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Composites of Engineering Plastics with Layered Silicate Nanofillers: Preparation and Study of Microstructure and Thermomechanical Properties

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1. Introduction

1.1 Polymer nanocomposites

Polymer/layered silicate nanocomposites have recently attracted a great deal of interest because of their unique properties, such as enhanced mechanical property, increased thermal stability, improved gas barrier properties and reduced flammability. According to the arrangement of silicate layers within the polymer matrix, two types of morphology can be achieved in nanocomposites: namely intercalated or exfoliated structures. Exfoliated structures have been well recognized as superior morphology for high performance at lower clay loadings, but are difficult to achieve. Attempts to improve processability and ensure efficient dispersion of the above fillers have led to modifications, e.g. with quaternary ammonium surfactants, which is expected to increase the inter-gallery spacing and provide enough hydrophobicity to clay particles in order to make them miscible with the polymer matrix.

A typical example is sodium montmorillonite (MMT), one of the most commonly used clays, which is hydrophilic and therefore shows restricted compatibility with many polymers. To obtain good interfacial adhesion for improved mechanical properties, the clay needs to be modified prior to incorporating into the usual organophilic polymer matrices. Clay modification can be achieved by an ion exchange reaction with organophilic cations (Utracki, 2004). There are two reasons for this modification: (i) the addition of an intercalating agent to increase the space between the layered silicates and make it more uniform and (ii) the addition of small organic molecules bonded to silicates to make MMT more miscible with the polymer matrix. Therefore, polymer molecules are allowed to enter the enlarged intergallery of silicates for further intercalation or exfoliation. In general the intercalated agents are small molecules of cationic surfactant, such dodecyl ammonium chloride and 1-hexadecyl ammonium blomide.

Clay possesses net negative charge on its lamellar surface and, therefore, it can absorb cations, such as Na^+ or Ca^{2+}. Alkyl ammonium ions can replace metal cations through a cation exchange process and occupy the gallery space between nanoscaled layers of the clay to alter the original silicate surface from hydrophilic to organophilic (Burnside and

Giannelis, 1995). Because of the negative charge of the silicate layer, the cations head group of an alkyl ammonium molecule preferentially resides at the layer surface with the aliphatic tails being removed from the surface (Chen and Yoon, 2005).

Nanocomposites can be prepared by solvent casting, by in situ polymerization or by melt compounding (Pinnavaia & Beall, 2002). So far, melt intercalation method has been the most commonly used procedure because of advantages especially in terms of commercial versatility and mass production ability.

Three types of polymer/clay composites are usually recognized: a)"conventional composites", in which the clay is added as a common filler, b)"intercalated nanocomposites", where a small portion of the polymer is inserted into the interlayer spacing between the layered silicates, and c)"exfoliated or delaminated nanocomposites", in which the silicate layers are almost or completely separated and dispersed in a continuous matrix.

While preparing nanocomposites by melt mixing, the exfoliation and dispersion of nanoclays in a polymer matrix depend on the type of organic modifier in the nanoclay, the initial interlayer spacing, the compatibility of the polymer matrix towards the nanoclay, the type and concentration of an added compatibilizer, the viscosity of the resin and the operational conditions. Although shear is, in general, a very important factor for efficient filler dispersion during mixing processes, it does not enable by itself to provide nanometric dispersion of the clay. Interfacial adhesion needs to be high enough in order to achieve better compatibility and, therefore, improved performance of the composite (Patiño-Soto et al., 2008).

Regarding melt processing, for polymers that require high melt temperatures, the thermal stability of the organic component of modified clay becomes a significant factor because it sets the top limit temperature for polymer processing.

1.2 Nanocomposites of poly(acrylonitrile-butadiene-styrene)

Poly(acrylonitrile-butadiene-styrene) (ABS) is a popular engineering thermoplastic because of its unique properties, including excellent mechanical response, good processing characteristics, chemical resistance and fine surface appearance. It consists of styrene-acrylonitrile (SAN) continuous phase partially grafted to a dispersed polybutadiene (PB) phase of elastomeric nature. The commercial ABS is produced in the main by emulsion copolymerization of styrene-acrylonitrile in the presence of rubber, and the final product is usually constructed with the physical mixture of styrene-acrylonitrile copolymer as well as the graft copolymer of styrene-acrylonitrile into the rubber. SAN exhibits the combined properties of the ease of processing of polystyrene and the rigidity and chemical resistance of acrylonitrile, whereas the incorporation of butadiene rubber into SAN imparts the high impact strength characteristic of ABS polymer. ABS is widely used in the automotive industry, telecommunications, business machines and consumer market, mainly because its property-price profile is intermediate between the lower priced commodity thermoplastics and the more expensive high performance engineering plastics. It is also used with the appropriate reinforcements that may be incorporated to the plastic matrix in order to enhance functional properties. One of the main drawbacks of ABS is its lower thermal stability and inherent flammability (Karahaliou & Tarantili, 2009). Therefore there is a need to increase its thermal stability and flame retardant properties (Owen & Harper, 1999).

The use of halogenated fire retardants (FR) are limited by the European Union legislation. The alternative inorganic FR's are often incorporated at such high loadings, i.e. up to 50 wt%, that there is a significant compromise in the final balance of properties for the composite, particularly toughness. Formation of ABS nanocomposite by addition of montmorillonite clay platelets, are believed to be a new approach in fire retardancy, which has been shown to be effective at low loadings and may lead to better balance of physical properties (Stretz et al., 2005).

1.2.1 Preparation

As already mentioned, melt blending is by far the most common method for preparation of polymer nanocomposites, because it involves the processing operations commonly adopted for the parent polymer.

A quick review of the related literature shows that ABS/MMT composites can be prepared by melt processing in a twin screw extruder (Wang et al., 2004b; Stretz et al., 2005; Kim et al., 2008; Patiño-Soto et al., 2007) or using a two-roll mill (Xiao et al., 2007; Yeh et al., 2005) or an internal mixer (Aalaie et al., 2007).

However, the high temperature, shear stress and local overheating induced by the shear itself can affect the clay through thermal degradation of the organic modifier, phase separation of the clay and possibly reduction of aspect ratio of the layered silicate (Dennis et al., 2001). In order to overcome these problems, a low temperature solvent/non-solvent method for preparation of ABS/clay nanocomposites has been developed by Pourabas and Raeesi, 2005, in which the organoclays were just dispersed in ethanol, a non solvent for ABS. Then the clay dispersion in ethanol was introduced to the ABS/THF solution and the ABS/clay nanocomposite was obtained after precipitation. 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 homogenizer operates as a wet twin-roll mill, and the precipitating polymer together with OMMT undergo high shear stresses when processed between the rotor and stator cylinders. In that way, it is said that intercalated structure nanocomposites with a uniform interlayer spacing of the silicate layers were obtained. The above authors also mentioned that this method is appropriate for polymers with moderate solubility in common solvents. Higher solubility will cause difficulties in the precipitation step as enormous volume of non-solvent will be needed.

A new two-step technique, namely SOAM method, was established by Lim et al., 2010, where the polymer matrix and organoclay were blended in solution and then compounded in melt in a torque rheometer. Comparative studies with nanocomposites prepared via solution blending showed that SOAM method is more effective in providing high degree of dispersion of organoclay in the polymer matrix.

Masterbatch approaches, as a means of improving exfoliation, have also been investigated by Wilkie & Zheng, 2003 as well as by Guo et al., 2004. Poly(ε-caprolactone) (PCL) nanocomposites were prepared either by melt blending of PCL with OMMT or by in situ ring opening polymerization of ε-caprolactone (CL) with organically modified clay. The new organically-modified clay was then blended with ABS melt and exfoliated structures were produced (Zheng & Wilkie, 2003). Guo et al., 2004 used amphiphilic poly(styrene-*b*-ethylene oxide) block copolymers, prepared by anionic copolymerization, to modify layered silicates via melt intercalation. XRD and microscopy studies on ABS/intercalated clay nanocomposites prepared by melt blending demonstrated a good dispersion of silicate

layers in the polymer matrix. The above researchers attributed this behaviour to strong interactions from hydrogen bonds between the layered silicate and PEO block chain segments, making the block copolymer to adhere to the interlayer and act as intercalating agent. They also observed that ABS nanocomposites showed considerable improvement in its tensile strength, modulus and thermal stability.

Emulsion and in situ polymerization processes for the preparation of ABS/clay nanocomposites have been reported by Jang et al., 2001 and Kim et al., 2011. Jang et al., 2001 prepared ABS/MMT-Na$^+$ nanocomposites by direct intercalation through one-step emulsion polymerization. The mixture of acrylonitrile and styrene monomers and 1,3-polybutadiene (PBD) rubber latex was copolymerized in the presence of MMT-Na$^+$. By SEM and TEM images it was observed homogeneous dispersion of MMT particles in the polymer matrix. TGA measurements indicated enhanced thermal stability, whereas DSC thermogram does not exhibited any thermal transition.

1.2.2 Effect of type of clay on the nanocomposites morphology

The effect of clay size on the dispersion morphology and emulsion stability during preparation of ABS/layered silicate nanocomposites through in situ emulsion polymerization was studied by Kim et al., 2011. Three types of silicates: Laponite, Cloisite-Na and Kunipia-F with particle sizes about 20-30, 70-150 and 300-500 nm, respectively were used. The obtained results indicated that, ABS layered silicate nanocomposites produced by using Cloisite-Na and Laponite showed exfoliated structures and stable emulsions. On the other hand, nanocomposites with Kunipia-F contain aggregated particles and separated phases. The nanocomposite reinforced with a mixture of Kunipia-F/Cloisite-Na or Kunipia-F/Laponite showed stable emulsion. This behaviour was attributed to the small sizes of Cloisite-Na and Laponite which also showed good efficiency to stabilize the emulsion particle during polymerization.

As stated above, the compatibility of polymer matrix towards the organic modification of clay reinforcement is a very critical parameter affecting the nanocomposite structure and the enhancement of final properties. Four different commercial clays (Cloisite-Na, 10A, 20A, 30B) were used by Patiño-Soto et al., 2008 for preparation of ABS matrix nanocomposites by processing in a twin-screw extruder. The above authors observed that Cloisite 20A and Cloisite 30B (the first owing greater initial intergallery spacing but lower polarity and the second with smaller intergallery spacing but greater polarity), produce ABS nanocomposites with maximum intergallery spacing, better thermal stability and fire retardancy.

On the other hand, Lim et al., 2010 have studied the solution technique followed by melt blending process for preparation of ABS nanocomposites and reported that the system ABS/Cloisite 30B gave more exfoliated structures and better thermal and mechanical properties in comparison with the results obtained for Cloisite 10A and Cloisite 25A reinforcements. The Flory-Huggins interaction parameter of the system ABS and Cloisite 30B was calculated and found smaller than that for ABS/Cloisite 10A as well as for ABS/Cloisite 25A. Therefore, thermodynamic interaction between ABS and Cloisite 30B was predicted more favourable than that of the other two systems.

1.2.3 Clay modification

Su et al., 2004 prepared new organically modified clays using copolymers of styrene (COPS) and methacrylate (MAPS) with vinylbenzyl chloride. Both these polymeric clays offer

advantages in thermal stability when compared to those treated with conventional ammonium salts and this may enable melt processing of polymers requiring higher temperatures. From TEM images it is clear that in styrene copolymer-containing clay/ABS nanocomposites individual clay layers are present, while the methacrylate copolymer gives some mixtures of immiscible and intercalated structures. Thermal stability is higher for the COPS systems, since styrene is inherently more thermally stable than methyl methacrylate.

In another work an oligomerically modified clay (with styrene, vinylbenzyl chloride and lauryl acrylate), has been used to fabricate ABS nanocomposites by melt blending and mixed delaminated/intercalated structures were obtained (Zhang et al., 2006a). The plasticizing effect from the oligomer was successfully suppressed by increasing the inorganic clay content to 50%. The decreased organic content of clays reduces plasticization, giving better mechanical properties, but also it creates an adverse effect on the dispersability of clay in the polymer, leading to morphological changes from nanocomposite to microcomposites (Zhang et al., 2006b).

A modified clay with enhanced thermal stability and larger d-spacing compared to commercially available clays, was developed by Chigwada et al., 2006, who used an ammonium salt containing 4-acetylbiphenyl (BPNC16). BPNC16 modified clay has enhanced thermal stability and large d-spacing compared to some commercially available clays. The nanocomposites prepared with this clay showed improved thermal stability and a significant reduction in the peak heat release rate from cone calorimetric measurements.

ABS/clay nanocomposites containing imidazolium-modified montmorillonite were prepared by Modesti et al., 2008, via the classic melt intercalation and a low-temperature solution process. WAXD and TEM show that with both processes, a mixed intercalated/exfoliated structure was obtained, however confocal microscopy showed that the clay is not homogeneous dispersed and that micrometer aggregates of clay tactoids are present. The sonication process reduces the size of these aggregates as compared to melt blending and improves the degree of dispersion. This effect was confirmed by the values of elongation at bleak and flexural elastic modulus obtained from composite specimens. Fluorescence spectroscopy has also been used to investigate the distribution of clay within the composite and results indicate that clay layers in ABS were preferentially located in the SAN phase, independently of the dispersion process.

Based on the structure characteristic of ABS resin and the principle "like dissolves like", hexadecyl triphenyl phosphonium bromide (P16) and cetyl pyridium chloride (CPC) were used by Cai et al., 2010 to prepare a high thermal stability OMMT. Intercalated structure for ABS/OMMT-P16 hybrids and intercalated-exfoliated structure for ABS/OMMT-CPC nanocomposites were respectively formed by melt mixing method. TGA results revealed that the onset temperature of thermal degradation and charred residue at $700^{\circ}C$ of the ABS nanocomposites were remarkably increased compared to pure ABS. It was also found from Cone calorimetry tests, that the peak of heat release rate (PHRR) decreased significantly, contributing to reduced flammability. In addition, DMA measurements indicated that the loading of silicate clays improved the storage modulus of ABS resin. Partial exfoliation of OMMT-CPC nanocomposites was, therefore, advantageous for increasing thermal stability, decreasing flammability and improving mechanical properties.

Other researchers, treated commercial OMMT (Cloisite25A) with bis(3-triethoxysilylpropyl) tetrasulfane (TSS), in order to enhance interactions between clay and ABS through the chemical reaction of tetra sulfide groups with vinyl groups present in ABS (Kim et al., 2008).

Intercalated/exfoliated coexisting structures were observed by TEM. The ABS/clay composites exhibited much higher tensile strength and elongation at break than that of neat ABS and especially the elongation at break of ABS/TSS-C25A composite was 5 times higher than that of neat ABS.

1.2.4 ABS modification to improve compatibility

One approach to induce attractive interactions between a polymer and layered silicates is to employ a third component, commonly referred as compatibilizing agent, which can help improve compatibility between the polymer and the organoclay. Specifically Lim & Park, 2001 employed polystyrene grafted with maleic anhydride, PS-g-MA, as compatibilizing agent to prepare nanocomposites consisting of PS and organoclays. Polypropylene grafted with MA, PP-g-MA, was employed as compatibilizing agent to prepare nanocomposites of PP and organoclays (Solomon et al., 2001; Galgali et al., 2001). A similar attempt to improve compatibility between clay reinforcement and ABS matrix has also been made by Ma et al. 2006, who tried to increase ABS polarity by appropriate modification. They performed grafting of maleic acid anhydride (MAH) to ABS and investigated the effect of this modification on the morphology, thermal stability, flammability and dynamic mechanical properties of the obtained ABS/OMMT nanocomposites. Maleic anhydride was successfully grafted into butadiene chains of the ABS backbone in the molten state using dicumyl peroxide as initiator and styrene as the comonomer. TEM images showed that the size of the dispersed rubber domains of ABS-g-MAH increase and the dispersion is more uniform than that taking place in pure ABS resin. Intercalated/exfoliated structures were formed in ABS-g-MAH/OMMT nanocomposites and the rubber phase intercalated into clay layers that were distributed in both SAN and rubber phase. The intercalation of clay in rubber phase is probably due to grafting of MAH to butadiene chain, thus improving the polarity of this phase, which results in stronger affinities between clay and PB and, therefore, rubber phase can intercalate into clay layers. These nanocomposites exhibit better barrier properties, thermal stability and significantly reduced flammability as compared with ABS/OMMT systems. The improvement of flame retardancy of ABS-g-MAH/OMMT nanocomposites can be ascribed to the better dispersion of clay layers and intercalation of clay in both PAN and PB phases. Moreover, T_g of ABS-g-MAH/OMMT was 1.5°C higher than that of ABS/OMMT nanocomposites, which suggests that intercalated/exfoliated structure is more effective in improving rigidity and barrier ability than intercalated structures of ABS/clay hybrids.

Other types of treatment were studied by Kim et al. 2003, who reported the synergistic effect of triphenyl phosphate (TPP) and nanosilicates on the enhancement of thermal stabilization of ABS/clay nanocomposites.

1.2.5 Effect of ABS monomers composition in the nanocomposites morphology

It is well known that among the three initial monomers of ABS, acrylonitrile (AN) is the most polar one and its content would affect polar interactions with modified clays in nanocomposite. The effect of AN content on the structure of ABS nanocomposites was studied by Patiño-Soto et al., 2007 and the obtained results confirmed that better intercalation and/or exfoliation can be obtained when using ABS with higher AN content, due to the higher content of polar groups, which allows more homogeneous dispersion and intercalation of polymer chains within OMMT layers and, furthermore, some exfoliation of the nanoclay. The study of

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properties using TGA and flammability tests showed that the nanodispersed silicate layers enhanced the thermal stability of the ABS matrix and that a grade of ABS with higher AN content was more effective in providing fire retardancy. DMA showed that the storage modulus of both, low and higher AN content ABS polymers, was quite similar. The incorporation of organoclay increases the modulus of both examined ABS and this effect is slightly stronger when ABS with higher AN content was used. Similar behaviour was observed for T_g calculated from the maximum of tan δ (Patiño-Soto et al., 2008).

As mentioned earlier, ABS is a complex system, with the rubber particles (polybutadiene) dispersed in the matrix of poly(styrene-co-acrylonitrile) (SAN). Therefore the addition of a third component, i.e. the nanoclay filler, makes the system more complicated. SAN is the matrix phase of the multiphase ABS, thus SAN/MMT could be considered a model system useful for understanding ABS/MMT compatibility. Stretz at al., 2005 concluded that clay particles reside predominantly in the SAN phase with some accumulation at the rubber particle surfaces. The effect of reinforcing was somewhat lower in ABS/clay nanocomposites when compared to SAN/clay hybrids. The reason has been attributed to the different moduli of ABS and SAN matrixes and to the random orientation of clay particles in ABS/MMT composites at the rubber particle surface. They concluded that the SAN/MMT composites represent a good model system for studying the more complex ABS/MMT composites.

In order to explore the effect of different phases of ABS on the preparation of ABS nanocomposites, an indirect method of preparation of SAN/clay nanocomposites followed by the addition of ABS, was studied in comparison with the direct method by which nanocomposites were prepared directly using commercial ABS. It was observed that with the indirect method, the compatibility between the components was reduced because clay layers were already dispersed inside the SAN matrix. In nanocomposites prepared by the direct method, less dispersion of the layers and accumulation of the clay particles in the interphase regions was observed (Pourabbas and Azimi, 2008). Kinetic analysis carried out with the data from dynamic TGA showed that the addition of gABS to SAN nanocomposites reduced the activation energy (E_a) but decreased the reaction order (n) on the global degradation reaction. Relatively higher E_a values were obtained for indirectly prepared ABS nanocomposites, however the steady values of n indicated that the thermal degradation mechanism remains unchanged independent of the preparation methods employed. It was also found that reduction of E_a and n, by increasing the clay content in the nanocomposites. Even though the effect of enhancement of thermal stability due to clay nanofillers, (observed in most of the polymeric nanocomposites and attributed to the barrier property and char promoting effect of the clay, which protects the inner materials from further decomposition or combustion), the reduced E_a values by increasing clay content showed their accelerating effect on thermal degradation reactions. Pourabbas & Azimi, 2008 concluded that clay particles or layers take part in thermal degradation mechanisms and they must not be regarded as inert material.

Many studies on ABS nanocomposites are concentrated on the scope to balance their mechanical and improve thermal and flammability properties. In a recent work (Stretz at al., 2005), detailed results on mechanical properties of ABS/clay nanocomposites were reported, showing a remarkable decrease in impact strength. Since the impact strength of ABS/clay nanocomposites is very important mechanical property for technical applications, the optimization of formulation seems to be necessary. One approach to improve the impact

strength is to increase rubber content in ABS/clay nanocomposites. Kim et al., 2009 investigated the effect of rubber content in ABS on the mechanical properties of ABS/clay nanocomposites, in an attempt to find the optimum content with good balance of mechanical properties. Three different types of ABS with different rubber content (25, 30 and 35 wt%) were tested and it was concluded that for addition of 3 % wt clay, ABS nanocomposite with 35% content of rubber displayed the highest reinforcing effect, in terms of tensile properties and impact strength. Furthermore, the addition of UV stabilizer further improved the impact strength of the optimum nanocomposite composition. The above researchers mentioned that increasing rubber content may lead to a lower degree of dispersion of clay and/or to a lower degree of orientation and this effect became stronger with increasing clay content.

1.2.6 Characterization of ABS/organoclay nanocomposites

Enhancement of improvement of the thermal stability and mechanical strength was observed by Yeh et al. 2006, by testing samples of a series of injection molded ABS/organoclay nanocomposites at low clay loading. In addition, they observed that incorporation of organoclay platelets into ABS matrix resulted in an increase of T_g, associated with the confinement of the intercalated polymer chains within the organoclay galleries that prevent the segmental motions of polymer chains. They also measured an increase of hydrophobicity of nanocomposites, based on the contact angle measurements.

Studies of thermal properties in intercalated/exfoliated ABS/OMMT nanocomposites by Wang et al., 2002 using thermogravimetric analysis showed that the pyrolysis of ABS was divided into two steps. They explained the improved thermal stability of ABS matrix in the formation of carbonaceous-silicate char on the surface during burning, which insulated the underlying material and slowed the escape of the volatile product generated during decomposition. The nanodispersed lamellae of clay in polymer matrix will result in a spatially more uniform and thicker char on decomposition.

The increase in decomposition temperature during TGA in ABS nanocomposites might be taken as measure of the occurrence of clay intercalation-exfoliation, since the intercalated or exfoliated clay will act as a barrier for the diffusion of atmospheric oxygen into the material, inhibiting the polymer decomposition (Morawiec et al., 2005). Since TGA is a dynamic experiment, another possible reason for the increase of decomposition temperature of the ABS nanocomposites, is the increase of viscosity due to the addition of clay, which will increase the difficulty for the inward diffusion of oxygen and the outward diffusion of the degradation by-products (Valdes et al., 2006).

Patiño-Soto et al., 2007, observed that in all cases ABS nanocomposites produce more char than pure ABS. Several studies have shown that the lower flammability of polymer-clay nanocomposites is related to the formation of char with a multilayer carbonaceous-silicate structure. This char builds up on the surface during burning, insulating the underlying material and slowing the escape of the volatile products generated during thermal decomposition. The observed increase in char formation in the ABS nanocomposites indicates that the clay enhances the formation of char on the surface of ABS and as a consequence, reduces the rate of decomposition and improves thermal stability.

As mentioned above, flammability of ABS restricts its application and, therefore, many halogenated organics have been used as flame retardant additives. Nowadays, a lot of emphasis has been placed on the replacement of halogen-type flame retardants by non-

halogen types and the flame retardants based on phosphorus-containing compounds are known to be the most acceptable candidates for this purpose, still having some problems with toxicity. Triphenyl phosphate (TPP) and its analogues are known to be the most effective candidate for many polymers including ABS. On the other hand, polymer/clay nanocomposites are believed to be a new promising approach to fire retardancy.

Kim et al., 2003 reported the synergistic effect of nano triphenyl phosphate and nanosilicates on the enhancement thermal stabilization of ABS/clay nanocomposites. Epoxy resin and silane coupling agents were incorporated as flame co-retardants. A very large increase in the limiting oxygen index (LOI) value was observed with epoxy addition and further enhancement in thermal stability was obtained for ABS compounds containing small amounts of coupling agent. It was also found that the enhancement was closely related to the morphologies of the chars formed after combustion.

TTP was also used by He et al., 2010, who tried to improve the thermal properties and flame retardancy of ABS/OMMT nanocomposites. The results by cone calorimetry analysis indicated that the reduction of peak heat release rate for ABS/OMMT and ABS/OMMT/TTP nanocomposites was 47.3 and 57.3% respectively, while the total heat released became lower to about 10 and 17% and the mass loss rate decreased by about 41 and 53% respectively, as compared to pristine ABS. The Limiting Oxygen Index (LOI) value of ABS/OMMT and ABS/OMMT/TTP nanocomposites increased to 22.8 and 28 from 18% respectively with respect to pristine ABS. The vertical burning test (UL-94V) results revealed that the nanocomposites could achieve V-0 grade.

Rheological investigation by Aalaie & Rahmatpour, 2007, on ABS/OMMT hybrids has shown that the prepared nanocomposites and their pristine counterpart have shear-thinning behaviour, obeying the power law equation. At low shear rates, the steady shear viscosity and shear stress of the nanocomposites increase with increasing the nanoclay content. However, at high shear rates they behave similar to pure ABS. It was shown that the flow activation energy (E_a) values increase with increasing nanoclay content. Mechanical tests showed that the flexural moduli of nanocomposites increase with increasing nanoclay loading, but flexural strength as well as tensile and impact properties decrease with the increase of nanoclay content.

Viscoelastic properties of ABS/organoclay nanocomposites prepared by the SOAM method and the solution blending method were studied by Lim et al., 2010, who measured the rheological properties under oscillatory shear condition. They observed that the storage modulus G' became less dependent on the frequency with increasing clay loading and this was due to the formation of network structure of the clay plates, indicating solid-like characteristics. Furthermore, nanocomposites prepared by the SOAM method showed more solid-like behaviour and exhibited higher increase of storage modulus throughout the frequency range, than those prepared by solution blending.

From the results of linear and nonlinear viscoelastic measurements in ABS/clay melts it was found that, in addition to the physical network originated from interconnection of rubber particles, a 3D network is formed between organoclay platelets and/or tactoids that causes reduced temperature dependence of linear viscoelastic properties of nanocomposite samples as compared with ABS matrix (Saadat et al., 2010).

Extrudate swell, also called die swell, is one of the most important viscoelastic responses of polymer melts and play a key role in processability of polymers and die design in extrusion process. According to Saadat et al., 2010 the presence of organoclay reduced die swell of

ABS/clay nanocomposites and this was explained in terms of great surface area and anisometric nature of organoclay tactoids and/or platelets, which promote energy consumption and less energy to be stored in chains.

The OMMT/ABS nanocomposite materials were subjected to a series of five succesive extrusion cycles, in a co-rotating twin screw extruder and the effect of reprocessing on the properties of this compound was investigated by Karahaliou & Tarantili, 2010. By ATR/FTIR analysis it was observed that the above reprocessing of OMMT/ABS composites resulted in a progressive increase of oxidation products. More specifically, the concentration of carbonyl groups increased gradually during the extrusion processing, but at a lower extent compared with the increase of ester-groups. On the other hand, the ester-groups showed a dramatic increase after the second extrusion process, followed by lower changes up to the fifth pass. The band corresponding to -C≡N group, present in AN, remained almost stable and, therefore, it can be concluded that this group is relatively resistant against these processing conditions. The color of samples was rather constant through the successive extrusion cycles. On the other hand, the melting temperature was slightly decreased, whereas glass transition temperature (T_g) was almost stable. Extrusion reprocessing did not have any significant effect on the temperature of the maximum thermal degradation rate (T_{max}), whereas a slight decrease in the onset temperature of thermal degradation (T_{onset}) as it was observed by TGA. Finally, the rheological and tensile properties of the investigated composites did not display any significant change by increasing the number of reprocessing cycles. The above researchers concluded that OMMT nanoparticles did not only act as reinforcement for ABS but also seemed to play a role on the ageing mechanism taking place during repeated melt processing. Therefore, the incorporation of the above nanofiller into ABS/PC blends could be considered as an alternative option for the mechanical recycling of ABS/PC wastes, providing low cost and easy processing.

1.3 Nanocomposites of polycarbonates
1.3.1 Basic aspects and preparation

Polycarbonate (PC) is commonly used as high-performance amorphous engineering thermoplastic because of its distinct properties, such as high-impact strength, transparency, heat resistance and dimensional stability. In addition, this family of polymers show excellent electrical properties, colorability, high-gloss, flame retardancy and high-heat distortion temperature (HDT). However, it is notch sensitive and, moreover, difficult to process, because its high-melt viscosity hinders fluidity and the residual stresses resulting from the process could be a potential hazard for fracture formation. Approaches were developed to decrease the notch sensitivity and enhance processability without reducing the superior toughness of PC. Polycarbonate has been modified and tailored in many different ways, particularly with other polymers for use in demanding applications particularly when its outstanding impact strength is a critical factor. Recently, nanocomposite technology has been applied to modifying PC. Polycarbonate nanocomposites, because of the nanoscopic length scale, offer the promise of improved physical properties, such as strength, modulus and scratch resistance without sacrificing optical clarity and toughness.

Recently, Huang et al. reported on polycarbonate-layered silicate nanocomposites prepared by two different methods. A partially exfoliated cyclic oligomer (OLS) nanocomposite was obtained by mixing cyclic carbonate and ditallow dimethyl exchanged MMT in a brabender

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mixer (Huang et al., 2000). Subsequent ring-opening polymerization of the cyclic oligomers preserved the exfoliated structure affording a route to polycarbonate-OLS nanocomposites. An analogous mixing experiment with linear polycarbonate and OLS only produced an intercalated structure. Conventional melt or solution processing of the above mentioned OMMT with either linear polycarbonate or cycling oligomers yielded intercalated nanocomposites.   These results demonstrate that consideration of molecular architecture (cyclic versus linear) and kinetics (medium viscosity and shear) are critical for nanocomposite formation.

1.3.2 Types of fillers and mixing techniques

In another work, the influence of various processing variables and that of organoclay structure on the degradation process and color formation of PC nanocomposites was studied by Yoon et al, 2003b, who used two different twin screw extruders and a series of organoclays based on sodium MMT, with relatively high iron content, exchanged with various amine surfactants. It was found that the extruder with longer residence time and broader residence time distribution was the most effective equipment for dispersing the clay but gave products with more color. Molecular weight degradation of the PC matrix during melt processing produces phenolic end groups and more extended dispersion of the clay generally lead to higher reduction in molecular weight due to the increased surface area of clay exposed. Double bonds in the hydrocarbon tail of the surfactants lead to more darkly colored materials than saturated surfactants. The most severe color change was observed when using a surfactant containing hydroxyethyl groups and a hydrocarbon tail derived from tallow.

A selected series of organoclays based on the synthetic clay Laponite® and calcium MMT from Texas (TX-MMT) were also prepared in an attempt to explore the effect of the clay structure on the overall behavior of final nanocomposite. Laponite® and TX-MMT produce less color polluted products of MC nanocomposites as compared with MMT, probably due to the lower content of iron (Yoon et al., 2003b).

Lee & Han, 2003 studied the linear dynamic viscoelastic properties and non-linear transient rheology of PC/organoclay (Cloisite 30B) and PC/natural clay nanocomposites prepared by melt blending in a twin-screw extruder. The results obtained by FTIR spectroscopy on extrudates, at temperatures ranging from 30 to 280°C, showed that carbonyl groups in PC and hydroxyl groups of Cloisite 30B in PC/Cloisite 30B nanocomposites can form hydrogen bonds, while no evidence of hydrogen bonding was observed in PC/Cloisite Na+ nanocomposites. TEM images showed that organoclay platelets are well dispersed in PC/Cloisite 30B nanocomposites, whereas the untreated clay platelets are poorly dispersed in PC/Cloisite Na+ nanocomposites. The rheological measurements supported the conclusion based on the results of XRD, TEM and FTIR spectroscopy. An increase in dynamic moduli of nanocomposites was observed with increasing concentrations of Cloisite 30B. This was attributed to an increase of the surface area of dispersed layered silicates of Cloisite 30B platelets as the concentration of clay increases and, consequently, an increase of the number of sites available for hydrogen bonding between carbonyl groups in PC and the hydroxyl groups in MT2EtOH of Cloisite 30B takes place.

An alternative technique for making PC nanocomposites was based on the melt polymerization of bisphenol-A with diphenyl carbonate. The prepolymers were intercalated with OMMT by melt mixing and solution mixing. Subsequently, micro-wave solid-state

polymerization converted the pre-intercalated into exfoliated nanocomposite, whereas conventional solid-state polymerization using oil heating only increased the gallery size of MMT (Yoo et al., 2004).

Carrión et al. 2008, prepared a new PC nanocomposite containing 3 wt% of OMMT bentone 2010 and shaped some samples from this system by extrusion and injection moulding. Then, its tribological properties were determined under a pin-on-disc configuration against stainless steel. The nanocomposite presented a 88% reduction of friction and up to two orders of magnitude reduction of wear rate with respect to the base polymer. The good tribological performance of the new composite was attributed to the uniform microstructure and to the increase of nanoclay stacking distance.

Wu et al., 2007, prepared PC/clay nanocomposites by melt intercalation using epoxy resin as a compatibilizer. The above researchers reported that the addition of epoxy can improve clay dispersion, enhancing the low-frequency viscoelastic responses, while high loadings of epoxy lead to severe degradation of PC matrix, decreasing the high frequency responses and, furthermore, creating a plasticizing effect due to excessive epoxy. Moreover, all samples showed high sensitivity to both, quiescent and large amplitude oscillatory shear deformation, despite enhanced percolation of tactoids due to the compatibilization of epoxy.

1.3.3 Thermal and mechanical properties

As already mentioned, OMMT is unstable at high processing temperature, tends to degrade and forms agglomerates on the high processing temperatures of PC, i.e. at about 220-260°C. Thus, it could suppress the dispersion of clays in the PC matrix and subsequently weaken the properties of composites. For achieving a good PC/MMT nanocomposite, two criteria should be met, that are good thermal stability of MMT and good compatibility between PC and MMT.

Severe et al., 2002 studied the thermal stability of polycarbonate nanocomposites formed in a twin screw extruder, using phosphonium exchanged montmorillonite and synthetic clays. They found that the former provided better thermal stability in comparison with synthetic clays. Also, a series of flame retardant formulations of solid bisphenol A bis(diphenyl phosphate) (S-BDP) and OMMT were prepared by melt compounding procedures. OMMT was well dispersed into the matrix showing an intercalated-exfoliated morphology. S-BDP and OMMT exhibit a synergistic effect in the vertical burning test (UL-94) but an antagonistic effect in the limiting oxygen index (LOI) evaluation. The introduction of OMMT could especially enhance the thermal-oxidative stability of the material (Feng et al., 2010).

Organoclay nanocomposites based on medium molecular weight PC (MMW-PC) and high molecular weight PC (HMW-PC) were prepared using a twin screw extruder (Yoon et al, 2003a). Tensile tests showed that HMW-PC gives better stiffness and ductility to the nanocomposite than MMW-PC. This effect was attributed to the higher shear stress generated during melt processing. The effect of chemical composition of the surfactant on the morphology and physical properties of nanocomposites were explored for systems formed from HMW-PC. The surfactant having polyoxyethylene and octadecyl alkyl tails produces the most significant improvement of modulus and lead to partially exfoliated platelets and this was attributed to the miscibility of poly(ethylene oxide) tail with PC. However, nanocomposites formed from a range of other organoclays contained both intercalated tactoids and collapsed clay particles with few, if any, exfoliated platelets.

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Chow & Neoh, 2009 used three different loadings of 3-aminopropyl-triethoxysilane (APS) to modify the MMTNa$^+$ via cation exchange technique. Nanocomposites were prepared by melt compounding and their morphology was characterized by using XRD and TEM, which revealed partial intercalation and exfoliation of silane-treated montmorillonite (STMMT) in the PC matrix. Increase of APS concentration significantly enhanced the storage modulus (E') and improved the thermal stability of PC nanocomposites. Their results indicated that APS was effectively interacting with PC resins and clay, and subsequently enhancing the thermal stability of PC nanocomposites. This was due to the crosslinked structure between APS and clay which made the degradation more difficult. The improvement in storage modulus could be associated to the stiffness of these layers on molecular motion of polymer chains, the high aspect ratio and degree of dispersion of STMMT. In highly intercalated and exfoliated nanocomposites, individual clay layers with high aspect ratio are dispersed homogeneously in the polymer matrix. Their results indicated that the stiffness of the nanocomposite was contributed by the clay loading instead of the concentration of the modifier.

A series of PC/organoclay nanocomposites from two commercial surface-modified MMT were prepared by melt compounding using a twin screw extruder (Nevalainen et al., 2009). The PC nanocomposites showed rather good dispersion of nanoclay, with a mixture of exfoliated, intercalated and confined morphology. The type of surfactant did not have a significant effect on the overall dispersion of nanoclay. The effect of clay reinforcement on the mechanical response of specimens subjected to tensile and impact test demonstrated an increase of Young's modulus and yield strength. A transition from ductile to brittle deformation Polycarbonate upon tensile loading occurred at the investigated concentrations of clay loadings. Notched impact strength experiments supported this behaviour, showing that impact strength decreases significantly as nanoclay content increases from 1 to 5%, regardless of the performed nanoclay surface modification. According to TGA results, PC nanocomposites showed a complex behaviour in comparison with pure PC. Incorporation of nanoclay lowers the initial decomposition temperature but at the final stages of decomposition the weight loss of PC nanocomposites shifted to some higher temperatures than those for with pure PC. Furthermore, T_g dropped as a function of clay loading probably because of the enhanced chain mobility in the presence of filler. The tribological properties of selected specimens were evaluated using a pin-on-disc and it was observed that nanoclay did not significantly change the tribological behavior of PC, possibly due to the tendency of the studied nanoclays to form micro-sized agglomerates in the PC.

1.4 Nanocomposites of ABS/PC blends
1.4.1 General characteristics and morphology
It also should be noted that ABS can be easily mixed with polycarbonate (PC) polymer and the obtained alloy is widely used in the production of electric and electronic equipment, due to a balanced combination of properties of the two components. ABS/PC blends are used in the computer and business equipment industry to mould housings, such computer monitors, printer peripherals, laptop cases and, more recently, flat panel LCD television bezels and housings. PC has high thermal stability and good impact behaviour whereas ABS shows easy processability and economical benefits. When PC is blended with ABS, the polycarbonate matrix contributes to mechanical and thermal properties, whereas the ABS contributes to processability, economy and more reliable impact strength. The desired mechanical properties and thermal stability properties can be achieved by changing

PC/ABS ratio. Thermoplastics including PC/ABS blends are easily combustible and, however, have several applications in electronics, electrical and car industries, where plastic parts must display low flammability. To achieve an optimum level or fire retardancy, a large amount of non-halogenated type flame retardants (FRs) is required in the formulation. However, the addition of large amounts of FRs could decrease mechanical properties of resin and also affects its rheological behaviour.

Extensive investigation of the morphology of PC/ABS blends throughout the entire composition range was carried out by Lee et al., 1992. The PC-rich blends showed that dispersed ABS obtained a "bead-and-string" structure. With increasing ABS content the bead-and-string structures became more densely arrayed and more interconnected. A transition was observed between the 70/30 and 60/40 compositions, from the bead-and-string structure to a coalesced configuration. For the 40/60 compositions, PC formed a dispersed phase with SAN inclusions (Lee et al., 1992).

From studies on different compositions of ABS/PC blends it was observed that ABS seems to act as plasticizer when incorporated to PC at concentrations above 20%, probably due to the dispersion of polybutadiene phase into the thermoplastic matrix of the blend (Tarantili et al., 2010). Differential Scanning Calorimetry tests showed dependence of the glass transition temperature (T_g) on the composition of the examined blend, which suggests certain interactions among the components of the mixture. Therefore, it was concluded that the ABS/PC system shows a wide range of miscibility of its components up to a minimum of 20%ABS concentration. The change of T_g was much more intense for PC phase, which was interpreted assuming the plasticizing effect of ABS on PC. Furthermore, this behaviour was confirmed by the determination of rheological characteristics of the blend via Melt Flow Index (MFI) measurements. A decrease in mechanical properties, in terms of tensile strength and elongation, was also recorded, whereas the modulus of elasticity showed some improvement.

As mentioned above PC/ABS mixtures display partial miscibility and, therefore, modification for the improvement of their performance is necessary. Elmaghor et al., 2004 studied the effect of maleic anhydride grafted ABS (ABS-g-MA)/PC blends. The above authors observed improved dispersion of ABS-*g*-MA in PC, resulting in excellent toughening. However, it was shown that the effect of grafting of MA to ABS was not the promotion of compatibility, but the creation of special morphology of ABS domains dispersed in PC matrix. At a certain PC/ABS-g-MA weight ratio, the ABS domains connected together to form a network and gave rise to a maximum of the notched impact strength.

Organoclay nanocomposites have attached considerably interest as an alternative method to improve FR performance and mechanical properties of polymers. Wang et al., 2003 prepared and studied nanocomposites based on alloys of ABS/PC blends reinforced with MMT nanoparticles. Intercalated structure was obtained and improvement in the thermal stability of the mixture ABS/PC was reported by the incorporation of MMT. The morphology of these alloys nanocomposites indicate that it is mainly the ABS molecules which are intercalated into the clay layers rather those of PC. Further study by Wang et al., 2004b on the dynamic self-assembly of clay layers in ABS/PC phases, made in samples of nanocomposites prepared by melt mixing in a twin screw extruder, revealed that in the interphase region, a higher density of the dispersed clay particles is observed as compared to the density inside the ABS phase. The excess silicate layers in the area of interphase is presumably the result of segregation of the clay particles from the surface, attributed to the

surface tension or from the crystal growth front attributed to the exclusion. This segregation phenomenon is greatly dependent on the choice of polymers and, more specifically, the more compatible or the greater the intercalation of polymer with OMMT, the more the density of clay layers is dispersed. They also reported that with the increase of melt-mixing time, the clay layers were self-organized from the PC phase to the ABS phase. It is well known that the presence of acidic or basic impurities will enhance depolymerization of carbonic ester in PC. However, OMMT can produce Lewis or Brönsted acid sites in the aluminosilicate when heated over 200°C, which have a positive contribution to the thermal degradation of PC. Thus, the self-organization of clay layers in ABS phase may be helpful for avoiding the enhancing effect of clay on PC during decomposition and enhance the thermal stability of ABS/PC.

Studies of the morphology on ABS/PC (70/30 wt%) clay nanocomposites by Hong et al., 2007, by TEM confirmed the fact that clay existed in the ABS phase and the interphase of ABS and PC. With further study using SEM, they mentioned that droplet size of the PC in the ABS/PC/clay nanocomposites did not change significantly with the presence of clay and has been found to be from 1.0 to 1.5 μm when the clay was added up to 5 phr. The small difference of the droplet size of the PC was attributed to the similar values of viscosities of the dispersed phase (PC) and continuous phase (ABS). From the results obtained by Dynamic Mechanical Analysis (DMA) of samples taken from ABS/PC clay nanocomposites, it was observed that the storage modulus was increased by the addition of clay at the rubbery state, i.e. at temperatures between 120 and 150°C. From the results obtained for tanδ of the ABS/PC/clay nanocomposites, it was shown that double tanδ peaks were observed. The height of the lower temperature tanδ peak was decreased from 4.5 to 3.3 when clay concentration was increased up to 5 phr, which suggests that the motion of ABS chain was restricted by the incorporation of clay in the ABS phase. The restriction of the ABS chain mobility by the clay was attributed to same conclusion drawn about the system morphology, i.e. to the fact that the clay accumulates within ABS and at the interface of ABS and PC.

1.4.2 Flame retardancy and thermal stability

In another work by Zong et al., 2204, PC/ABS/clay nanocomposites were prepared through direct melt intercalation in a twin screw extruder and detailed kinetic analysis of their thermal stability has been performed using thermogravimetric analysis. The activation energies were determined using the Kissinger method and the Flynn-Wall-Ozawa method. It was clearly observed that activation energies of the thermal degradation for nanocomposites are greater than those of the pure polymer. These data indicate an important role of clay in improving the flame retardancy of the alloy. This increasing tendency coincides with the results obtained by thermal analysis, indicating that the polymer/clay nanocomposite has higher thermal stability and lower flammability. The above authors confirmed previous studies which have shown that the lower flammability of polymer/clay nanocomposites is not due to retention of a large fraction of fuel, but rather to the form of carbonaceous char, in the condensed phase. The nano-dispersed lamellae of clay in polymer matrix may change the decomposition process of polymer since the nano-dispersed silicate layers acted as thermal hinder in polymer matrix. The nano-dispersed silicate layers slow the decomposition rate and increase the temperature of degradation by acting as an excellent thermal insulator and mass transport barrier (Zong et al., 2004).

Zong et al., 2005, studied the pyrolytic and thermo-oxidative degradation of ABS/PC alloy and ABS/PC/MMT nanocomposites by thermogravimetric analysis. The kinetic evaluations were performed by the model-free kinetic analysis and the multivariate non-linear regression. The investigation shows that thermal degradation behavior and kinetic parameters were greatly dependent on the nature of the purge gas as well as on the montmorillonite loadings. The activation energy values of samples in air were smaller than that in nitrogen, indicating that the thermal degradation mechanism was different in the above two gases. Oxygen seemed to play a key role in initiating depolymerization during the thermo-oxidative degradation of the material. This promotional effect is in agreement with the lower activation energy. In the case of nanocomposites, clay acts as a char promoter slowing down degradation and providing a transient protective barrier to both mass and energy transport in the nanocomposites. The experimental results of the above authors showed that there is an obvious tendency for the apparent activation energy of nanocomposites to increase. This increasing tendency is consistent with the thermal analysis results, suggesting that the polymer/clay nanocomposites have higher thermal stability and lower flammability. The kinetic analysis also indicated that pyrolytic degradation and thermo-oxidative degradation of PC/ABS alloy and ABS/PC/OMMT nanocomposites are two kinds of different reaction models. Pyrolytic degradation reaction of the polymer follows a two-step parallel reaction model: nth-order reaction model, and the ath-degree autocatalytic reaction with an nth-order reaction autocatalytic reaction, whereas the thermo-oxidative degradation reaction of the polymer is a two-step following reaction model: A→B→C of nth-order reaction model, and autocatalytic reaction model.

In the literature, it is reported that when polymer-layered silicate nanocomposites are evaluated for their FR properties by some test methods, such as limited oxygen index and vertical burning test (UL-94), they do not perform better than polymers without nanocaly reinforcement. Because of the aforementioned drawbacks, researchers have been focused on the combined use of nanoclay and conventional FRs systems (Wang et al., 2004a).

1.4.3 The effect of various additives

The effect of triphenyl phosphate (TPP) and MMT nanoclay on the morphology and rheological properties of ABS/PC blends was investigated by Feyz et al., 2010a. Improvement of the polymer intercalation was achieved by the presence of TPP. The results of complex viscosity (η^*) with angular frequency (ω) showed good agreement with those obtained with Carreau model. A plateau modulus (G_N^o) was observed for blends containing nanoclay, indicating the formation of network structure that increases the modulus as the result of intercalation of nanoclay. The complex viscosity is increased with the inclusion of nanoclay and TPP, but this effect was more evident with nanoclay. The above authors also observed that the addition of nanoclay enhances the non Newtonian behavior of ABS/PC blends, particularly at low-frequencies. They concluded that for composites containing both, nanoclay and TPP, the rheological behaviour of the blend was mainly controlled by the presence of nanoclay than TPP.

The thermal stability of ABS/PC/TPP/organoclay was studied using TGA and the degradation kinetic parameters were determined using the Kissinger, Flynn-Wall-Ozawa and Coats-Redfern methods (Feyz et al., 2010b). It was found that samples containing both TPP and nanoclay have the highest activation energy. Cone calorimetry, limited oxygen

index (LOI) and UL 94 methods were used to investigate the fire behaviour and flammability of materials. The reduced mass loss rate (MLR), peak heat release rate (PHRR) and enhanced LOI of the composite containing a mixture system, confirmed the synergistic effect of TPP and nanoclay. This formulation showed immediate self-extinguishing properties with V-0 classification.

2. Results and discussion

2.1 Introduction

From the above presented literature survey as well as from the discussion of experimental results, it was clearly shown that clay nanoparticles do no naturally delaminate into various polymeric matrices and this may be attributed to their chemical structure or to processing conditions. On the other hand, it is obvious that in order to achieve the expected property improvement in nanocomposites, stacked clay platelets must be dispersed into the polymeric mass and strong interactions between the polymer and mineral phase must be promoted. Therefore, the existing commercial grades of nanoclays are usually modified by several organic reagents (e.g. with quaternary ammonium surfactants) as a means to increase the inter-gallery spacing and to achieve enough hydrophobicity that further promotes miscibility with the polymer matrix. In addition to the above approach, the processing parameters during the incorporation of nanofillers into polymers are often adjusted, so that the appropriate shear is developed in order to create maximum exfoliation and adequate dispersion of the clay nanoparticles. However, as mentioned above shear alone does not enable to provide an efficient and nanometric dispersion of the clay. Interfacial adhesion needs to be high enough in order to achieve better compatibility and, therefore, improved performance of the composite. Some other factors influencing the obtained microstructure of the system are the initial spacing between layers, the affinity between polymer matrix and filler, the type and concentration of modifiers etc.

As a result, the experimental design of the study of the related nanocomposites was based on the investigation of the combined effect of processing characteristics as well as of the type and amount of nanofiller on the structure and final properties of the obtained nanocomposite. More specifically, systems processed by melt blending techniques were investigated for the preparation of organically modified montmorillonite (OMMT)/ABS nanocomposites. A commercial OMMT named Cloisite 30B was used, being a natural montmorillonite modified with a surfactant, namely (MT2EtOH): methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium chloride. Tallow (T) consists of ~65% C18, ~30% C16 and ~5% C14.

Mixing took place in a powerful and efficient machine, i.e. a twin screw extruder suitable for processing of thermoplastics. The following factors that affect nanocomposite structure were examined: (i) the extruder rotation speed and (ii) the clay content, in an attempt to elucidate the interrelations of composition and processing conditions. Characterization of nanocomposites was performed using X-ray diffraction (XRD), Scanning Electron Spectroscopy (SEM), Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) analysis, Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Rheological properties of the above blends were investigated via Melt Flow Index (MFI) tests, as a measure of their processability during melt mixing and moulding processing. Furthermore, the mechanical strength of the obtained hybrids was explored. Intercalated or/and partial exfoliated composite structures of OMMT/ABS can be prepared by melt mixing in a twin screw extruder. Screw rotation speed does not have

significant effect on the composite structure; however the second extrusion cycle improves the dispersion efficiency of the system.

In addition to the above, ABS/PC/OMMT nanocomposites were prepared and the effect of PC incorporation was assessed in comparison with unfilled ABS/PC blends. The observed interactions were interpreted in terms of the influence of each component on the functional properties of the final mixture. This attempt might also be a contribution to the effective recycling of ABS/PC blends via upgrading of the relevant waste stream using layered silicate reinforcement.

2.2 ABS nanocomposites
2.2.1 X-ray diffraction (XRD)

XRD analysis was performed to assess the status of clay dispersion within the polymer matrix. Further analysis of the obtained diffractographs, by the use of Bragg's rule, i.e. $2d\sin\theta = n\lambda$, can give the basal spacing for the clay layers.

Cloisite 30B pattern in Figure 1, shows an intense peak around $2\theta = 4.89^{o}$, which denotes that basal spacing in silicate layers is 1.8 nm. It can also be seen that, after melt mixing, the three studied screw rotation speeds (35, 100 and 200 RPM) does not have any significant effect on the dispersion of clay into the ABS matrix. Similarly, no significant effect of screw rotation speed on the obtained morphology of nanocomposites was observed.
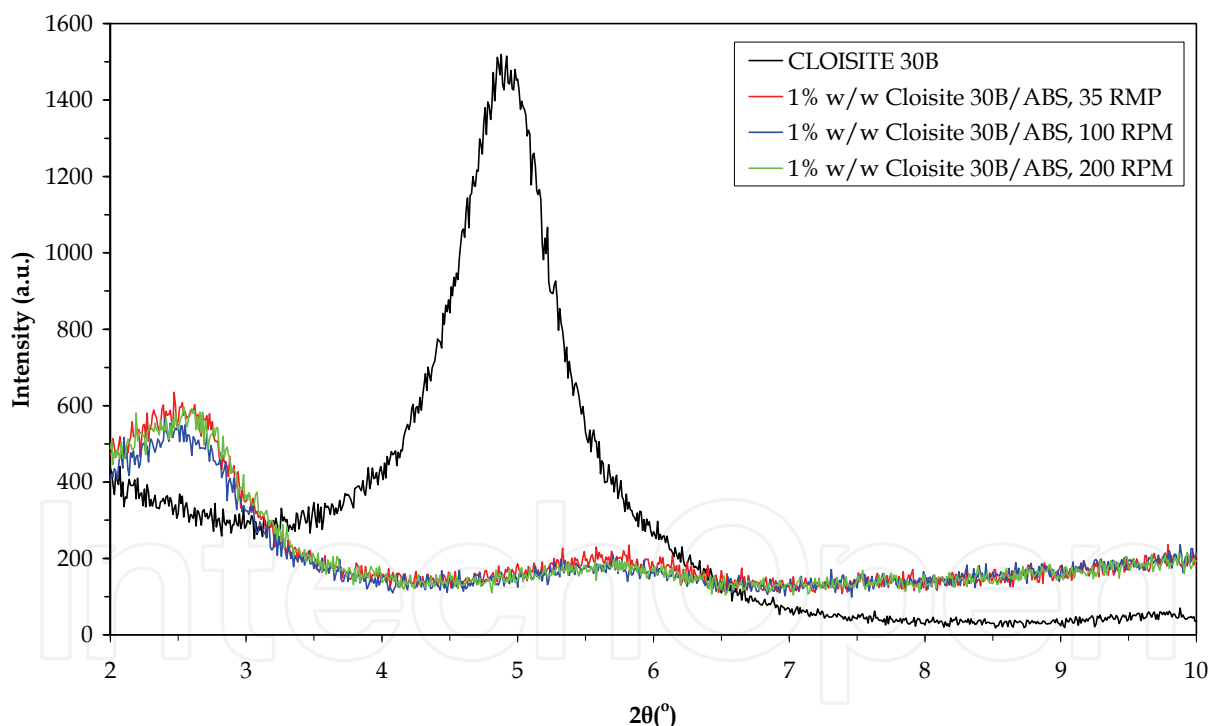

Fig. 1. XRD patterns of Cloisite 30B and its composites with ABS using different screw rotation speeds.

From Figure 2 it can be observed that the sample with 2% w/w clay shows a well defined peak at 2.61^{o}, with decreased intensity and intergallery spacing of 3.38 nm. The sample with 1% w/w Cloisite 30B shows a significant decrease in intensity of the diffraction peak, with an intergallery spacing of 3.55 nm. This probably suggests the formation of mixed exfoliated/intercalated silicate nanolayers of the clay particles dispersed within the ABS matrix.
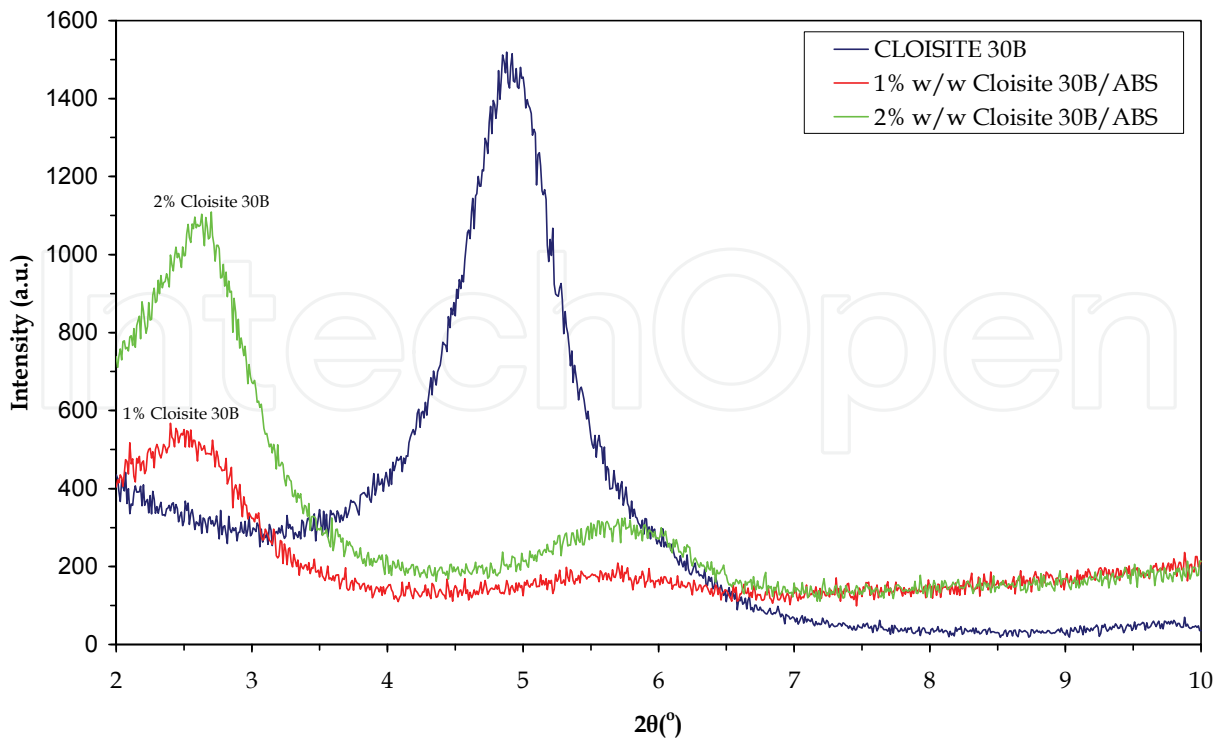
Fig. 2. XRD patterns of Cloisite 30B/ABS nanocomposites as function of clay content, at 200 RPM.

However, reprocessing in the twin screw extruder improves dispersion and intercalation of clay in the polymer matrix, after this second cycle, as can be clearly seen in Figure 3.
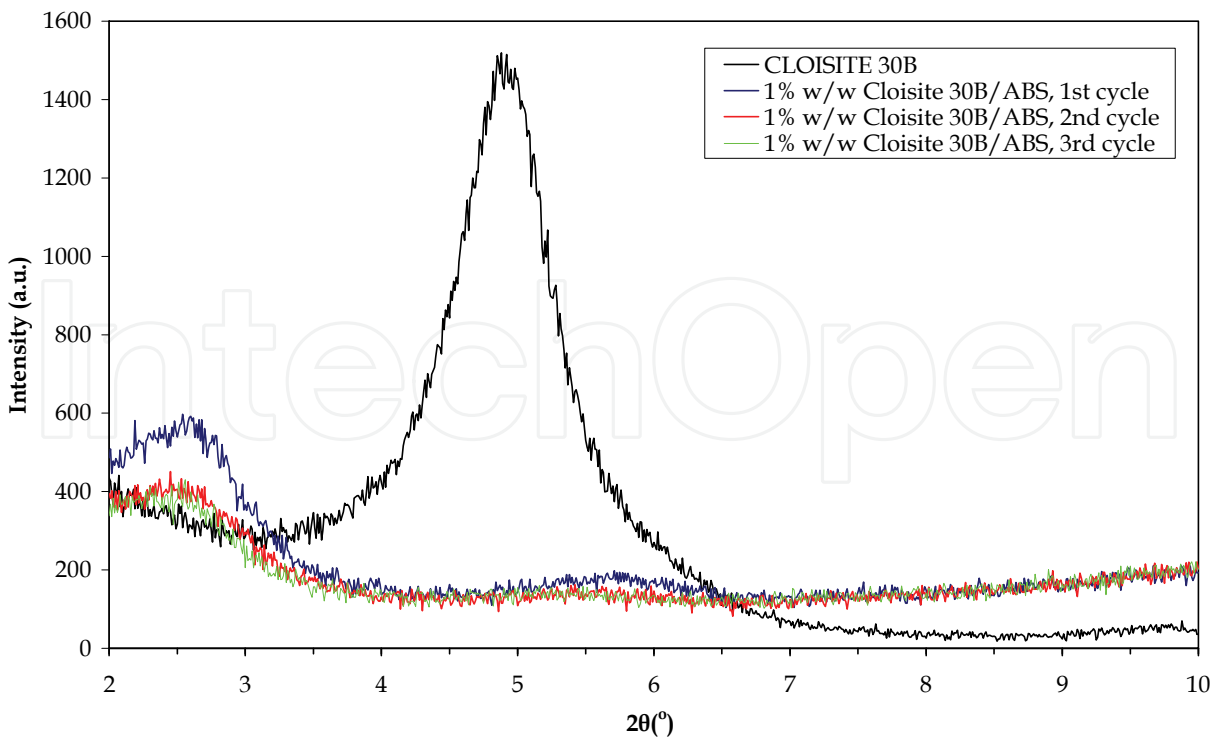

Fig. 3. XRD patterns of 1% w/w Cloisite 30B/ABS nanocomposites after extrusion reprocessing at 100 RPM.

Vaia et al., 1993 proposed that an increase in the intergallery spacing, which is related to the intercalation of the polymer through the clay galleries, results in a new diffraction pattern, corresponding to the increased spacing of the clay galleries. According to these authors, the degree of intercalation in the hybrid composite could be determined by changes in sharpness and intensity of the corresponding reflection peaks.

2.2.2 MFI
The incorporation of 1% w/w nanoclays in ABS results in a decrease of the flow rate of the mixture compared with pure ABS, which is due to the increase of viscosity (Table 1).

	MFI (g/10 min)
ABS	1.507 ±0.181
1% w/w Cl 30B/ABS	1.161 ±0.165

Table 1. MFI measurements of OMMT/ABS composites.

Similar results were reported by Aalaie & Rahmatpour, 2007 who studied the rheological behaviour of ABS nanocomposites at low shear rates. Confinement of polymer chains motion caused by organoclay platelets and tactoids in the ABS matrix, together with interactions between polar groups of ABS and oxygen groups of Cloisite 30B, may cause this effect. However, at high shear rates, flow properties of the composite are comparable to those of pure ABS. This behaviour can be attributed to preferential orientation of clay layers, or even anisotropic tactoids, parallel to flow direction.

2.2.3 ATR-FTIR
Representative ATR spectra of Cloisite 30B, ABS and 1% w/w Cloisite 30B/ABS composites, are presented in Figure 4a. Cloisite 30B reveals absorption bands at 3630 and 3367 cm^{-1} deriving from O-H stretching for the silicate group and water respectively, 1643 cm^{-1} (related to O-H bending), 1018 cm^{-1} (stretching vibration of Si-O-Si from silicate) and 920 cm^{-1} (Al-OH-Al deformation of aluminates) (Bora et al., 2000). The organic modification is responsible for the bands located at 2927, 2853 and 1470 cm^{-1}, which were assigned to C-H vibrations of methylene groups (asymmetric stretching, symmetric stretching and bending respectively).
In Figure 4b&c are also presented the spectra of 1% Cloisite 30B/ABS composites and pure ABS. The aromatic and aliphatic C-H stretching can clearly be seen in the range 3200-3000 cm^{-1} and 3000-2800 cm^{-1}, respectively. The intense and well-defined C≡N stretching from acrylonitrile (AN) is located at 2237 cm^{-1}. The scissoring mode of CH$_2$ groups is at 1457 cm^{-1} and the intense ring bends are visible at 798 and 698 cm^{-1}. Typical dienic rubber bands are easy to identify in the range 1000-900 cm^{-1} as follows: absorption peak at 998 cm^{-1} corresponds to off-frequency vibrations of CH in CH=CH groups, band at 967 cm^{-1} is due to off-frequency vibrations of CH in *trans*-CH=CH- moieties, band at 913 cm^{-1} is determined by off-frequency vibrations for =CH$_2$. The deformation vibration for =CH$_2$, which usually appears at wavelengths under 1465 cm^{-1}, shifts to 1457 cm^{-1} due to the influence of the double bond. The bands in the interval 2950-2800 cm^{-1} can be attributed to asymmetric and symmetric –CH$_2$ groups. The hydroxyl peak appears as a broad signal with a maximum at ≈3650 cm^{-1}, typical of an OH stretch. The hydroxyl peak appears as a broad signal with a maximum at ≈3650 cm^{-1}, typical of an OH stretch.

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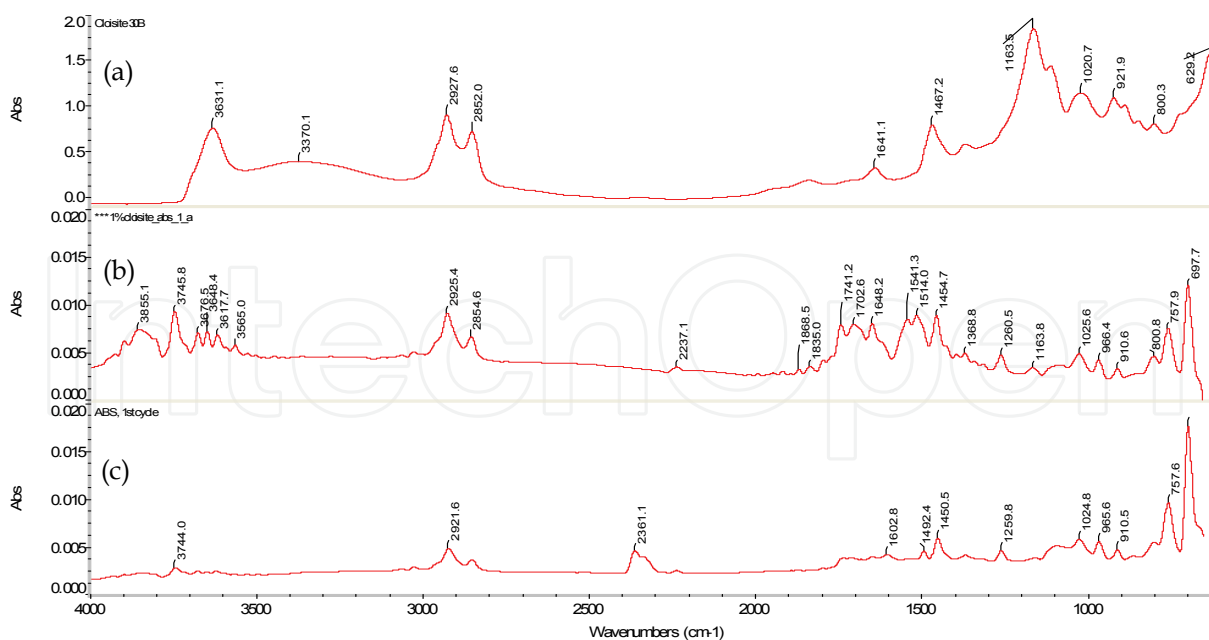
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Fig. 4. ATR-FTIR spectra of (a) Cloisite 30B, (b) ABS and 1% w/w Cloisite 30B/ABS composite and (c) pure ABS.

2.2.4 Color test

The color changes in terms of Lab scale were presented in Table 2. The incorporation of montmorillonite has a clear effect by changing the color texture of pure ABS. The observed changes in red saturation index a, yellow saturation index b and total color change ΔE, may also be the result of degradation phenomena of organic modification of nanoclay occurred during melt mixing.

	ΔL	Δα	Δb	ΔE
ABS	-2.73 ±1.06	0.60 ±0.15	5.25±0.71	6.05 ±0.61
1% w/w Cl 30B/ABS	-5.91 ±1.94	3.62 ±0.66	13.176 ±2.20	14.92 ±2.79

Table 2. The change of total color (ΔE) of 1% w/w OMMT/ABS composites.

2.2.5 DSC

The glass transition temperatures of ABS as derived from the DSC runs, are listed in Table 3. The glass transition of SAN phase was found to be at ~103ºC. The DSC thermographs revealed a fairly constant glass transition temperature (T_g) of 103 (±1) ºC for ABS nanocomposites, which is expected for the SAN-phase of ABS.

	T_g (ºC)	T_{onset}(ºC)	T_{max}(ºC)	Residue %
ABS	102.38	407.29	428.33	2.893
1% w/w Cl 30B/ABS	103.50	403.03	427.33	3.574

Table 3. DSC & TGA results of ABS and 1% OMMT/ABS composites.

2.2.6 TGA

The decomposition temperature of Cloisite 30B is above 300ºC and seems to be initiated by decomposition of the organic modifier. This suggests that during melt processing, which

was carried out around 200ºC, the organic modifier in the clay remains active, facilitating dispersion and further assisting the formation of exfoliated or intercalated structures, as it was somehow confirmed by the XRD patterns. Finally, the char residue increases to about 0.7%, which is obviously a result of the incorporation of the inorganic clay that remains as residue and contributes to the final weight (Table 3). It should be noted that, TGA studies of Yeh et al., 2006 made with ABS nanocomposites in air, have also shown an enhancement of thermal stability as well as an increase of the remaining residue.

Similarly, Patiño-Soto et al., 2007 observed that dispersed clay enhances the thermal stability of ABS, since the intercalated or exfoliated clays display barrier properties against the diffusion of atmospheric oxygen into the material, inhibiting oxidative attack of the system. Similar results were reported by Kim et al., 2008 and the observed effect was attributed to the shielding effect of clay layers. According to Zanetti et al., 2001 the layers of organo-modified silicate are impermeable from small molecules, generated during the thermal degradation process and, therefore, degradation products have to take a long way around the clay layers. According to these authors, the addition of organoclay to polymer matrix is expected to slow down the release rate of decomposed products to endow the degradation products more chance to bind back to undecomposed original polymer matrix. Moreover, given that TGA is a dynamic experiment, another possible reason for the increase in the decomposition temperature of ABS nanocomposites is the increase in viscosity due to the addition of clay, which will inhibit transmission, i.e. it will increase the difficulty for the inward diffusion of oxygen and the outward diffusion of the degradation by-products.

The ABS samples with higher AN content produce a greater increase of decomposition temperature, which was attributed to better clay intercalation-exfoliation, due to the higher polarity brought about by the higher AN content.

Based on the above review of the related literature, we can draw the conclusion that our nanocomposites did not display a clear improvement of their thermal stability because of the insufficient dispersion of nanofiller taking place under the experimental conditions followed in our experiments. In fact, the data obtained from XRD analysis revealed that melt mixing with the operational parameters of this work, did not succeed to produce fully exfoliated structures, which would probably have led to essential improvement of thermal resistance and prevention of thermal degradation during TGA experiments.

2.2.7 Tensile test

From Table 4 it can be seen that the incorporation of Cloisite 30B in ABS does not have any significant effect in tensile strength, but increases the tensile modulus and decreases the elongation at break of the reinforced samples in comparison with pure ABS.

	Tensile strength (MPa)	Modulus of elasticity (MPa)	Strain at break (%)
ABS	50.33 ±1.794	1939.75 ±103.84	12.15 ±5.805
1% w/w Cl 30B/ABS	50.78 ±0.619	2117.91 ± 159.05	6.69 ±2.581

Table 4. Tensile test results of 1% w/w OMMT/ABS composites.

Aalaie & Rahmatroup, 2007 reported a decrease of tensile strength and elongation of ABS/Cloisite 30B nanocomposites , in comparison with specimens of pure ABS. Su et al., 2004 reported a decrease of tensile properties of ABS/clay hybrids despite the intercalated/exfoliated structure formation. On the other hand, Zhang et al., 2006a claim

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that nanocomposite formation did not improve the mechanical properties of ABS reinforced with oligomerically-modified clay with high organic content. They observed in most cases decrease in tensile strength, Young's modulus and elongation at break. In addition, they reported that a plasticization effect of organically modified clay may reduce the mechanical properties of nanocomposites (Zhang et al., 2006b). In case the plasticization from the oligomeric surfactant was suppressed the tensile properties were improved, compared to similar oligomerically-modified clays with higher organic content.

Using different types of surfactant-modified clays for ABS reinforcement, Stretz et al., 2005 observed that the elongation at break decreases and the yield strength remains about the same. However, for some clays, increased MMT content resulted in a slight increase of yield strength. Yeh et al., 2006 found that the incorporation of organoclay platelets into polymer matrix increased the tensile strength of ABS for concentrations up to 3 wt %. Further amounts of organoclay loading (e.g. 5 wt %) were found to decrease tensile strength of the nanocomposite material. On the other hand, elongation at break was decreasing as the organoclay loading increased in the composite.

Interestingly, Kim et al., 2008 reported increase in tensile strength and elongation at break of ABS composites reinforced with unmodified Cloisite 25A and modified with tetrasulfane.

2.3 ABS/PC blends nanocomposites
2.3.1 XRD

The XRD patterns of Cloisite 30B and the 1phr Cloisite 30B/ABS/PC nanocomposite are shown in Figure 5.
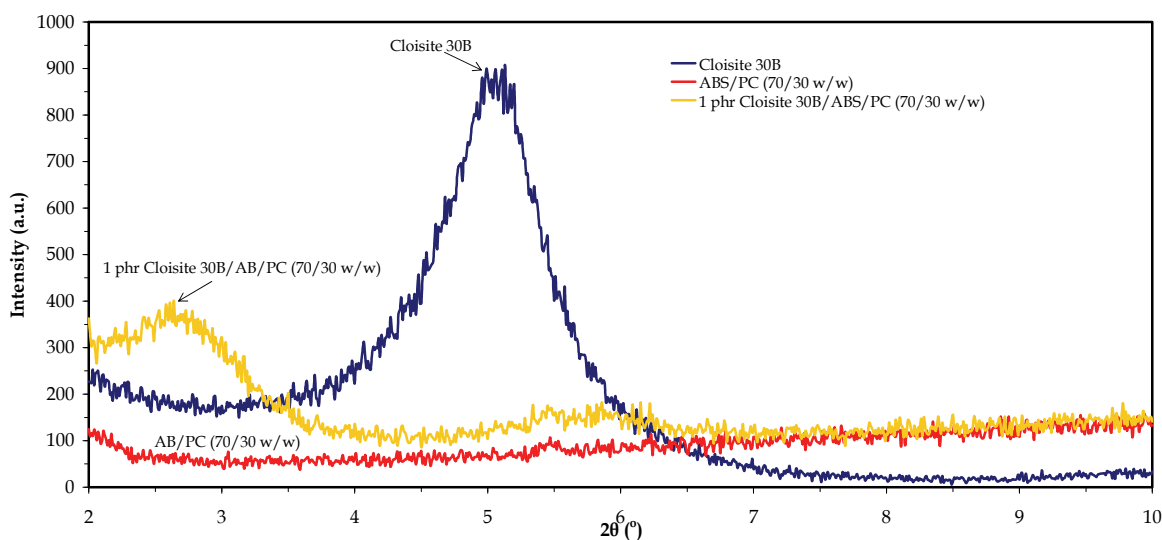

Fig. 5. XRD patterns of Cloisite 30B, ABS/PC and 1% w/w Cloisite 30B/ABS nanocomposite.

It can be observed that the diffraction peaks of silicate clay in the ABS/PC blend nanocomposite shift to lower angle values. The corresponding average basal spacing of MMT increased from 1.8 to 3.36 nm. The XRD results indicated that ABS/PC blend intercalates into the silicate clay layers and enlarges the interlayer spacing of OMMT.

2.3.2 SEM

Microscopic investigation of gold coated surfaces deriving from cryogenic fracture of ABS/PC specimens, as well as of their nanocomposite system containing 1 phr Cloisite 30B,

revealed a slight increase of surface roughness of the later. This probably suggests inhomogenity of filler dispersion, which is consistent with the fact of preferential accumulation of clay nanoparticles in the ABS phase (Hong et al., 2007).
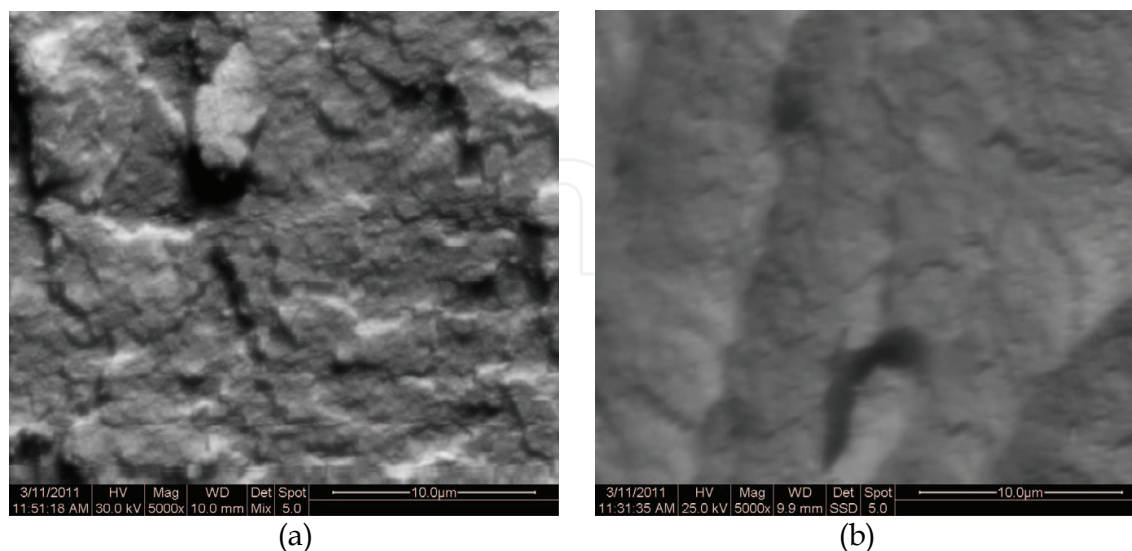

Fig. 6. SEM images of (a) ABS/PC (70/30, w/w) blend and (b) its 1phr Cloisite 30B nanocomposite.

2.3.3 DSC

DSC studies on ABS/PC blends and their nanocomposite containing 1phr Cloisite 30B show a slight increase of the T_g of PC phase, whereas the T_g of ABS phase remains stable (Figure 7).
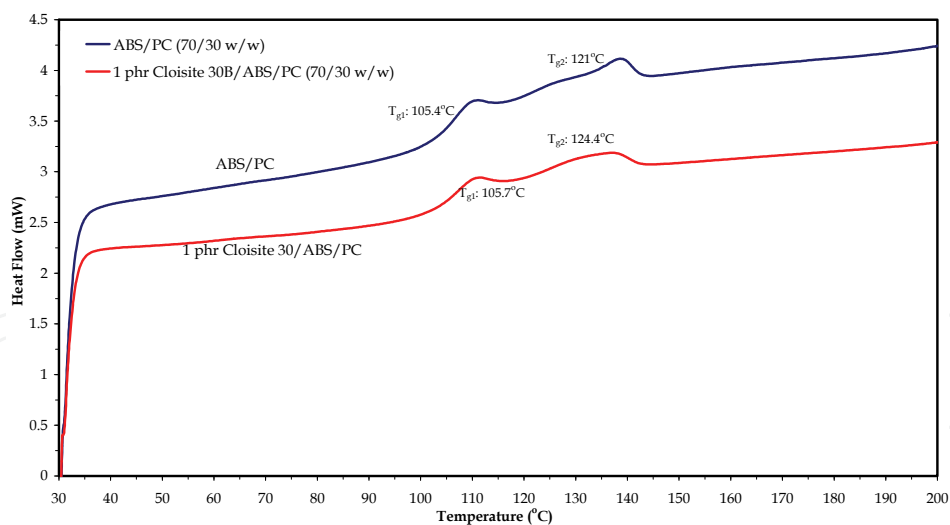
Fig. 7. DSC curves of ABS/PC (70/30 w/w) and 1 phr Cloisite 30B/ABS/PC (70/30 w/w) composite.

Studies on ABS/PC nanocomposites have shown that most of the nanoclay accumulates in the ABS phase and the T_g of this phase is influenced, due to restriction of ABS chain mobility by the presence of reinforcement. Investigation of the T_g changes, performed with Dynamic Mechanical Analysis, revealed a decrease on the height of peak corresponded to ABS phase (Hong at al., 2007).

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2.3.4 TGA

The thermal stability is an important characteristic strongly influenced by the nanocomposite morphology. The decomposition temperature of ABS is about 300-450°C, while PC shows higher thermal stability and decomposes at 500-600°C. It is believed that the thermal degradation of PC/ABS blends consists of several complex processes, such as hydrolysis and thermal degradation, each becoming predominant during different stages of the overall process (Balart et al., 2005).

TGA results for ABS/PC blend, at 70/30 w/w composition, showed that the thermal degradation behaviour of mixture is mainly controlled by the content of ABS, which is the main constituent of the mixture. It can also be observed from Figure 9 and Table 5 that the incorporation of 1 phr montmorillonite in ABS/PC blends improves the thermal resistance especially in the high temperatures zone of thermal degradation. In the case of nanocomposite, an increase in the temperature of maximum thermal degradation rate to about 2°C and a shifting of thermal degradation to higher temperatures were observed. The increase of residue in the case of nanocomposite is related with the presence of clay in polymer matrix that may change the decomposition process of polymer, since the nanodispersed silicate layers contribute to hinder heat transfer within the polymer matrix.
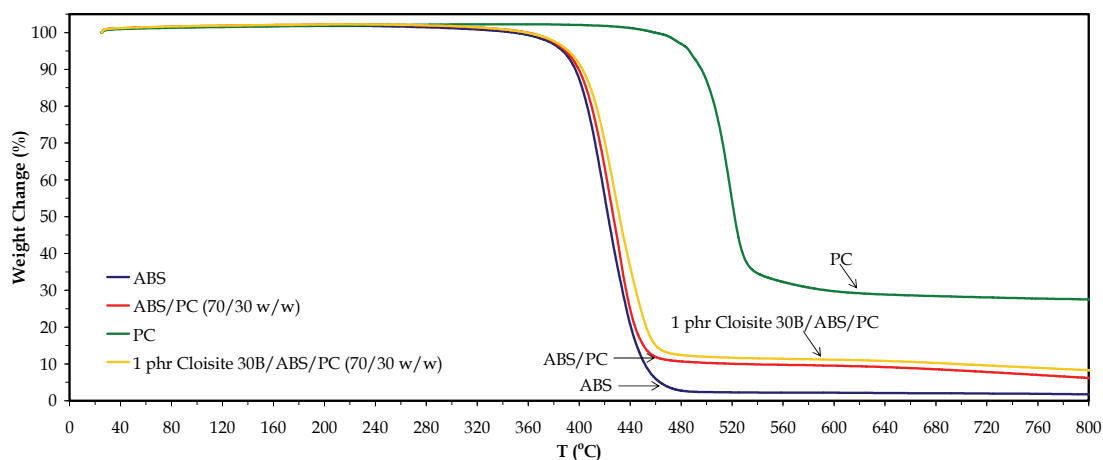

Fig. 8. TGA curves of ABS, PC, of ABS/PC (70/30 w/w) blend and 1 phr Cloisite 30B/ABS/PC (70/30 w/w) nanocomposite.
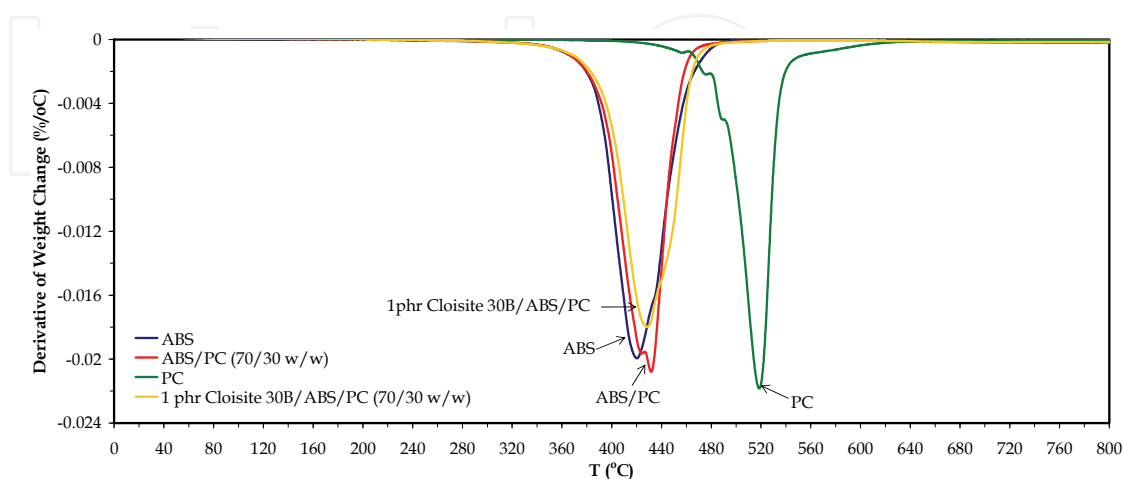

Fig. 9. Derivative of weight change versus temperature of ABS, PC, ABS/PC (70/30 w/w) blend and 1 phr Cloisite 30B/ABS/PC (70/30 w/w) nanocomposite.

Two distinct peaks were observed in TGA graphs obtained from ABS/PC nanocomposites at 434 and 500°C, whereas ABS/PC showed a main peak at 433°C (Wang et al., 2003). The higher peaks were attributed to the nanodispersed silicate layers, which could slow the decomposition and increase the temperature of degradation by acting as an excellent thermal insulator and mass transport barrier, as stated above.

One step of thermal degradation of PC/ABS/OMMT hybrids under pyrolytic conditions was reported by Zong et al., 2005. The onset temperature of thermal degradation was slightly higher for the nanocomposites than for virgin PC/ABS alloy. Under thermo-oxidative conditions PC/ABS alloy and PC/ABS/OMMT hybrids degrade in two steps. In that case, the onset temperature of thermal degradation was not enhanced but charring was increased. The above researchers pointed out the important role of oxygen in the degradation of ABS/PC alloy and ABS/PC/OMMT hybrids. They observed that the onset temperature corresponding to the main degradation was higher under nitrogen than in air for the alloy and nanocomposites. The calculated activation energy for samples in air was smaller than that in nitrogen, indicating that the thermal degradation mechanism was different in these two gases. Enhanced residues in air were also observed in the temperature range 470-540°C, suggesting that oxygen reacted with PC/ABS alloy and/or its degradation products to yield char. Oxygen initiates depolymerization leading to the formation of hydroperoxides, which can yield char. This char undergoes subsequent degradation at high temperatures and as a result, the reaction of oxygen with the polymeric matrix initiates earlier degradation of the material and then, yielding more char, stabilization takes place in a particular temperature range. In the case of nanocomposites, the obtained results suggest that the role of clay is to promote char formation, during the thermo-oxidative degradation of the material, slowing down degradation and providing a transient protective barrier to both mass and energy transport in nanocomposites.

	T_{onset} (°C)	T_{peak} (°C)	Residue (%)
PC	503.8±0.785	524.42±0.099	27.59±0.118
ABS	402.23±0.106	422.64±0.502	0.91±1.280
ABS/PC (70/30 w/w)	408.32±0.806	429.8±0.028	6.47±0.017
1 phr Cloisite 30B/ABS/PC (70/30 w/w)	408.01±0.884	431.3±0.856	8.41±0.035

Table 5. TGA results in PC, ABS, ABS/PC (70/30 w/w) and 1 phr Cloisite 30B/ABS/PC (70/30 w/w) nanocomposite.

The synergistic effect of triphenyl phosphate (TPP) flame retardant and nanoclay reinforcement in improving the thermal resistance of ABS/PC blends was observed by Feyz et al., 2010 using TGA. They also observed that decomposition of PC/ABS is a single step process, whereas decomposition of the flame-retarded PC/ABS having nanoclay is a two step process: the first step takes place in the range of 400-500°C and the second in the range of 500-600°C. The two step decomposition determined with TGA experiments, was attributed to the interaction between nanoclay and the polymeric matrix, leading to changes of the thermal stability of ABS resin. The initial weight loss of ABS/PC/nanoclay occurring at 200°C is related to the thermal decomposition of alkyl ammonium salt present in the nanoclay as a modifier. The decomposition of alkyl ammonium salt causes a delay in the thermal decomposition of the nanocomposite at higher temperatures and by doing this, an increase of the activation energy of the matrix decomposition can be observed in the subsequent steps.

2.3.5 Tensile test

The incorporation of montmorillonite in ABS/PC blend has a positive effect in tensile strength, whereas the modulus of elasticity and strain at break remain almost stable.

	Tensile strength (MPa)	Modulus of elasticity (MPa)	Strain at break (%)
ABS/PC (70/30 w/w)	51.96±0.62	2181.15±103.40	13.04±1.22
1 phr Cloisite 30B/ABS/PC (70/30 w/w)	53.45±0.35	2108.78±129.46	12.44±0.80

Table 6. Tensile test results of ABS/PC (70/30 w/w) and 1 phr OMMT/ABS/PC (70/30 w/w) nanocomposite.

3. Conclusions

The above literature review on polymeric nanocomposites and the presented results deriving from the experimental work on the related systems, can lead to the following conclusions:

The use of nanostructured montmorillonite as a filler for making composites with high performance polymeric systems, such as ABS, PC and their mixtures, is a promising procedure, leading to products with increased scientific and technical significance.

Mixed intercalated or/and partial exfoliated composite structures of organic modified montmorillonite/ABS can be prepared by melt mixing in a twin screw extruder, especially designed for processing thermoplastic melts. Such machines, are today the most powerful melt mixing system for continuous work, whereas internal mixers could be tested alternatively, as batch systems.

Screw rotation speed does not have significant effect in the composite structure, however the second extrusion cycle improves the dispersion efficiency of the system. This suggests, that longer residence time, i.e. a higher L/D ratio in the extruder design would probably be beneficial. It should be noted that the screw geometry must be considered stable for those experiments and the same applies for screw rotation speed, since it controls shear stresses.

No obvious effect of the nanoclay loadings on the T_g of SAN phase in ABS terpolymer was observed. A decrease of the temperature of thermal degradation in the case of nanocomposites was observed and this effect was attributed to the degradation of the organic modification of clay. However, the increase of the amount of residue in the case of nanocomposite indicates a change in the thermal degradation mechanism of ABS, due to the contribution of nanoclay, that seems to have a protective action to the polymer. Improvement of the modulus of elasticity was also observed as a result of organoclay reinforcement.

The incorporation of PC in ABS shifted the thermal degradation of the latter to higher temperature range and this behaviour was further enhanced with the addition of 1 phr nanoclay. DSC thermographs in ABS/PC blend reinforced with 1 phr OMMT showed an increase in the T_g of PC phase, whereas the lower temperature T_g, corresponding to the ABS phase, does not show any change.

The mechanical properties of ABS/PC nanocomposite present an increase, in terms of tensile strength but without any obvious effect in the modulus of elasticity.

All the above results are considered as a very promising option for improving applications of ABS and ABS/PC blends, towards the design of thermally stable materials with improved mechanical performance through the preparation of nanocomposites with

hydrophilic clay by continuous melt blending in a twin screw extruder. Based on the above, the OMMT nanoparticles have shown to act not only as reinforcement for ABS, but also they seemed to play a significant role on the interactions taking place during the thermo-mechanical ageing of ABS that naturally occurs when it takes repeated cycles of melt processing. Therefore, this technology could also be applied for upgrading plastic waste by mechanical recycling.

In future research work, improvement of the nanoclay intercalation in pure ABS as well as in ABS/PC blends should be examined, with special focus on parameters such as the content of ABS terpolymer and molecular weight of PC. In addition the incorporation of a polar compatibilizer like maleic anhydride grafted ABS (MA-*g*-ABS), might also have an interesting effect and, therefore, it also should be examined.

4. Acknowledgment

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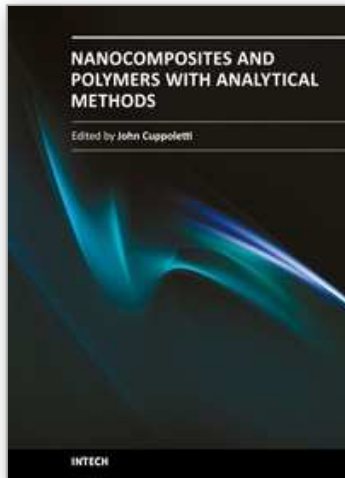
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