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Characterization of Nanoclays and Incorporation in Copolymer of Styrene-Ethylene-Propylene-Styrene (SEPS)

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Abstract

The objective of this work is to evaluate the effect nanoclays inclusion on copolymer of Styrene-Ethylene-Propylene-Styrene (SEPS) at two compositions of nanoclay (0 and 3%, w/w). The resulting nanoclay was characterized by XRD, SEM, EDX. Membranes modified with nanoclay were studied by water uptake, porosity and DSC analysis. The XRD patterns indicated that both samples of nanoclays, obtenied of cosmetic and molding clay, were suitable for the modification because of the increasing of the polymer-nanoclay surface area after this procedure. SEM analysis revealed an agglomeration phenomenon after contacting the surfactant-modified nanoclays with air. The incorporation of surfactant hydrocarbon chains in the MMT structure was confirmed by the EDX results. Finally, DSC analysis showed good stability of modified membranes at temperature changes, suggesting that this material could be used in applications that require temperatures range less than 150 °C.

Keywords: Nanoclay, copolymer, montmorillonite, SEPS.

INTRODUCTION

Clay minerals have been used in multiple applications such as nanocomposites [1], drug carrier in pharmaceutical industry [2], catalyst in organic synthesis [3], food additive, as adsorbent for nonionic, anionic, cationic dyes and metal ions [4], modification of cementitious materials [5] and in food packaging material [6]. This material has attached great attention in several scientific and technological areas due to their low cost, availability, and feasibility for nanosized conversion of particles [2]. On the other hand, the copolymer of Styrene-Ethylene-Propylene-Styrene (SEPS) has unique properties resulting from their morphological features. Because of the properties of block copolymers have been used in a wide range of application, such as thermoplastic elastomers for impact modification, compatibilization and pressure-sensitive adhesion [7–9]. Several studies have been focused on developing new kinds of functional materials, i.e porous, nano-structured damping materials [10], nano-scale templates [11] and nanocomposites based on block copolymers have shown promising results in these fields [12–14]. In this work, nanoparticles based on two types of clays were obtained and characterized by SEM, XRD and EDX studies. SEPS membranes modified with nanoclays at 0 and 3 %w/w were studied by as water adsorption, porosity, and DSC analysis in order to analyze the final properties of the membrane obtained.

EXPERIMENTAL PROCEDURES

Materials

Two types of clays were used: cosmetic clay (sample 1) and molding clay (sample 2), to obtain nanoclays and determine the differences in their properties. Silver nitrate was purchased from Panreac; hydrogen peroxide, sodium hydroxide, sodium chloride, ethyl alcohol and hydrochloric acid, were purchased from Chemi. The surfactant Arquad HTL8-MS has been donated by AkzoNobel (See Figure 1). The SEPS copolymer was donated by the company Kraton Polymers and diethanolamine (DEA) has been provided from Panreac.

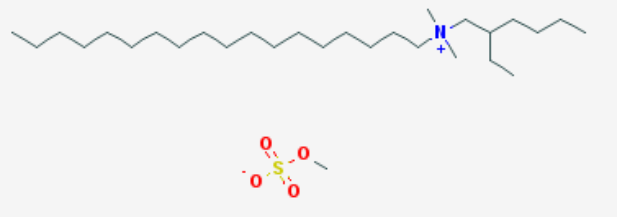

Figure 1. Arquad HTL8-MS molecule. Source: [16]

Nanoclays preparation

To preparate the nanoclay, the process was divided into three steps according to the methodology proposed by Perugachi [15]. The first step attempted to obtain the clay fraction. In brief, oxygenated water and hydrochloric acid were used to eliminate organic matter and carbonates, respectively. Afterward, sodium hydroxide was required to determine the fraction of area. The second step was carried out by adding sodium chloride solution and distillated water obtain a purified montmorillonite (MMT) clay with a conductivity of 10 µS/cm. In third step, a water /ethanol solution was prepared and mixed with sodium montmorillonite clay to homogenize it. The resulting mixture was added to distilled water and Arquad HTL8-MS solution. Finally, the excess of water was removed and the clay was washed with a water/ethanol solution, dried and stored.

Characterization

The samples were analyzed using a diffractometer with a horizontal goniometer. The interlayer spaces were determined using a Panalytical X'Pert Pro Diffractometer (CuKα radiation;

λ=0.15418 at 45 kV and 40mA) with a scanning speed of 0.02 2θ/s and a time per step of 8 seconds with a sweep of 1.8 to 6°.

The changes in surface morphologies of the samples after the modification were observed under scanning electron microscope (SEM, model JSM-6490, JEOL 1) at an accelerated voltage of 20 kV.

Energy dispersive X-ray spectroscopy (EDX, JEOL 1 JSM-6490) was used to determine the nanoclays samples composition after SEPS modification.

The thermal analysis of Films of Copolymer SEPS with nanoclays was carried out using a using differential scanning calorimeter [Model-DSC Q200 V24.4 Build 116] with a heating rate of 10ºC/ min between temperature ranges of 0ºC to 300ºC.

RESULTS AND DISCUSSIONS

X-ray Diffraction (XRD)

Figure 2 shows the XRD patterns of the treated clays. Both samples have the same interlayer space. The sample 1 exhibited two peaks (3.31° and 3.39°), which indicates interlayer spaces between 2.6 nm and 2.7 nm (Table 1). The interlayer space for both samples proved to be greater than the results obtained in previous work using unmodified (1.17nm) [17, 18]. Furthermore, this interlayer space is greater than values presented by commercial nanoclays such as Na-MMT (1.05 nm), 10AMMT (1.95nm) [19], Cloisite 30B (1.813nm) [20], Cloisite 20A (2.42 nm) [21] and Na + Cloisite (1.17 nm) [22]. This result is attributed to the long-chain hydrocarbon substitutions (C18 and C8) of the modifying agent (Figure 1) located in paraffinic monolayer type form [23–25].

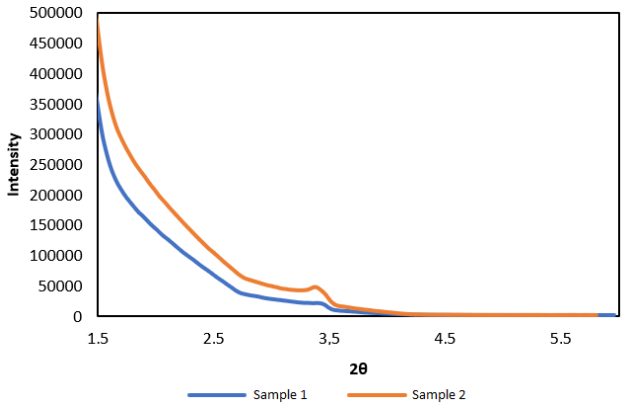

Figure 2. XRD pattern for sample 1 (cosmetic clay) and sample 2 (molding clay)

Table 1. Difraction peaks and interlayer space

Sample	Diffraction angle (2θ degrees)	Interlayer space (nm)
No. 1	3.31	2.7
	3.39	2.6
No. 2	3.39	2.6

According to these results, the sample type does not affect the interlayer space. Although in sample 1 a slight greater spacing is detected, it is not a relevant factor to identify it as more suitable with respect to sample 2 for being used as an additive in the copolymer of SEPS. Both samples are suitable for the modification of polymers because they have a high interlaminar space that promotes diffusion of the polymer and provides a greater surface area for the increase of the polymer-nanoclay contact area. The presence of the surfactant or modifier chains in the interlayers of the nanoclay influences Van der Walls interactions with the non-polar hydrocarbon structures of polymers such as polyethylene [26], whose block is contained in the SEPS.

Energy-dispersive X-ray spectroscopy (EDX)

The results of EDX for both samples are presented in Table 2. The compositions of the samples are compared with others reported by Kim et al. [27]. The samples contain carbon due to the modification with the ionic liquid Arquad HTL8-MS ($C_{29}H_{63}NO_4S$) which confirms the presence of surfactant hydrocarbon chains between the layers of the two samples of nanoclays (Figure 2). Nitrogen was not detected due to the high C:N ratio of the surfactant used (29:1). On the other hand, a higher silica composition was observed in sample 2 than those reported for aluminum. In addition, the ratio of silicon/aluminum (Si/Al) is greater for molding clay suggesting greater similarity with the compositions shown in Table 2. In contradistinction to amino group, the hydrocarbon chains of the surfactant become part of the structure of the montmorillonite. The magnesium composition was proportional to that reported by other researchers [17], and other elements common in this material were identified in the samples, such as iron, sodium, calcium and titanium.

Table 2. Elemental Analysis (%) of the clay mineral studied and its comparison with published values [17]

	Sample 1	Sample 2	MMT reference		
C (w%)	22.18	26.2	10.7245	13.475	17.694
O (w%)	33.19	36.15	51.195	46.505	45.495
Na (w%)	0.56	0.68			
Mg (w%)	0.62	1.23	1.23	0.7	1.005
N (w%)			3.465	3.42	3.51
K (w%)	7.81	1.37			
Ca (w%)		0.32			
Ti (w%)	1.57	0.38			
Fe (w%)	5.6	4.87			
Al (w%)	11.48	7.81	9.2	9.34	8.225
Si (w%)	17.38	21.24	24.415	26.06	24.075
Si/Al ratio	1.51	21.24	2.65	2.79	2.93

Scanning Electron Microscopy (SEM)

Figures 3 and 4 obtained from the scanning electron microscope show a phenomenon of agglomeration in both samples, this occurs because of contacting surfactant-modified nanoclays with air [28]. Also, different particle sizes formed agglomerates (large circles) and some nanoscale particles are found on the surface (small circles). It should be noted that the phenomenon of agglomeration between particles at the nanoscale is observed more clearly in sample 2.

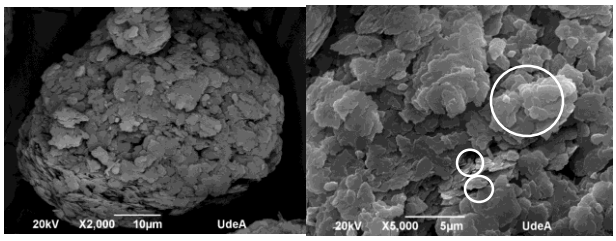

Figure 3. SEM micrograph for sample 1 of modified nanoclays

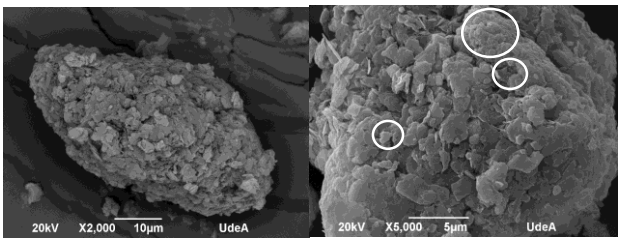

Figure 4. SEM micrograph for sample 2 of modified nanoclays

Characterization of SEPS membranes modified with nanoclays

Table 3 summarizes the results for water absorption and porosity for some membranes. As we can observe, there is an increase in water absorption and porosity in the membranes, the inclusion of nanoclays (NC) and DEA favored the absorption of water in the copolymer due to the creation of available spaces in the polymer chains and the inclusion of amino groups facilities the formation of hydrogen bridges, respectively.

Table 3. Results of Water Absorption and Porosity

Membrane	Water absorption (%)	Porosity
SEPS	0	0.069
SEPS 3% NC	0.777	1.986
SEPS 3% NC 25% DEA	1.787	10.34

The results of membrane thermograms with 0% NC, 3% NC and 3% NC with 25% DEA showed melting temperatures at 257, 245 and 214 °C, respectively (Figure 5). The presence of DEA improves the plasticization of the copolymer generating a significant change in the order-disorder transition temperature (TODT). The thermogram reported a change of 12 °C in the TODT with the presence of 3% nanoclays, which has been pointed out by Jin & Song [14], who detected a reduction of 1°C in the TODT of SEPS copolymer because of the presence of oil with only 0.5% of nanoclays. On the other hand, modified membranes exhibited stability at temperature changes, for example, the order-to-disorder transition temperature did not decrease dramatically, which means that the polymeric material will exhibit adequate performance in a temperature range of less than 150 °C.

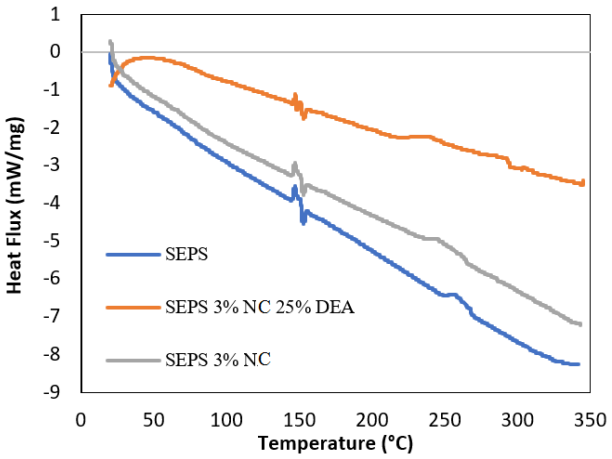

Figure 5. DSC thermograms for unmodified and modified SEPS copolymer

CONCLUSION

Two different types of clays (cosmetic and molding) were used to prepared nanoclays that were modified with SEPS to increase their properties and be used in different technological applications. The X-ray diffraction showed that both samples were suitable for modifying the polymer with these clays because they have a high interlaminar space, which increased the polymer-nanoclay contact area. Also, the EDX analysis confirmed the incorporation of hydrocarbon chains of the surfactant in the MMT structure and SEM analysis reported a phenomenon of agglomeration because of contacting the surfactant-modified nanoclay with air. Finally, modified membranes exhibited stability at temperature changes, which suggested that the polymeric material could be used for different applications in a temperature range of less than 150 °C.

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