing so to make room for the polymer to penetrate into the gallery space during the preparation of polymer/clay nanocomposites [3].

Polystyrene is an important engineering thermoplastic. It is a strong plastic, which can be easily injected, extruded or blow moulded thus making it a very useful and versatile manufacturing material. PS-clay nanocomposites have been prepared in different ways: solution blending method

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0014-3057/$ - see front matter © 2008 Published by Elsevier Ltd.
doi:10.1016/j.eurpolymj.2008.10.001

[4], in-situ polymerization [5], and direct melt intercalation [6,7]. The modification of clay with various surfactants and/or the grafting of various polar groups onto polymer chains are necessary steps for preparing PS-clay nanocomposites. However, it is still difficult to achieve an exfoliated morphology, even though in the case of in-situ polymerization method.

The aims of the present study were: (A) the synthesis of polystyrene/organo-montmorillonite nanocomposites, via the 'solution blending method' using two different solvents and (B) the investigation of the effect of (i) solvent's polarity, (ii) organoclay's surfactant concentration and (iii) organoclay/polymer ratio, on the nanocomposite morphology and the thermal stability of the received materials. Furthermore the water vapor transmission through nanocomposite's film was examined.

2. Experimental

2.1. Raw materials – organic modification of clay

The raw clay used in this study was a bentonite (brand Zenith, S&B Co., Athens) from the Greek island of Milos in the Aegean Sea. According to the supplier, the mineralogical composition was as follows: 85% montmorillonite, 5% plagioclase, 3% calcite, 2.5% quartz, 2% illite, 2% cristobalite and some amorphous mater. After carbonates removal, Na-exchanged montmorillonite was obtained after equilibration in a large excess of 0.1 M NaCl for two days under continuous stirring. Removal of the excess salt was performed by using a dialysis tube. Na-montmorillonite with particle size <2 μm was received by gravity sedimentation and drying under vacuum at 45 °C [8]. The cation exchange capacity (CEC) of the resulted clay was 85 meq/100 g.

To prepare the organo-modified clay (organoclay), a water solution of hexadecyltrimethyl-ammonium bromide (CTAB-obtained from Merck), after 2 h stirring at 50 °C, was added slowly to an aqueous 1 wt% clay suspension under vigorous stirring. The mixture was stirred for 24 h at 50 °C, centrifuged, washed with deionized water four times and once with ethanol in order to remove the excess of surfactant and dried under vacuum at 45 °C. After drying every organoclay was tested with silver nitrate and Bromine presence was never evidenced. Following the above route three organoclays were prepared with various surfactant content concentrations in the ion-exchange solution, corresponding to 0.8, 1.5 and 3.0 times the CEC of the clay.

Polystyrene (PS) was obtained from Aldrich Chemical Company, with weight and number average molecular weights of $M_w = 230,000$ g/mol and $M_n = 140,000$ g/mol, respectively.

2.2. Preparation of PS/organoclay nanocomposites

The preparation method of polystyrene nanocomposites was described in Ref. [9]. Two series of materials, using chloroform or carbon tetrachloride as solvent, with 2 and 10 wt% organoclay loading were prepared as follows: appropriate amount of PS was diluted in $CHCl_3$ or CCl_4 and the solution was mixed, under vigorous stirring, with the organoclay suspension in the corresponding solvent. Carbon tetrachloride gave more stable suspensions compared to those of chloroform. Especially in the case of high surfactant loading (3.0xCEC) the obtained suspension of organoclay and polymer was found to be stable (no sedimentation was observed) for months. This observation will be discussed next. After 24 h stirring, the mixtures were precipitated with methanol addition and dried at room temperature.

2.3. Characterization

SEM images of clay and organoclays surface microstrucure were taken using a JEOL JSM 5600 microscope.

Samples for XRD analysis were prepared by spreading about 1 ml of suspension of each sample on glass slides. The interlayer *d*-spacing of these sample films orientated along the (001) direction, was measured using a D8 Advanced Bruker diffractometer with CuK_α radiation ($\lambda = 1.5418$ Å). The scanning parameters concerning 2θ range, scanning rate and step time were 1.6–20°, 0.03°/s and 1 s, respectively.

Thermogravimetric (TGA) analysis was carried out using a NETZSCH STA 449C apparatus. Samples of about 10 mg were heated in air from 25–650 °C at a rate of 10 $°C\ min^{-1}$. Generally the TGA experiments were carried out once. Some of the experiments were repeated, always with excellent reproducibility. The temperature accuracy of the instrument was <1 K and the mass reproducibility within ±0.5%.

Water vapor transmission (WVT) of neat PS and PS-nanocomposite films was determined at 38 °C using the apparatus and methodology described in the ASTM E96/E 96M-05 and Ref. [10]. Films with 0.1 mm thickness were sealed by a rubber O-ring on top of Plexiglas test bottles containing dried silica gel and then placed in a glass desiccator with 200 ml saturated magnesium nitrate solution (50% relative humidity (RH)). Test bottles were weighed periodically for 24 h and the WVT was calculated according to equation:

$$\mathrm{WVT} = (G/t)/A$$

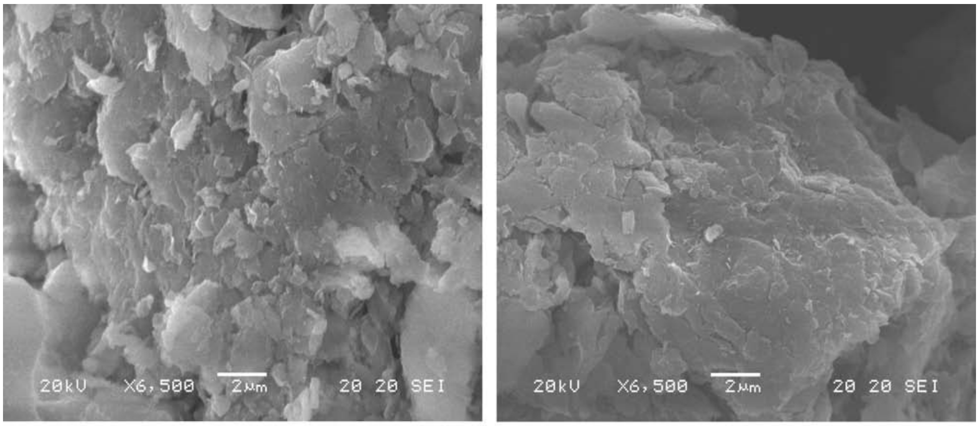
where: G is the weight gain of the tested bottles, t is the time during which G occurred, G/t is the slope of the straight line in the diagram $G = f(t)$ and A is the permeation area.

3. Results and discussion

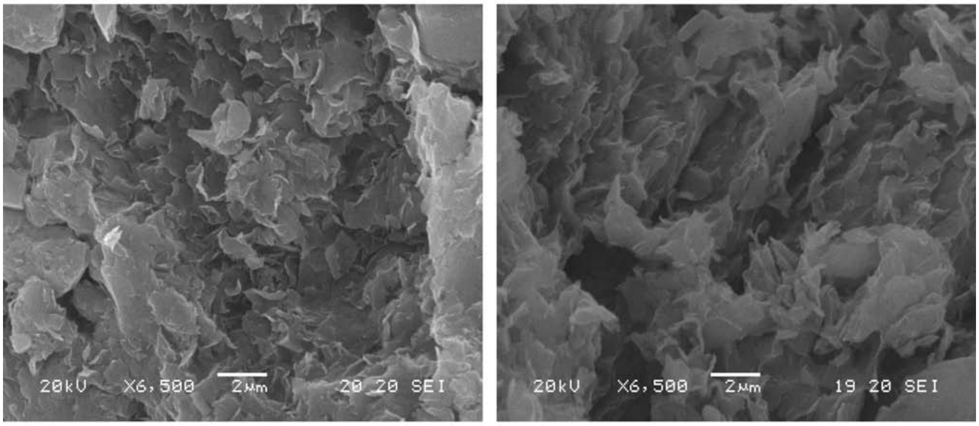
3.1. Organic modified clay

Fig. 1 shows some typical SEM microphotographs of Na-montmorillonite and the organo-modified clays with CTAB at various surfactant's content. For all surfactant loadings the presence of layered structure was revealed.

Fig. 2 shows the XRD patterns of the parent material and the organoclays at various organic phase loadings. An increase of the basal spacing (d_{001}) of the clay is observed after the insertion of the surfactant. More specifi-



Na–Montmorillonite **CTAB-0.8×CEC-Mt**



CTAB-1.5×CEC-Mt **CTAB-3.0×CEC-Mt**

Fig. 1. Characteristic SEM images of the parent clay and the organically modified clays.

cally, the pristine Na-Montmorillonite (Na-Mt) shows a d_{001}-spacing of 12.5 Å which correspond to an interlayer space $D = 12.5 - 9.6 = 2.9$ Å, where 9.6 Å is the thickness of the individual clay sheet. In the case of the organoclay, the basal spacing d_{001} becomes 18.1 Å for 0.8xCEC-Mt, 19.5 Å for 1.5xCEC-Mt and 38.8 Å for 3.0xCEC-Mt, with corresponding interlayer space: $D_1 = 8.5$ Å, $D_2 = 9.9$ Å and $D_3 = 29.2$ Å. For 3.0xCEC-Mt except of the first order (d_{001}) reflection, d_{002} and d_{003} are also clearly shown in the XRD pattern indicating a highly ordered structure.

Taking into account the chain length of CTAB, which is 25 Å [11], the distances D_1 and D_2 of the organoclays arise from a conformation where the organic chains are inclined (at a certain angle) to the surface. $D_3 = 29.2$ Å distance of the 3.0xCEC-Mt organoclay corresponds to a solid-like paraffinic arrangement of the chains with high packing density [12].

In the case of organoclays with medium and high surfactant loading (namely 1.5 and 3.0xCEC) except of the ion-exchanged alkylammonium ions there is an unconfined fraction of alkylammonium bromine which has not ion-exchanged and is present in the organoclay either inside the interlayer space or within void spaces between primary clay particles [13].

The organic phase content, in the organoclay, was estimated by thermogravimetric analysis. The obtained curves are shown in Fig. 3 and the corresponding weight losses (theoretical and experimental) are tabulated in Table 1.

3.2. *PS/organoclay nanocomposites*

XRD patterns of the prepared nanocomposites are shown in Fig. 4. On the left hand part of Fig. 4, i.e. (a), (c) and (e) graphs correspond to materials prepared using chloroform as solvent, while on the right hand part i.e. (b), (d) and (f) to materials prepared using carbon tetrachloride as solvent. XRD patterns in (e) and (f) graphs correspond to materials with low (0.8xCEC), surfactant concentration. Graphs (c) and (d) correspond to materials with normal 1.5xCEC, and (a) and (b) to materials with high 3.0xCEC surfactant concentration. For all graphs, patterns (i) correspond to organoclay, OMt, (ii) to PS-OMt with 2 wt% filler loading and (iii) to PS-OMt with 10 wt% filler loading. The estimated d-spacing from the XRD analysis as well as the temperatures for starting of decomposition (T_{onset}) and 50% weight loss (T_{50}), from the thermogravimetric experiments, of the prepared materials, are presented in Table 2.

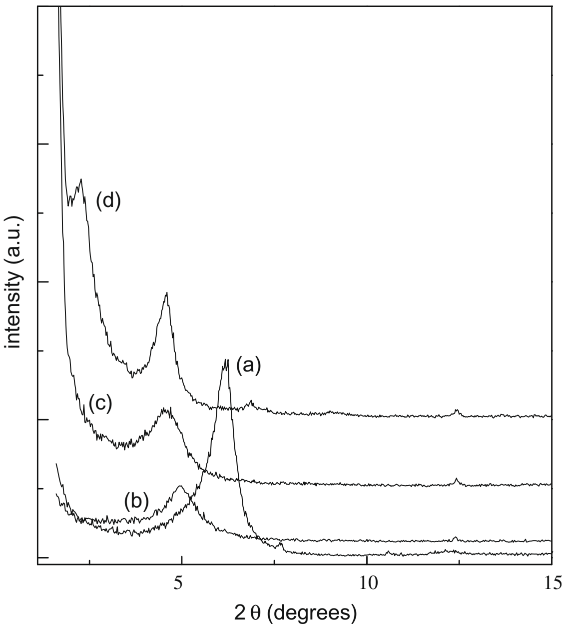


Fig. 2. XRD patterns of the parent clay (a) and the organoclays at various organic phase loading: (b) -0.8xCEC; (c) -1.5xCEC and (d) -3.0xCEC.

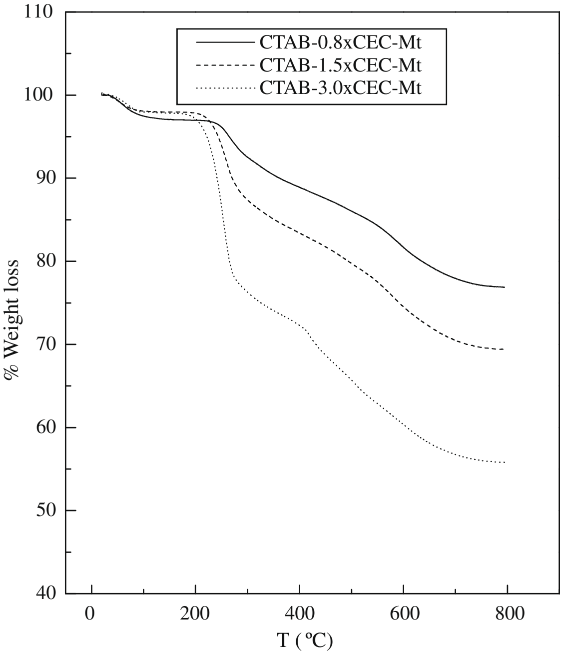


Fig. 3. TGA curves of the three organoclays used.

Table 1
Water content (wt% loss at the temperature area 30–160 °C), experimental organic content (wt% loss at the temperature range 160–700 °C), theoretical organic content, (wt% of organic surfactant added on clay) and *d*-spacing values of parent clay and organoclays.

Material	Water content (wt%)	Experimental organic content (wt%)	Theoretical organic content (wt%)	*d*-spacing (Å)	
				d_{001}	d_{002}
Na-Mt	–	–	–	12.5	–
CTAB-0.8xCEC-Mt	3.1	16.3	18.2	18.1	–
CTAB-1.5xCEC-Mt	2.1	25.2	29.5	19.5	–
CTAB-3.0xCEC-Mt	2.2	39.2	45.5	38.8	19.3

From the XRD patterns (Fig. 4) and the corresponding results (Table 2) it is shown an increase in *d*-spacing for the PS-nanocomposites prepared using $CHCl_3$ as solvent, compared to the corresponding OMts. From 18.1 Å for the organoclays with 0.8xCEC and 19.5 Å for 1.5xCEC surfactant loading, to 32.5 Å for the PS-nanocomposites. This is what one may expect for intercalated structure where the polymer chains are incorporated between the silicate layers, increasing their gallery height but maintaining their layered stacking with alternating polymer/silicate layers. In the case of PS-CTAB-3.0xCEC-2%OMt or 10%OMt a small decrement in the d_{001}-spacing from 38.8 (for the corresponding organoclay) to 38.1 Å is observed. This decrement in the d_{001}-spacing after mixing with the polymeric matrix may be attributed to a decrease in the mobility of the carbon chain of the surfactant with a concomitant reduction from their arrangements in the clay layers. Also this shift to lower d_{001}-spacing is usually attributed to loss of unbound surfactant from the gallery or to surfactant degradation [14].

Using CCl_4 as solvent (b), (d) and (f) graphs of Fig. 4) and 2 wt% OMt loading, the absence of peaks in the XRD patterns, is indicative for probable formation of exfoliated structure. Complete exfoliation of the clay layers, in which the individual clay layers lose their ordered stacking and are exfoliated and dispersed in the continuous polymer matrix, is the desired goal of the formation process. However, this ideal morphology is frequently not achieved and varying degrees of dispersion are more common. For completely exfoliated organoclay, no X-ray peak is expected for the nanocomposite since there is no regular spacing of the platelets. However, the absence of such a peak is not conclusive evidence for a highly exfoliated structure. If the sensitivity or counting time, of the scan is low, then an existing peak may not be seen [14]. For nanocomposites with 10 wt% OMt loading, the presence of a very low intensity peak, at the same angle with that of pure OMt, indicates probably the formation of a partially exfoliated structure.

Moreover in Fig. 4 four other patterns (dotted lines) designated as (iib), correspond to XRD patterns obtained from films prepared using a manual hydraulic press with heated platens. A proper quantity of the received nanocomposites (according the preparation method described in Section 2.2), was placed on the heated platens at 180 °C and pressed at 2 ton pressure for 5 min. For the PS-CTAB-1.5xCEC-2%OMt sample (c-iib), prepared with $CHCl_3$ as solvent, the heating/pressing process did not play any significant role at the final received material, except of a minor increase of the *d*-spacing. This is probably a result of a different arrangement of the polymer chains in the interlayer space, due to melting of PS after heating at 180 °C. On the other hand the materials prepared using CCl_4 as solvent, presented totally differentiated XRD patterns. In the cases of PS-CTAB-0.8xCEC-2%OMt, (f-iib) and

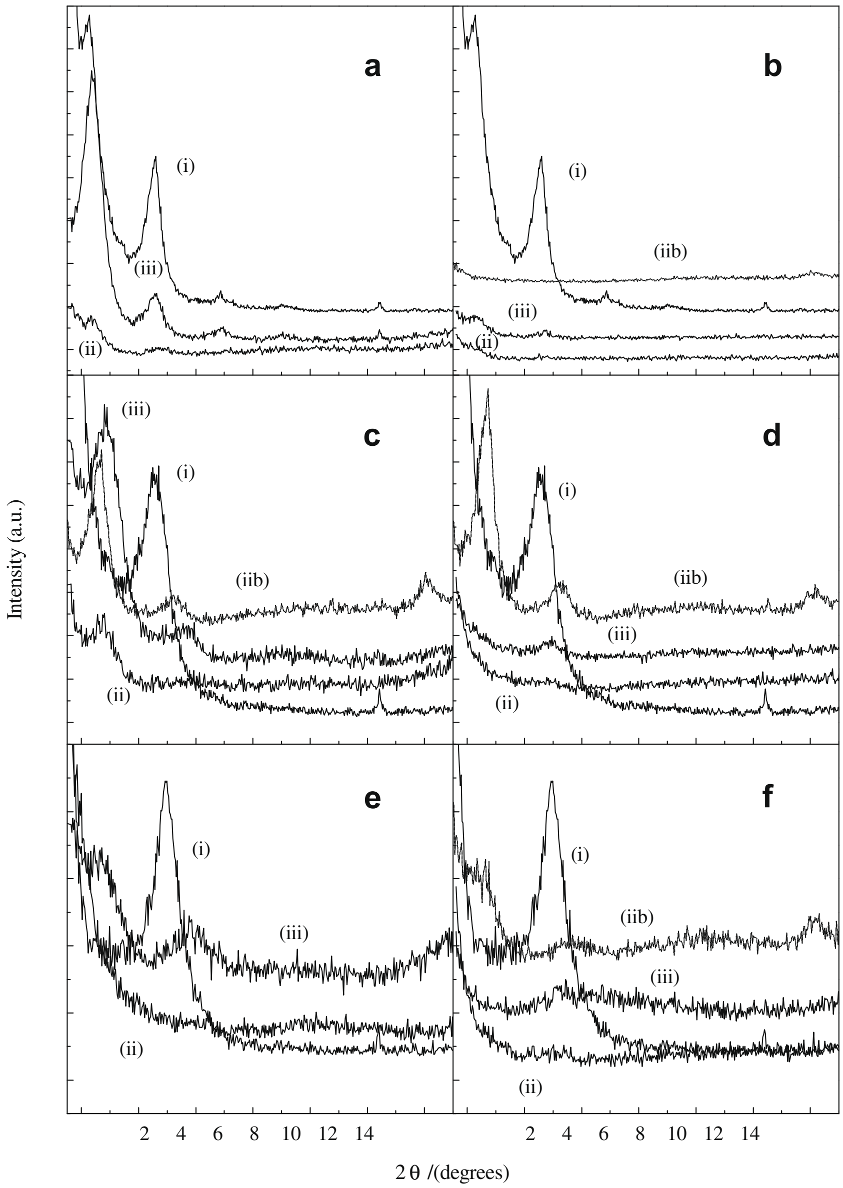


Fig. 4. XRD patterns of materials with low 0.8xCEC (e and f), normal 1.5xCEC (c and d) and high 3.0xCEC (a and b) surfactant concentration. For all graphs, patterns (i) correspond to OMt, (ii) and (iib) to PS-OMt with 2 wt% filler loading for films prepared as usual or using a hydraulic heated press, respectively, and (iii) to PS-OMt with 10 wt% filler loading. XRD patterns in (a, c and e) graphs correspond to materials prepared using chloroform as solvent, and (b, d and f) to materials prepared using carbon tetrachloride as solvent.

Table 2

d-spacing from XRD patterns, T_{onset} (starting of decomposition) and T_{50} (50 wt% loss) from thermogravimetric analysis and water vapor transmission (WVT) values for materials prepared using $CHCl_3$ or CCl_4 as solvent. Numbers in parentheses correspond to values of *d*-spacing received for films prepared using a hydraulic heated press

Materials	solvent:$CHCl_3$		solvent:CCl_4		solvent:$CHCl_3$		solvent:CCl_4		solvent:CCl_4	
	$d_{(001)}$ (Å)	2nd order, (Å)	$d_{(001)}$ (Å)	2nd order, (Å)	T_{onset} (°C)	T_{50} (°C)	WVT (g/hm^2)	T_{onset} (°C)	T_{50} (°C)	WVT (g/hm^2)
PS-pure	np[a]	np	np	np	338	380	3.17	349	385	3.15
PS-CTAB-0.8xCEC-2%OMt	np	np	np (32.7)	np (15.8)	372	407	2.68	371	404	2.44
PS-CTAB-0.8xCEC-10%OMt	32.5	15.5	np	np	387	414	2.09	391	421	1.98
PS-CTAB-1.5xCEC-2%OMt	32.5 (32.7)	np(16.6)	np (32.4)	np (16.5)	385	412	2.57	378	409	2.36
PS-CTAB-1.5xCEC-10%OMt	32.5	15.8	18.1	np	314	360	1.97	388	420	1.78
PS-CTAB-3.0xCEC-2% OMt	38.1	19.2	np (np)	np (np)	360	387	2.30	370	403	2.15
PS-CTAB-3.0xCEC-10% OMt	38.1	19.2	39.1	19.0	327	372	1.76	368	403	1.44

[a] no peak.

PS-CTAB-1.5xCEC-2%OMt, (d-iib), first (001) and second order (002) peaks are revealed at the same angle with the corresponding materials prepared using $CHCl_3$ as solvent. These results are in agreement with the results published by Wilkie et. al. [3], where intercalated and/or partially delaminated structures are observed more readily, and the clay layers exhibit an increased *d*-spacing (an intercalated structure) or a delaminated structure after in-situ polymerization. They noted that the materials that have been prepared by in-situ polymerization are not at thermodynamic equilibrium, and if they are subjected to melt-blending, they can revert to an intercalated morphology.

The absence of peaks in the diffraction pattern of PS-CTAB-3.0xCEC-2%OMt, (b-iib), indicates that the disordered structure of the layered silicate remains, despite of heating/pressing process of the nanocomposite. This result can be related to the observation, described in experimental part (2.2 §), for very stable organoclay-PS suspension in carbon tetrachloride (no sedimentation was observed). CTAB-3.0xCEC-Mt is a material with ~40 wt% organic phase content, and CCl_4 is an absolutely non polar solvent which favors the formation of stable suspensions or solutions of organophilic compounds or composites such the former. Such suspensions, where the individual clay layers are separated in the solvent matrix, are very effective for exfoliated nanocomposites preparation. According Ho and Glinka [15] the dispersion force of the solvent is the principal factor determining whether the organically modified clay layers remain suspended in the solvent, whereas the forces of polarity and hydrogen bond induce the tactoid formation (intercalated structure) of the clay in solution. Probably a thermodynamic equilibrium was achieved for the pristine suspension in CCl_4, which led to a stable exfoliated morphology for PS-CTAB-3.0xCEC-2%OMt nanocomposite, which was not altered significantly by the subsequent melting process applied.

Characteristic TGA curves of PS-nanocomposites are shown in Fig. 5. TGA results indicate improvement of the thermal stability for PS-nanocomposites compared to neat polystyrene. The decomposition temperatures T_{onset} or T_{50}, of nanocomposites increased by 20–50 °C. This increment is more prevalent for nanocomposites prepared with carbon tetrachloride as solvent. This is in agreement with previous works [16,17]. For intercalated nanocomposites prepared with chloroform (as solvent) we observe improvement of the thermal stability, except for PS-1.5x(CEC)-10%OMt and PS-3.0x(CEC)-10%OMt.

The lower thermal stability of PS-1.5x(CEC)-10%OMt and PS-3.0x(CEC)-10%OMt nanocomposites prepared using $CHCl_3$ as solvent, if compared to neat polymer or to the other nanocomposites could be attributed to the poor dispersion of silicate layers into the polymer matrix in the case of high filler (OMt) loading. According Bellucci et. al. [13] the thermal stability as well as the combustion behavior of the polymer-clay nanocomposite is affected by the degradation mechanism of the surfactant molecules. During the thermal treatment of nanocomposites at elevated temperatures, acidic proton sites are formed via the Hoffman decomposition of the alkylammonium modifier of clay, giving protonated montmorillonite that can act as a protonic acid catalyst. Camino et al. [18] ascribed the lower thermal stability of an epoxy resin composite, if compared to the other filled composites, to the larger catalytic activity related to the monoalkyl structure of its organic modifier as compared to the di to tetraalkyl substitution of the other clays.

In our study, the excess of surfactant in the organoclay did not seem to play any significant role on the thermal stability of the nanocomposites. The effect of the presence of high surfactant concentration on the mechanical properties of the prepared nanocomposites, is under investigation.

The relatively low weight loss in the temperature range 100–180 °C observed in the TGA curves could be attributed to the evaporation of solvent's molecules trapped by the polymer chains or into the organophilic interlayer space of the clay.

Water vapor transmission of the films was calculated and the results are tabulated in Table 2. All nanocomposite films exhibit a significant reduction in water permeability, compared to pristine polymer which fluctuates between 23% and 54% for nanocomposites prepared using CCl_4 and 15–44% for nanocomposites using $CHCl_3$ as solvent. Also

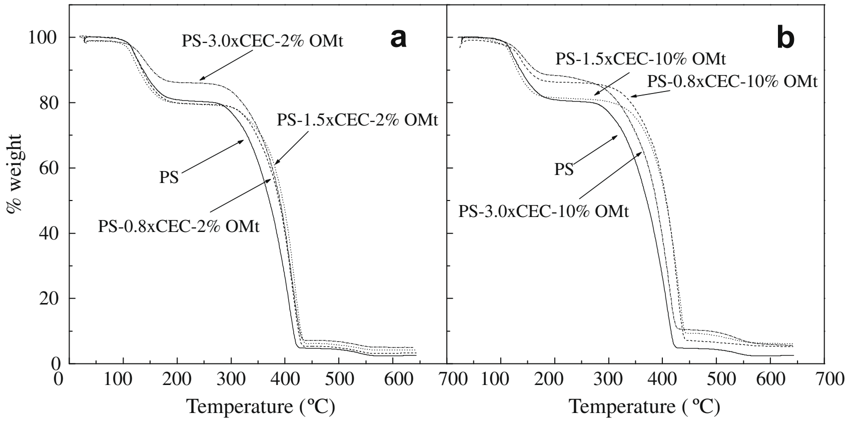


Fig. 5. Characteristic TGA curves of pristine polymer and PS-nanocomposites with 2 wt% filler loading (a) and 10 wt% filler loading (b) prepared using carbon tetrachloride as solvent.

water vapor transmission is considerably decreased with increasing OMt loading from 2% to 10% and with increasing the surfactant loading in the OMt. These results attributed first of all to the fact that in nanocomposites, gas molecules have to take a long and tortuous way around the impermeable clay layers which are distributed in the polymer matrix in comparison with pristine polymer where the penetration of the film is much easier [19]. In Ref. [19] a study of the correlation between the aspect ratio of the clay and the barrier properties was conducted and it was shown that the best barrier properties obtained in polymer nanocomposites with fully exfoliated clay minerals.

In accordance with the above mentioned conclusions, in our study the nanocomposite which exhibits the lower water vapor transmission value is PS-CTAB-3.0xCEC-10% OMt, prepared using CCl_4 as solvent. This nanocomposite combines a probable exfoliated structure, high OMt loading and high hydrophobic nature of OMt layers because of the increased surfactant loading.

4. Conclusions

PS-organoclay nanocomposites were prepared through the solution blending process in two different solvents $CHCl_3$ and CCl_4. Intercalated nanocomposite structure was obtained using $CHCl_3$ as solvent. Probably exfoliated or partially exfoliated morphology was more prevalent for nanocomposites prepared using CCl_4 as solvent.

TGA results indicate improvement in thermal stability, of PS-nanocomposites compared to pristine polymer. This enhancement is more prevalent for nanocomposites prepared with carbon tetrachloride as solvent. The excess of surfactant in the organoclay did not seem to play any significant role on the thermal stability of the nanocomposites.

Water vapor transmission results indicate improvement in water barrier properties for all nanocomposites. WVT is considerably decreased with increasing OMt loading from 2% to 10% and with increasing the surfactant loading in the OMt. The best barrier properties obtained for nanocomposite with high OMt and high surfactant loading, prepared using CCl_4 as solvent.

Acknowledgments

We acknowledge financial support from the project "PENED03" of the General Secretariat for Research and Technology. The authors thank the Ring of the Laboratory Units and Centers of the U.I. for the XRD and TGA experiments.

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