

## Nanocomposites Based on an Algerian Bentonite and Poly(Methyl Methacrylate-CO-4-Vinylpyridine) Initiated by Ni(II) $\alpha$ -Benzoinoxime Complex

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Poly(methyl methacrylate-co-4-vinylpyridine) containing various 4-vinylpyridine contents (PMM4VP) were synthesized in dioxan at room temperature using a neutral Ni(II) $\alpha$ -benzoinoxime complex as a single component initiator and used to elaborate via solution intercalation method nanocomposites based on an organically modified bentonite from Maghnia Algeria (OBT).

Mixed exfoliated and intercalated PMM4VP/OBT nanocomposites were elaborated as confirmed by X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) investigations. The degree of exfoliation of these nanocomposites depended on both the OBT loading and the content of 4-vinylpyridine within the polymer matrix. Higher degree of OBT dispersion was obtained with nanocomposites based on PMM4VP19 containing 19 mol % of 4-vinylpyridine in presence of 2 % of OBT. Differential Scanning Calorimetry analysis showed an increase of about 20 °C in their glass transition temperatures compared to their virgin copolymers. Moreover, these nanocomposites exhibited a significant improvement of their thermal stability

**Keywords:** Poly (Methyl Methacrylate-co-4-Vinylpyridine), Hexadecylammonium Chloride, Intercalated, Partially Exfoliated Nanocomposite, Maghnia Bentonite and Thermal Degradation.

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### 1. INTRODUCTION

The elaboration of nanocomposites via solution intercalation is mostly carried out with water soluble polymers [1-3] and recommended in some circumstances only where in-situ polymerization or intercalation methods cannot be used.

Although nanocomposites based on poly(methyl methacrylate) and an organically modified bentonite (from Algeria) were prepared via in situ intercalative polymerization initiated by a neutral Ni(II) $\alpha$ -benzoinoxime complex (NBO) as a single component initiator in dioxan at room temperature[4], we did not succeeded so far after several attempts to elaborate via in-situ polymerization, nanocomposites based on 4-vinylpyridine and methyl methacrylate under similar conditions. Yet copolymers of various compositions of 4-vinylpyridine and methyl methacrylate were successfully prepared using this complex (NBO) as a single component initiator [5].

We will, in the present contribution, report on the preparation of nanocomposites based poly(methyl methacrylate-co-4-vinylpyridine) previously prepared and characterized using NBO as initiator at room temperature, via solution intercalation using THF as the solvent THF in presence of different loadings of a bentonite from Algeria, organically modified by hexadecylammonium chloride (OBT).

Investigations on the effects of OBT loading and 4-vinylpyridine contents within the polymer matrix on the structure, morphology and thermal behavior of the elaborated materials in nitrogen atmosphere, were carried by XRD, TEM, DSC and TGA and compared to the pure copolymers.

### 2. EXPERIMENTAL

#### 2.1 Materials

Poly(methyl methacrylate-co-4-vinylpyridine) containing 19 and 11 mol % of 4-vinylpyridine (PMM4VP19 or PMM4VP11) were synthesized and characterized as previously reported[5] at 30 °C using a neutral Ni(II) $\alpha$ -benzoinoxime complex (NBO) as a single component initiator, prepared according to literature.

Bentonite from Maghnia (Algeria) was kindly supplied by Bentonite Company of Algeria and analyzed by the central laboratory of the ENOF. This clay containing SiO<sub>2</sub> (55-65 %), Al<sub>2</sub>O<sub>3</sub> (12-18 %), Fe<sub>2</sub>O<sub>3</sub> (1-3 %), Na<sub>2</sub>O (1-3 %), CaO (1-5 %), K<sub>2</sub>O (0.76-1.75 %) and MgO (2-3 %), was organically modified by Hexadecylammonium chloride as previously described.

PMM4VP19/OBT and PMM4VP11/OBT systems were prepared by solution intercalation method using THF as the solvent for these copolymers and the dispersing medium for clay particles. The copolymers and the OBT were separately dissolved in THF to form dilute solutions during 24 h. The OBT/THF solution was then added to the dissolved copolymer. After solvent evaporation, the obtained materials (films) were dried to constant weight in a vacuum oven at 60 °C during several days to remove any trace of solvent. All these materials were characterized by FTIR, XRD, TEM, DSC and TGA.

## 2.2 Characterizations

The content of 4-vinylpyridine in these copolymers was determined using  $^1\text{H-NMR}$  performed on a Bruker Advanced spectrometer operating at 200 MHz in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ , using tetramethylsilane (TMS) as the internal reference standard. Typical weight average molecular weight and polymolecularity obtained by size exclusion chromatography (SEC) were respectively  $5,25 \times 10^4$  and 2,99 for PMM4VP11.

X-Ray diffractograms of pure (PBT) and modified Maghnia bentonite (OBT), and their nanocomposites PMM4VP11/OBT and PMM4VP19/OBT (in presence of 2% and 4% by weight of OBT) were recorded on a Philips PW3710 diffractometer in the range of 2 Theta (2-50). The monochromatic radiation applied was  $\text{CuK}\alpha$  ( $\lambda = 1.5406\text{\AA}$  under  $0.5^\circ\text{C}/\text{min}$  scan rate).

The morphology of the PMM4VP11/OBT and PMM4VP19/OBT nanocomposites was examined by transmission electron microscopy (TEM) as a complementary technique to XRD carried out on a JEOL 1400 equipped with a MORADA SIS numerical camera at an acceleration voltage of 120 Kv.

The glass transition temperatures ( $T_g$ ) of these copolymers and of their corresponding nanocomposites were determined by differential scanning calorimetry using a Mettler Toledo 821 DSC calorimeter under nitrogen at  $10^\circ\text{C}/\text{min}$ . The  $T_g$  values were determined at the midpoint of the second scan.

The thermal stability of these copolymers and their hexadecylammonium chloride Maghnia bentonite materials was analyzed by thermogravimetry using a TA Instruments thermal analyzer TGA 500 under nitrogen atmosphere at a scanning rate of  $10^\circ\text{C}/\text{min}$  from  $30^\circ\text{C}$  to  $650^\circ\text{C}$ .

## 3. RESULTS AND DISCUSSION

### 3.1 X-ray diffraction

Fig. 1 shows X-Ray diffraction patterns of PBT, OBT, binary PMM4VP11/OBT and PMM4VP19/OBT materials. A relatively broad peak appearing at  $2\theta = 6.60^\circ$  and corresponding to a d-spacing of 1.34 nm is observed with pure PBT. The intercalation of the Hexadecylammonium ion into the layer of this clay shifted this peak to a lower angle of  $5.20^\circ$  with OBT, increasing the d-spacing to 1.70 nm. The absence of the major peak of OBT with all these hybrids materials and the appearance of only weak peaks at lower angles may be considered at this step as due to the presence of mixed intercalated and partially exfoliated nanocomposites.

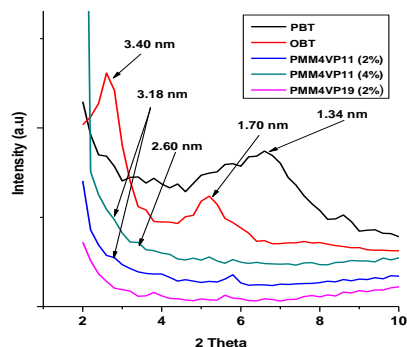


Fig. 1 – X-Ray diffraction patterns of PBT, OBT, PMM4VP11/OBT (2 and 4%) and PMM4VP19/OBT (2%)

### 3.2 TEM

The absence of the major XRD peak and the appearance of weak peaks at lower angles were not sufficient for the identification of the structures of these materials and a complementary characterization was carried out by TEM. Several TEM images were analyzed and Fig. 2 displays typical ones for PMM4VP11/OBT (2% and 4%) nanocomposites at high magnifications.

Mixed exfoliated/intercalated nanocomposite structures were evidenced with PMM4VP11/OBT (2%) by the presence of stacks of relatively small thickness randomly dispersed coexisting with a significant fraction of exfoliated silicate sheets. The thickness of the stacks of these nanocomposites varied between 7.6 nm to 15 nm while the d-spacing between clay layers of these stacks estimated by TEM varied between 2 nm and 3.70 nm and were in agreement with those observed by XRD.

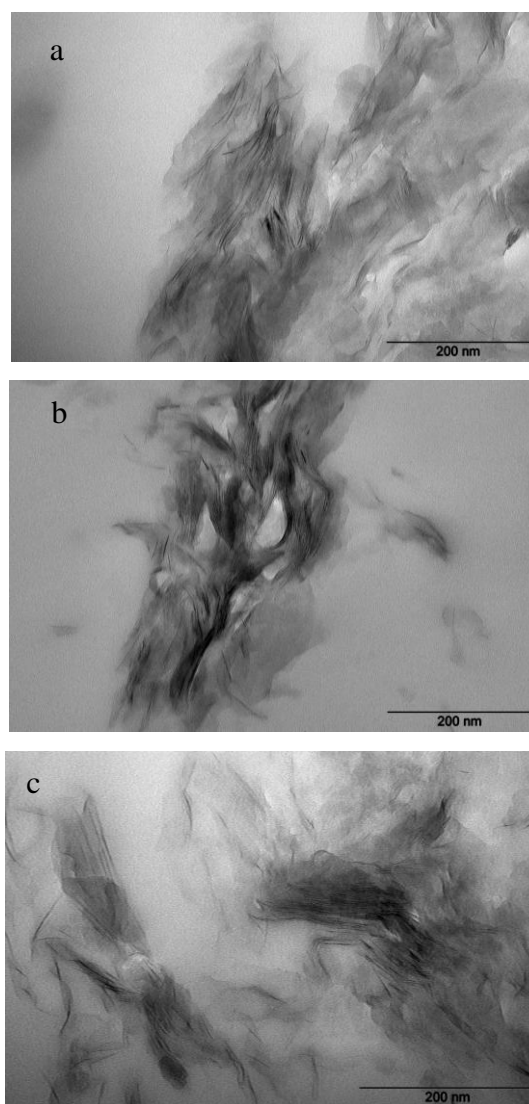


Fig. 2 – TEM micrographs of PMM4VP19/OBT (2) (a) and PMM4VP11/OBT (2, 4%) (b, c) nanocomposites.

A Higher number of relatively thicker stacked layers with d-spacing of different sizes of an average value smaller than that obtained with a lower clay loading, were shown with PMM4VP11/OBT (4%)

nanocomposites. A limited number of larger intercalated stacks as well as weakly intercalated agglomerates were also observed.

A better dispersion of OBT was observed with PMM4VP19/OBT (2 %) of higher 4-vinylpyridine content, characteristic of more exfoliated individual and thinner stacked clay layers of a length and a thickness varying between 67 nm and 105 nm and 3.54 nm and 8.70 nm respectively and a d-spacing estimated by TEM varying between 2.5 nm and 4.2 nm difficult to assess by XRD.

### 3.3 DSC analysis

DSC analysis showed that the glass transition temperatures of all nanocomposites increased by more than 20 °C compared to their virgin copolymers as shown in Fig. 3 for a typical PMM4VP19/OBT system.

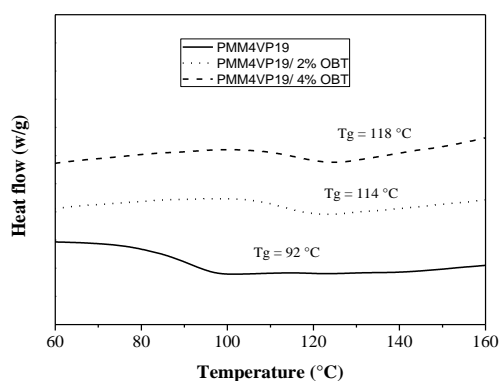


Fig. 3 – DSC curves of PMM4VP19 copolymer and its corresponding nanocomposites

### 3.4 TGA Analysis

A thermogravimetric analysis was carried for all studied systems under nitrogen from 30 °C to 650 °C and Fig.4 shows for illustration the TG and respective derivative curves of PMM4VP19 and its corresponding nanocomposites (2 and 4 % of OBT). The PMM4VP19 decomposition occurred in three stages in similar way as that of PMMA [4] with peaks appearing at about 170 °C, 310 °C and 346 °C.

In addition to the decomposition peak of the surfactant observed at 226 °C, the PMM4VP19/OBT nanocomposite degradation appeared slightly different from that of virgin copolymer and with OBT loading. A shift to lower temperatures is depicted with PMM4VP11/OBT (2 %) while PMM4VP19/OBT (4 %) shifted to higher temperature by 5°C in the first step compared to virgin PMM4VP19. A tendency toward a single step is observed in the second stage around

307 °C with an increase of OBT loading. Indeed, the intensity of the first and third peak decreases with an increase of OBT. Although practically no change occurred at T50 %, a significant increase of 40 °C in  $T_d$  (10%), considered as a measure of the onset degradation temperature, was observed for PMM4VP19 (4 %) as compared to its virgin copolymer.

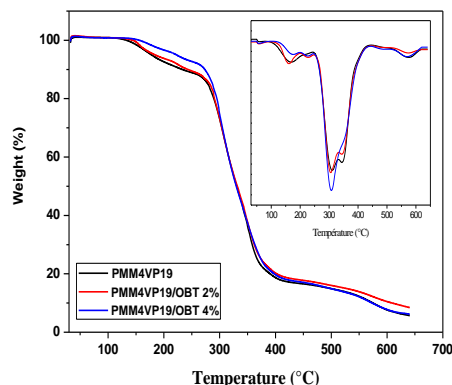


Fig. 4 – TG and d(TG) thermograms of PMM4VP19 and their corresponding nanocomposites (2 and 4 %) of OBT

## 4. CONCLUSIONS

Intercalated and partially exfoliated nanocomposites based on poly (methyl methacrylate-co-4-vinylpyridine) containing 11 and 19 mol % of 4-vinylpyridine were successfully prepared by solution intercalation, using a bentonite from Maghnia (Algeria), modified by hexadecylammonium chloride and THF as solvent.

All elaborated nanocomposites exhibited an increase in  $T_g$  and an enhanced thermal stability at T 10%, compared to their virgin copolymers.

Better dispersion was evidenced by TEM for nanocomposites based on copolymers containing 19 mol % of 4-vinylpyridine in presence of 2 % of OBT. The dispersion of OBT decreases with a decrease of 4-vinylpyridine content in the copolymer matrix and with its increase in the mixture of elaboration.

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