Preparation of ABS/montmorillonite nanocomposite using a solvent/non-solvent method

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Abstract

Polymer layered silicate nanocomposites have been studied for many years and due to their distinguished properties and applications, it is still the subject of many research programs. There are different methods of preparation, with the melt intercalation method as the mostly used method. Due to the thermal destructive effects of melt mixing on the polymer chains there are currently efforts to develop some new methods of preparation. A solvent/non-solvent method has been developed in this study for the preparation of ABS/clay nanocomposites. ABS nanocomposite is precipitated after addition of ethanol (non-solvent) containing organic modified montmorillonite from a THF solution while it is stirring. A kind of mixing system known as homogenizer has been used in this work. The final product has been determined having an intercalated structure with a uniform interlayer spacing of the silicate layers. The ABS nanocomposites prepared in this work has been studied by X-ray diffraction, FTIR, transmission electron microscope and thermogravimetric analysis. The effect of using homogenizer on the characteristics of the nanocomposites also has been investigated and discussed in several parts of the present work.
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1. Introduction

Polymer based composites are a class of materials with fillers dispersed in a polymer matrix to improve the mechanical and physical properties. Nanocomposites are a new class of composites that are filled with nanometric particles in which at least one dimension of the dispersed particles is in the nanometer range [1]. A clay mineral is a potential nanoscale additive because it comprises silicate layers in which fundamental unit is a 1 nm thick planner structure [2]. Among the many types of layered silicates, montmorillonite (MMT) is the most commonly used. Natural MMT is hydrophilic and not compatible with most organic molecules. Sodium cations in the interlayer space (gallery ions) of MMT can be exchanged with organic cations to yield organophilic MMT. Several types of organophilic MMT's are now available commercially.

Polymer/clay nanocomposites have their origin in the pioneering research conducted at Toyota Central Research Laboratories and the first historical record goes back to 1987. The matrix was nylon-6 and the filler MMT. Because of its many advantages such as high mechanical properties, good gas barrier, flame retardation, etc. polymer/clay nanocomposites have been intensely investigated [1,3] and is currently the subject of many research programs. Nanocomposite materials are commercially important and several types of products with different shapes and applications including food packaging films and containers, engine parts, dental materials, etc. are now available in markets [2].

According to the dispersion level of mineral in the polymer mixture, three types of polymer/clay mixture are available: conventional, intercalated and exfoliated composites [4]. In the intercalated level, the silicate layers maintain their stacking except that the basal spacings are increased due to the intercalation of polymer chains between the silicate layers. However, when the individual silicate layers are dispersed almost homogeneously in the polymer matrix, the exfoliated nanocomposite is produced. Usually, the percentage of intercalation and exfoliation would be expected in real nanocomposites.

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Several strategies have been considered to prepare polymer–clay nanocomposites. Four main processes are: exfoliation-adsorption, in situ polymerization, melt intercalation and template synthesis. Exfoliation-adsorption method is a solvent based process in which the polymer matrix and modified clay become in contact with a solution and after evaporating the solvent (or precipitating) nanocomposite is produced as a film or bulk material [1]. So far, melt intercalation method was the most commonly used procedure because of its advantages especially from commercial point of view and mass production ability. In this process, molten polymer is mixed with modified clay while applying high shear stresses by using an internal mixer (or in small gap between the hot rotating rolls (twin-roll mill)). Polymer chains intercalate between the silicate layers of the modified clay and usually a high level of exfoliation would be achieved. High temperatures used in mixing process may lead to some destructive influences on the polymeric molecules of the matrix. Therefore, low temperature methods of preparation need to be developed. The present work has a new approach to the solvent-based preparation method of nanocomposites.

A solvent/non-solvent method has been developed in this study for the preparation of ABS/clay nanocomposites. ABS nanocomposite is precipitated after addition of ethanol (non-solvent) containing organic modified montmorillonite from a THF solution while it is stirring. The method utilized a special mechanical tool known as homogenizer, which consists of two co-axial cylindrical stator and rotating parts with a small gap between them. The rotating cylinder rotation rate can be increased up to 45,000 rpm. Therefore, the material (precipitating polymer and the OMT) undergoes high shear stresses between the rotor and stator cylinders. In other words, homogenizer operates as a wet twin-roll mill.

ABS is a widely used thermoplastic material due to good mechanical properties, chemical resistance, and easy processing characteristics. However, only a few records are available for synthesis and characterization of ABS/clay nanocomposites [5–10]. Thermal and flammability properties of ABS/clay nanocomposites have already been investigated widely by Hu and co-workers [6–8,10].

2. Experimental

2.1. Materials

ABS (SD-0150) was supplied by Tabriz Petrochemical Company, Iran. Montmorillonite K-10 was purchased from Aldrich Chemical Co. and used after modification (ion exchange reaction) with hexadecyl trimethyl ammonium bromide. All other chemicals were laboratory grades from Merck and Fluka chemical companies.

2.2. Modification of MMT

MMT (5 g) was dispersed in distilled water (150 ml) and was mixed using homogenizer at 10,500 rpm for 1 h at 30 °C (wetting stage). Hexadecyl trimethyl ammonium (4 mmol) was added and while mixing was continued for additional 2 h at the same homogenizing condition at 60 °C (ion exchange reaction). After precipitation, the solution was decanted and filtered. Organic modified MMT (OMT) was dried for 24 h at 60 °C after washing with distilled water.

In order to study the homogenizing effect (using homogenizer) on the modification of MMT, the same process was repeated by using a mechanical mixture by rotation speed of 200 rpm for 24 h (wetting stage) and 7 h (ion exchange reaction).

2.3. Preparation of nanocomposites

ABS (10 g) was dissolved in 200 ml THF by mixing at 50 °C. A dispersed mixture of OMT (0.5 g) in ethanol (200 ml) was prepared separately by using the homogenizer and subsequently by a magnetic stirrer in order to prevent coagulation and precipitation. To the ABS/THF solution, under homogenizing (10,500 rpm) condition at 60 °C, the dispersion solution of OMT/ethanol was added drop wise during 0.5 h overall time. After precipitation, the upper liquid was decanted and the solids collected over a filter paper. After washing several times with ethanol, and distilled water, the product was dried at 80 °C for 24 h in an oven (ABS-OMT-H, Table 1). In order to obtain weight ratio of OMT to ABS in the final product, the procedure was repeated by adding of 200 ml ethanol (without OMT) to a solution of ABS (10 g) in THF (200 ml). Precipitated polymer was collected, dried and weighed. In this way, the final composition of the composites was evaluated as 7.15 wt% OMT.

For comparative purposes, and in order to investigate the homogenizer effect, the same procedure was repeated using a mechanical stirrer (200 rpm) instead of homogenizer, leading to composite ABS-OMT-M in Table 1.

2.4. Characterization

The homogenizer used in this work was Mikra-8, Germany, with a stator outer diameter of 2.5 cm. FTIR spectroscopies were carried out using Unicam Matteson 1000, and specimens were prepared as KBr pellets.

Basal spacing of the MMT, OMT and also that of OMT in the ABS nanocomposites were measured using a X-ray diffractometer (Bruker D-8 and Siemens Kristallo Flex), Cu K$_\alpha$ ($\lambda = 0.154$ nm), generated at a voltage of 30 kV, 10 mA. The basal spacing was calculated by using Bragg's law, $n\lambda = 2d \sin \theta$.

Thermal gravimetric analyses were carried out by using Perkin–Elmer, Pyris Diamond TGA/DTA analyzer with $\pm$

Table 1
Encoding and specifications of materials used or prepared in this study

Sample code	Remarks	Overall preparation time
MMT	Commercial montmorillonite K-10 purchased from Aldrich Chemical Co.	–
OMT-M	Organic modified montmorillonite, prepared by using mechanical stirrer	24+7 h
OMT-H	Organic modified montmorillonite, prepared by using homogenizer	1+2 h
ABS-PRE	Precipitated ABS in the same condition as used in the preparation of nanocomposites (without filler)	0.5 h
ABS-ORG	Orginal (commercial) ABS without any further treatment	–
ABS-OMT-M	ABS/OMT nanocomposite prepared by using mechanical stirrer	0.5 h
ABS-OMT-H	ABS/OMT nanocomposite prepared by using homogenizer	0.5 h

0.06 μV equal to 2% error in reading temperature and $\pm 2\%$ error in reading weights, at a heating rate of 20 °C/min under stream of N_2.

TEM specimens were cut from an epoxy block with the embedded ABS nanocomposite powders using an ultra-microtome with a diamond knife. Thin specimens, were collected in a trough filled with water and placed on 200 mesh copper girds. TEM images were obtained with a Leo 906 microscope at an acceleration voltage of 60 kV.

Table 1 is the encoding table for different materials used or prepared in this work.

3. Results and discussion

The main objective of the present work was the preparation and characterization of ABS/OMT nanocomposites by using the described solvent/non-solvent method. In this way, effect of homogenizer on the modification of MMT and also its effect on the nanocomposites characteristics were investigated and being discussed in the following sections.

3.1. Precipitated ABS

Acrylonitrile–butadiene–styrene terpolymer (ABS) is a complex system comprising an amount of *graft*-acrylonitrile–butadiene–styrene (*g*-ABS) and styrene–acrylonitrile copolymer (SAN). The used commercial ABS in this work was 35% *g*-ABS and 65% SAN. Being involved a precipitation process from a polymer solution in the procedure; there was a possibility of changing for the composition during the precipitation. Therefore, it was necessary to determine the composition of the precipitated ABS, ABS-PRE. The purpose was done by using FTIR analysis. Several mixtures of *g*-ABS and SAN were prepared with different weights of *g*-ABS, varying from 10 to 40%. Fig. 1 shows the FTIR spectra between 1160 and 900 cm^{-1} for those samples. As it is understood, the intensity of the peak centered at 965 cm^{-1} increases as the weight percent of *g*-ABS is increased. The peak was attributed to the *trans*-CH=CH positions on the *g*-ABS portion of the samples. The ratio of peak areas, i.e. the peaks between 992–938 and 1138–992 cm^{-1} were obtained for

each sample and calibrated with respect to *g*-ABS content in the samples. Calculating the ratio of the peak areas for the same peaks showed that ABS-PRE had nearly the same composition as ABS-ORG, about 33% *g*-ABS and 67% SAN. This showed that the composition had been changed upon precipitation but not by a large amount. This is due to the different solubility of the ABS ingredients in THF. Some differences on the thermal properties of ABS-PRE and ABS-ORG also were observed which is discussed in Section 3.5.

3.2. XRD investigations

Fig. 2 shows the XRD patterns of (a) MMT, (b) OMT-M and (c) OMT-H. The diffraction peaks are due to (001) plane. As it is observed the peaks are shifted toward lower 2θ by modification, showing the larger interlayer spacing in comparison with MMT. By using Bragg's rule, basal spacing for MMT, OMT-M and OMT-H was estimated
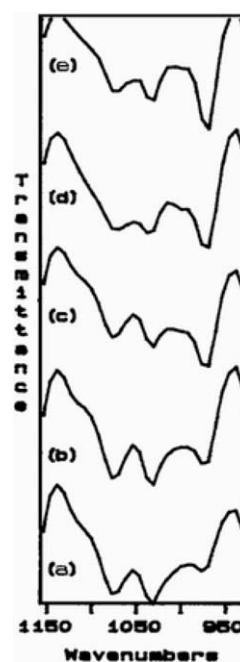

Fig. 1. FTIR spectra for several mixtures of *g*-ABS and SAN, (a), (b) and (c) 20, 30 and 40 wt% of *g*-ABS, respectively in SAN, (d) ABS-PRE and (e) ABS-ORG.
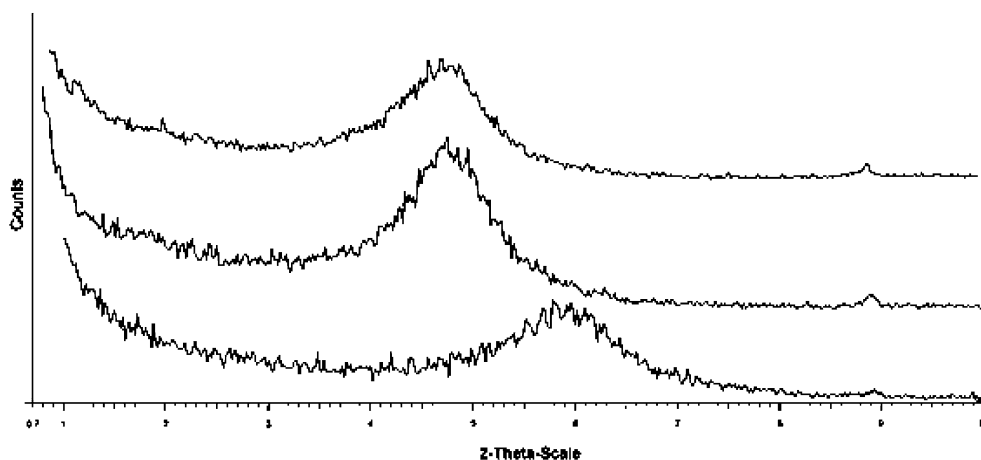
Fig. 2. XRD diffraction patterns for MMT (lower), OMT-M (middle) and OMT-H (upper).

1.53, 1.83 and 1.84 nm, respectively. Results show that homogenizer did not lead to a further modification or in turn larger interlayer spacing in ion exchange process which took place between MMT and ammonium ion. However, it should be noted that homogenizer had at least a time shortening effect (2 h overall time against 32 h, Table 1). In other words, it can be concluded that applying shear stresses (through homogenizer, for example) is ineffective for cation exchange promotion and the process seems to be a thermodynamically controlled process.

Fig. 3 shows the XRD patterns for ABS-OMT-H and ABS-OMT-M. The peaks attributed to the basal spacing of the silicate layers were the same for ABS-OMT-H and ABS-OMT-M around 3 and 3.1 (broad peak), respectively, in 2θ scales. These peaks prove an intercalated structure for both of the nanocomposites with a larger interlayer spacing with respect to OMT itself. From the same location of the peaks, an equal interlayer spacing could be estimated for both of the nanocomposites (roughly 3 nm). However, the peak for ABS-OMT-H is more eminent than that of ABS-OMT-M. This may occur because of several reasons, among them, partial exfoliation and disordered stacking of the silicate layers are the most probable in this case. By the fact that ABS-OMT-H and ABS-OMT-M did not show any evi-

dences of exfoliation based on results of TEM, the latter become the most important reason. In other words, the stacking order of the silicate layers are more regular and uniform in the nanocomposite ABS-OMT-H leading to a narrower peak on XRD diffractogram.

Therefore, homogenizer was effective not only on overall process time reduction but also in production of nanocomposites with more monotonic intercalated structure. By the fact that both the XRD peaks (Fig. 3(a) and (b)) are located around a same value on the 2θ scale, which in turn results in a same interlayer spacing for both of the nanocomposites, it can be concluded that initial intercalation of polymer molecules between the silicate layers is a thermodynamically favored process rather than kinetically. The same result has also been obtained by Yoon et al. and references cited therein [4].

3.3. FTIR characteristics

Fig. 4 shows the FTIR spectra for (a) OMT-H, (b) ABS-PRE, (c) ABS-OMT-H and (d) ABS-OMT-M. IR characteristic peaks for ABS system are 3150–3020 (aromatic C–H vibrations), 3000–2800 and 1478 cm^{-1} (aliphatic C–H vibrations), 2238 cm^{-1} (C≡N stretching), 1730 cm^{-1}
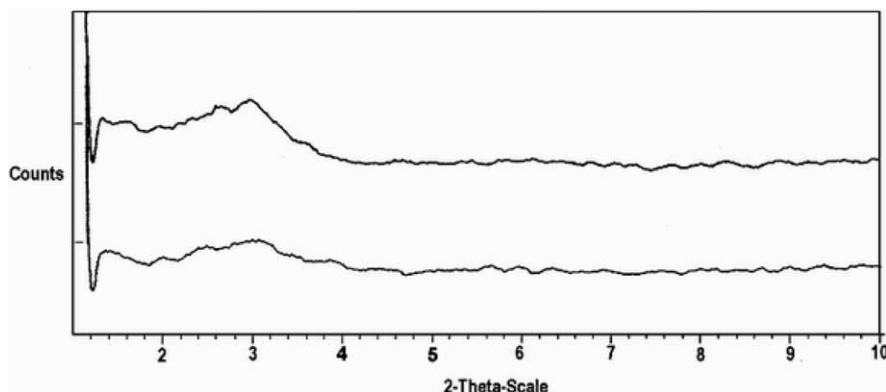

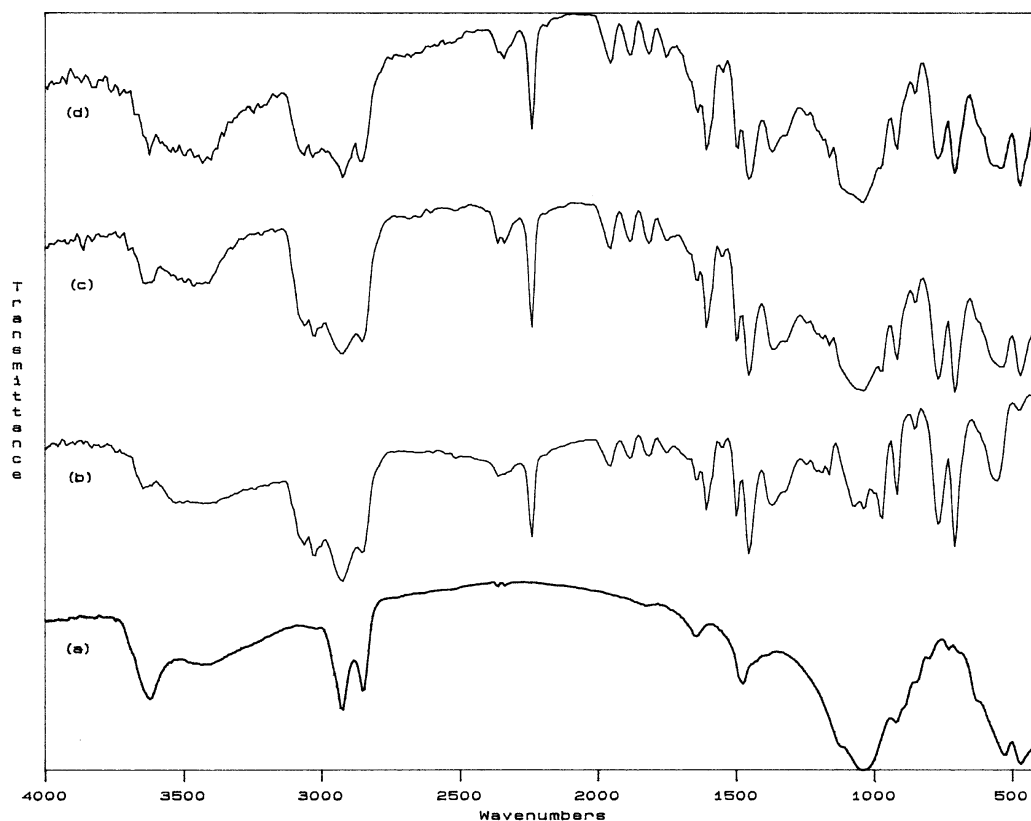Fig. 3. XRD diffraction patterns for ABS-OMT-H (upper) and ABS-OMT-M (lower).

Fig. 4. FTIR spectra for (a) OMT-H, (b) ABS-PRE, (c) ABS-OMT-H and (d) ABS-OMT-M.

(C=O stretching), and 1300–1100 cm^{-1} (C–O stretching). OMT has its characteristic peaks: 3000–2800 and 1482 cm^{-1} (aliphatic C–H vibrations due to organic modifier aliphatic chains), Si–O stretching vibrations around 1046, 600–500 cm^{-1} (Al–O stretching) and 461 cm^{-1} (Si–O bending vibrations). According to peak assignments, Fig. 4 confirms the formation of ABS/clay composites. The peak centered at 461 cm^{-1} is appeared in both of the spectra for ABS-OMT-H and ABS-OMT-M and, peaks centered at 1053 and 561 cm^{-1} are deformed and broadened due to overlapping with peaks of MMT in the same regions. In contrast to the results obtained from XRD analysis (Section 3.2), no any significant differences are detectable in the FTIR spectra for ABS-OMT-H and ABS-OMT-M. Whereas, other tools of investigation including TEM microscopy and thermal analysis show some differences between them which are discussed in the following sections.

3.4. TEM analysis of the nanocomposites

TEM micrographs of the nanocomposite ABS-OMT-H is shown in Fig. 5 in two levels of magnification. Distinguishable clay particles in Fig. 5(a), show the extent of clay particle dispersion in the polymeric matrix. Individual particles are apparent in the micrograph with different sizes spreading from 50 to 100 nm diameters. No agglomeration of the particles is seen in micrograph 5a. Fig. 5(b) is obtained with higher magnification. Intercalation of the matrix molecules between clay layers have led to a structure with an average basal spacing of about 3 nm (Section 3.2). No individual silicate layers are seen in the composite and it means that no exfoliation is occurred for the nanocomposite.

Briefly, the nanocomposite is a dispersion of clay particles with an intercalated structure.

Fig. 6 shows the TEM micrograph obtained for ABS-OMT-M.

No individual silicate layers also have been seen in this sample; however, comparison of Figs. 5(b) and 6 reveals more uniform spacings for the silicate layers of the clay in ABS-OMT-H. It is equal to a more disordered intercalated structure leading to a wider XRD peak as is discussed in Section 3.2 for ABS-OMT-M.

As an important result, homogenizer leads to a more uniform structure or more uniform intercalated structure. However, the same average interlayer spacing obtained for both of the nanocomposites (ABS-OMT-H and ABS-OMT-M) shows that the process is probably a thermodynamically controlled one. Therefore, thermodynamic properties such as temperature, concentration, solvent, chemical structure of the polymeric matrix, modified clay properties, etc. are most likely the predominant parameters. Though, applying subsequent shear stresses, for example, by using a hot twin-roll mill may lead to complete exfoliation, it is
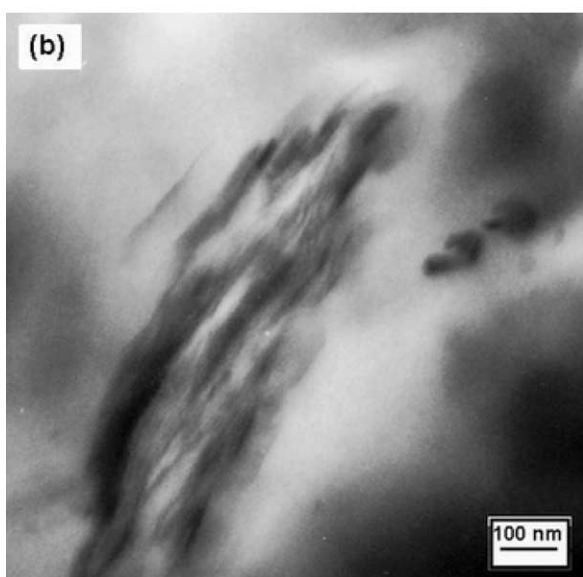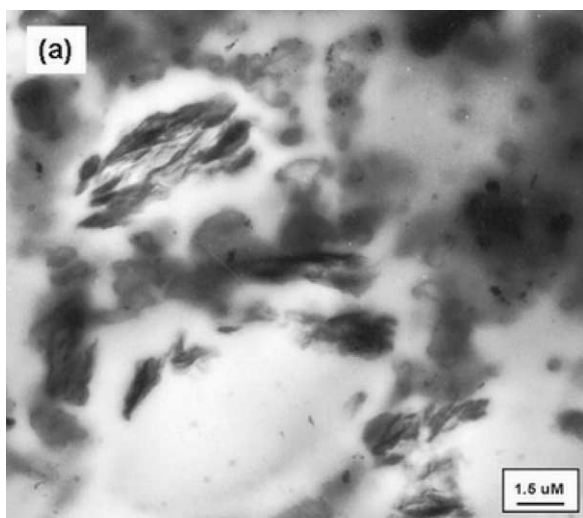
Fig. 5. TEM micrographs for ABS-OMT-H with lower (a) and higher magnification (b).

ineffective for initial thermodynamically controlled process of intercalation. In the used procedure, homogenizer has led to a uniform spacing of intercalated layers (uniform structure) but not to a wider spacing (more polymer chains between layers). The result is the same as that of obtained by previous researchers [4]. Nanocomposite prepared by using homogenizer has also been investigated by other researchers [11]. While the only investigated feature was the level of
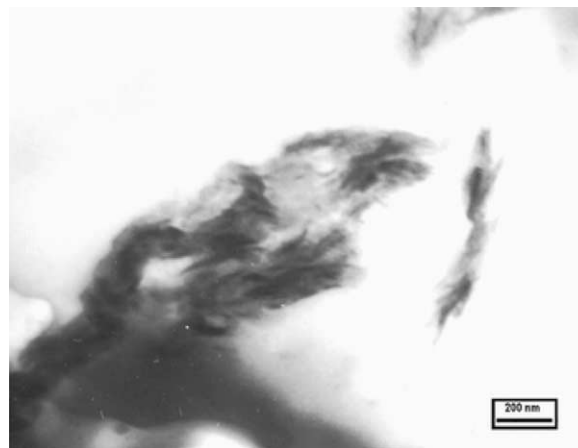

Fig. 6. TEM micrograph for ABS-OMT-M.

particle dispersion, the effect of homogenizer on the structure of the individual particles has not been discussed.

3.5. Thermal properties of the nanocomposites

Thermal properties of nanocomposites are among the most interesting features of nanocomposites and they are usually considered by investigators [1]. Thermogravimetric analysis (TGA) results obtained for ABS-ORG, ABS-PER, ABS-OMT-M and ABS-OMT-H are shown in Fig. 7(a)–(d), between 25 and 600 °C. Thermal properties of ABS [12–14] and ABS/OMT nanocomposites have been investigated previously [10] by other researchers.

According to Fig. 7 two steps of degradation, one around 300 500 °C and the other upper than 500 °C exist for all the TGA traces, in complete agreement with results obtained by Hu et al. [10]. Table 2 summarizes the TGA data for thermograms provided in Fig. 7. TGA traces are different for ABS-ORG and ABS-PRE. For ABS-PRE the first step degradation commences at lower temperatures but the weight percent residue at the end of this step is higher with respect to that of ABS-ORG. This may be due to the differences in composition, which was changed after precipitation (Section 3.1). TGA traces for nanocomposites are different not only with each other but also with ABS's. In the case of nanocomposites, there is an early weight loss completely before 300 °C, which is attributed to thermal decomposition of organic modifiers of the clay [15]. The first step degradation commences at lower temperatures with respect to ABS-ORG but at higher temperatures with

Table 2
The data of the thermal properties for TGA curves shown in Fig. 7

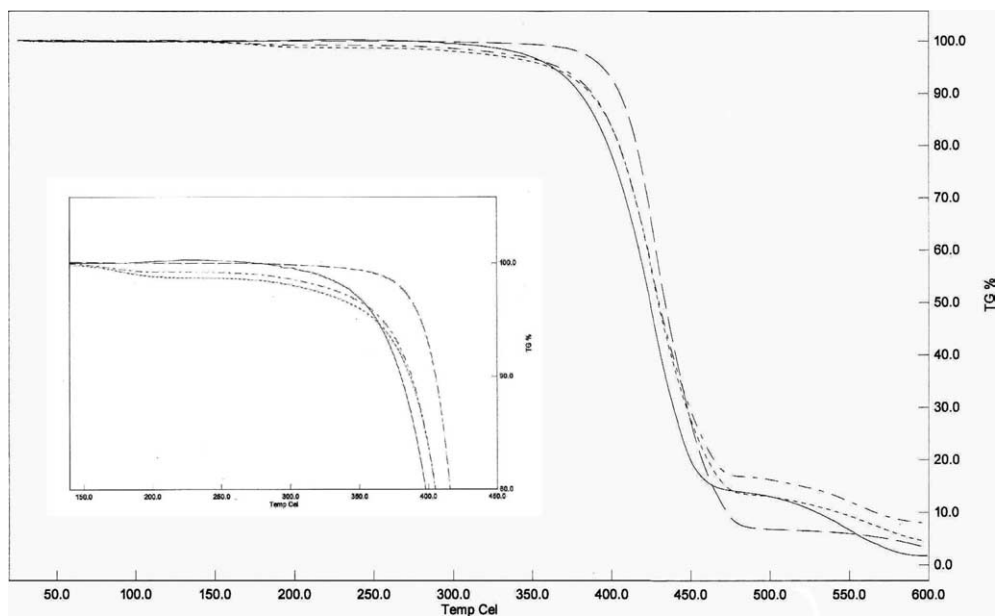| Sample	Beginning of the first step decomposition/°C (wt%)	End Of the first step decomposition/°C (wt%)	Beginning of the second step decomposition/°C (wt%)	Char yield at 600 °C (wt%)
ABS-ORG	405 (99.6%)	475 (7.1%)	562 (5.9%)	(3.2%)
ABS-PRE	376 (97.8%)	455 (15.4%)	514 (12.5%)	(1.7%)
ABS-OMT-M	380 (96.1%)	469 (14.4%)	534 (11.1%)	(4.7%)
ABS-OMT-H	392 (97.9%)	468 (17.7%)	532 (14.4%)	(8%)

Fig. 7. TGA results for polymers and nanocomposites: (— —) ABS-ORG, (—) ABS-PRE, (– –) ABS-OMT-M and (– —) ABS-OMT-H. The inset is the larger view of the region between 150 and 450 °C.

respect to ABS-ORG. At the end of the first step degradation, nanocomposites were accompanied by a larger residue showing an enhanced thermal stability. The char yield at 600 °C was also higher for nanocomposites, which can be attributed to highly resistance of MMT filler. Fig. 7 shows different thermal properties for nanocomposites ABS-OMT-M and ABS-OMT-H. While the first step is almost identical, a higher residue is observed for ABS-OMT-H at the end of this step. Higher amount of char yield is also detectable for the latter at 600 °C. Differences between thermal properties of the nanocomposites ABS-OMT-H and ABS-OMT-M can be attributed to the different contents of OMT in them. Therefore, an isothermal thermal gravimetric analysis at 400 °C in air was carried out on these two products in order to investigate. The results are shown in Fig. 8. The same pattern of degradation can be seen from Fig. 8 for both the composites. However, the thermal degradation curve for ABS-OMT-H is appeared over than that of ABS-OMT-M in all temperature regions. The temperature has risen gradually from room temperature to 400 °C during first 40 min period and was kept constant for
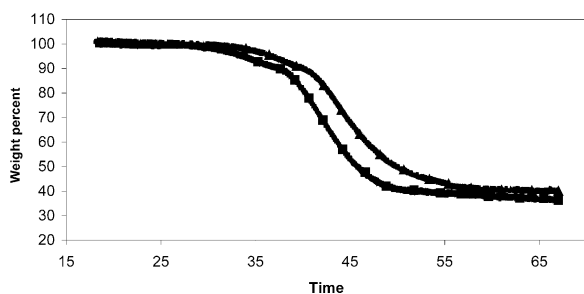
after then. After sharp degradation, both of the curves reach to a plateau region, which the weight remains constant later on. ABS-OMT-M reaches to this region before than 50 min while ABS-OMT-H reaches around 55 min. The main part in Fig. 8 is the differences between the weights percentages of char yield after long time thermolysis, i.e. at the end of plateau region. This will be an indication of incombustible compounds in the samples. This quantity is 39.8 (at 67 min) for ABS-OMT-H and 36.4 (at 67 min) for ABS-OMT-M. By the fact that at this region, weight percentage of the two composites differs only by 3.4% and this is a little larger than instrumental error (2 wt%), it must be interpreted carefully. The best and reliable interpretation would be: OMT content is a little higher in nanocomposites ABS-OMT-H. The difference in OMT content would have an origin in the different synthetic method, and using homogenizer in synthesis.

Results obtained from Fig. 8, show that thermal properties of nanocomposite ABS-OMT-H and differences with ABS-OMT-M (Fig. 7) may be due to the different amount of OMT in these two nanocomposites. In this case, another advantage appears for using homogenizer in solvent production of nanocomposites. It provides a better condition for OMT particles to be adsorbed by dissolved polymer during precipitation.

4. Conclusion

A new low-temperature solvent/non-solvent preparation method for ABS/clay nanocomposite has been described. An intercalated structure has been determined as final product by several ways of investigation. Special feature of

Fig. 8. Isothermal thermal gravimetric analysis for ABS-OMT-M (■) and ABS-OMT-H (▲).

the procedure was using of homogenizer, a special mechanical tool, in order to apply shear stress during the modification process of MMT and preparation of nanocomposite. Investigations showed that shear stress does not lead to further modification of MMT during ion exchange process. A same interlayer spacing was finally achieved with or without using homogenizer. The same interlayer spacing in a shorter time (2 h against 32 h) was the main advantages of using homogenizer in the modification reaction. In the preparation of the nanocomposites, homogenizer led to an intercalated structure with more uniform interlayer spacing of the clay silicate layers. This uniformity can be detected by XRD diffraction peak shape and TEM micrography. From thermal properties point of view, silicate layers work as thermal shield for intercalated polymer chains which in turn lead to an enhanced thermal resistance for the nanocomposites. Isothermal degradation analysis showed that the nanocomposites prepared by using homogenizer must contain higher amount of OMT, which influence the thermal properties of the product totally. As a conclusion, the investigations showed that ion exchange process and polymer intercalation between the silicate layers are thermodynamically controlled process. In other words and by taking the results obtained by other researchers into account, it seems that two steps are involved, a preliminary intercalation step and subsequent complete delaminating process. In the first step an equilibrium state, which can be established between the materials incorporating in the modification or polymer intercalation process, is the final attitude. Applying severe mixing or shear stresses in this step by using, for example, homogenizer has just an accelerator effect for the equilibrium to be reached. After that initial intercalation, further shear stresses via, for example, a twin-roll mill or an internal mixer may lead to the final and complete exfoliated state [16].

By using solvent/non-solvent method, polymers with moderate level of solubility in common solvents can be converted into corresponding nanocomposites. Higher solubility will cause difficulties in the precipitation step so as enormous volume of the non-solvent will be needed. On the other hand, solubility in non-common solvents will not be economically feasible because of the solvent high cost.

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