Swelling of organoclays in styrene. Effect on flammability in polystyrene nanocomposites

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Abstract. In this work the effect of the compatibility between organoclays and styrene on the flammability of polystyrene/clay nanocomposites obtained through *in situ* incorporation was investigated. The reactions were carried out by bulk polymerization. The compatibility between organoclays and styrene was inferred from swelling of the organoclay in styrene. The nanocomposites were characterized by X-ray diffraction and Transmission Electron Microscopy. The heat release rate was obtained by Cone Calorimeter and the nanocomposites were tested by UL94 horizontal burn test. Results showed that intercalated and partially exfoliated polystyrene/clay nanocomposites were obtained depending on the swelling behavior of the organoclay in styrene. The nanocomposites submitted to UL94 burning test presented a burning rate faster than the virgin polystyrene (PS), however an increase of the decomposition temperature and an accentuated decrease on the peak of heat release of the nanocomposites were also observed compared to virgin PS. These results indicate that PS/clay nanocomposites, either intercalated or partially exfoliated, reduced the flammability approximately by the same extent, although reduced the ignition resistance of the PS.

Keywords: nanocomposites, flammability, polystyrene, organoclay, swelling

1. Introduction

In situ incorporation is an effective route to obtain polystyrene/clay nanocomposites [1–10]. Nonetheless, the compatibility between monomer and organoclay is a critical factor in determining the microstructure of nanocomposites obtained through *in situ* incorporation [1]. A good compatibility between monomer and organoclay is fundamental to disperse the clay in the reaction medium, avoiding its agglomeration. In addition, the penetration of the monomer into the basal space of lamellae allows the entrance of oligomeric radicals and the consequent intercalation of lamellae with polymer. If the separation of the lamellae is high enough, delamination (exfoliation) occurs.

Liauw *et al.* [2] had measured the swelling volume and the viscosity of organoclays in toluene considering that the compatibility of organoclays with styrene can be considered in the same way as with toluene and therefore can be a predictor of state of clay dispersion within the resulting composite. Fu and Qutubuddin [1] determined the swelling behavior of organoclays in styrene comparing wettability and rheology measurements and observed that the organoclay prepared with a styryl group had the highest compatibility with styrene and formed exfoliated polystyrene nanocomposites while the organoclays that presented weaker interaction formed intercalated polystyrene nanocomposites after polymerization of styrene and organoclay

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mixtures. Similar results were observed by Arioli *et al.* [3] when comparing the swelling volume of organoclays in styrene. The higher the swelling volume the higher the degree of organoclay exfoliation in polymer matrix after polymerization of styrene in the presence of organoclay. The use of other solvent mixtures (tetrahydrofuran and water) resulted in different clay intercalation with styrene-vinylpyridine (SVP, 36.40 wt% styrene and 63.60 wt% 4-vinylpyridine) block copolymers in the *in situ* formation of polystyrene/clay nanocomposite and the most effective exfoliated nanocomposite, showed the highest thermal stability and the best dynamic mechanical responses [11]. The significant enhancement of both tensile and flexural strength in polymer/clay nanocomposites is usually attributed to the delaminated clay formation [12].

The good dispersion of clay produces a substantial improvement in fire performance in polymeric matrices such as polystyrene [10, 13–18] at least in terms of peak heat release rate (Peak HRR) accessed by cone calorimeter. The suggested mechanism by which clay nanocomposites reduce the heat release rate involves the formation of a char that serves as a barrier to both mass and energy transport [10]. According to Levchik and Weil [19] flame retardancy achieved with nanocomposites alone is not enough for the ignition resistance inferred by the UL-94 test and they suggest a better approach to combine the nanocomposite with another flame retardant, such that the nanocomposite provides the base reduction in flammability, and the secondary flame retardant provides the ignition resistance. Several papers [20–22] investigated the effect of the chemical and physical structure of polymer/clay interfaces on the flammability of polymer composites and nanocomposites. Some of these papers showed that the clay/polymer nanocomposite improved not only the cone calorimetry results, but the UL94 performance as well. One of the reasons is the increase of viscosity caused by clay that arrests the dripping of the polymer during burning which is reflected by the UL94 rating [21]. The objective of this work is to investigate the correlation of the compatibility between monomer and organoclay and the flammability properties of the polystyrene/clay nanocomposite obtained through *in situ* incorporation. To attain this objective, different organoclays were incorporated to the polymer matrix through styrene bulk polymerization.

The compatibility between organoclays and styrene was inferred from swelling of the organoclay in styrene. The nanocomposites were characterized and the thermal stability and flammability were studied.

2. Material and methods

Styrene was provided by Innova S.A., Brazil, with a purity about 99.6% and inhibitor (p-terc-butylcatechol) concentration equal to 12 ppm. Benzoyl peroxide (BPO) with 75% of active oxygen P.A. grade (Elf Atochem Chemicals, USA) was used as initiator. The montmorillonite (MMT) containing exchangeable cations of primarily Na^+ was provided by Southern Clay Products, USA. The organoclays were prepared and supplied by Southern Clay (Cloisite 10A and Cloisite 15A), USA, and by SüdChemie (Nanofil 15), Germany. All reactants, including the clays, were used as received, without any previous treatment. The Cloisite 10A and Cloisite 15A clays were the SWy-1 montmorillonite modified by 2MBHT (dimethyl-benzyl-hydrogenated-tallow, quaternary ammonium) and 2M2HT (dimethyl-dihydrogenatedtallow, quaternary ammonium), respectively. The hydrogenated tallow was a mixture of ~65% of C18, ~30% of C16 and ~5% of C14 and the anion was the chloride. The Nanofil 15 clay was a montmorillonite modified with C18 chains (distearyl-dimethyl ammonium chloride).

2.1. Bulk polymerization

At first 3.0% of clay in relation to the total mass of polymer was dispersed in styrene (S) during two hours under vigorous stirring (1200 rpm) in a jacketed reactor at 25°C. This step was conducted to allow the dispersion and swelling of the clay with the styrene. After this initial dispersion step, the reactor temperature was raised up to 90°C and initiator (0.5% w/w related to the total mass of monomer) was added to the reaction medium. Reaction was kept at 90°C for 2 hours after which the reaction medium was transferred to an aluminum vessel and immersed in an oil bath with a gradual temperature increase (20°C/hour) up to 180°C, maintained for 2 additional hours. Nitrogen was fed to the reactor during the whole reaction to avoid inhibition by oxygen.

2.2. Characterization

The swelling volume of organoclays in styrene was measured using a 100 ml measuring cylinder. The sample (1.0 g) was sprinkled onto the styrene surface (100 ml) and it slowly fell to the bottom of the cylinder. The swelling volume was recorded after 24 h (a swelling equilibrium was reached by this time). XRD patterns of organoclays and polystyrene nanocomposites were obtained by using Philips X'Pert X-ray diffractometer, with a Cu tube source (wavelength λ of 1.54056 Å) operated at 1 kW. Transmission electron microscopy (TEM) images of polystyrene/layered silicate (clay) nanocomposites were obtained at 100 kV, with a JEOL electron microscope. The samples were ultramicrotomed with a diamond knife on a Leica Ultracut UCT microtome at room temperature to give 70 nm thick sections. The sections were transferred to carbon-coated Cu grids of 200 mesh. The contrast between the layered silicates and the polymer phase was sufficient for imaging, so no heavy metal staining of sections prior to imaging was required.

Thermogravimetric analyses (TGA) were conducted on a Shimadzu TGA-50 equipment, under inert atmosphere with a N₂ flux of 50 ml/min and heating rate of 10°C/min, until the final temperature, 600°C, was reached. The horizontal burning test UL94 [23] was conducted according to the ASTM D635 procedure [24]. The dimension of the standard bar samples were 125×13×3 mm. The flammability data reported here were the averages of five samples. Combustion behavior was assessed according to the ASTM E 1354 [25] procedure in a Fire Testing Technology (FTT) dual cone calorimeter apparatus. During the test, the materials were subjected to irradiated heat plus the feedback heat from the flame starting from the ignition of the volatile products (ignition time). The aim was to simulate the conditions likely to occur in a real fire [26]. The samples were irradiated at 35 kW/m², and the data were collected for the first 250 s, this being regarded as representative of the initial stage of a fire when it can still be stopped before becoming uncontrollable after flashover. The exhaust gas flow rate was 24 l/s. The heat released was calculated from the consumption of oxygen due to combustion. The analysis by cone calorimeter gives the ignition time (T_{ig}), the heat release rate (HRR) and its peak value (Peak HRR), the average value of heat release rate over the entire heat release rate

curve for the material during combustion of the sample (Avg HRR) and the total heat release.

3. Results and discussion

Swelling tests were performed in order to characterize the organoclays in respect to their affinity towards styrene. The values of swelling of the three tested clays might be observed in Table 1. According to the results shown in Table 1, two samples (Nanofil 15 and Cloisite 15A) presented moderate swelling values, whereas clay Cloisite 10A presented the highest value. The naturally occurring Na-MMT did not swell in styrene. The higher the swelling volume, the higher the compatibility between the organoclay and styrene. All clays tested in this work were montmorillonite modified with quaternary ammonium salts. The salts used to modify the organophilicity of the clays Nanofil 15 and Cloisite 15A presented dimethyl-dehydrogenated-tallows, being the tallow of Cloisite 15A a mixture of ~65% of C18, ~30% of C16 and ~5% of C14 and the tallow of Nanofil 15 clay was composed by C18 chains. As the swelling value provides an information about the affinity of the clay towards the monomer, Cloisite 10A presented the higher swelling value as its quaternary ammonium salt was composed by a dimethyl-benzyl-hydrogenated-tallow that presents a high compatibility with styrene as observed before by other authors [1, 2]. Similar results were obtained by Fu and Qutubuddin [4] that observed that montmorillonite modified with vinylbenzyl dodecyl dimethyl ammonium chloride gave the highest styrene dispersion viscosity by a wide margin (more than 10 times), when compared to montmorillonite clays modified with quaternary ammonium salts featuring alkyl chains of C16 to C18. The high degree of styrene compatibility afforded by the styryl group of the quaternary ammonium salt illustrates the importance of matching monomer/polymer structure to that of the intercalant [2].

Table 1. Swelling volumes of Na-MMT and organoclays in Styrene at 25°C

Clay	ml clay/100 ml Sty
Na-MMT	–
Cloisite 10A	26
Cloisite 15A	12
Nanofil 15	15

Figure 1. XRD patterns of clays

The interlamellar layer (d) of the clay was measured by X-ray diffraction (XRD). The d_{001} spacing of clay particles was calculated according to Bragg's law where $d = \lambda/2\sin(\theta)$ at peak positions. The wave-length (λ) of X-ray is 1.5418 Å. In Figure 1 it is possible to observe that all organoclays show sharp peaks and the peak positions shift to lower angles when compared to natural occurring montmorillonite (Na-MMT) which contains exchangeable cations of primarily Na^+ . Nanofil 15 and Cloisite 15A presented different diffractograms, although the values of d_{001} spacing (3.03 and 3.07 nm, respectively) were quite similar. The diffractograms of both clays presented a small peak around 1.2 nm that do not correspond to d_{002} spacing and seems to be quite similar to the crystallographic spacing of Na-MMT (1.18 nm). This means that both clays could contain small amounts of tactoids with clays platelets intercalated with cations of Na^+ . Cloisite 10A presented just a single peak corresponding to a d_{001} spacing value of 1.91 nm.

In order to determine the effect of the swelling volume of the clay in the monomer, the styrene dispersions were polymerized *in situ*. XRD and TEM were used to characterize the dispersions of the organoclays in polystyrene (PS). The *in situ* incorporation of Na-MMT resulted in a very heterogeneous composite, when the stirring of the reaction medium was stopped the Na-MMT clay sedimented to the bottom of the reaction vessel. No further analysis was performed on this resulting composite. On contrary, the organoclays were very well dispersed in the polystyrene matrix. Figure 2 shows

Figure 2. XRD patterns of nanocomposites

the diffractograms of the resulting nanocomposites. No clearly defined peak can be observed in the curve of PS/Cloisite 10A nanocomposite indicating that the clay could be delaminated. The PS/Cloisite 15A nanocomposite presented the displacement of the peak to 2.58° , corresponding to a basal spacing of 3.42 nm. This means that an increase of the interlayer distance has occurred by PS polymer chains polymerized in the interlayer of clay platelets. A similar diffractogram was observed for PS/Nanofil 15 nanocomposite with a well defined peak at 2θ equal to 2.91° ($d_{001} = 3.38$ nm). These results indicate that both nanocomposites (PS/Cloisite 15A and PS/Nanofil 15) presented an intercalated structure.

TEM micrographs of the nanocomposites show similar dispersion of all clays in polystyrene. The thin dark lines of Figure 3 suggest that some clay layers of the organophilic clays are exfoliated in polystyrene, while other layers have intercalated structure as it is possible to observe MMT stacks dispersed in polymer matrix. TEM and XRD results suggest that the nanocomposite PS/Cloisite 10A was partially exfoliated whereas the nanocomposites PS/Cloisite 15A and PS/Nanofil 15 presented a predominant intercalated structure.

Thermogravimetric analysis: The TGA data of the samples (Figure 4) showed that the polymer nanocomposites, decompose at higher temperatures compared to virgin PS. The temperature at which 5% degradation occurred, representative of the onset temperature of degradation, and the midpoint degradation temperature, corresponding to the temperature at which the weight loss of the sample

Figure 3. TEM micrographs of the nanocomposites: PS/Cloisite 10A (a), PS/Cloisite 15A (b) and PS/Nanofil 15 (c)

Figure 4. TGA of virgin polystyrene (PS) and of PS/clay nanocomposites

attains 50%, were found to be highest for PS/Cloisite 15A (410.6 and 464.5°C, respectively). The higher degradation temperatures may probably be attributed to extensive interaction of PS with nanodispersed and large surface area organophilic clays that resulted in inhibition of the diffusion of the decomposed product in the polymer matrix. Although all nanocomposites (PS/Cloisite 10A, PS/Cloisite 15A and PS/Nanofil 15) had high mid-point degradation temperatures (459.8, 464.5 and 457.6°C, respectively), when compared to virgin PS (418.1°C), nanocomposite PS/Cloisite 10A lost initial 5% weight at a temperature (382.2°C) just 5.8°C higher than virgin PS (376.4°C).

UL94 test: The results of the flammability analysis assessed by UL94 horizontal burning test are presented in Table 2. These results show that the burning rate was faster for the nanocomposites than for the virgin polystyrene. Similar result was previously reported by other authors that credit the poor UL94 performance of the clay/polymer composite to the presence of the compatibilizers present in the organoclays. These compatibilizers are added to the clay in order to increase the affinity of the clay for the monomer. As UL94 burning test should be regarded primarily as an ignition test and since the

Table 2. Burning rate (UL94)

Sample	Burning rate [mm/min]
PS	12.9
PS/Cloisite 10A	21.2
PS/Cloisite 15A	27.1
PS/Nanofil 15	16.7

organoclays shorten the ignition time they can degrade UL94 performance [27, 28]. Nevertheless, a very different behavior was observed during the burning of virgin PS and PS/organoclay nanocomposites, as during the burning of PS/organoclay nanocomposites, a char structure was formed and no dripping was observed, whereas during the burning of virgin PS specimen dripping of melted polystyrene in flame was constant.

Cone calorimeter: The heat release rates (HRRs) of the virgin polymer (PS) and the nanocomposite (PS/organoclay) during the combustion tests are shown in Figure 5. When the organoclays are present, the ignition time (T_{ig}) decreases from 66 to 52–59 s (see Table 3). Just after ignition, however, the virgin polystyrene heat release rate (HRR) increases much more quickly. The heat release rate of the PS overtakes that of the nanocomposite after 60 s of T_{ig} (HRR = 600 kW/m²), peaks at 1303 kW/m² after 202 s of T_{ig} , and then falls very sharply after 240 s of T_{ig} . The heat release rate of the composite rises regularly to a maximum of 663–704 kW/m² after 171–178 s of T_{ig} . Reduction of the peak heat release rate is a typical feature of polymer layered silicate nanocomposites, as reported in the literature [14–18]. The combustion behavior of the nanocomposite is due to a reduction in the mass loss rate, compared to that of the poly-

Figure 5. HRR of virgin polystyrene (PS) and of PS/clay nanocomposites

mer. This greater thermal stability stems from the chemical and physical action of the crystalline layers of the silicate dispersed in the matrix that inhibited the diffusion of the decomposed product in the polymer matrix. Thermal decomposition of the organically modified montmorillonites starts at around 200°C and proceeds according to the Hofmann degradation mechanism [19]. The decomposition products are combustibles that feed the combustion in the flame. Despite a larger heat release rate in the early stage of combustion, the nanocomposite shows an improvement of fire behavior compared to those of the virgin polymer (Table 3). The average heat release rate (Avg. HRR) decreases from 807 kW/m² (virgin PS) to 448–475 kW/m² (PS/organoclay).

During the cone calorimeter analysis it was observed that once the virgin PS specimen ignited the sample surface did begin to boil rapidly as the polymer burned away, but the flames were steady (not turbulent) as the material burned. After burning no significant char was noted, just some soot and ash in the aluminum sample pan. Whereas for the nanocomposites, once sample ignited the flames were steady and no boiling of polymer underneath the flame front was noted. Formation of condensed phase char was noticeable during the entire burning process. The final char was black and highly cracked, with the aluminum foil clearly seen underneath (see Figure 6). The fire behavior of the nanocomposite PS/Nanofil 15 was identical to that of the others nanocomposites but the char was more pronounced and could be seen sticking up in the flame front area as the sample burned. Char formation is good for fire retardancy purposes as the char prevents the entry of flammable gases into the gas phase and insulates the underlying polymer from the flame [29].

Char formation in cone experiments corroborates the observations during UL94 tests, where a char structure formed during burning was observed for the nanocomposites but not for the virgin PS. The apparently contradictory results of cone calorimeter and UL94 horizontal burning test regarding the

Table 3. Results of the cone calorimeter analysis

Sample	Time to ignition [s]	Time to peak [s]	Peak HRR [kW/m ²]	Avg. HRR [kW/m ²]
PS	66	202	1303	807
PS/Cloisite 10A	59	171	704	475
PS/Cloisite 15A	52	178	669	461
PS/Nanofil 15	55	175	663	448

Figure 6. Pictures of the residues of nanocomposites after the cone experiment. a) PS/Cloisite 10A, b) PS/Cloisite 15A, c) PS/Nanofil 15 (pictures size of 75×75 mm)

flammability of the nanocomposites could be explained because UL94 is primarily an ignition test. The thermal degradation of the excess of quaternary ammonium surfactants used to disperse the clays form flammable volatile vapors increasing the probability of early ignition, this behavior was observed in the reduced time to ignition measured by cone calorimeter.

Results indicate that intercalated and partially exfoliated polystyrene/clay nanocomposites presented similar flammability properties assessed by cone calorimeter analysis. These results are in accordance with a recent work of Samyn *et al.* [30] where it was observed that polyamide-6/organoclay nanocomposites exhibit significant reduction of Peak HRR but the nanomorphology (exfoliation, intercalation and presence of tactoids) did not play any significant role. It means that if the nanodispersion is achieved, the polymer/organoclay nanocomposite should exhibit flame retardancy properties, at least in terms of Peak HRR.

4. Conclusions

Results showed that intercalated and partially exfoliated polystyrene/clay nanocomposites were obtained depending on the swelling behavior of the organoclay in styrene. UL94 burning test showed that the burning rate was faster for the nanocomposites than for the virgin polystyrene and that during the burning of PS/organoclay nanocomposites, a char structure was formed and no dripping was observed, whereas during the burning of virgin PS specimen dripping of melted polystyrene in flame was constant.

It was also observed an increase of the higher decomposition temperature and an accentuated decrease on the peak of heat release of the nanocomposites when comparing to the virgin polymer. These results indicate that polystyrene/clay nanocomposite, either intercalated or partially exfoliated, reduced the flammability approximately at the same extent, although reduced the ignition resistance of the polystyrene.

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