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Study Of Thermal And Mechanical Properties Of Clay/Polymer Nanocomposite Synthesized Via Modified Solution Blending

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ABSTRACT

The incorporation of layered nano-silicates in polymer matrix greatly enhances the properties of the polymer. At present, there are many applications of polymer nanocomposites including coatings and architectural, they are also parts of automotive and construction industry among others. The acrylics employed at the present study were based on butyl acrylate (BA), styrene (STY), and methacrylic acid (MAA), and the nano-clay was Na-montomorillonite (MMT). The MMT clay was added to the polymer, which is the mixing matrix in a physical state solution called blend. Furthermore, their mechanical, thermal and wettability of especially prepared acrylic montmorillonite (MMT) nanocomposites were performed. By increasing the MMT in the polymer matrix concentration the Young’s modulus tends to increase it by an order of magnitude. However, by Differential Scanning Calorimetry (DSC), the thermograms show an increase in the glass transition temperature of nanocomposites for all weight percentages of MMT. Also, the wetting angle was determined, in order to know how much water is retained on the surface of the nanocomposite; the results showed that by increasing the particle of nano clay in the polymer matrix will induce a hydrophobic property to the nanocomposite.

INTRODUCTION

A typical polymer composite is a combination of a polymer and filler, and represents a new class of materials. Polymer-clay nanocomposites (PCNs) are materials which consist of organic polymeric matrix and inorganic nano-layered clay platelets [1-2]. Polymer nanocomposites with small percentage (<5 wt%) of nanoparticles embedded in a polymer matrix can exhibit significant improvement in material properties like dimensional stability, mechanical properties, increased glass transition, flame retardancy, gas barrier properties, compared to the neat polymer [3-4]. Montmorillonite (MMT), hectorite and saponite are the most commonly used layered silicates. In PCNs, their molecules can intercalate into the galleries of the layered silicates, pushing the layers apart and creating a nanocomposite with high aspect ratio. Depending on the nature of the components used, i.e. layered silicate and polymer matrix, and the method of preparation, three main types of composites can be obtained when layered clay is associated with a polymer. They are: a) phase-separated nanocomposites, b) intercalated and c) exfoliated nanocomposites [5-6]. In the present work, polyacrylic-layered silicate nanocomposites are investigated. Being, the processing blending solution with nanoparticles of MMT (sodium montmorillonite). Several properties were analyzed such as the mechanical and wettability properties, and their thermal properties.

EXPERIMENT

The polymer is an acrylic binder with composition 65BA/33.5MMA/1.5MAA synthesized via a staged-acid redox emulsion polymerization process at the former Rohm & Haas R&D Laboratories (Spring House PA, USA). The clay is a sodium montmorillonite (MMT), PVG grade, manufactured by Nanocor. In order to study, the solution blending process, the in-situ nanocomposite latex was produced via synthesis of the polymer in the presence of nano-clay. The blend nanocomposite latex was produced by low speeding mixing of a clay-free polymer latex and a dispersion of nanoclay in water [7, 11]. Films of about 2 mm in thickness were formed in 100 mm diameter Petri dishes by drying 15.9 grams of wet sample under constant temperature and humidity conditions (24 ºC and 50% humidity).

The thermal transitions were determined by differential scanning calorimetry (DSC). For DSC experiments the DSC6000™ calorimeter manufactured by Perkin Elmer (Connecticut, USA) was used. Temperature and enthalpy calibration were carried out using analytical grade In (T_m = 156.6 °C). The thermal transitions were determined at a heating rate of 20 °C/min under dry nitrogen atmosphere. The morphology was investigated by scanning electron microscopy (SEM) using a XL 30 ESEM Philips Xl series SEM with electron voltage of 15 KV. The samples were fractured under liquid nitrogen and subsequently sputter-coated with a thin layer of gold prior to SEM examination. Image analyses of the micrographs were carried out using the software ImageJ®.

Contact angle measurements were conducted with an in-house instrument which consists of an optical microscope Stereomaster II, Fisher Scientific Model SPT-ITH [6]. The images were acquired with a Motic1000 digital camera manufactured by Motic (P.R. China). The volume of the drop was maintained at 1 μL in all cases using a microsyringe. For accuracy and reproducibility, measurements were repeated 5 times on different regions of the same sample.

Elastic mechanical modulus was determined by uniaxial tensile deformation using the mini-tensile tester TST-350 manufactured by Linkam Scientific Instruments (Tadworth, Surrey, UK). Tensile deformation was carried out at 5 mm/min, room temperature.

RESULTS AND DISCUSSION

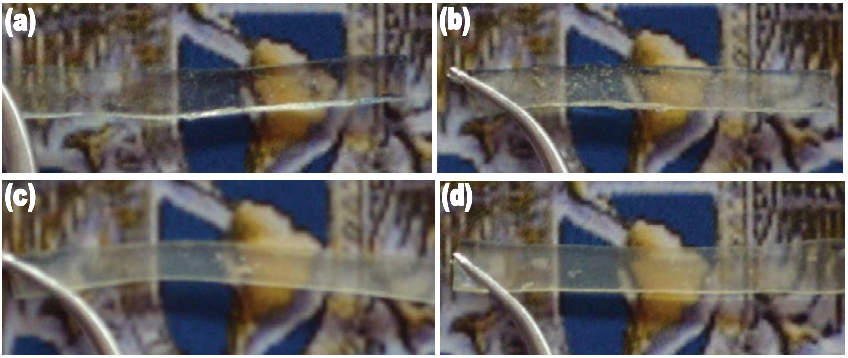

Figure1. Photographs of nanocomposite films of 2 mm in thickness obtained by the blending solution process. (a) acrylic coating control (b) 5%, (c) 10% and (d) 15% clay montmorillonite (MMT) obtained by mixing the solution.

Figure 1 shows the photographs obtained from the films of 2 mm thick montmorillonite (MMT), and it is observed that the concentration of 10% and 15% by weight remain optically transparent despite the brown color of the nanoparticle, this is typical Of a coating always preserve its transparency, even when adding any particles. On the other hand, it could be suggested that a good dispersion of the clay silicates is obtained since no cumulus is found in the polymer matrix according to figure 1 shown.

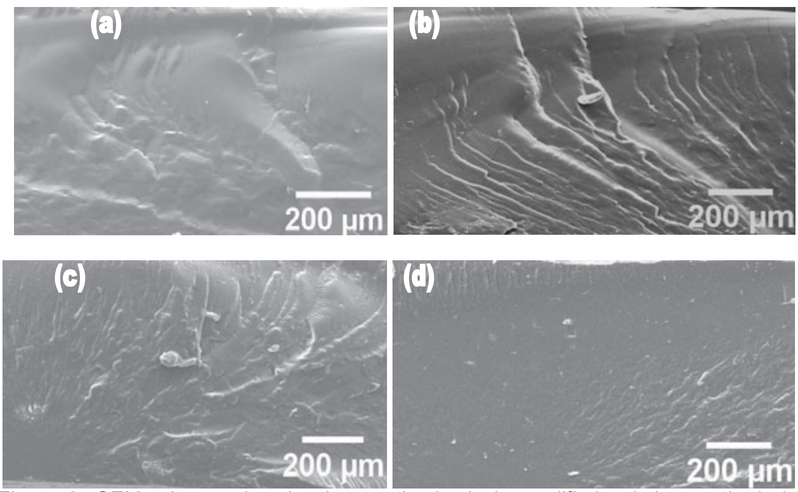

Figure 2. SEM micrographs showing synthesized via modified solution method: (a) polymer pristine (b) PCNs 5% (c) PCNs 10% y (d) PCNs 15% wt.

Figures 2 (a), (b), (c) and (d) show the surface morphology of (PCNs) nanocomposites prepared by solution blending. It can be seen from Figure 2 (a) The clean pristine polymer is shown to match that optical transparency of a coating, compared to Figures (b), (c) and (d), it is noted that the organoclay particles are uniformly dispersed in the polymer matrix. This is expected as solution blending allows the molecular chains to freely move in the solution at room temperature. The disordered mobility of polymer chain therefore easily penetrate through gallery spacing and thus resulting in a more exfoliated morphology.

The glass transition temperature, T_g, of the acrylic nanocomposites was determined by DSC. Figure 3 shows DSC heating scans of the acrylic coatings. The scans were carried at 10°C/min under dried N_2 atmosphere; the scans correspond to second heating. The pristine polyacrylic showed a glass transition temperature. T_g, of ≈ 8.4°C. The results showed that T_g slightly increases by the addition of nanoclay montmorillonite (MMT). It is important to note, that this mixing process solution mixture produces nanocomposites with slightly higher glass transition temperature, and the T_g values are shown in Table 1.

Table 1. Represents the results obtained of: DSC (Glass transition temperature), water contact angle and the Young's modulus of polyacrylic layered-silicate nanocomposites.

Samples	DSC T_g (ºC) Second heat	Contact Angle (º)	Young´s Modulus (MPa)
control	8.44	59º	.80
(PCNs) 5%	9.61	70º	1.00
(PCNs) 10%	10.41	73º	1.42
(PCNs) 15%	10.28	72º	1.30

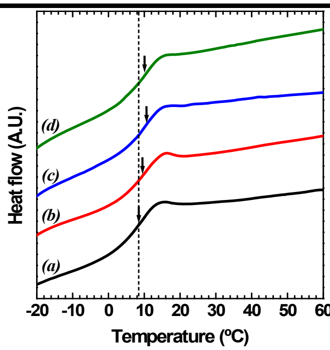

Figure 3. DSC heating scans, polyacrilic-layered silicate nanocomposites obtained by mixing the solution*. The concentration of MMT is (a) 0, (b) 5%, (c) 10%, and (d) 15% in weigh.*

Since the coatings studied in this work are polyacrylic and in turn these are classified as amorphous polymers, the thermal properties exhibited by these materials, will be only the temperature associated with their glass transition temperature (T_g). This is due, because its chains are not arranged in a crystalline structure. The nanocomposites exhibited an endothermic step associated with the glass transition temperature with an increment of about 2 °C, when MMT is incorporated at 10 % and 15% [9,10], as shown in table 1.

On the other hand the angle of wettability was determined, in order to study how much water was retain on the surface of the nanocomposite. This was carried out by incorporating a micro drop of water on the surface of the material and the results are shown in Figure 4(a). It can be observed, that the increment of the nano-particles clay in the polymer matrix will induce a hydrophobic condition, despite the amount of MMT incorporated.

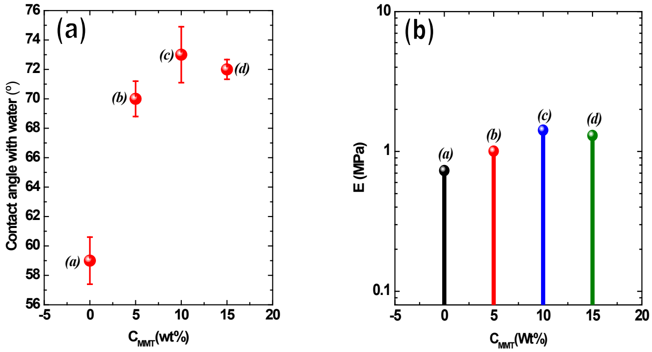

Figure 4. Contact angle with water (a) y mechanical properties (b)*, polyacrilic-layered silicate nanocomposites obtained by mixing the solution. The concentration of MMT is (a) 0, (b) 5%, (c) 10%, and (d) 15% in weigh.*

Also their mechanical properties were determined, obtaining their Young's modulus from stress-strain curves obtained initially and the results are shown in figure 4. (b). It is clear that there is a slightly increment obtained in the Young's modulus [8], by rising the concentration of montmorillonite clay.

CONCLUSIONS

The PCNs have been synthesized via modified solution method, as well as studied by SEM, DSC, Angle of wettability and, mechanical properties results showed that the modified solution method is an efficient method to obtain nanocomposite with the exfoliated morphology of the silicate layers and in high concentrations holds and retains its optical transparency. On the other hand, these nanocomposites increase up to an order of magnitude in reinforcement mechanical Young's modulus by increasing the concentration of nanoparticle.
By DSC, the glass transition has a significant increase, however, this nanoparticle by the wettability angle, it induces property of hydrophobicity to the polymer matrix.

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