



Effect of sonication on the synthesis of exfoliated polymer clay nanocomposites

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Research efforts on polymer clay nanocomposites have been drawing a great deal of attention due to their great enhancement of properties in many areas. Here, we synthesized exfoliated polymer clay nanocomposites (PCNs) by *in situ* polymerization of oil based vinyl macromonomer with styrene in the presence of clay. In order to facilitate the clay dispersion mixing was carried out by sonication besides classical mixing. The polymer clay nanocomposites were characterized by Fourier transform infrared spectroscopy (FTIR), transmission electron microscopy (TEM), X-ray diffraction spectroscopy (XRD) and thermal gravimetric analysis (TGA). The samples prepared by mixing in sonication bath gave lower char yield compared to the samples of classical mixing.

Keywords: Polymer clay nanocomposite, exfoliated, sonication, X-ray diffraction spectroscopy, thermal gravimetric analysis.

Introduction

Polymer-clay nanocomposites (PCNs) have attracted much attention recently due to their excellent properties such as high dimensional stability, thermal resistance, gas barrier performance, optical clarity and enhanced mechanical properties when compared with the pure polymer or conventional composites¹⁻⁶. These materials can find applications in a large area such as automotive, aerospace, transportation, construction and electronic industries⁷⁻¹⁰. The properties of the PCNs depend on various factors, such as kind of clay and its loading, processes of composite preparation, surface modification and the type of surface modifier^{3,11}. In addition, dispersion of the clay in the polymer matrix has also a great effect on the composite properties¹². Strong interactions between polymer matrix and exfoliated nanolayers having large interfacial area lead to superior mechanical properties and higher thermal stability^{13,14}. Although property enhancement is really very exciting for the exfoliated polymer-clay nanocomposites, it is not easy to synthesize truly exfoliated structures. The majority of the reported polymer-clay nanocomposites contain a mixture of platelets and tactoids, and these nanocomposites are called as partially exfoliated nanocomposites¹⁵.

In this study, we successfully synthesized oil based polymer-clay nanocomposites by using *in situ* polymerization. The nanocomposite samples were also prepared in sonication bath in order to provide better dispersion of the clay platelets. The chemical structure and thermal characteristics of the obtained composite samples were determined and the results were evaluated.

Experimental

Refined sunflower oil purchased from the local market was used as received. Toluene diisocyanate (TDI) and silver nitrate (AgNO₃), styrene (St) and 2-hydroxyethyl methacrylate (HEMA) were purchased from Aldrich Chemicals. 2,2'-Azobisobutyronitrile (AIBN, Fluka) was recrystallized from ethanol prior to use. Montmorillonite (MMT) was purchased from Aldrich Chemicals and was modified with hexadecyltrimethylammonium chloride (HDTMA, 25%, Aldrich) was used as a cationic surfactant.

Partial glyceride was prepared by glycerolysis reaction between sunflower oil and glycerol. For the urethane oil preparation, the reactant ratio given by Stanton¹⁶ was applied. Thus, oil and glycerol, were placed into the reaction flask and heated. When the temperature reached 218°C, calcium

hydroxide (0.1 wt% of the oil) was added as catalyst. The temperature was then set at 232°C and kept constant. At predetermined time intervals, samples were taken and poured into three-fold ethanol. Transesterification reaction was ended when the alcohol solution became clear. The flask content was taken into diethyl ether and washed first with dilute sulphuric acid and then with distilled water to remove the catalyst and free glycerol. In order to understand that the glycerol was removed completely, the spot test based on selective oxidation of glycerol with periodic acid was applied to the washings¹⁷. The ethereal solution was dried over Na₂SO₄ and the solvent was removed. The hydroxyl value of the dry and glycerol free sample was determined. The hydroxyl value is the number of mg of potassium hydroxide required to neutralize the amount of acetic acid capable of combining by acetylation with 1 g of sample. For this determination, an acetic anhydride solution in pyridine was used as an acetylation agent¹⁸.

In order to prepare oil based macromonomer; partial glycerides and HEMA were combined through urethane linkage by the reaction with TDI. The reactants (TDI, HEMA, and [OH] contributed by partial glyceride) were used in equimolar amounts. Partial glyceride and HEMA mixture were heated in dry xylene to 40–50°C, and TDI was added slowly over a 30 min period. Lead naphthenate as a 24 wt% solution in white spirit was added as a catalyst in the amount of 0.02 wt% of the oil portion. The temperature was set at 90°C and reaction was continued for 4 h.

Organomodified clay (OCLAY) was prepared by cationic exchange of sodium MMT with HDTMA in distilled water at 75°C for 2 h. Then mixture is cooled to room temperature and stirred for 24 h. The exchanged clays were filtered and washed with distilled water several times until no chloride ion was detected (white color) with 0.1 M AgNO₃ solution. After drying the OCLAY in an oven for 24 h at 60°C, it was ground to powder with a mortar.

Oil based macromonomer was stirred with magnetic stirrer at room temperature overnight until macromonomer was completely dissolved in styrene. Organomodified clay (0.75, 1.5, and 3 wt% of total weight of styrene and macromonomer) and AIBN (0.5 wt% of styrene) was added and mixed by mechanical stirring for 2 h. Finally, films with 300 micron wet film thicknesses were prepared on the glass plates. The film samples were then placed in an oven and cured at 95°C for

8 h. Additional film samples were prepared in same route by mixing in sonication bath (Sonorex Super RK 106 35Hz BANDELIN Electronic GmbH & Co KG).

Molecular weight was determined by gel permeation chromatography (GPC) instrument equipped with a Waters styragel column (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 0.3 mL min⁻¹ and a Waters 410 Differential Refractometer detector. The structure of macromonomer was characterized by using Fourier-transform infrared spectroscopy (recorded on a Perkin-Elmer FT-IR Spectrum One B spectrometer). The powder XRD measurements were performed on a PANalytical X'Pert PRO X-ray diffractometer equipped with graphite-monochromatized Cu K_α radiation ($\lambda = 1.15 \text{ \AA}$) at a general voltage of 40 kV and current of 120 mA at room temperature. TEM imaging of the samples was carried out by JEOL JEM 1011 instrument operating at an acceleration voltage of 200 kV. For the TEM measurements, film samples were prepared by cutting the cross-linked nanocomposite by using microtome apparatus. Then samples were placed on a thin copper grid covered by a carbon film that supports the sample to be viewed. The thermal stability of the oil based polymer-clay nanocomposites (OBPCNs) was measured using a TGA instrument (TA Instrument, TGA 2050) under a nitrogen atmosphere at a heating rate of 50°C/min.

Results and discussion

As stated previously, triglyceride oil-based vinyl macromonomer was prepared in two successive steps. First, partial glycerides were obtained by glycerolysis reaction. The hydroxyl and acid values (acid value, number of mg of potassium hydroxide to neutralize the acids present in 1 g of sample) of the partial glyceride were found to be 113 and 2.45, respectively.

Subsequently, these partial glycerides were combined with HEMA through urethane linkage by using TDI in equivalent amount to total hydroxyl groups. The reaction between isocyanates and hydroxyl groups forming urethane linkage was monitored by FT-IR. In Fig. 1, FT-IR spectra of initial reaction mixture containing partial glyceride, TDI and HEMA and the end product obtained after 4 h were given. As seen, the free isocyanate peak at 2270 cm⁻¹ disappeared after 4 h indicating completion of the reaction. Polymerizable methacrylate double bonds were inserted into the structure through

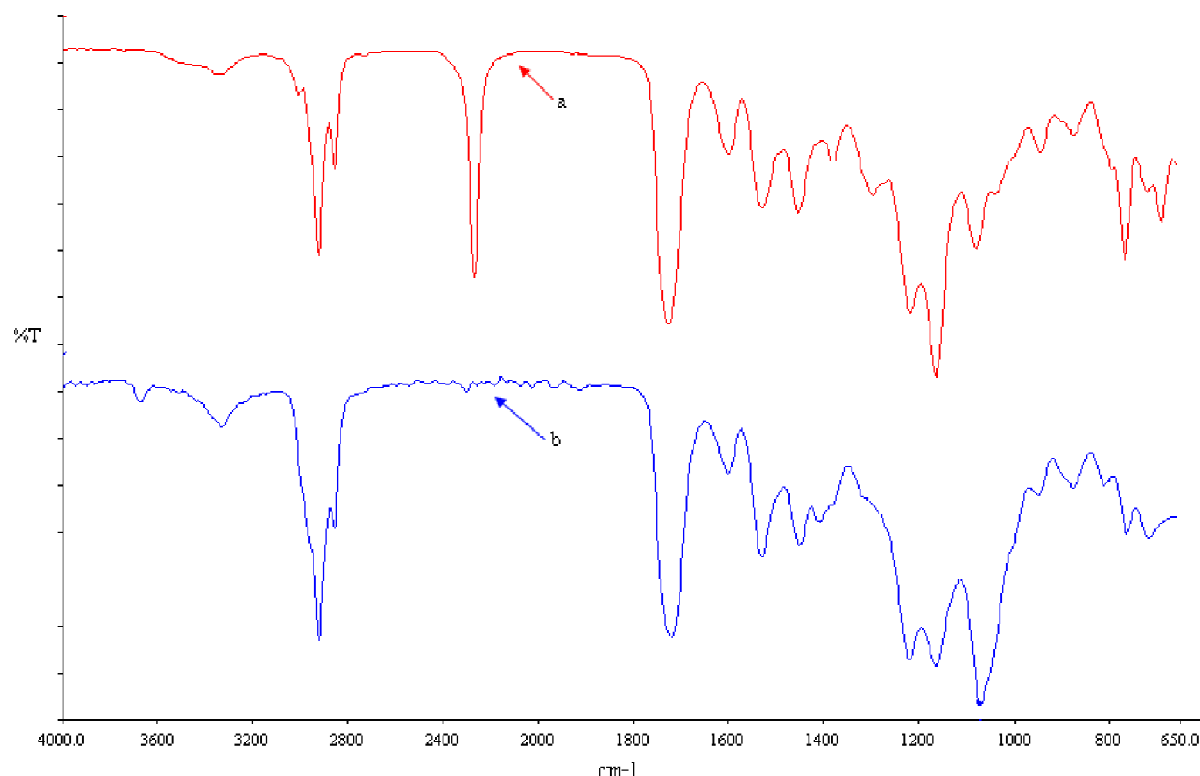
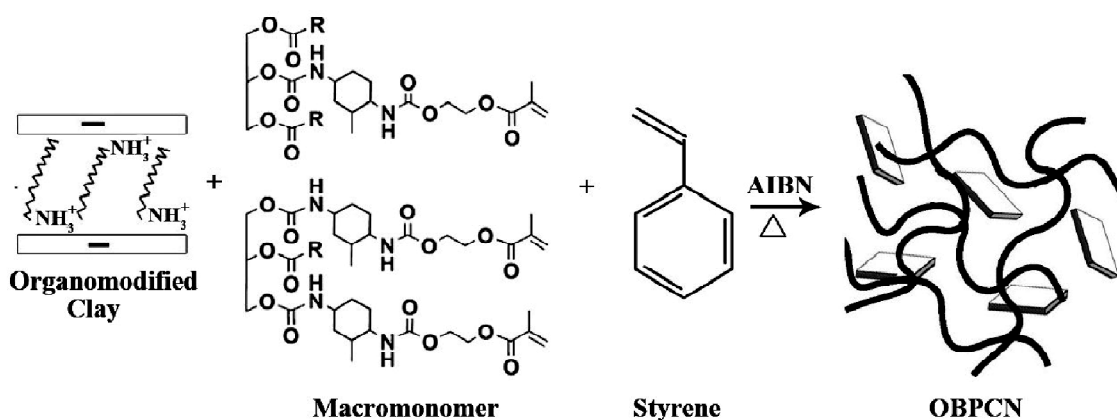


Fig. 1. FTIR spectra of TDI based reaction mixture: (a) at the beginning and (b) final product after 4 h.

the hydroxyl groups of mono- and diglycerides. The unsaturated terminal groups are expected also to act as cross-linker in the subsequent polymerization step. The number average molecular weight of the macromonomer was determined by GPC and found to be 3280 with a polydispersity of 2.21. The observed relatively high polydispersity is expected since the partial glycerides used to obtain macromonomer is a mix-

ture of mono-, di- and triglycerides. Styrene monomer was copolymerized with the macromonomer by using AIBN as free radical initiator in the presence of OCLAY. The radicals stemming from the thermal decomposition of AIBN initiate the polymerization. The overall process for the *in situ* synthesis of oil based polymer-clay nanocomposite is represented in Scheme 1.



Scheme 1. *In situ* synthesis of triglyceride oil based polymer clay nanocomposite.

FTIR analysis was also applied to the OCLAY and OBPCNs with different clay loadings. The obtained spectra were given in Fig. 2 for OBPCNs. As seen in Fig. 2, CH₂ asymmetric stretching (2924 cm⁻¹), CH₂ symmetric stretching (2854 cm⁻¹), and CH₂ plane scissoring (1452 cm⁻¹) appeared. In addition to the peaks, the bands appeared at 1036 or 1045 cm⁻¹ belong to Si-O-Si stretching indicates the presence of clay portion in the nanocomposite samples.

For the preparation of oil based nanocomposite sample, as explained before first clay was organically modified with alkylammonium cation to promote the insertion of macromer into the interlayer spaces of clay. XRD curves of MMT clay, OCLAY and OBPCN with loadings of 0.75% of clay are illustrated in Fig. 3. In the XRD diffraction pattern, the change in the value of 2θ, reflects the changes in the gallery distance of the clay. In Fig. 4, the XRD diagrams of MMT clay, OCLAY

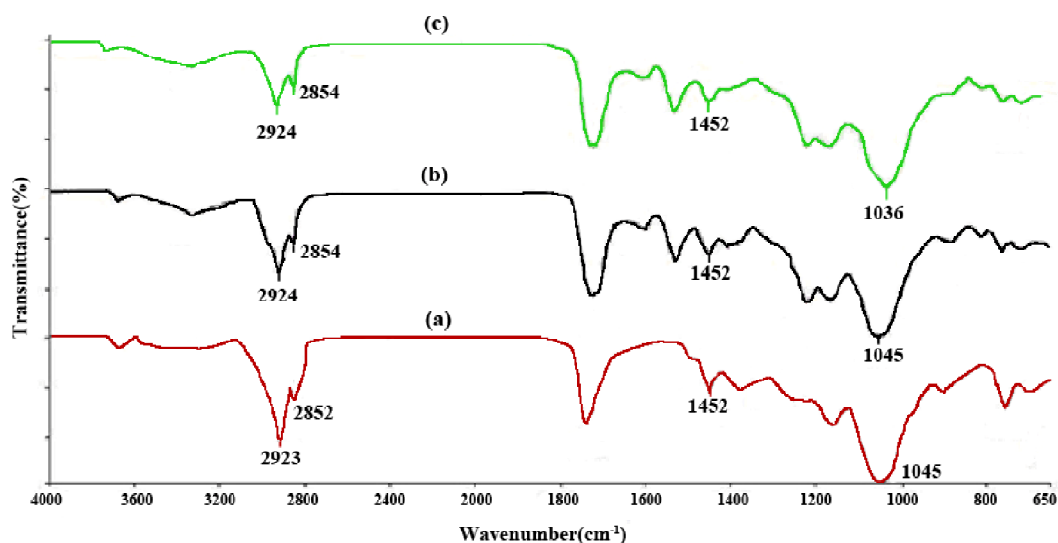


Fig. 2. FTIR spectra of OCLAY.

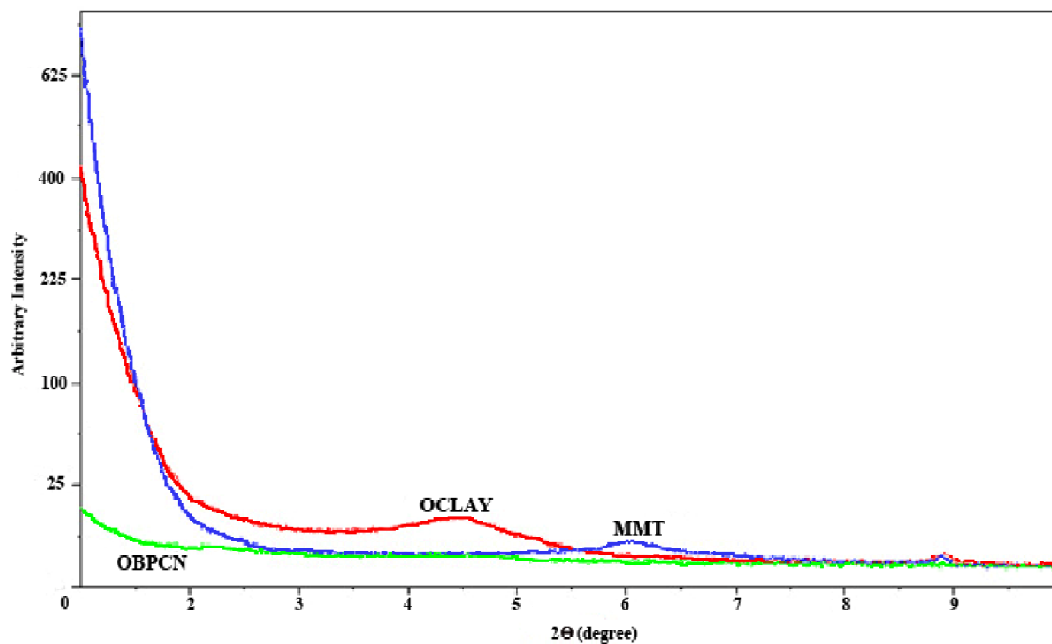


Fig. 3. XRD diffractograms of the MMT, OCLAY and OBPCN.

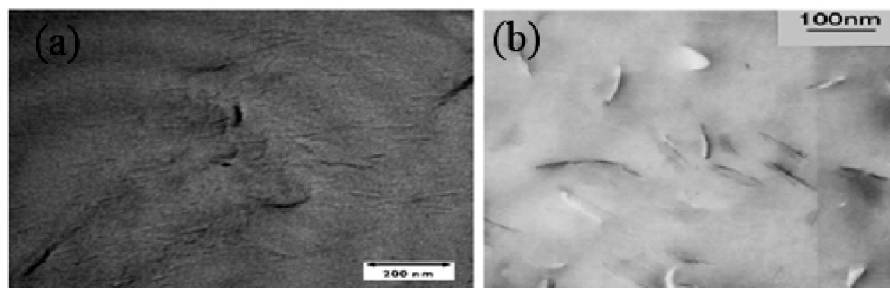


Fig. 4. TEM images of oil based polymer-clay nanocomposites: (a) 200 nm and (b) 100 nm.

and OBPCN samples were given. As seen, the organically modified clay and MMT samples exhibit peaks, which corresponds to a basal space (d_{001}) of 18.47 Å and 14.3 Å, respectively.

The increased basal spacing of OCLAY compared to the MT indicates that the organic modifiers came to reside between silicate layers. Additionally, OBPCN sample did not give any peak due to completely exfoliation of the clay in the polymer matrix.

However, XRD measurements alone may not be conclusive for understanding the level of dispersion of the silica platelets. For this reason, structural analysis of polymer-clay nanocomposite was also performed with TEM. TEM images in Fig. 4 corroborated the nanometer-scale dispersion of the

clay within the polymer matrix. In this image, dark lines correspond to silicate layers, while the lighter portion represents oil based polymer (OBP) matrix. This result implies that the exfoliated structure was formed in OBPCN.

In order to achieve a good dispersion of the clay particles in OBPCN, initial reaction mixture was subjected to sonication by using a sonication bath. TGA analysis of OBPCN samples, prepared with and without sonication were given in Fig. 5 and Fig. 6 the overall results are collected in Table 1. As seen from Table 1, the char yield at 550°C was effected by the type of mixing. The samples prepared by mixing in sonication bath gave lower char yield compared to the samples of classical mixing, since the sonication mixing cause clay particles to be well dispersed in the polymer matrix and

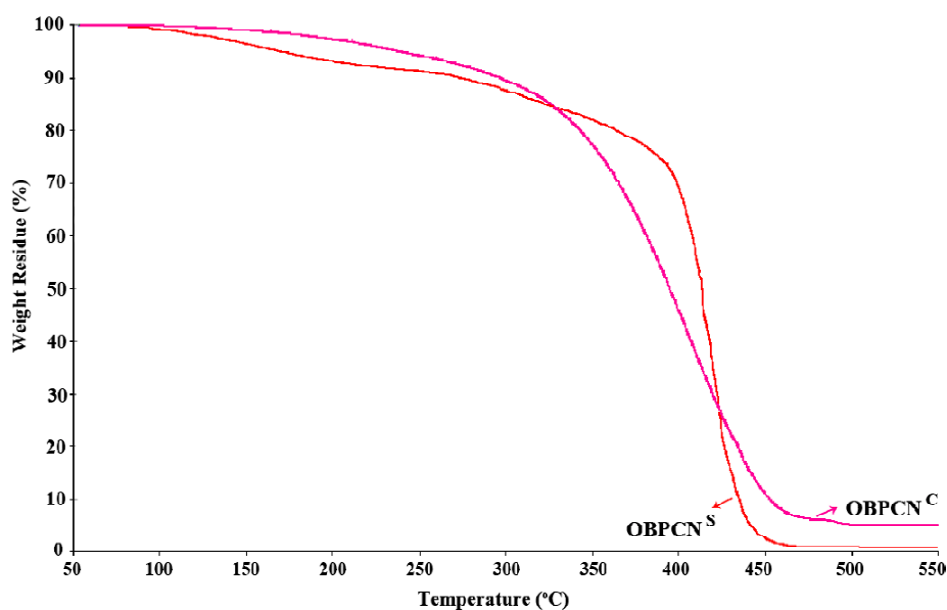


Fig. 5. TGA curves of OBPCN containing 0.75 wt% of clay.

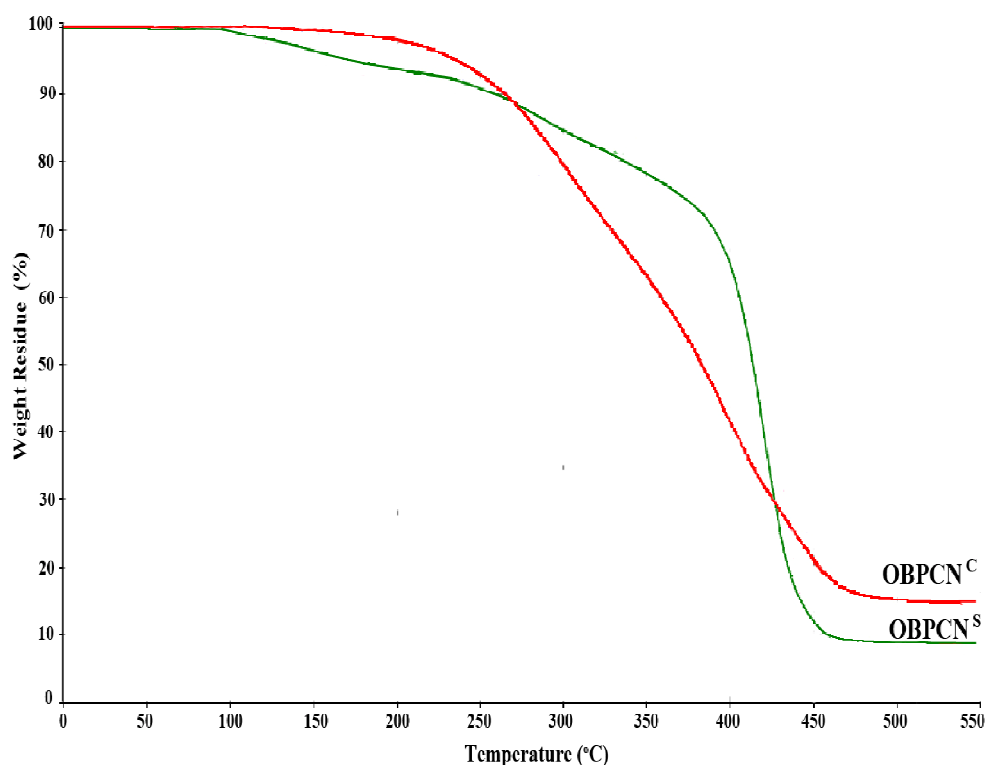


Fig. 6. TGA curves of OBPCN containing 3 wt% of clay.

Table 1. TGA analysis of OBPCN and its nanocomposites with different clay loadings

Sample	Clay content (%)	% Char yield at 550°C	T ₁₀ wt. % (°C)
OBPCN ^C	0.75	5.232	294
OBPCN ^S	0.75	0.45	274
OBPCN ^C	3	14.482	268
OBPCN ^S	3	8.669	260

OBPCN^C: Composite sample prepared with classical mixing.
 OBPCN^S: Composite sample prepared with sonication mixing.

most probably up to 3% clay loading, particles might not show enough barrier effect. Due to this fact, char yield was decreased in the samples prepared by sonication mixing. Similar results were also reported by Dean *et al.*¹⁹.

Conclusions

In this study oil based polymer was used in the preparation of polymer-clay nanocomposites. In the synthesis of oil based polymer, a strategy based on macromonomer technique was applied. Macromonomer was obtained by com-

binning the partial glyceride with HEMA through the reaction with TDI. The macromonomer thus obtained was copolymerized with styrene in the presence of clay. The resulting product is a polymer-clay nanocomposite material. Also, the effects of sonication during solvent blending in regards to degree of clay exfoliation was discussed. This study established that sonication method gave lower char yield compared to the classical mixing method. The preliminary results obtain in study showed that oil based polymer could be used for the production of nanocomposite materials.

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