ORIGINAL ARTICLE

The effects of processing and using different types of clay on the mechanical, thermal and rheological properties of high-impact polystyrene nanocomposites

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High-impact polystyrene (HIPS) nanocomposites were prepared by melt compounding two grades of organoclays (Cloisite 10A (C10A) and Cloisite 30B (C30B)) in a Haake internal mixer or a corotating twin screw extruder. The nanocomposites were characterized by transmission electron microscopy, small-angle X-ray diffraction, thermogravimetric analysis, rheometer analysis and tensile and impact testing. The correlation between the morphological and the rheological properties of the nanocomposites was also investigated. As the exfoliation of the samples processed by the twin screw extruder was greater than the exfoliation of the samples processed by the Haake internal mixer, the extruded samples were of better quality than the samples subjected to internal mixing. Furthermore, the HIPS nanocomposite material that was prepared with C10A showed better mechanical properties and thermal stability than the HIPS nanocomposite material that was prepared with C30B. By increasing the clay content, it was observed that the zero shear viscosity increased, whereas the initial slope of the storage modulus ($g' = \partial G'/\partial \omega$) decreased. A high degree of clay dispersion was obtained for HIPS samples containing a concentration of 2 wt% C10A with an aspect ratio of 177.1, whereas the exfoliated nanocomposite material had an aspect ratio of approximately 300.

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INTRODUCTION

A polymer nanocomposite material is a polymer matrix with a reinforcing phase consisting of at least one type of particle with nanometer-sized dimensions. Recent studies have focused on the processing of polymer nanocomposite materials in the hope of exploiting the unique properties of materials that are within the nano-sized regime.^{1–8} The key to achieve such performance is in the ability to exfoliate and disperse individual, high aspect ratio silicate platelets within the polymer matrix.^{9–11} Montmorillonite (MMT), the most commonly used clay in such processes, causes the intercalation, exfoliation or formation of micro composite structures because it does not disperse well within the polymer matrix. The hydrophilic nature of a pristine MMT surface and the strong electrostatic interactions between silicate layers impede the movement of the polymer chains, which therefore interrupt the synthesis of the exfoliated nanocomposites. This difficulty can be overcome by using an organoclay, which replaces the interlayer cations such as Na^+ , Ca^+ or K^+ with long alkyl chains. This organoclay has a low surface polarity and an enhanced compatibility with hydrophobic polymers for the production of nanocomposite polymers.^{8,12–16}

Although the use of an organically treated clay can improve the miscibility of the clay with the polymer matrix, the main limitation of such clay is lower thermal stability relative to the high melting

temperatures of many polymers.¹⁷ Polymer nanocomposites may be subjected to high temperatures during melt blending and further processing. Decomposition will occur when the organoclay is not thermally stable at the processing temperature, causing the interface between the organoclays and the polymer matrix to be effectively altered. There has been substantial work conducted on studying the degradation process of organoclays and nanocomposites, which clarifies that the thermal stability of the organoclays is dependent on both the processing conditions and the organic modifier that is used between the silicate layers.

Study by Achilias and group¹⁸ synthesized PMMA nanocomposites using different grades of commercial organically modified clay through *in situ* polymerization. The thermogravimetric analysis (TGA) curve in their results showed that the PMMA/Cloisite 25A nanocomposite material was more thermally stable than the PMMA/Cloisite 30B (C30B) nanocomposite material. They believed that this difference in stability was related to the higher thermal stability of the organic modifier. The Cloisite 25A clay consists of a single tallow with an ethylhexyl side chain, whereas the C30B clay consists of a single tallow with two hydroxyethyl side chains. Su and Wilkie¹⁹ prepared HIPS/organically modified MMT nanocomposites using two oligomeric groups containing either styrene: copolymer of styrene and vinyl benzyl chloride (COPS), or methyl methacrylate: copolymer

of methyl methacrylate and vinyl benzyl chloride (MAPS), as a modifier. The thermal stability of the MAPS system was lower presumably because of its instability in comparison with the COPS system.

Delozer *et al.*²⁰ observed that the decomposition of the organic modifier caused an agglomeration of clay platelets into larger particles during their preparation of polyamide/clay nanocomposite materials. This agglomeration might affect the morphological and mechanical properties of the nanocomposite materials by reducing the interaction between the clay and the polymer matrix. In other works, wide-angle X-ray diffraction (XRD) analyses of polystyrene nanocomposite materials have shown that there were increases in the 2θ degree peak positions relative to the 2θ degree peak positions of the pristine organoclay. Utracki²¹ suggested that a decomposition of the onium intercalants caused a reduction in the height of the interlamellar gallery, and this phenomenon was also observed in other works.^{22,23}

The rheological properties of nanocomposite materials have been extensively investigated because knowledge of the rheological properties possessed by the silicate that is layered with the polymer melt in gaining a fundamental understanding of the processability and structure property relations of these materials. Many articles reported a correlation between the morphological and rheological properties of nanocomposite materials.^{24–27}

Hoffmann *et al.*²⁸ considered the effect of material morphology on the rheological properties of the material. They correlated the slope of the storage modulus to the formation of the network structure. Tanoue *et al.*²⁹ investigated several rheological methods used to detect the degree of clay dispersion in the polymer matrix. They noted that there was a decrease in the initial slope of the storage modulus ($g' = \partial G' / \partial \omega$), and the loss modulus ($g'' = \partial G'' / \partial \omega$) was caused by the increase in G' and G'' at the lowest frequencies, which was a result of forming a three-dimensional structure. They also used the aspect ratio of the clay platelets in the polymer matrix to quantify dispersion.

To the best of our knowledge, the influence of processing conditions such as rotor speed and residence time on the thermal stability of HIPS nanocomposites has not been reported. Although there have been studies investigating the effects of different organically modified clays on the morphology and mechanical and thermal properties of nanocomposite materials, there appear to be no publications that compare the effects of processing and different types of clay on the formation of HIPS-organically modified MMT nanocomposites. Therefore, the aim of this work was to explore the variation in processing conditions for the preparation of HIPS/clay nanocomposite materials using a Haake internal mixer (Thermo Fisher Scientific Inc, Waltham, MA, USA) or a twin screw extruder. Two different commercial organoclays (Cloisite 10A (C10A) and C30B) were employed. The rheological properties of the nanocomposite materials were investigated and the diverse rheological methods for characterizing high-impact polystyrene (HIPS) nanocomposites were also studied.

Figure 1 Alkyl ammonium cations in the C10A clay and the C30B clay.

EXPERIMENTAL PROCEDURE

Materials

HIPS 7240 with a melt flow index of $4.5 \text{ g } 10 \text{ min}^{-1}$ was supplied by the Tabriz petrochemical company of Iran. Organically modified Cloisite clays were acquired from Southern Clay Products, Inc (Gonzales, TX, USA). C10A and C30B are O-MMT-containing quaternary ammonium salts. C10A contains two methyl groups, a benzyl group and a hydrogenated tallow, whereas C30B contains a methyl group, two 2-hydroxyethyl groups and a hydrogenated tallow (as shown in Figure 1). The cation-exchange capacity of the C10A and C30B are reported by the supplier to be 125 and 90 mequiv per 100 g of clay, respectively.

Sample preparation

The organically modified clays were dried overnight in a vacuum oven before compounding. Compounded samples were prepared in two ways. First, the clays were tumble mixed with HIPS and the compounded polymer was then processed in a Haake plastograph internal mixer at 200°C . The processed samples containing C10A and C30B were designated as αRA and αRB , respectively, where α is the weight percent of clays (ranging from 2 to 8 wt%) and R refers to the rotor speed of the internal mixer. Secondly, other samples containing 5 wt% C10A and C30B were prepared using a Brabender corotating twin screw extruder (Duisburg, Germany) with an L/D ratio of 40 at a barrel profile temperature of $175\text{--}200^\circ\text{C}$ and a screw speed of 70 r.p.m. These samples were classified as 5Ae and 5Be, respectively. All compounded samples from the Haake internal mixer and the extruder were injection-molded into the standard tensile bars (ASTM D638, type I) and tested according to the ASTM D256 notched impact test. Rheological samples were prepared discs that had a diameter of 25 mm and a thickness of 1 mm via compression molding at 210°C . The discs were heated for 4 min as a preheating step and then compressed at pressure of 25 MPa for 1 min by a Toyosiki press (Tokyo, Japan).

Measurements

The XRD patterns were obtained with small-angle XRD (S3-micro pix; Hecus, Karlsruhe, Germany) using Cu K α ($\lambda = 1.542 \text{ \AA}$) as the X-ray source. The diffraction angle that was used ranged from 0° to 9° . The morphology of the nanocomposite materials was examined by transmission electron microscopy (TEM) on a Philips CM200 instrument (Amsterdam, The Netherlands) at an acceleration voltage of 200 kV. Tensile tests were conducted with an Instron 6025 instrument (Instron Worldwide Headquarters, Norwood, MA, USA) using a 1-kN loading cell according to the ASTM D638 method at a speed of 50 mm min^{-1} . Impact testing was carried out with a Zwick 5102 pendulum impact testing machine (Ulm, Germany) using a 4-J hammer according to the ASTM D256 method. The TGA was conducted using a TGA-PL instrument at a heating rate of $10^\circ\text{C min}^{-1}$ from 25 to 600°C under an N_2 atmosphere. The rheological properties of the nanocomposite materials were measured on an Anton Paar Physica, MCR300 (Anton Paar company, Graz, Austria), rotational rheometer in the dynamic state. The samples were placed in parallel plates, and different rotational speeds were exerted on the samples to determine their rheological–dynamical properties. The results are shown in figures generated by the US200 software (Anton Paar company). The samples were tested at 200°C using a 10% shear rate at different frequencies ranging from 0.01 to 600 rad s^{-1} .

RESULTS AND DISCUSSION

Small-angle XRD is the primary method for characterizing the morphology of nanocomposite materials. Figure 2 shows the small-angle XRD scans for the HIPS nanocomposites produced from the two different clay grades used. Samples prepared by the Haake internal mixer showed peaks (d_{001}) located at 2θ values $>4.6^\circ$ and $>4.78^\circ$. The absence of peaks at $2\theta <4.6^\circ$ and $<4.78^\circ$ suggests that some organoclay may have been exfoliated. There are two possible explanations for the appearance of the second peak. One possibility is that the intercalant was extracted from the interlamellar space under high shear rates, whereas the second possibility is that there was a

Figure 2 Small-angle XRD (SAXS) variation data for the HIPS nanocomposite materials.

decomposition of the onium intercalant according to the Hoffmann elimination mechanism.²¹ This phenomenon was observed by other researchers, who thought that the annealing process caused the organically modified MMT in the melting process to progressively degrade the alkyl surfactants, which resulted in a collapse of the clay platelets.^{13,23} The second peak was also more dominant for the 5100B sample than the 5100A sample, which indicates that the nanocomposite material containing the C10A clay was more thermally stable than the nanocomposite material containing the C30B clay. According to Figure 1, the surfactant in the C10A clay contains a toluene group, which is more stable than the hydroxyl groups in the C30B clay.

Figure 2 shows the small-angle XRD scans for the samples prepared by the internal mixer operating at different rotor speeds. The second peak for these samples exhibited no changes in location or intensity, which suggested that the shear rate was not a significant factor in causing the collapse of the clay platelets. However, the extruded samples 5Ae and 5Be did not show peaks at $2\theta > 4.6^\circ$ or $> 4.78^\circ$, and there is only one peak in the 5Ae sample scan that can be related to the intercalation structure. This phenomenon shows that thermal degradation is occurring in the internal mixer, which is absent from the extruder because the polymers and clays are mixed in the extruder for a shorter period of time.

As the clay loading was increased for the HIPS nanocomposites, an extremely broad peak was observed to emerge at $2\theta = 3.2\text{--}4.7^\circ$, as shown in Figure 3. This peak was thought to be caused by an increased stacking of regular platelets at higher clay loadings because the volume of the HIPS matrix available for expansion was fixed but the clay loading increased.

The TEM micrographs for the HIPS/C10A and HIPS/C30B nanocomposite materials are shown in Figure 4. These micrographs show the degree to which the silicate layers are dispersed inside the host polymers. The intercalated structures for samples 5100A and 5100B are shown in the TEM images. Although an intercalated structure is present in the micrograph of sample 5100A, some individual platelets within the matrix can also be observed in the micrograph because the material remains thermally stable when it undergoes melt compounding.

Tensile and impact tests were conducted on these materials and the results were tabulated in Table 1. The incorporation of the clay increased the tensile modulus of the modified HIPS notably in comparison with the virgin HIPS, whereas there were no significant

Figure 3 SAXS diffraction data for the HIPS/C30B clay nanocomposite materials produced with different concentrations of C30B clay.

Figure 4 TEM micrographs of the HIPS/organically modified MMT (OMMT) nanocomposites containing (a) 5 wt% C30B clay and (b) 5 wt% C10A clay.

Table 1 The tensile and impact properties of the HIPS polymer and its nanocomposites

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Impact strength (J m^{-2})
HIPS	811.5 ± 64.9	15.95 ± 0.83	52.0 ± 4.8	11.00 ± 0.56
2100B	921.6 ± 102.4	15.48 ± 0.89	24.5 ± 2.9	4.99 ± 0.31
5100B	914.0 ± 98.1	14.37 ± 1.08	24.4 ± 3.1	4.65 ± 0.27
8100B	873.6 ± 107.3	14.11 ± 1.73	18.6 ± 3.6	3.73 ± 0.46
550B	997.8 ± 106.6	14.64 ± 1.21	21.3 ± 2.2	4.40 ± 0.29
5150B	891.0 ± 103.1	14.24 ± 1.37	19.6 ± 1.4	4.46 ± 0.21
2100A	952.2 ± 93.1	16.30 ± 1.11	43.5 ± 4.1	5.68 ± 0.13
5100A	958.1 ± 99.0	16.51 ± 1.43	41.6 ± 5.3	4.91 ± 0.37
8100A	921.3 ± 81.2	15.63 ± 1.32	21.4 ± 3.4	3.85 ± 0.22
5Ae	1032.0 ± 73.1	19.73 ± 0.63	43.4 ± 3.1	6.22 ± 0.60
5Be	971.2 ± 100.8	17.66 ± 1.79	34.7 ± 2.4	6.07 ± 0.49

Abbreviation: HIPS, high-impact polystyrene.

differences in the tensile strength. The enhancement of the tensile modulus at a low clay concentration is attributed to the high resistance exerted by the organoclay against deformation coupled with the stretching resistance of the polymer chains in the galleries.^{1,5} By increasing the clay content in the nanocomposite material, the following two factors may negate the changes in the tensile modulus. The clay particles may form agglomerates, which destroy the adhesion

between the matrix and the filler, thus resulting in a decrease in the tensile modulus. However, the agglomerates are still acting as fillers, which cause an increase in the tensile modulus conversely.⁵ Nevertheless, with a further increase in the organoclay loading from 5 to 8%, a marginal decrease in the tensile strength and the tensile modulus of the nanocomposites was observed. This behavior can most likely be attributed to the interactions between the fillers, which results in the formation of agglomerates and induces a local stress concentration in the nanocomposites, leading to a reduction in the clay aspect ratio and therefore reducing the contact surface area between the organoclay and the polymer matrix.

Other studies^{5,14,30,31} have shown that the elongation at break is greatly decreased upon addition of clay. It can therefore be postulated that the decrease in the impact strength is a result of the organoclay degradation during melt processing, in which the collapsed organoclay structures cause a buildup of stress in the system.³² In contrast, the reduction of impact strength is thought to be a result of the silicate portion existing within the rubber domain, which invalidates its ability to absorb energy when the material is subjected to impacting forces.^{30,32}

A comparison of 550B, 5100B and 5150B suggests that the tensile modulus undergoes the most significant changes of all of the properties analyzed. An increase in the rotor speed during mixing causes the tensile modulus to decrease, and this decline may be attributed to the degradation of the organoclay during melt processing. As the rotor speed is increased during melt processing, the samples experience greater shear rates, which result in an increase in shear heating occurring through blending.³³ Therefore, the shear heat that was produced caused the samples to degrade to different extents, in the order 5150B > 5100B > 550B.

C10A has a better miscibility with HIPS and a lower thermal degradation based on its structure, hence the HIPS/C10A nanocomposite materials are mechanically stronger than the HIPS/C30B materials. This benefit that the C10A clay has over the C30B clay causes more individual platelets to experience intercalation during the formation of the nanocomposite material, thus leading to the HIPS/C10A nanocomposite materials possessing better mechanical properties. The extruded samples also exhibit better mechanical properties, which signify more exfoliation occurring on the material structure during extrusion.

Figures 5 and 6 exhibit curves for the TGA of the nanocomposite materials that were used to determine the loss in sample mass (a) or the differential loss in sample mass (b) as a result of the nanocomposite materials undergoing thermal degradation. The effect of varying the C30B clay loading is presented in Figures 5a and b, and the effect of the type of organoclays added to the HIPS is shown in Figures 6a and b. From both figures, it is clear that the thermal stability of the HIPS/clay nanocomposite materials is substantially improved in comparison with pure HIPS, where the degradation curve is moved to a higher temperature. The effect of the clay in enhancing thermal stability can be explained by the silicate layers with a high aspect ratio, which could hinder the diffusion of volatile degradation matter out of the polymer matrix.^{18,30,34}

From the results included in Figure 5a, it is clear that the temperature where the material is degraded by 10% ($T_{10\%}$) increases by as much as 25 °C with the addition of 2 wt% C30B, whereas a further increase in the C30B clay loading to 5 wt% does not improve the thermal stability of the nanocomposite material significantly. The differential thermogravimetric analysis (DTGA) curves showed a double peak when the HIPS material was undergoing degradation, indicating that there was a degradation mechanism taking place in

Figure 5 TGA (a) and DTGA (b) scans of the HIPS/C30B nanocomposite materials produced with different concentrations of C30B clay.

two separate steps. The first peak is attributed to the degradation of weak links in the polymer chains. It is clear that as the clay content in the nanocomposite material increases to 2 wt%, the first initial step completely disappears, whereas the intensity of the second peak is increased. This phenomenon means that the incorporation of clay with HIPS enhanced the thermal stability of HIPS. However, an increase in the C30B clay content to 8 wt% caused the intensity of the second peak to be reduced, whereas the first peak reappeared, which explains the lower thermal stability of nanocomposite material as a result of clay stack formation.

It can be observed that the HIPS/C10A nanocomposite material had the best thermal stability. Figure 6b shows that the nanocomposite material containing C10A had the greatest peak intensity at higher temperatures. One explanation for this behavior could be the higher thermal stability of the organic modifier, which in the case of the C10A clay consists of a single hydrogenated tallow with a benzyl group, whereas the C30B clay consists of a single tallow with two ethanol groups. Finally, it was noticed that HIPS nanocomposite materials produce more charred residues than is expected from the inorganic clay, which is related to the presence of butadiene in HIPS.³¹ The amount of residual matter left by the nanocomposite materials was found to increase with increasing clay content in the polymer matrix because the quantity of inorganic matter in the nanocomposite materials was also increased.

Understanding the rheological properties of the nanocomposite materials is important for developing useful applications for the materials as well as the necessary processing steps. Figure 7 shows the

Figure 6 TGA (a) and DTGA (b) scans of HIPS nanocomposite materials containing various OMMTs. The amount of clay added was 5 wt% C10A and 5 wt% C30B.

Figure 7 Complex viscosity as a function of angular frequency for the HIPS nanocomposite materials. -- 8100A, --♦-- 5100A, --▲-- 5100B, --■-- 2100B and — HIPS.

complex viscosity (η^*) as a function of angular frequency (ω) for the HIPS/organically modified MMT nanocomposite materials at 200 °C. It can be seen from Figure 7 that the complex viscosity decreases substantially with an increasing angular frequency, but increases monotonically with the loading of C30B clay. By increasing the C30B clay content from 2 to 8 wt%, the Newtonian plateau region

Figure 8 Storage modulus as a function of angular frequency for the HIPS/OMMT nanocomposite materials. --▲-- 8100B, --●-- 5100A, --■-- 5100B, --♦-- 2100B and --*-- HIPS.

Figure 9 Storage modulus as a function of the loss modulus for the HIPS/OMMT nanocomposite materials at 200 °C. --■-- 8100B, --●-- 5100A, --▲-- 5100B, --*-- 2100B and --♦-- HIPS.

decreases, and the polymer experiences a transition from Newtonian to power law behavior at a lower frequency. The 5100A sample has a higher viscosity than 5100B, possibly because there is a higher affinity of the C10A modifier for the HIPS polymer, which enhances the interfacial interaction. The complex viscosity decreases irregularly with an increasing frequency, indicating a shear thinning effect caused by the orientation of the silicate layers parallel to the flow direction.^{24,26}

Figure 8 shows how the storage modulus (G') varies as a function of the angular frequency. The storage modulus exhibits a similar trend when compared with the complex viscosity, where the values of the storage modulus for all blends studied at all frequency regions increases with increasing clay content. This enhancement is more dominant at low angular frequencies, but an increase in the storage modulus was detected in comparison with the neat HIPS at a higher angular frequency, indicating that the segmental motion of the polymer matrix determines the material response at short time scales.

However, the storage modulus of the 5100A nanocomposite material is higher than the storage modulus for the 5100B nanocomposite material, confirming that the C10A modifier effectively improves the interfacial adhesion between the dispersed clay and the HIPS polymer matrix.

Figure 9 shows a comparison of G' as a function of G'' for the HIPS/organoclay nanocomposite materials at 200 °C. It can be seen from Figure 9 that all of the blends are viscous in the low frequency region but indicate elasticity in the intermediate frequency region. Moreover, this figure shows that the addition of clay enhances the elasticity of the material. The 8100B sample shows a lower slope and a higher elasticity than other materials, as has been confirmed by previous results. It is expected that the 8100B sample crosses the bisector at a lower frequency than the other materials, except for the virgin HIPS sample, which indicates that the virgin HIPS material is more elastic than the other nanocomposite materials within the intermediate frequency region. The low elasticity of the nanocomposite materials may be caused by the phenomenon that the interaction of the clay with polymer chains results in a more dissipative response at intermediate frequencies.³⁵

Rheological measurements at low frequency provide substantial information for the characterization of the nanocomposite materials. These measurements are also more beneficial for processing the nanocomposite materials than the more commonly used XRD and TEM methods. XRD and TEM are traditional methods for investigating the degree of intercalation, exfoliation and dispersion of clay in nanocomposite materials. Although both of these methods are effective tools, they can probe only a small volume of the sample and can be costly for the routine characterization of nanocomposite materials. Moreover, neither XRD nor TEM can precisely determine the levels of clay dispersion within the nanocomposite material structure. Therefore, researchers have used multiple techniques such as a combination of XRD, TEM and another technique that can adequately characterize a system. The melt rheology of the polymer could quantify the degree of dispersion across the whole test specimen of the nanocomposite material, which usually contains approximately 2 g of sample. In this work, two rheological methods for detecting the degree of clay dispersion were used.

Some researchers have focused on calculating the values of the initial slope of the storage modulus ($g' = \partial G' / \partial \omega$) and the loss modulus ($g'' = \partial G'' / \partial \omega$), as indicators of clay dispersion.^{25,28,35} They consider the values of g' and g'' to represent the extent of interaction between the organoclay platelets and the polymer chains. The slope of the storage modulus is expected to have a value of 2, whereas the slope of the loss modulus is expected to have a value of 1 for monodispersed polymers,²⁶ which decreases to 0 for three-dimensional nanocomposite structures.^{30,35} Table 2 shows the slope of the storage modulus for HIPS and HIPS nanocomposites. The value of g' for HIPS is reported to be 1.42, with the deviation from a theoretical g' of 2 resulting from the polydispersity of HIPS. The decrease in g' when clay is loaded is a result of the clay forming a nanocomposite three-dimensional structure. The formation of a three-dimensional structure originates from the interactions occurring between clay platelets within the polymer matrix in a polymer clay nanocomposite.²⁹ The C10A clay also has a greater effect on decreasing the initial slope because it experiences more interactions with the HIPS polymer matrix. Moreover, the extruded samples also possess lower initial slopes in comparison with the samples that were mixed in the Haake mixer, which confirmed that the extruded nanocomposite materials contained more exfoliated clay platelets and a more effective aspect ratio.

The preparation of polymer/clay nanocomposite materials can be considered to be a dispersion of clay platelets in molten polymer. Therefore, the aspect ratio of clay, which can vary from $P \cong 1$ to a value of approximately 300²⁹ (a common value for commercial

Table 2 The initial slope of the G' modulus for the HIPS nanocomposite materials

Sample	g' (Pa.s)
HIPS	1.42
2100B	0.94
5100B	0.90
8100B	0.67
2100A	0.83
5100A	0.76
8100A	0.59
5Be	0.81
5Ae	0.63

Abbreviation: HIPS, high-impact polystyrene.

Table 3 The aspect ratio of clay platelets for the HIPS nanocomposite materials

Sample	ϕ	η_0 (Pa.s)	$[\eta]$	P
HIPS	—	12181	—	—
2100B	0.0106	17312	39.7	144.0
5100B	0.0258	21663	30.17	117.8
8100B	0.0437	39556	51.43	173.5
2100A	0.0110	19278	52.97	177.1
5100A	0.0280	25943	40.35	145.7
8100A	0.0454	45522	60.29	194.2
5Be	0.0258	24711	31.66	122.0
5Ae	0.0258	28941	43.71	154.4

Abbreviation: HIPS, high-impact polystyrene.

organoclays) could be used to determine the level of clay dispersion in the nanocomposites.

Several theoretical and empirical relations exist for calculating the aspect ratio. For discs, the following relations were proposed:²⁹

$$[\eta] = 2.5 + a(p^b - 1) \quad (1)$$

where $a = 0.025 \pm 0.004$ and $b = 1.47 \pm 0.03$. $[\eta]$ is the intrinsic viscosity, which in its simple form is given by an Einsteinian relation for the relative viscosity of a hard sphere suspension:²⁹

$$\eta_r \equiv \frac{\eta}{\eta_0} = 1 + [\eta]\phi + O(\phi^2) \dots \quad (2)$$

where ϕ is the volume fraction of dispersed solid and η and η_0 are the zero shear viscosities of the nanocomposite material and the polymer matrix, respectively.

The Carreau–Yasuda model was used to extrapolate the viscosity of each material to its zero shear limits.³⁶ The extrapolated zero shear viscosity data were used to calculate the intrinsic viscosity and the aspect ratio of the organoclays.

$$\eta = \frac{\eta_0 - \eta_{\text{inf}}}{[1 + (\lambda\dot{\gamma})^a]^{(1-n)}} \quad (3)$$

where η_0 and η_{inf} refer to the zero shear viscosity and infinite shear viscosity, respectively, and a , n and λ are the width of the transition range between the zero shear viscosity and power law region, power law exponent and relaxation time, respectively.

As the degree of particle symmetry decreases, the aspect ratio (P) increases, as shown in Table 3. The 2-wt% C10A clay nanocomposite

Figure 10 Relaxation time spectra of the HIPS/OMMT nanocomposite materials at 200 °C.

material has the highest aspect ratio, which means that it has the highest exfoliated structure. However, an increase in the clay content to 5 wt% decreases the aspect ratio, which shows that there are interactions between fillers and that stacks are also formed. The C10A nanocomposite materials also demonstrate higher aspect ratios than their C30B nanocomposite material counterparts, which is attributed to a higher count of individual platelets in the C10A/HIPS nanocomposite materials. The extruded samples have higher aspect ratios than the samples treated by internal mixing, which denotes more individual platelets with a well-defined particle density, confirming that the clays experience less agglomeration in the extruder than in the internal mixer.

The relaxation time spectra provided more information about the miscibility of the organoclays with the polymer matrix. Figure 10 shows the relaxation time spectra $H(\lambda) \cdot \lambda$ as a function of λ (relaxation time) for the HIPS nanocomposite materials at 200 °C was calculated from the experimental storage modulus data obtained by a nonlinear spectrum calculation method, available in the US200 rheometer software. The location of the maximum point in the resulting curves was selected as the relaxation time for the polymer chains.³⁷ Furthermore, the relaxation time increased as the C30B clay content in the nanocomposite material increased from 2 to 8 wt%. This time increase is attributable to an enhancement of the interactions occurring between the organoclay and the polymer chains and to the confinement of the motion and the relaxation of the polymer chains.³⁸ An increased relaxation time means that non-Newtonian flow commences at a lower frequency, which also means that the material exhibits a smaller Newtonian region.²⁷

CONCLUSIONS

In this study, the effects of melt processing on the morphological, mechanical and rheological properties of HIPS nanocomposite materials based on the addition of two different organoclays were investigated. The nanocomposite materials were prepared separately in a Haake internal mixer and a corotating twin screw extruder. TEM and XRD analysis show the development of an intercalated structure in the materials processed by both the internal mixer and the extruder, and exfoliation was likely to occur during extrusion. The HIPS/C10A nanocomposite materials possessed higher tensile moduli and greater mechanical strengths than the HIPS/C30B nanocomposite materials because the C10A clay had a stronger affinity for the polymer matrix. The extruded samples possessed higher ultimate

tensile strengths, moduli and impact resistances in comparison with the samples that were prepared in the Haake mixer, originating from the presence of more exfoliated clay platelets in the polymer matrix and less thermal degradation occurring. The impact strength was reduced in all samples because of the clay in the nanocomposite materials interacting with the rubber domains. The incorporation of clay into the HIPS polymer enhances the thermal stability of the HIPS polymer. The C10A nanocomposite materials exhibit a higher thermal stability than the C30B nanocomposite materials; this stability is related to the modifier present in C10A, which is more temperature-resistant. By increasing the clay content in the nanocomposite materials, the zero shear viscosity and storage modulus increases and the initial slope of G' decreases. The C10A nanocomposite material containing 2 wt% C10A has the highest aspect ratio of all of the samples, which also means that its structure has the most exfoliation of all of the samples synthesized.

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