Surface Modification of Sodium Montmorillonite Nanoclay by Plasma Polymerization and Its Effect on the Properties of Polystyrene Nanocomposites

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Sodium montmorillonite nanoclay (Na⁺-MMT) was modified by plasma polymerization with methyl methacrylate (MMA) and styrene (St) as monomers and was denominated as Na⁺-MMT/MMA and Na⁺-MMT/St, respectively. This plasma modified nanoclay was used as reinforcement for polystyrene (PS) nanocomposites that were prepared by melt mixing. Pristine and modified Na⁺-MMT nanoclay were analyzed by the dispersion in various solvents, Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and scanning electron microscopy (SEM). The results confirmed a change in hydrophilicity of the modified Na⁺-MMT, as well as the presence of a polymeric material over its surface. The pristine PS/Na⁺-MMT and modified PS/Na⁺-MMT/MMA and PS/Na⁺-MMT/St nanocomposites were studied with X-ray diffraction (XRD), differential scanning calorimetry (DSC), and TGA, as well as mechanical properties. It was found that the PS/Na⁺-MMT/St nanocomposites presented better thermal properties and an improvement in Young’s modulus (YM) in compared to PS/Na⁺-MMT/MMA nanocomposites.

1. Introduction

Research and development of polymeric materials with better properties have led to the reinforcement of polymeric matrices with particles at nanometer scale, which facilitates the exchange and transference of properties between the phases [1, 2]. The success of nanostructures as reinforcement agents is because of the intrinsic properties of each type of nanoparticle and low levels of loadings compared to conventional reinforced composites and, above all, because of their high surface area-volume ratio.

Na⁺-MMT has been one of the reinforcement agents most used in polymeric and other matrices to obtain nanocomposites with unique properties such as a gas and liquid barrier, flame retardant, and mechanical improvement [2–9]. Na⁺-MMT is a swelling clay with three layers, which has a great surface and an elevated capacity for cation exchange; with Na⁺ and Ca²⁺ as typical exchangeable cations, for this, it is also used to remove components in contaminated waters [6–10]. Other different nanostructures than clays like carbon nanotubes (CNTs), noble metal nanoparticles, nanofibers, and so forth are equally used to obtain polymeric nanocomposites [11–17]. However, one of the best advantages of Na⁺-MMT nanoclay is that it is a material that is found in great abundance in the five continents, for which its cost-performance ratio is considerably
low with respect to many other nanometer-scale structures [10].

On the other hand, even if the physical and performance properties of nanocomposites can be improved upon addition of nanostructure reinforcement agents, the experimental values of force and efficiency are still lower than theoretical predictions because of aggregation and compatibility problems between the interfacial union of nanoparticles and polymeric matrices. Within the most used techniques to promote the interaction between phases is the ion exchange of the dispersive phase with organophilic cations [18–20]. Another line of investigation is the use of a third substance that serves as a phase compatibilist [21, 22]. Afterwards is the mixture process. In this stage, there is in situ polymerization, solution mixing, and melt blending as the main techniques of nanocomposite preparation which have revealed favorable levels of dispersion [23, 24]. Particularly polymer/clay composites are generally divided in three types: conventional composite materials, where the clay acts as a normal reinforcement material [23, 25], intercalated nanocomposites, where a small quantity of polymer moves into the gallery spaces of the clay [26, 27], and exfoliated nanocomposites, where the sheets of clay are completely dispersed in a polymer matrix [27, 28].

In the improvement of the dispersive phase, a recent alternative is polymerization on the nanoparticle by surface modification with plasma [5, 16, 17, 29, 30]. Plasma presents certain advantages in this area compared to conventional surface modification methods. It is a relatively simple, rapid, dry, and environment-friendly technique that is used to modify the surface of a great variety of materials. Even if this technique is normally used to modify the surface of different polymeric substrates, it has been used with success to modify different nanoparticles and other surfaces like zinc oxide, iron oxide, aluminum oxide, titanium oxide, carbon nanofibers (CNFs), CNTs, nanoclays [5, 7, 15, 16, 31–36], and quartz [37, 38]. Treatment with plasma can add a nanometric film that covers nanoparticles, modifying their surface properties. If the plasma modification is carried out by using a monomer (plasma polymerization), this can generate a polymeric coating like the specific polymeric matrix over the nanoparticle with a desired increase in surface interaction, promoting an improvement in the adhesion between phases and the transferance of properties between them [15, 16]. For example, Jarvis and Majewski [37, 38] have recently investigated changing the surface of quartz particles from hydrophobic to a hydrophilic character by using plasma treatment of allylamine. Longer polymerization times increased the number of positively charged groups and their hydrophilic behavior.

Reported works using plasma modification of nanoclays and other nanoparticles to prepare polymer composites have presented favorable improvements in particle dispersion as well as thermal, mechanical, and gas barrier properties [5, 15, 16, 39–41]. According to Ramos-de Valle et al., these dispersion improvements have allowed the investigation of the effects of styrene plasma modified CNFs to investigate the effects on the tensile properties of polystyrene/CNF composites [5]. In this report, the plasma treatment greatly enhances the nanofiber dispersion within the PS matrix by helping the nanofiber compatibilization, which in turn highly increased the tensile modulus.

However, in the reported investigations, there have been no references that include the comparative study of modified Na⁺-MMT with St (Na⁺-MMT/St) and with MMA (Na⁺-MMT/MMA) added to PS for the purpose of evaluating the differences between the modifications on the two modified nanoclays and their interaction in the PS matrix.

2. Experimental

2.1. Materials. The used polymer was general purpose PS, with a molecular weight, $M_w = 168,000$ g/mol, and a glass transition temperature ($T_g$) of 98°C. The Na⁺-MMT nanoclay was acquired from Southern Nanoclay Products, Inc., and presented the following characteristics: purity = 99.5%, tactoid size = 2–13 μm, sheet width = 1 nm, and sheet longitude = 150–600 nm. The monomers that were used for plasma polymerization were MMA (CH$_2$=C(CH$_3$)COOCH$_3$) and St (C$_6$H$_5$-CH=CH$_2$). Said monomers were acquired from Sigma-Aldrich with a purity of 99.9%.

2.2. Plasma Polymerization. Na⁺-MMT was surface-modified by plasma polymerization using MMA monomer and St monomer. To achieve this, the MMA and St monomers were polymerized in a plasma reactor at low pressure. The modification of Na⁺-MMT with these monomers was done in order to change the hydrophilic nature of the nanoclay to hydrophobic and thus promote greater compatibility with the PS matrix which is hydrophobic to obtain thus nanocomposites with better mechanical properties.

The plasma reactor used for modification of Na⁺-MMT was composed mainly of a power controller coupled to a radiofrequency generator of 13.56 MHz, a vacuum pump, a controlled gas flow valve, and a 500 mL glass flask, which was used as a reactor. A copper wire that acts as an inductive electrode was placed around the glass flask and one end connected to the radiofrequency generator (Advance Energy RFX600). Figure 1 illustrates the plasma reactor. The process of plasma polymerization of MMA and St to modify Na⁺-MMT was done as follows: 1.5 g of Na⁺-MMT was introduced in the glass flask and the vacuum pump was turned on. The initial internal base pressure of the system was 10 Pa. Afterwards, the MMA or St monomer flow was held until the pressure of the system was kept constant at 17 Pa. This pressure leads to a constant flow of MMA or St at 1.25 cm$^3$/min. The Na⁺-MMT nanoclay was modified at different plasma power intensities (50, 100, and 150 W) and each one applied the following times: 1, 1.5, and 2 h. This reaction was done with constant agitation by magnetic stirrer to obtain a surface modification of Na⁺-MMT with plasma polymers of polymethyl methacrylate (PMMA) or PS.

2.3. Preparation of Nanocomposites. The nanocomposites were prepared in a Brabender mixture chamber using CAM-type rotators at 190°C with 60 rpm during 10 min. In all cases, 75 mL chamber was filled to 93% of its capacity, (which is 70 mL). The PS/Na⁺-MMT nanocomposites were
prepared with a 3% wt. concentration of Na⁺-MMT and 97% of PS. The mixing procedure was the following: the PS was introduced to the mixing chamber. When the PS was melted, the pristine Na⁺-MMT and modified Na⁺-MMT (Na⁺-MMT/MMA and Na⁺-MMT/St) were introduced during a period of 2 min; after this, the mixing was continued during 8 more min to complete the mixing time of 10 min. Then the nanocomposites were extracted, ground, and molded by compression molding to obtain plaques of 150 × 150 × 3 mm

2.4. Solvent Dispersion. The pristine Na⁺-MMT and modified Na⁺-MMT nanoclays were examined by dispersion in various solvents with different solubility parameters (δ): water (H₂O), chloroform (CHCl₃), and tetrahydrofuran (THF), with δ of 23.5, 9.52, and 9.21, respectively. In this procedure, 3 mg of the Na⁺-MMT was placed in 10 mL of each solvent and stirred. After 5 min, pictures were taken to observe the dispersion grade.

2.5. FTIR Spectroscopy. An Nicolet Magna 550 FT-IR spectrophotometer was used to obtain infrared spectra and observe the functional groups present in the pristine Na⁺-MMT and modified Na⁺-MMT nanoclays. The samples were previously dried in a vacuum oven at 100°C during 12 h. Each sample was supported with potassium bromide (KBr).

2.6. Scanning Electron Microscopy (SEM). The micrographic and morphological analysis of the nanoclay samples (pristine and plasma treated) was carried out by SEM in a field emission scanning electron microscope (FESEM, Hitachi SU8010) at a voltage of 3 kV for the pristine, while for the plasma modified nanoclay it was of 10 kV.

2.7. Thermogravimetric Analysis. Thermal stability of Na⁺-MMT and the nanocomposites was obtained with a Q500 thermogravimetric instrument at a heating velocity of 10°C/min within the range of 25–600°C in nitrogen atmosphere at 50 mL/min and within the range of 600–800°C in oxygen atmosphere to favor the oxidation process.

2.8. X-Ray Diffraction. The effect of pristine and plasma modified Na-MMt on the structural properties of PS was determined using Wide Angle X-ray Diffraction (WAXD) in a Siemens D500. Pristine and plasma treated Na-MMT were also analyzed by WAXD. The equipment consists of a Cu anode with a wavelength of 1.5406 Å. The samples were analyzed in a range of 2θ from 2 to 35°. The runs were performed with a pitch size of 0.5 and time of 5.0 sec.

2.9. Differential Scanning Calorimetry. Thermal analysis of the nanocomposites was also carried out by DSC analysis of TA Instruments model MDCS-2920. A small amount of the nanocomposite of about 10 mg was used for each experiment. The samples were heated twice; the first heating was used to erase the thermal history of the sample. The heating rate was 10°C/min. During the second heating, the samples were heated to a temperature of 180°C at 10°C/min. The glass transition (Tg) temperature of the sample was obtained from the thermograms.

2.10. Mechanical Properties. The tensile-strain properties were studied with a Universal machine model 3M-10, equipped with a charging cell of 450 kg at an extension velocity of 5 mm/min. All of the tests were done in accordance with the ASTM-D638 norm. All of the samples were modified for 40 h in a 50% relative humidity environment. Six samples were tested for each set of data and the average was reported.

2.11. UV Spectroscopy. The UV analysis of the pristine PS and the nanocomposites were measured (300–800 nm) with a UV-visible Spectrophotometer (UV-Vis-NIR Cary 5000); the background was run in air. Films of neat PS and PS/MMT nanocomposites of ~300 μm thickness were used for optical clarity measurements.
3. Results and Discussion

3.1. Characterization of Nanoclay

3.1.1. Dispersion Tests. For the dispersion tests, $\delta$ of the polymers and solvents were used in this work. $\delta$ is a measure of the attractive strength between molecules of the material; it allows the prediction of miscibility. It is also called cohesion parameter, a term which is often preferred to solubility parameter when referring to nonliquid materials such as polymers [42–44]. This is a qualitative estimation to the interaction degree between materials, since the organic films deposited on the Na$^+$-MMT using MMA and St monomers that crosslink due to plasma polymerization cause the modified Na$^+$-MMT to interact in solvents with similar solubility parameter. This study is expected to see an increase in interaction between the nanoclay modified with plasma and the matrix, when $\delta$ of both phases are the same. In previous studies, this polymeric coating has already been confirmed on other different nanomaterials using plasma polymerization [5, 15, 39].

In Figure 2, the dispersions in water at room temperature of pristine Na$^+$-MMT and of modified Na$^+$-MMT/MMA before (Figure 2(a)) and after agitation (Figure 2(b)) both with different times of plasma polymerization are presented. In these images, we can observe that the pristine Na$^+$-MMT is highly hydrophilic and disperses well in water after agitation. This is due to the high content of Na$^+$ cations present in the clay which have been hydrated (solvated with water, Figure 2(b)) [27, 28, 45]. For Na$^+$-MMT/MMA, with different time of plasma modification, it is observed that they stay on the surface of the water before and after agitation, which identifies their hydrophobic property; the presence of the polymer on the surface of Na$^+$-MMT indicates a difference in $\delta$ between the coating of PMMA ($\delta = 9.25$) and H$_2$O ($\delta = 23.5$), which avoids the diffusion of water between the sheets and consequently their interaction with the sodium ions. In this figure, a part of Na$^+$-MMT/MMA were sedimented, which indicated a fraction of them agglomerated during the modification and are denser than water.

According to the results of Figures 2(a) and 2(b), there is no significant difference due to the time treatments between the behaviors of the modified Na$^+$-MMT nanoclay. This suggests that the treatment time only will increase the thickness of polymer films (PMMA or PS) deposited on the surface of Na$^+$-MMT. Figures 2(c) and 2(d) show that Na$^+$-MMT/MMA treated at 50, 100, and 150 W remains on the water surface before and after agitation. It is noted that all the modified Na$^+$-MMT nanoclays treated at different plasma powers have the same hydrophobicity; this is due to the fact that the plasma coatings probably present very similar chemical structures at any power used in the reaction.

Figure 3 shows the dispersion in water at room temperature of pristine Na$^+$-MMT and Na$^+$-MMT modified with St
According to the images, Na⁺-MMT/St is more hydrophobic than that with the coating of PMMA; this can be due to PS presenting a solubility parameter ($\delta = 9.12$) lower than PMMA ($\delta = 9.25$). Also, unlike PMMA, the coating of PS does not present electron fluctuations (instantaneous dipoles) because of the absence of molecules with free electron pairs that can present interaction with the hydrogen of water.

Figure 4 shows the vials that contain the pristine Na⁺-MMT, Na⁺-MMT/MMA, and Na⁺-MMT/St dispersed in CHCl₃ (Figures 4(a) and 4(b)) and THF (Figures 4(c) and 4(d)). These figures show that the pristine Na⁺-MMT nanoclay dispersed in CHCl₃ is deposited on the bottom almost immediately, while those modified with MMA plasma or St plasma stay dispersed after 5 min of resting; meanwhile the pristine and modified Na⁺-MMT dispersed in THF show a good interaction with the solvent (Figures 4(c) and 4(d)). This is because the THF is a dipolar aprotic protophilic solvent,
which means it is capable of accepting protons, given the unshared electron pairs of the oxygen atom which give Lewis-base features and enable the THF interaction with a wide range of compounds.

In general, it was observed that the dispersion of Na\textsuperscript{+}-MMT/MMA or Na\textsuperscript{+}-MMT/St was poor with solvents of high polarity like water $\delta = 23.5$, while their dispersion was better in a medium of low polarity such as THF ($\delta = 9.52$) or chloroform ($\delta = 9.21$), as $\delta$ of PMMA and PS are 9.25 and 9.12, respectively. $\delta$ are very similar to the last two solvents causing a good dispersion between them [5, 15, 39].

The dispersion tests do not give a quantity of Na\textsuperscript{+}-MMT modification degree; however, they give a clear idea on whether the modification of Na\textsuperscript{+}-MMT nanoclay was accomplished or not.

3.1.2. FTIR Spectroscopy. In Figure 5, the FTIR spectra of pristine Na\textsuperscript{+}-MMT and Na\textsuperscript{+}-MMT/MMA are shown. In these spectra, the previously reported characteristic signals of nanoclay can be observed [36, 46]. The signal at 3640 cm\textsuperscript{-1} is attributed to the Al-OH bond stretching, while the presence of absorbed humidity is observed at 3440 cm\textsuperscript{-1}. The band at 1640 cm\textsuperscript{-1} corresponds to the bending of the OH proceeding from the water situated on the surface layers of the nanoclay. The bands that are found in 1117 cm\textsuperscript{-1} and 1039 cm\textsuperscript{-1} are generated by the stretching of the Si-O bond out of and within the plane, respectively. Comparing spectra “a” and “b” from Figure 5, it can be observed that there is a decrease in intensity of the signals of Al-OH and OH, indicating a slight dehydration and dehydroxylation of the nanoclay; meanwhile the band located at 2947 cm\textsuperscript{-1} is due to the stretching of the C-H bond. Finally, the presence of PMMA on the surface of Na\textsuperscript{+}-MMT/MMA nanoclay is defined by the carbonyl (C=O) group signal of the PMMA ester at 1745 cm\textsuperscript{-1} and a band corresponding to the C-O stretching between 1300 and 1050 cm\textsuperscript{-1}.

In Figure 6, the spectra of pristine Na\textsuperscript{+}-MMT (described previously) and Na\textsuperscript{+}-MMT/St are shown. Comparing these spectra, it can be observed that there is an increase in the Al-OH/OH signal ratio in Na\textsuperscript{+}-MMT/St (Figure 6(b)) regarding Na\textsuperscript{+}-MMT/MMA in Figure 5, which is caused by the change in chemical environment of the Na\textsuperscript{+}-MMT nanoclay by the presence of PS. In relation to the deposit of the plasma polymer, a low intensity band can be seen at 3025 cm\textsuperscript{-1} corresponding to aromatic C-H bond and a band at 1600 cm\textsuperscript{-1} corresponding to aromatic C=C bond. The bands situated at 2919 cm\textsuperscript{-1} and 2849 cm\textsuperscript{-1} refer to the C-H and CH\textsubscript{3} bonds, with which the presence of these characteristic groups of PS on the surface of Na\textsuperscript{+}-MMT/St nanoclay can be confirmed.

Even if the presence of characteristic bands of PMMA and PS can be appreciated by infrared, it is important to point out that plasma polymerization occurs only on the surface of the nanoparticle. Figures 5 and 6 confirmed the presence of the coatings of plasma polymers of PMMA and PS on the surface of the nanoclay.

3.1.3. Thermogravimetric Analysis. In Figure 7, the thermograms of pristine Na\textsuperscript{+}-MMT, Na\textsuperscript{+}-MMT/MMA, and Na\textsuperscript{+}-MMT/St nanoclays are shown. According to Ros et al. (2002) [47] and Toebes et al. (2004) [48], weight loss between 50 and 160°C is mainly attributed to humidity loss. The difference in humidity loss between the pristine Na\textsuperscript{+}-MMT and modified Na\textsuperscript{+}-MMT nanoclay can be attributed to the decrease in water absorption of the modified nanoclay due to the presence of the plasma coating at the surface of Na\textsuperscript{+}-MMT/St or Na\textsuperscript{+}-MMT/MMA; the plasma coating acts as a water barrier, and coated nanoclay absorbs less amount of water. Na\textsuperscript{+}-MMT/MMA exhibit an average ($\overline{X}$) weight loss of 8.25% between 200 and 400°C; this is related to the
nanoclay, clearly confirms that plasma coatings of PMMA respectively. The observed roughness at the surface of the ∼+ray diffractograms of PS/Na
3.2.1. X-Ray Diffraction Analysis.
3.2. Characterization of Polymer Nanocomposites
CNF and that it was also confirmed by SEM. The coating with plasma polymer covalently crosslinking of PMMA by plasma but on the surface of the work that the 100 W treatment for 30 minutes resulted in the thermal stability is observed when compared to that of PS/nanocomposite prepared with Na
3.2.2. Thermal Stability. For the thermogravimetric analysis, the temperatures of degradation for all polymers were obtained at 10% loss in weight as can be seen in Figure 10, where for the PS/Na
+ -MMT/St nanocomposite it is 402.9 C, for PS/Na
+ -MMT/MMA nanocomposite it is 387.5 C, and for the PS it is 377.5 C. These results are in accordance with previous reports, where nanoparticles have been mixed with polymers in order to improve their thermal properties such as CNFs modified with plasma methyl methacrylate in a PMMA matrix [15] or nanoclays dispersed in a polypropylene matrix [23]; however, in none of them, there is mention of nanocomposites formulated by the materials combination and methodologies of this investigation, giving a new scientific contribution about polymeric nanocomposites, especially those formed by plasma modification of the dispersed phase.

The results obtained by TGA show an improvement in thermal stability of PS in presence of modified or unmodified Na
+ -MMT. It is clear that the incorporation of the nanoclay and its dispersion by mixing give the thermal stability to the PS, but the polymerization with St plasma on the surface of the Na
+ -MMT presents an extra signal. These results are in accordance with the JCPDS cards (29-1498); the polymer, in this case PS, is amorphous and does not present any signal.

In samples of PS/Na
+ -MMT/MMA and PS/Na
+ -MMT/St nanocomposites, the results indicate that there is no evidence of a significant level of exfoliation or intercalation of Na
+ -MMT modified by plasma in the PS/Na
+ -MMT nanocomposites, possibly because the coating formed by plasma on the nanoclay does not allow the introduction of the St or MMA polymer in-between the nanoclay galleries. This, however, does not contradict the surface interaction results demonstrated by the article which are attributed to the compatibility of the coating of the nanoclay Na
+ -MMT/St with the PS matrix, as well as the shear stress during melt mixing [39].

3.2.2. Thermal Stability. For the thermogravimetric analysis, the temperatures of degradation for all polymers were obtained at 10% loss in weight as can be seen in Figure 10, where for the PS/Na
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The results obtained by TGA show an improvement in thermal stability of PS in presence of modified or unmodified Na
+ -MMT. It is clear that the incorporation of the nanoclay and its dispersion by mixing give the thermal stability to the PS, but the polymerization with St plasma on the surface of the Na
+ -MMT presents a better interaction with the PS matrix, since both present the same functional group (St) that interact within themselves, provoking a better compatibility between both phases, promoting an improvement in the dispersion of the analyzed sample. Consequently, it causes significant improvement in the transfer of thermal properties from the Na
+ -MMT/St to the PS polymer, as shown in Figure 10.

Referring to pristine PS/Na
+ -MMT, an improvement in thermal stability is observed when compared to that of PS and PS/Na
+ -MMT/MMA; this suggests that the pristine Na
+ -MMT nanoclay has a better dispersion in the PS matrix than the PS nanocomposite prepared with Na
+ -MMT/MMA nanoclay (PS/Na
+ -MMT/MMA). This can be explained by the increase in repulsion energy of the PS and Na
+ -MMT/MMA nanoclay compared to the pristine Na
+ -MMT nanoclay, provoking more agglomeration of the Na
+ -MMT/MMA, lowering the transfer of thermal properties. The increase in repulsion energy is due to the difference in the solubility parameter, as mentioned in Dispersion Tests (Section 3.1.1).
Figure 8: SEM micrographs of (a) pristine Na\(^+-\)MMT, (b) Na\(^+-\)MMT/MMA plasma coated at 150 W for 1.5 h, and (c) Na\(^+-\)MMT/St coated at 150 W for 1.5 h.

Figure 9: X-ray diffraction patterns of pristine PS/Na\(^+-\)MMT, PS/Na\(^+-\)MMT/MMA, and PS/Na\(^+-\)MMT/St nanocomposites.

The appreciable difference of weight loss between 450 and 500°C for the PS and the PS/Na\(^+-\)MMT nanocomposites confirms the presence of the Na\(^+-\)MMT nanoclay. In the nanocomposites, it is observed that around 465°C the weight loss is completely ceased, due to the thermal resistance of the nanoclay, leaving around 3% of Na\(^+-\)MMT weight.

3.2.3. Glass Transition Temperature. In Figure 11, the DSC thermograms for pristine PS and PS/Na\(^+-\)MMT nanocomposites are shown. Since PS is amorphous, it does not present
a melting point, so upon analysis we can only observe its glass transition temperature ($T_g$), which is around 100°C [49]. The most marked shift of $T_g$ is shown by the PS/Na$^+$-MMT/St composite, where $T_g$ increases approximately from 100.1°C to 103.9°C with respect to the pristine PS. The endothermic slope shift is due to the interaction of the PS molecules with the nanoclay that has been modified with a PS coating thanks to St plasma modification, which provokes the polymerization upon Na$^+$-MMT. $T_g$ shift observed confirms the interfacial adhesion between the PS polymeric matrix and the modified Na$^+$-MMT nanoclay. This phenomenon is not observed with the PS/Na$^+$-MMT and PS/Na$^+$-MMT/MMA nanocomposites, which demonstrates the lack of interfacial interaction, as explained in Figure 14. The results about the increase of $T_g$ are similar to previous investigations of nanocomposites with clay/polymer formulations [49].

3.2.4. Mechanical Properties. Figure 12 shows the tensile-strain diagrams of PS/Na$^+$-MMT, PS/Na$^+$-MMT/MMA, and PS/Na$^+$-MMT/St nanocomposites. PS is a polymer that does not suffer large deformations [5]; since it is a rigid polymer, it only suffers elastic deformation, so Figure 12 presents the changes that occur in the slope in deformation percentages, and the values of deformation were lower than 2%. In this research, increment values of 0.2% deformation were intentionally chosen to make evident the instantaneous changes in the tensile stress, as can be seen in Figure 12. This indicates that the presence of Na$^+$-MMT in the PS matrix modifies the YM and the elastic deformation percentage.

The nanocomposites presented a gradual increase in the YM and a decrease in the deformation compared to PS. This effect is most notable in the PS/Na$^+$-MMT/St nanocomposite that is shown in Figures 12 and 13. This is due to the surface modification of the Na$^+$-MMT nanoclay with St plasma which provoked a better dispersion and a greater interfacial interaction between this modified nanoclay and the PS polymeric matrix owing to the similarity and compatibility of the St monomer to PS. Meanwhile the MMA-modified Na$^+$-MMT nanoclay was not as compatible with the polymeric matrix. These results are similar to those obtained from the TGA, where the PS/Na$^+$-MMT/St nanocomposite presents the highest thermal stability, and, in this analysis, PS/Na$^+$-MMT/St nanocomposite presents higher YM too. This increase in the slope upon the addition of the nanoclay is in accordance with previous reports [5,15,16].

In Figure 13, the calculations of YM obtained for the PS/Na$^+$-MMT/MMA and PS/Na$^+$-MMT/St nanocomposites at a time treatment of 1.5 h are reported. The PS/Na$^+$-MMT/St nanocomposite modified at 100 W for 1.5 h has an increase of 32% in its YM compared to PS; meanwhile PS/Na$^+$-MMT/MMA and pristine
PS/Na⁺-MMT have an increase of 23 and 27%, respectively. In Figure 13, it is notable that the best results are presented for the Na⁺-MMT nanocomposites modified at 50 W, where the YM has an increase of 34 and 30.5% for PS/Na⁺-MMT/St and PS/Na⁺-MMT/MMA, respectively, at a time treatment of 1.5 h. However, the data suggests after examining results that the modifications with plasma at 100 or 150 W do not affect noticeably the YM and thermal stability of the studied nanocomposites; however, it is recommended to use the lower parameter of plasma power (50 W), which is optimal in terms of energy savings.

A proposed mechanism of the modification and interaction of pristine Na⁺-MMT and plasma modified nanoclay (Na⁺-MMT/MMA, Na⁺-MMT/St) with the matrix of PS is represented by a schematic in Figure 14, in which the compatibility between the different composites is briefly explained.

3.2.5. Optical Properties. The optical properties of pristine PS and PS/Na⁺-MMT nanocomposites were measured with a UV-visible Spectrophotometer. The results are presented in Figure 15; it is appreciated that pristine PS has the higher optical clarity, as expected; however, the presence of untreated and plasma treated MMT affected the optical clarity of the nanocomposites as it is shown in Figure 15. But it is important to point out that PS nanocomposites containing the plasma treated MMT (PS/Na⁺-MMT/MMA 100 W and PS/Na⁺-MMT/St 100 W) presented higher optical clarity than PS nanocomposites containing untreated MMT (PS/Na⁺-MMT); this somehow indicates that treated MMT particles
presented higher dispersion in the PS matrix, and as a result of this dispersion these nanocomposites presented better optical clarity. In conclusion, the plasma treatment of MMT with St and MMA increased the compatibility towards PS, and as a result these nanocomposites presented better dispersion and optical properties.

4. Conclusions

The Na\textsuperscript{+}-MMT nanoclay was modified by plasma polymerization with MMA and St as monomers. According to the studies of dispersion and thermal properties as well as the FTIR carried out, the presence of organic material (plasma polymer) over modified Na\textsuperscript{+}-MMT was found. It was clear that the PS or PMMA plasma coating deposited on the Na\textsuperscript{+}-MMT via plasma treatment changes the hydrophilic character of the nanoclay into hydrophobic character. The modified Na\textsuperscript{+}-MMT showed poor dispersion in high polarity solvents, whereas it showed a better dispersion in low polarity solvents. On the other hand, when comparing the effects of the type of monomer used for the modification of the nanoclay, it was found that the coating formed by each type of monomer plays a fundamental role; the St monomer polymerizes to PS over Na\textsuperscript{+}-MMT and promotes a greater affinity between the PS matrix and the nanoclay. This greater interfacial interaction and dispersion of the Na\textsuperscript{+}-MMT nanoclay modified by St plasma in the PS matrix gave way to an improvement in thermal stability as well as an increase in 34% of YM for the PS/Na\textsuperscript{+}-MMT/St. In the PS/Na\textsuperscript{+}-MMT/St nanocomposites, the plasma modified Na\textsuperscript{+}-MMT nanoclay with St is scattered in the PS polymeric matrix due to the intercalation that was done. A greater interaction between the phases and better scattering are two of the most important factors for the improvement of nanocomposite properties. It was concluded that the properties of the modified PS/Na\textsuperscript{+}-MMT nanocomposites were significantly affected by the type of monomers used.

Data Availability

Data of this paper are available on request; please contact Rosa Idalia Narro-Céspedes (email: rinarro@uadec.edu.mx) for any more information.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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