Montmorillonite/polystyrene nanocomposites were prepared by in situ photopolymerization of styrene in the presence of 2% by weight of clay organomodified by two new imidazolium surfactants having in their structure an alkyl chain with 20 or 22 carbon atoms, respectively. Thermogravimetry showed that the new surfactants are more thermally stable than conventional alkylammonium surfactants. The properties of the obtained nanocomposites were compared with those of pristine polystyrene, with those of a microcomposite obtained by in situ polymerization of styrene in the presence of unmodified clay, and with those of a nanocomposite obtained starting from an organomodified clay with a short alkyl chain (12 carbon atoms) imidazolium surfactant. XRD, TEM, and rheological analysis showed that the clay/PS nanocomposites have a mixture of intercalated and partially exfoliated structure layers, where the higher the surfactant alkyl chain length, the higher the exfoliation degree. Kinetics curve of accelerated UV aging, obtained by following through infrared spectroscopy the increase of carbonyl functions during aging, showed that the rate of photooxidation of clay containing samples is higher than neat polystyrene. The rate is higher as a function of the degree of dispersion of the filler in the polymer matrix.

1. Introduction

In recent decades there has been a considerable interest in polymer nanocomposites [1–5]. The interest has involved both academic and industrial communities because of the significant application perspectives that the development of this new class of materials made it possible to glimpse. The high performances that the filler dispersion at the nanometer level allows to achieve affect physical, mechanical, optical, and economic fields [6–8].

The predictions of using these materials on large-scale have been progressively revised downwards, and the estimate of 2002 of reaching, in the US alone, a turnover of $4 billion for 2010 [9] was recently updated [10] and global market consumption of nanocomposites in 2013 reached 190 ktons, or $1.2 billion, and now is expected to grow in unit terms from nearly 225 ktons in 2014 to nearly 585 ktons, or $4.2 billion, in 2019, with a compound annual growth rate (CAGR) of 21.1% for the period from 2014 to 2019. The postposition of predictions made in 2002 is in part due to emerging problems relating to the production and durability of these materials.

Among the various classes of polymeric nanocomposites, the polymer-clay ones have seemed the most promising in relation to production costs and achievable performances, and clay nanocomposites accounted for more than 50% of total nanocomposite consumption by value in 2010. Their market share is expected to increase to approximately 58% in 2016. The raw materials from which the filler is obtained are widely available and the best performance aspects relate to the mechanical properties, such as Young's modulus and toughness, and, among others, to those relating to a particular aspect watched with interest by the market of plastic materials, that is, the possibility of contributing to replace the halogenated flame retardant additives to enhance fire resistance of plastic materials [11].

The research has shown, however, that in order to achieve a substantial improvement of the mechanical performance it is necessary to obtain a nanometric dispersion of individual
clay layers, obtaining the so-called exfoliated structure, rather than having the more easily obtainable but less performing morphologies, that is, the intercalated ones, in which the layers remain well ordered and the polymer chains are inserted into the gallery space of the silicate [12, 13].

To obtain intercalated and/or exfoliated structures it is necessary to organically modify the clay in order to increase the affinity with the polymer matrix. The organic modification of the clay is most commonly made with quaternary ammonium salts. Due to this organic modification the thermal stage of the production process becomes even more relevant. In fact, alongside the well-known steps that must be taken because of the relative thermal stability of the polymer matrices, it is also necessary to pay attention to the thermal degradation processes faced by the surfactants used in the organic modification of the clay. The quaternary ammonium salts, in fact, begin to decompose, resulting in a Hoffman degradation processes faced by the surfactants used in the surfactants used in the organic modification of the clay [13]. This decomposition process involves the collapse of the clay layers that prevents the achievement of the desired exfoliated structures [17]. To overcome this problem, cationic surfactants, such as phosphonium [18, 19], pyridinium [20], and imidazolium [21, 22], have been used to modify layered silicate because of their higher thermal stabilities.

Another issue that has emerged from the study of this class of nanocomposites is that the presence of the nanofiller determines the deterioration of the resistance of the polymer matrix to UV photooxidation [23–25]. In literature, several authors have tried to explain the mechanism of this decrease of durability and various explanations have been proposed. Some authors consider, for example, that this phenomenon is attributed to the presence of the surfactant, while others attribute it to the catalytic action of metal ions present in the clay layers [26, 27]. We have contributed to this debate and our previous studies have shown that a lower stability to UV radiation is also determined by the presence of the clay only and may also be in relation to the degree of exfoliation achieved in the nanocomposite [28].

Continuing our studies we now present the results obtained using two new imidazole surfactants with a thermal stability higher than the one of conventional surfactants based on quaternary ammonium salts, and that, due to the long alkyl chains present in their structure, should allow reaching a high degree of exfoliation. Using these new surfactants we have realized the organic modification of montmorillonite and with the obtained clay we have prepared, by in situ polymerization, polystyrene-montmorillonite nanocomposites with a clay concentration of 2% by weight. The nanocomposites were characterized by GPC analysis to determine the average molecular weight of the matrix, XRD, TEM, and rheological analysis to obtain information on the relative degree of exfoliation. FT-IR spectroscopy was used to follow accelerated UV aging of pristine PS and of nanocomposites.

2. Materials and Methods

The chemicals used in this study were acquired from Aldrich Chemical Co. The MMT (Na/MMT) is a fine powder with a particle size of 10–15 μm in a dry state and a cation exchange capacity (CEC) of 100 mEq/100 g. Styrene monomer was purified using an inhibitor removal column, also acquired from Aldrich. AIBN was purified crystallizing it twice from dry ethanol at a temperature lower than 40°C and out of direct light.

2.1. Instruments. 1H- NMR spectra were recorded in a Varian Unity Inova 500 MHz spectrometer, without an internal standard, at room temperature, using DMSO-d6 (deuterated dimethyl sulfoxide) and CDCl3 (deuterated chloroform) as a solvent.

Thermal degradations were performed in a Mettler TA 3000 thermogravimetric analyzer coupled with a Mettler TC 10A processor. Degradations were performed in dynamic heating conditions, from 35 up to 600°C, in flowing nitrogen (0.02 L min⁻¹) or static air at a heating rate of 10°C min⁻¹. The thermogravimetric (TG) and differential thermogravimetric (DTG) curves were immediately printed at the end of each experiment and the mass of sample at various temperatures was then transferred to a PC. These data were later used to plot the percentage of undegraded sample (1 − D)% as a function of temperature, where D = (W₀ − W)/W₀, and W₀ and W were the masses at the starting point and during scanning.

XRD measurements were recorded on a Bruker AXS D5005 θ-θ X-ray diffractometer, using Cu Kα radiation operating at 20 kV and 30 mA.

The molecular weight results were determined using an HP 1100 GPC instrument, equipped with a refractive index detector, operating at 30°C, using tetrahydrofuran (THF) as a carrier at a flow rate of 1 mL min⁻¹. Separation was accomplished using a PLgel 3 μm mixed-D column connected with a PLgel 5 μm 500 Å column (Polymer Labs). The measurement utilized a refractive index detector and toluene as internal standard. Solution concentrations were 2 mg/mL in THF; they were filtered through 0.45 μm PTFE membranes and injected into the columns in 20 μL aliquots. Calibration was performed using narrow polydispersity polystyrene standards in weight average molecular weights in the range 2500–400000 Da.

For rheological analysis, sample disks were produced by compression and performed with a rheometer ARES (Advanced Rheometric Expansion System), in the plate-plate geometry, using plates of 25 mm in diameter and a sample thickness of ~1 mm. The measurements were conducted under isothermal and variable frequency (from 0.1 to 100 rad/s). The temperatures used for the tests ranged from 170°C to 240°C and an amplitude of deformation of 1% has been applied to obtain a linear viscoelastic response.

Films of the samples with a thickness of 25, 50, and 100 μm were obtained by means of a Grave specat P/N15800 press, heating the material, reducing it to powder, at 170°C for 2 minutes and then applying a force of 2 tons for another 2 minutes.

The accelerated exposure device used in the experiments was a Xenotest Alpha (Atlas), equipped with a Xenon lamp set up for simulated sunlight exposure conditions (λ ≥ 300 nm)
with six infrared filter plates and one dark UV filter glass inserted in the filter lantern. The irradiance was 80 W/m². The black panel temperature was 60°C and the relative humidity was 60%, without rain. The specimen holders turned on their own axis, which resulted in alternating dark/light cycles. The exposures were conducted for 400 h and the chemical degradations were periodically checked by FT-IR.

FT-IR spectra were recorded from exposed sample films by a Perkin-Elmer Spectrum-100 spectrophotometer. They were recorded from 4000 cm⁻¹ to 400 cm⁻¹ with a resolution of 2.0 cm⁻¹. To compare the spectra of different nanocomposites an internal calibration of the thickness of each sample was performed by measuring the absorbance at 539 cm⁻¹.

2.2. Synthesis of Imidazolium Salts. Imidazolium salts (C
_{20}

 and C
_{22}
 , Scheme 1) were prepared as follows: 0.02237 mol of alkyl bromide, 0.02125 mol of 1-vinylimidazole, and 5.000 mL of ethyl acetate were put in a 50.00 mL round-bottom flask and stirred at room temperature for 12 hrs in inert atmosphere. After heating to 55°C, it was allowed to react for 24 hrs to give, after cooling, a white precipitate of the imidazolium salt. This solid was filtered, washed several times with ethyl acetate to remove the unreacted compounds, and finally dried under vacuum at 45°C. The synthesized products were characterized via mass spectroscopy, ¹H NMR spectroscopy, and elemental analysis.

\[
C_{20}: C_{22}H_{17}N_2Br (455.56): \text{Calcd.} C 65.91, H 10.40, N 6.15; \text{Found} C 65.60, H 10.50, N 6.09
\]

¹H NMR (DMSO-d₆): δ = 0.88 (t, H²), 1.34 (m, H³–H¹⁹), 1.96 (m, H²), 4.41 (t, H¹), 5.42 (dd, H¹), 5.91 (dd, H⁸), 7.27 (dd, H⁹), 7.51 (m, H⁷ and H⁸), 11.35 (s, H⁵).

MS: m/z = 375.3 (M⁺).

\[
C_{22}: C_{27}H_{20}N_2Br (483.61): \text{Calcd.} C 67.06, H 10.63, N 5.79; \text{Found} C 66.9, H 10.49, N 5.76.
\]

¹H NMR (DMSO-d₆): δ = 0.88 (t, H²²), 1.25 (m, H³–H¹¹), 1.96 (m, H²), 4.41 (t, H¹), 5.43 (dd, H¹), 5.92 (dd, H⁸), 7.30 (dd, H⁹), 7.53 (m, H⁷ and H⁸), 11.30 (s, H⁵).

MS: m/z = 403.4 (M⁺).

2.3. Preparation of o-MMT. An aqueous suspension of 2.088 g of prewashed Na/MMT in 200.0 mL of deionized water was added to a solution obtained dissolving 2.506 mmol of imidazolium salt in 10.00 mL of a 50:50 mixture of ethanol and deionized H₂O at 50°C. After the solution was stirred in inert atmosphere for 6 hrs at 50°C, the white powder was filtered, washed several times with a mixture of ethanol and deionized water until no bromide ion could be detected by an AgNO₃ aqueous solution, and then dried in a vacuum oven overnight at room temperature.

2.4. Preparation of PS/o-MMT Nanocomposites. As a typical procedure for the preparation of PS materials via in situ free radical polymerization, an appropriate amount of organophilic clay, calculated by 2 wt% (0.240 g), with respect to styrene was thoroughly dispersed in 12.00 g of styrene monomer. First, the suspension was stirred at room temperature under flowing N₂ gas until it became homogeneous (7 hrs); then it was sonicated for 1 h; finally 0.6060 g (0.5 wt%) of AIBN initiator was added to monomer clay mixture. The tube was degassed by three freeze-thaw cycles, sealed at 0.01 mmHg, and placed in a constant temperature bath at 60°C for 16 hrs to obtain PS/clay nanocomposites. A bulk polymerization of styrene was carried out at the same conditions used for the nanocomposites except for the absence of the clay.

The samples used for GPC measurements were obtained as follows: the nanocomposites were extracted using toluene at room temperature and were repeatedly filtered to ensure the removal of the clay. The PSs obtained by precipitation in methanol were used to prepare the solutions.

3. Results and Discussion

The studied nanocomposite samples were prepared by polymerization in situ of styrene in the presence of 2% by weight of organically modified montmorillonite with imidazole cations (Scheme 1) and 0.5% of AIBN.

In this regard, we proceeded to the synthesis of two new imidazolium surfactants 1H-imidazolium, 1-eicosyl-3-ethenyl and 1H-Imidazolium, and 1-docosyl-3-ethenyl (C
_{20}
 and C
_{22}
, resp.) with the purpose of reaching a higher degree of exfoliation in nanocomposite by the increased baseline distance between the lamellae of modified montmorillonite. These two new surfactants, bearing aliphatic chains, respectively, of 20 or 22 carbon atoms linked to one of the nitrogen atoms of the imidazole ring and obtained according to the procedures described in the materials and methods part, were characterized by ¹H NMR spectroscopy (Figure 1, Scheme 1), Mass Spectrometry (MS), and elemental analysis (EA). Both MS and EA results fit the data associated with the surfactant structure that has been definitively confirmed by NMR results. The ¹H NMR spectra of C
_{20}
 and C
_{22}
 showed that the signals relative to H⁶, H⁷, and H⁸ were shifted downfield of about 1 ppm with respect to the 1-vinylimidazole ones. A similar result was observed also for the signal associated with H⁵ (from 7.16 δ to 7.30 δ) and for the double doublets relative
to H$^\varepsilon$ and H$^\eta$ (from 4.85 δ and 5.47 δ to 5.43 δ and 5.92 δ, resp.). These shifts are in agreement with the cationic character of C$_{20}$ and C$_{22}$.

In order to check that the two new imidazole surfactants have a thermal stability higher than the one of conventional surfactants based on quaternary ammonium salts, the cation thermal stabilities were studied by TGA in both flowing nitrogen and static air atmosphere. In all the samples studied by thermogravimetry a weight loss was detected in the range 80–120°C. It corresponds to the loss of adsorbed water into the sample. Since this kind of water is not a decomposition product, its presence can be neglected. For this reason the determination of the decomposition temperatures ($T_{d5}$ and $T_{d10}$) has been done considering the starting weight of the sample as the weight detected at 120°C. The results of C$_{12}$, C$_{20}$, and C$_{22}$ samples, compared with the ones of a standard alkylammonium cation (octadecyltrimethylammonium bromide, ODTA), clearly show the great improvement in thermal stability for C$_{20}$ and C$_{22}$, compared with ODTA (Figure 2).

In fact, considering as temperature of decomposition the temperature at which the residue percentage reaches 95% ($T_{d5}$) or 90% ($T_{d10}$) with respect to the initial weight, both $T_{d5}$ and $T_{d10}$ of the ODTA sample in nitrogen (236°C and 245°C) are clearly lower than the decomposition temperatures of the C$_{20}$ and C$_{22}$ samples (265–282°C and 264–281°C, resp.). A similar trend is also observed in the TGA experiment carried out in static air. Moreover, the maximum speed of weight loss during the first stage of decomposition (from DTGA data) for the ODTA is at about 261°C while for C$_{20}$ and C$_{22}$ it is at 303 and 301°C, respectively.

Sodium cations in the interlayer space of MMT were exchanged with C$_{12}$, C$_{20}$, and C$_{18}$, via standard ion exchange methods [29], to yield o-MMTs (MMT/C$_{12}$, C$_{20}$, and C$_{22}$). As shown by the XRD patterns (Figure 3) the interlayer $d$ spacings increased with the alkyl chain length. This suggested that the imidazolium surfactants successfully intercalated among the layers of MMTs.

The determination of the surfactant amount intercalated among MMT layers was carried out by TGA and elemental analyses. TGA and DTGA (in static air atmosphere) of organically modified clays are shown in Figure 4. The amount of surfactants was determined from TGA following what was reported in literature [30] and the values were compared with the ones obtained through the elemental nitrogen determination. The results of both determinations were in good agreement and showed the following concentrations of surfactants: 91, 94, 81, and 81 meq/100g clay in ODTA, C$_{12}$, C$_{20}$, and C$_{22}$/MMT, respectively.

The properties of the nanocomposites obtained by organically modifying the clay with the new surfactants (PS/MMT/C$_{20}$ and PS/MMT/C$_{22}$) were compared with those of samples of virgin PS, of PS unmodified clay microcomposite (PS/MMT/Na$^+$), and of a nanocomposite obtained from a clay
modified with a surfactant having in its imidazole structure a short chain alkyl (PS/MMT/C12) (Scheme 1).

Nanocomposites were characterized through the use of XRD, GPC, TEM, rheological analysis, accelerated aging in Xenotest, and FT-IR.

The XRD analysis of PS/MMT/C12, C20, and C22 nanocomposites showed the absence of any diffraction peak thus suggesting a possible exfoliated morphology, while in the case of PS/MMT/ODTA sample the diffraction peak associated with a \( d \) value of 4.72 nm, shifted with respect to the value of 2.05 nm observed in the ODTA/MMT sample, is indicative of the PS intercalation among MMT layers.

TEM micrographs of the ultrathin section of PS/MMT/ODTA, PS/MMT/C12, PS/MMT/C20, and PS/MMT/C22 (Figure 5, 40000x), where the parallel dark lines represent the intersection of the MMT layers and the grey part represents the PS matrix, were used to get information on the phase morphology. The micrographs of PS/MMT/ODTA sample mainly present an intercalated morphology with stacks containing parallel oriented layers with various degrees of intercalation, and PS/MMT/C12 sample micrographs show very few exfoliated layers in the polymer matrix besides intercalated tactoids. In the case of PS/MMT/C20 and PS/MMT/C22 micrographs it is possible to identify a nonuniform distribution of the silicate layers in the matrix where individual silicate layers along with two, three, and four layer stacks exfoliating in the PS are present. These results show that the last two samples have a partially exfoliated nanomorphology.

Traditionally, the techniques used to study the dispersion of the clay in the matrix are XRD and TEM. However both have limitations: the former because the absence of diffraction peaks can only reveal a possible exfoliation of the clay and the latter because it can provide information on the morphology of small volume fractions only. We have already shown [28, 31] that thermogravimetric studies, by comparing the \( E_a \) values of the samples, give the possibility of building a qualitative scale of exfoliation and then assist in the characterization of these materials. In the literature it has been shown that rheological analysis is another useful investigation tool to provide information on the state of the dispersion of the clay in the matrix [32]. In this study we have used this tool to characterize our samples. At the outset, in order to assess whether there are influences on the rheological behavior arising from the molecular weight of the clay, we determined by GPC analysis the average molecular weights of the PS in the different samples.

GPC analysis showed that the presence of organically modified clay during in situ polymerization does not determine an appreciable variation of the average molecular weights and polydispersity (\( M_w/M_n \)) (Table 1).

Rheological analyses were conducted by recording several frequency sweeps at temperatures ranging from 190 to 220°C and analyzing the storage modulus (\( G' \)), loss modulus (\( G'' \)), and complex viscosity (\( \eta^* \)).

Considering, first of all, the complex viscosity (\( \eta^* \)) data (Figure 6), it is evident that PS and PS/MMT/C12 samples show quite similar values, while PS/MMT/C20 and PS/MMT/C22 samples show a marked increase in viscosity. These initial results suggest that since the various samples have close values of molecular weight, the different viscosity is due to a different distribution of the clay layers. Then, while PS/MMT/C12 has a structure close to the one of a microcomposite and it is poorly intercalated, the nanoscale dispersion of modified
Figure 4: TGA (a) and DTGA (b) plots of MMT/ODTA, MMT/C\textsubscript{12}, MMT/C\textsubscript{20}, and MMT/C\textsubscript{22} thermogravimetric analyses in static air atmosphere.

Figure 5: TEM microphotographs of PS/MMT/ODTA (a), PS/MMT/C\textsubscript{12} (b), PS/MMT/C\textsubscript{20} (c), and PS/MMT/C\textsubscript{22} (d).
Table 1: Average molecular weights of the PS, PS/MMT/Na⁺, and PS/MMT nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(M_p) (k)</th>
<th>(M_n) (k)</th>
<th>(M_w) (k)</th>
<th>(M_z) (k)</th>
<th>(M_{z+1}) (k)</th>
<th>(M_v) (k)</th>
<th>(M_w/M_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>151</td>
<td>136</td>
<td>231</td>
<td>351</td>
<td>475</td>
<td>216</td>
<td>1.70</td>
</tr>
<tr>
<td>PS/MMT/Na⁺</td>
<td>210</td>
<td>161</td>
<td>261</td>
<td>385</td>
<td>503</td>
<td>245</td>
<td>1.62</td>
</tr>
<tr>
<td>PS/MMT/C_{12}</td>
<td>146</td>
<td>135</td>
<td>221</td>
<td>338</td>
<td>465</td>
<td>206</td>
<td>1.63</td>
</tr>
<tr>
<td>PS/MMT/C_{20}</td>
<td>153</td>
<td>148</td>
<td>227</td>
<td>332</td>
<td>444</td>
<td>214</td>
<td>1.54</td>
</tr>
<tr>
<td>PS/MMT/C_{22}</td>
<td>148</td>
<td>127</td>
<td>213</td>
<td>321</td>
<td>438</td>
<td>199</td>
<td>1.68</td>
</tr>
</tbody>
</table>

Table 2: Crossover frequencies and relaxation times of the PS and its nanocomposites at different temperatures (°C).

<table>
<thead>
<tr>
<th>(T) (°C)</th>
<th>(\omega_\phi) (rad/s)</th>
<th>Relax. time (s)</th>
<th>(\omega_\phi) (rad/s)</th>
<th>Relax. time (s)</th>
<th>(\omega_\phi) (rad/s)</th>
<th>Relax. time (s)</th>
<th>(\omega_\phi) (rad/s)</th>
<th>Relax. time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>20.3 [3.24]</td>
<td>0.31</td>
<td>22.9 [3.65]</td>
<td>0.27</td>
<td>5.9 [0.93]</td>
<td>1.07</td>
<td>1.0 [0.15]</td>
<td>6.54</td>
</tr>
<tr>
<td>200</td>
<td>40.4 [6.43]</td>
<td>0.16</td>
<td>44.2 [7.04]</td>
<td>0.14</td>
<td>11.1 [1.78]</td>
<td>0.56</td>
<td>1.7 [0.27]</td>
<td>3.74</td>
</tr>
<tr>
<td>210</td>
<td>92.3 [14.7]</td>
<td>0.07</td>
<td>73.5 [11.7]</td>
<td>0.09</td>
<td>13.9 [2.21]</td>
<td>0.45</td>
<td>7.61 [1.21]</td>
<td>0.83</td>
</tr>
<tr>
<td>220</td>
<td>115.4 [18.36]</td>
<td>0.05</td>
<td>75.4 [11.7]</td>
<td>0.09</td>
<td>35.8 [5.70]</td>
<td>0.18</td>
<td>12.6 [2.00]</td>
<td>0.50</td>
</tr>
</tbody>
</table>

Figure 6: Complex viscosity \(\eta^*\) at 190°C of PS, PS/MMT/C_{12}, PS/MMT/C_{20}, and PS/MMT/C_{22}.

clay nanoplatelets in PS/MMT/C_{20} and PS/MMT/C_{22} samples gradually increases (higher degree of exfoliation).

Considering now the \(G'\) and \(G''\) data, some interesting results emerge. For the polystyrene and its nanocomposites both the elastic and viscous components of the complex modulus show values which testify a mainly viscous behavior at low frequencies \((G'' > G')\) and a mainly elastic one at high frequencies \((G' > G'')\), with characteristic frequencies at which a reversal of the behavior is achieved (crossover frequency) (Figure 7).

It is known that incorporation of nanofillers in a polymer matrix induces an alteration in molecular mobility and, when present, the crystallinity of the matrix. Polymer nanocomposites exhibit pronounced elastic properties as well as delayed relaxation time as compared to the neat resin [33]. It is therefore logical to expect that as the degree of exfoliation increases, with the consequent increasing of the polymer chain-nanofiller interactions, the molecular mobility is more hindered with a consequent increase of the moduli, especially in the region at low frequencies, and an extension of the interval in which a solid-like viscoelastic behavior prevails.

Then, a better clay exfoliation should promote an increase of moduli and a shift of crossover frequencies toward lower values (delayed relaxation times). This is indeed the trend presented by our samples, with sample PS/MMT/C_{22} showing the higher values (Figure 7 and Table 2). The increase of moduli and of relaxation times could be influenced by the average molecular weight. In fact the increase of the average length of the polymer chains is expected to increase the number of entanglements, thus resulting in a decrease of the frequencies at which the chains remain immobilized. Our samples have similar molecular weight and so this contribution must not be considered.

Furthermore, the rheological behavior of a polymer in the molten state is also dependent on the temperature at which the measurement is taken. In fact, the examination of the experimental data shows that as the temperature increases, the absolute values of \(G'\) and \(G''\) decrease, even if with different speeds. Naturally, as the temperature increases, the viscous contribution \((G'')\) prevails in a gradually increasing extent with respect to the elastic one \((G')\) leading to a shift of the crossover frequency toward higher values (Table 2).
This behavior is due to the fact that the micro-Brownian motions of discrete elements of the macromolecular chains are more favored at high temperatures; this implies more macroscopic deformation and the fact that the elastic component prevails at even higher frequencies.

However, observing the results shown by PS and PS/MMT/C\textsubscript{12} samples, an interesting trend emerges: while in the measurements carried out at lower temperatures (190 and 200°C) PS crossover frequencies values are a little bit lower than the PS/MMT/C\textsubscript{12} ones, at higher temperatures (210 and 220°C) the results are reversed. This result could allow hypothesizing that from one side since in the experiments conducted at 190 and 200°C the crossover frequencies, and consequently the relaxation times, are very close in the two samples, both the low concentration of the filler and its poor dispersion do not influence significantly the bulk polystyrene chain mobilities and from the other side that the increase of the macromolecular mobility due to a higher temperature promotes the insertion of polymer chains into clay galleries, slightly increasing the clay dispersion into the matrix.

It is well known that the rheological response of a nanocomposite depends on the number of silicate particles per unit volume within the matrix and on the number of layers of clay per particle of clay.

The difference among the various samples lies in the different chain length of the surfactant used to modify the clay. So it can be assumed that the increase of the chain length in the surfactant promotes the separation of the layers of clay; this leads to a better dispersion of the silicate platelets in the matrix and consequently an increase in aspect ratio.

A confirmation of these results can be drawn from the Cole-Cole plot that can be used as a measure to assess the dispersion of filler into polymer matrix [34]. Since neat polymer and nanocomposites have different morphologies exhibiting different relaxation mechanisms, their Cole-Cole plots, which describe the relationship between the imaginary part $\eta''$ ($= G''/\omega$) and the real part $\eta'$ ($= G'/\omega$) of $\eta^*$, should display different shapes. Figure 8 displays the Cole-Cole plots of PS and its nanocomposites. While, as expected, PS plot presents a circular arc shape, the other samples present plots deviating from an arc-like shape. Since the deviation from an arc-like shape in the Cole-Cole plot is a measure of solid-like behavior, in our case deriving from a more efficient hindrance of polymer chains motion due to an increase of the number of clay platelets produced by exfoliation, we can conclude that the degree of exfoliation follows the order PS/MMT/C\textsubscript{22} > PS/MMT/C\textsubscript{20} > PS/MMT/C\textsubscript{12}, as already hypothesized from complex viscosity, moduli, and relaxation time data.
Films of all the samples were prepared with a thickness of 100 microns in order to be subjected to UV accelerated aging test in a Xenotest. The experiment was conducted for 400 hours and the evolution of the process of photodegradation was followed by registration of the infrared spectra. At the end of the aging stage, GPC analyses were carried out. A decrease of the average molecular weights was observed following the photodegradation process. The magnitude of the decrease of the average molecular weights was observed at the end of the photodegradation. It is known that polymer photodegradation involves two processes: chain scission and/or crosslinking, which changes the molecular weight $M_n$ and $M_w$ number and weight average molecular weight resp.). In the absence of crosslinking, only main chain scissions occur and the $M_n$ and $M_w$ drift toward smaller values. For random scission, polydispersity index ($M_w/M_n$) tends to 2. If simultaneous chain scission and crosslinking reactions occur and the probability of chain scission is smaller than the probability of crosslinking, $M_w/M_n$ increases [36]. From the data for PS films reported in Table 3, it was evident that $M_w/M_n$ had increased indicating that chain scission and crosslinking reactions were simultaneous with a probability of chain scission smaller than the probability of crosslinking. This indicated that the degradation took place with simultaneous occurrence both of branching reactions, which produced higher molecular weight molecules, and of chain scissions but with different trends: the presence of unmodified clay (sample PS/MMT/Na⁺ ox) seems to partially inhibit crosslinking, while as the degree of exfoliation increases, with a consequent increasing of polystyrene-surfactant interactions, the branching reactions become even more probable.

With regard to the kinetics of the UV photodegradation, it is already known that, with the proceeding of polystyrene UV accelerated aging, the formation of bands due to the hydroxyl groups (3600 to 3330 cm⁻¹) and carbonyl groups (1800–1600 cm⁻¹ and 1250 cm⁻¹) is observed. This trend is observed in all our samples, but with different kinetics.

First of all, the microcomposite behavior (where no surfactant is present) shows an interesting feature emerging during the very first hours of accelerated aging: the rapid increasing, with respect to neat polystyrene, of several peaks among which the more important ones are centered at 1690, 1704, and 1732 cm⁻¹ (Figure 9). As reported by Mailhot and Gardette [37] in their study on polystyrene photooxidation, these peaks can be assigned to the increase of concentration of aromatic ketones, benzaldehyde, and δ-lactone, respectively. This rapid growth has to be attributed to a catalytic action of sites present in the clay.

The kinetic curves (Figure 10), obtained plotting the carbonyl band area variation as a function of exposure time, show that the rate of photooxidation of all the clay containing samples is higher with respect to neat polystyrene sample. The rate is higher as a function of the degree of dispersion of the filler in the polymer matrix and then it increases with the increasing alkyl chain length present in the structure of the surfactant. In fact, the samples having the highest degree of dispersion of the silicate layers in the polymer matrix, that is,
the PS/MMT/C_{20} and PS/MMT/C_{22} samples, degrade faster than the PS/MMT/C_{12} one, with the microcomposite (PS/MMT/Na^+) showing a relatively lower rate.

4. Conclusions

The preparation of montmorillonite/PS nanocomposites by the use of two new thermally stable imidazolium surfactants (C_{20} and C_{22}) showed that it is possible to increase the exfoliation degree by increasing the length of the alkyl chain present in thermally stable surfactant structure. The higher exfoliation degree allows hindering more efficiently the macromolecular motion determining an increase of the relaxation times of the polymer melt and of its viscosity. In addition, a higher exfoliation promotes faster UV degradation of the nanocomposite that can depend on both higher polymer-clay interactions (especially during the very first hours of UV exposure) and higher polymer-surfactants interactions. Studies are in progress to address the contribution deriving from the structure of the surfactants to the enhanced UV photodegradation and to test other properties that have strong interest from an application point of view as, for example, mechanical performance, fire resistance, or barrier properties of the nanocomposites prepared starting from clay organically modified with these new surfactants in other properties.

Competing Interests

The authors declare that they have no competing interests.

Acknowledgments

The authors gratefully acknowledge the support of this work by University of Catania through PRA funding and Dr. Elena Fabbri for TEM microphotographs.

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