Elaboration and Thermal Analysis of Nanocomposites Based on Poly(methyl methacrylate-*co*-4-vinylpyridine) and Maghnia Bentonite

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ABSTRACT: Nanocomposites based on an organically modified bentonite, from Maghnia Algeria (OBT) and a copolymer of methyl methacrylate with 4-vinylpyridine (PMM4VP) synthesized in dioxan at room temperature using a neutral Ni(II)α-benzoinoxime complex as a single component initiator, were elaborated via solution intercalation method and characterized by several techniques. X-ray diffraction and transmission electron microscopy investigations indicate that mainly exfoliated and intercalated PMM4VP/OBT nanocomposites were elaborated and that the degree of exfoliation decreases with an increase of the OBT loading. Thermal analyses of these nanocomposites compared with their virgin copolymer confirmed a significant improvement of their thermal stability as evidenced by an increase of 28°C in their onset degradation temperatures. In addition, differential scanning calorimetry displayed an increase in the range of 12–18°C in their glass transition temperatures relative to their virgin copolymer. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

INTRODUCTION

Extensive research has been carried during the last two decades on various polymer-organoclay nanocomposites.[1–6] Many of them showed significant improvements mainly in their mechanical, barrier and thermal properties compared to micro composites.[7–9]

Depending on the method of elaboration via *in situ* polymerization, solution blending or melt blending and the degree of dispersion of clay within a polymer matrix, intercalated, or exfoliated nanocomposites may be prepared. Exfoliation is generally preferred to intercalation since it usually leads to significantly improved physical properties of nanocomposites. The elaboration of an exfoliated organoclay nanocomposite requires however a good compatibility between the polymer matrix and the organoclay surface.

Solution intercalation, often environmentally unfriendly, is not the recommended method for the preparation of large scale commercial nanocomposites. This method is however reported to give a good control on the homogeneity of the constituents; helps understand the intercalation process[10–12] and is used in particular circumstances in the design of tailored materials with specific properties where *in situ* polymerization or intercalation methods cannot be used.

Poly(methyl methacrylate) PMMA is one of the largely investigated thermoplastic-clay nanocomposites, due to its important applications in many fields.[13] Various methods of preparation of poly(methyl methacrylate)/clay nanocomposites that produced intercalated or exfoliated structures of improved properties have been reported.[14–17]

We have in a previous study prepared intercalated nanocomposite, with enhanced thermal stability, based on poly(methyl methacrylate) and an organically modified bentonite (from Algeria) via *in situ* intercalative polymerization initiated by a neutral Ni(II)α-benzoinoxime complex (NBO) as a single component initiator in dioxan at room temperature.[18] Copolymers of various compositions of 4-vinyl pyridine and methyl methacrylate of increased glass transition temperatures (T_gs) and enhanced thermal stability were successfully prepared at 30°C using this complex (NBO) as a single component initiator.[19] These types of copolymers are of importance as reported in the literature by several authors[20–23] as candidates in several applications as polyelectrolytes and catalyst supports.

Poly(methyl methacrylate-co-vinylpyridine)-montmorillonite nanocomposites of enhanced thermal stability compared to virgin corresponding copolymers were prepared and used as reducing agents by Salahuddin.[20] Fournaris et al.[21] have carried out aqueous *in situ* polymerization of protonated 4-vinylpyridine (4VP) in presence of 10% or less sodium montmorillonite and obtained exfoliated montmorillonite-polyelectrolyte heterostructures. Hassanein et al.[23] have prepared Cobalt(II) phthalocyaninetetrasulfonate supported on poly-*N*-alkyl-4-vinylpyridinium/montmorillonite intercalates and used it as catalyst for the oxidation of 2-mercaptoethanol in aqueous medium. This latter showed a good catalytic activity. Moreover, it is important to mention the potential applications of these materials in the field of nanoblends of tailored morphology and properties in the presence of another hybrid containing proton acceptors through specific interactions.

Synthetic nano-structured conducting polymers and polymer composites and their potential applications in the field of nanosensors were reported very recently by Rajesh et al.[24]

We have carried out various attempts to elaborate via *in situ* polymerization nanocomposites based on methyl methacrylate and 4-vinyl pyridine via *in situ* intercalative polymerization initiated by a neutral Ni(II) α-benzoinoxime complex (NBO) as initiator in dioxan at room temperature but without success.

We then have in a first step of the present work, investigated the possibility of elaborating nanocomposites via solution intercalation, based on a bentonite originated from Algeria, modified with Hexadecylammonium chloride (OBT) and a typical copolymer of 4VP and methyl methacrylate (PMM4VP32) containing 32 mol % of 4VP, synthesized radically at 30°C using a neutral Ni(II) α-benzoinoxime complex as initiator.

To our knowledge, the elaboration of such materials using this complex at room temperature and Maghnia bentonite, originated from Algeria, is original and has not been reported in the literature yet. This investigation, considered as a preliminary one, will be extended to the synthesis of copolymers at a much larger scale and to the elaboration of copolymer/clay nanocomposites prepared by melt intercalation.

We then reported in a second step on the characterization by different and complementary techniques, of these nanocomposites containing 2 or 4% of this modified bentonite.

The effect of OBT loading on the structure, morphology, and thermal behavior of the elaborated materials in nitrogen atmosphere, was then investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), and TGA and compared to the pure copolymer.

EXPERIMENTAL

Materials

A copolymer of methyl methacrylate containing 32 mol % of 4VP (PMM4VP32) was synthesized as previously reported[18] at 30°C using a neutral NBO as a single component initiator, prepared according to literature.[25] This copolymer obtained by precipitation in a large excess of methanol or petroleum ether were purified by dissolution/precipitation and dried in a vacuum oven at 50°C for several days. This latter was in this study kept in a vacuum oven for 8 days prior its FTIR, NMR, DSC, and TGA analysis.

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_2 (55–65%), Al_2O_3 (12–18%), Fe_2O_3 (1–3%), Na_2O (1–3%), CaO (1–5%), K_2O (0.76–1.75%), and MgO (2–3%), was organically modified by Hexadecylammonium chloride (HDAC) as follows.

HDAC was prepared by mixing appropriate amounts of hexadecylamine with concentrated HCl in 150 mL of distilled water and then added to an already separately dispersed bentonite into the hot clay–water mixture at 80°C and stirred vigorously for 1 h. The mixture was then filtered and washed with water in ethanol (50/50 vol %) until negative chloride test was obtained using AgNO3. The hexadecylammonium-exchanged clay (OBT) was then dried at 75°C for 3 days in a vacuum oven and kept in a dessicator.

PMM4VP32/OBT systems were prepared by solution intercalation method using THF as the solvent for these copolymers and the dispersing medium for clay particles. PMM4VP32 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. The mixture was then stirred during another 24 h and spread on a Teflon plate. After solvent evaporation, the obtained materials (films) were dried to constant weight in a vacuum oven at 50°C during 6 days to remove any trace of solvent. All these materials were characterized by FTIR, XRD, TEM, DSC, and TGA.

Characterizations

PMM4VP32 was characterized as previously[19] reported by UV spectroscopy, ^{1}H-NMR and ^{13}C-NMR spectra performed on a Bruker 500 MHz spectrometer at room temperature with CDCl$_3$ as the solvent and tetramethylsilane (TMS) as internal standard and elemental analysis. Its weight average molecular weight and polymoleculairy obtained by size exclusion chromatography were of 6.2×10^3 and 1.67, respectively.

^{1}H-NMR spectra PMM4VP32/OBT nanocomposites were performed on a Brucker Advanced spectrometer operating at 200 MHz in CDCl$_3$ at 25°C, using TMS as the internal reference standard.

FTIR

FTIR spectra of thin films of PMM4VP32 and of its corresponding binary nanocomposites cast from THF solutions onto KBr disks, with a spectral resolution of 2 cm^{-1} and 32 scans were signal averaged on a Perkin-Elmer Spectrum one spectrometer.

XRD

X-ray diffractograms of pure bentonite (PBT) and modified Maghnia bentonite (OBT), virgin PMM4VP32 copolymer and its PMM4VP32/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 CuKα ($\lambda = 1.5406$ Å under 0.5°C/min scan rate).

DSC

The T_gs of the synthesized PMM4VP32 copolymer and of its corresponding organo-modified materials were determined by DSC using a Metler Toledo 821 DSC calorimeter under nitrogen at 10°C/min. The samples were heated and cooled twice in the temperature range from 25 to 200°C. The T_g values were determined at the midpoint of the second scan.

TGA

The thermal stability of PMM4VP32 copolymer and its hexadecyl ammonium 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°C/min from 30 to 580°C.

TEM

The morphology of the PMM4VP32/OBT nanocomposites was examined by TEM as a complementary technique to XRD on a JEOL 1400 equipped with a MORADA SIS numerical camera at an acceleration voltage of 120 Kv.

RESULTS AND DISCUSSION

FTIR

Figure 1(a,b) shows FTIR spectra of PBT, organically modified bentonite (OBT), PMM4VP32 and its PMM4VP32/OBT materials. Figure 1(a) shows the FTIR spectra of PBT and OBT (modified bentonite) that confirm with only slight differences the characteristic vibration bands of PBT and of its organo-modification by the ammonium salt (HDAC) from the bands shown at 3630, 3349, 1034, 525, 465 cm^{-1} and the appearance of new bands at 2852 and 2920 cm^{-1} as well as at 1473 cm^{-1} corresponding to the stretching and deformation vibration of the saturated C[sbond]H, respectively.

As illustrated in Figure 1(b), the bands observed at 1450, 1300–1100, and 1732 cm^{-1} with PMM4VP32 are attributed to the stretching and deformation vibration of the C[dbond]O and C[sbond]O (ester group of MMA) while those at 1598, 1558, and 1416 cm^{-1} characterize the 4-substituted pyridine moiety. The characteristic absorptions of clay, slightly affected in the presence of the copolymer matrix, were observed in the PMM4VP32/OBT nanocomposite at 1037, 518, and 476 cm^{-1}. In addition, the carbonyl band appearing at 1732 cm^{-1} with virgin PMM4VP32 shifted to 1727 cm^{-1} with PMM4VP32/OBT nanocomposite, indicating the presence of interaction between this copolymer and the bentonite. Moreover, the broadening towards higher wavenumbers of the band at 1598 cm^{-1}, characteristic of free pyridine, observed with PMM4VP32/OBT, may also be attributed to the presence of specific interactions that occurred between the OBT and the pyridine moiety of PMM4VP32.

Zha et al. have depicted similar type of interaction between block poly(styrene-block 2-vinylpyridine) copolymers and natural clay (montmorillonite, MMT) or commercial organoclays (Cloisite 30B, Cloisite 10A, Cloisite 15A, and Cloisite 25A from Southern Clay Products).[10]
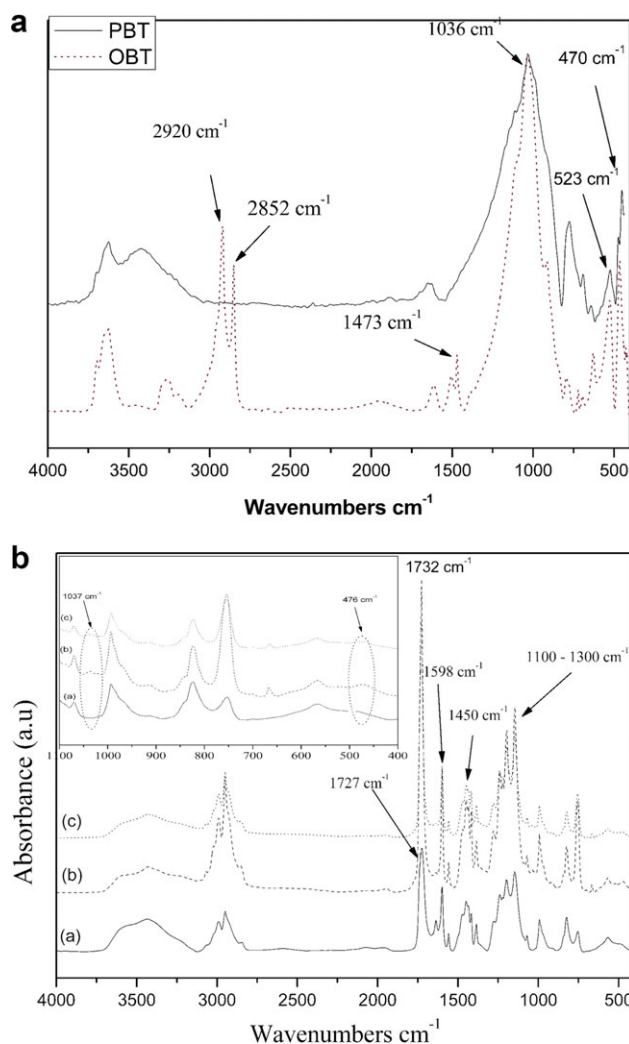

Figure 1. (a) FTIR spectra of pure (PBT) and organically modified bentonite (OBT). (b) FTIR spectra of (a) PMM4VP32, (b) PMM4VP32/2% OBT and (c) PMMA4VP32/4% OBT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

^{1}H-NMR

Figure 2 exhibits ^{1}H-NMR spectra of PMM4VP32 and its corresponding PMM4VP32/OBT nanocomposites including the assignments of the resonance signals. The presence of the organo-modified bentonite in the copolymer matrix is identified from the peak observed at 1.24 ppm attributed to the hydrogens of the HDAC, which intensity increased with an increase of clay content in agreement with data reported in the literature.[26–28]

The shifts of the meta and ortho proton signals of PMM4VP32 to lower fields, observed with PMM4VP32/OBT are also an evidence of the presence of interactions that occurred between the clay and the copolymer matrix.

XRD

Figure 3 shows XRD patterns of PBT, OBT, and binary PMM4VP32/OBT materials. A relatively broad peak appearing at $2\theta = 6.60°$ and corresponding to a d-spacing of 1.34 nm is
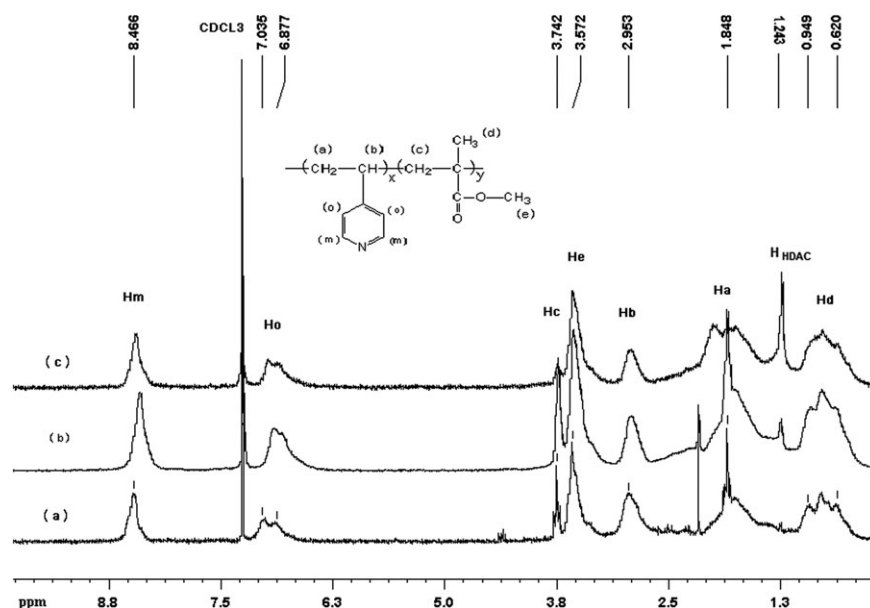
Figure 2. ^{1}H RMN spectra of (a) PMM4VP32, (b) PMM4VP32/2% OBT and (c) PMMA4VP32/4% OBT.

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° with OBT, increasing the d-spacing to 1.70 nm. An intercalated nanocomposite can in a first step be characterized by the observation of a XRD peak at 2θ lower than the one of the modified clay. The absence of XRD peak is not however sufficient for the identification of an exfoliated nanocomposite and a complementary characterization has to be carried out by TEM. The interpretation from XRD patterns of the only weak peak, observed with PMM4VP32/OBT, prepared in the presence of 2 or 4% by weight of OBT, at a d-spacing of 1.43 nm, intermediate between those of PBT and OBT is difficult. It may however be due to parts of surfactant that fled from the galleries of the clay as well as some left over weakly intercalated tactoids that did not participate to the formation of the nanocomposite as were evidenced by TEM as a complementary technique. The absence of the major peak of OBT may be considered at this step as due to the presence of exfoliated nanocomposites.

TEM
Figure 4a illustrates TEM micrographs of PMM4VP32/OBT (2%) nanocomposites at low and high magnifications. At low magnification (2000 or 1000 nm scale bar), the OBT exists as relatively small tactoids, randomly dispersed and coexisting with some aggregates weakly intercalated within the PMM4VP32 co-polymer matrix.

In agreement with XRD, TEM images confirmed at higher magnification (500 or 200 nm scale bar), the formation of mixed exfoliated/intercalated nanocomposite structures, evidenced by the presence of stacks of relatively small dimensions and a significant portion of exfoliated silicate sheets highlighted by circles.

A better dispersion of OBT was observed with PMM4VP32/OBT (2%) that contained a higher density of exfoliated thinner

stackded clay layers of a length and a thickness varying between 67 and 105 nm and 3.95 and 6.70 nm, respectively. In agreement with XRD analysis, the d-spacing between clay layers of these stacks, of mostly parallel individual layers, varied between 2.47 and 3.64 nm.The distance between these platelet stacks, randomly dispersed, estimated from a semi-quantitative TEM analysis, higher than 8 nm, confirmed their exfoliated structures.A significant number of individual platelets of a length varying between 73 and 109 nm and a thichness of 1.97 nm were also observed.

A limited number of intercalated stacks of a length varying between 61 and 85 nm and a thickness less than 11.50 nm as well as weakly intercalated agglomerates were also observed.

When the OBT concentration is increased to 4%, relatively thicker stacked OBT layers were observed with PMM4VP32/OBT (4%) nanocomposite, containing relatively more
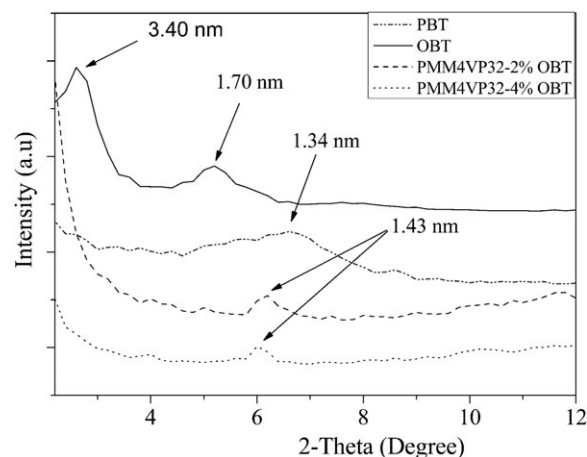

Figure 3. XRD patterns of PBT, OBT and PMM4VP32/OBT nanocomposites.
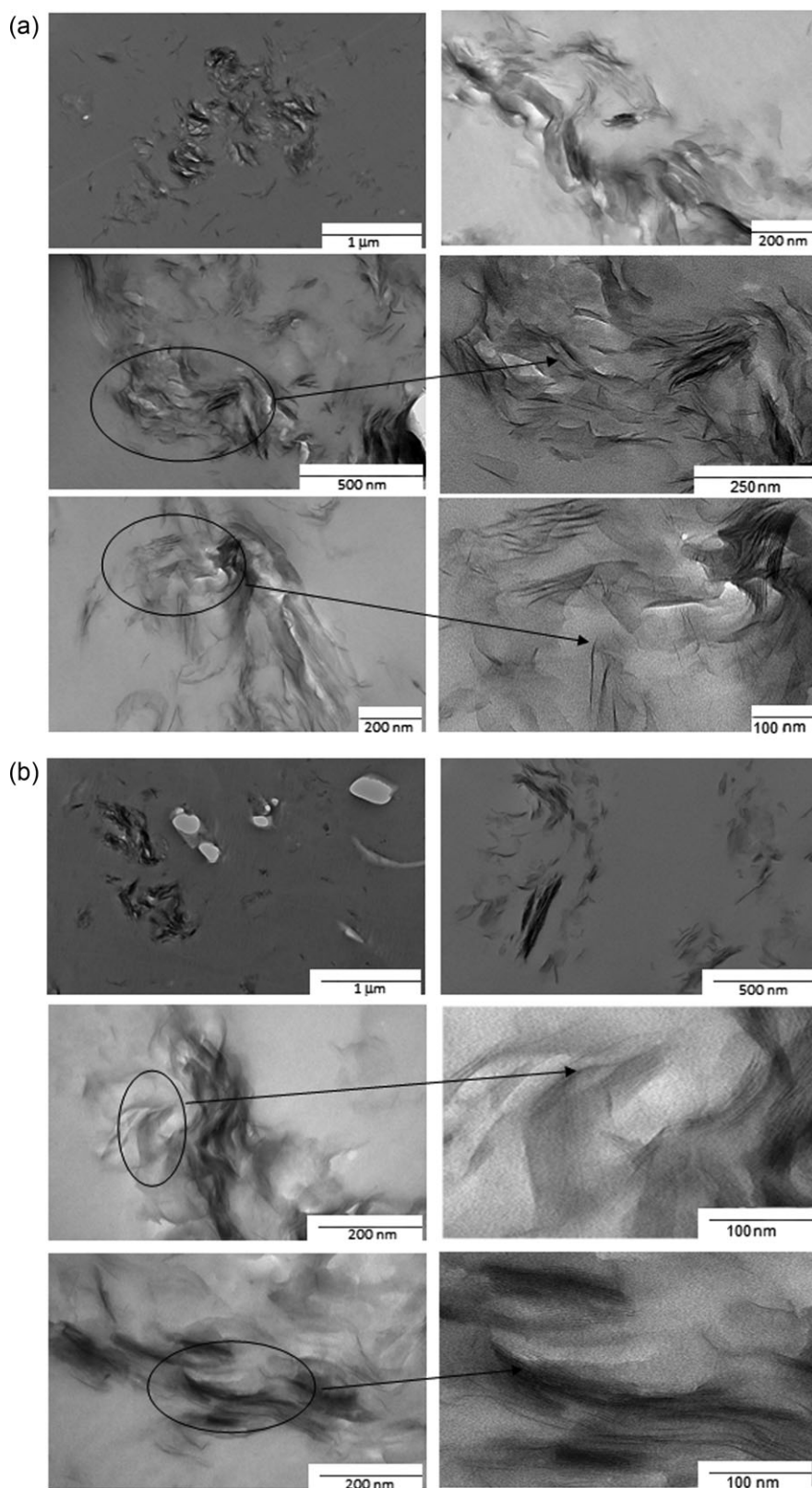
Figure 4. (a) TEM micrographs of typical PMM4VP32/2% OBT nanocomposite. (b) TEM micrographs of typical PMM4VP32/4% OBT nanocomposite.
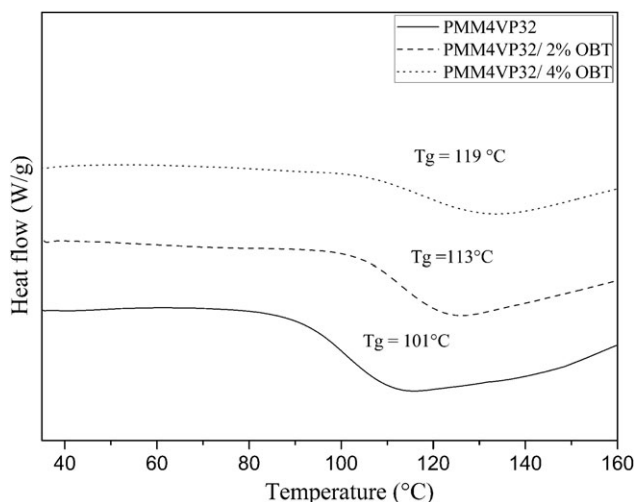
Figure 5. DSC thermograms of PMM4VP32 and its PMM4VP32/OBT nanocomposites.

intercalated layers. As displayed in Figure 4(b), less individual platelets and higher density of stacks randomly dispersed in the polymer matrix, with a relatively larger average thickness, a length varying between 45 and 72 nm and a distance between these relatively thicker stacks varying between 2.5 and 6.5 nm.The average length of the elaborated nanocomposites decreased with an increase of OBT loading as shorter individual platelets were observed with PMM4VP32/OBT 4%.

Thermal Behavior

DSC Analysis. PMM4VP32 copolymer previously synthesized[19] was purified again and recharacterized in this study as a film cast from THF that may still contain some solvent traces or moisture even though dried for several days. Its T_g determined by a different DSC apparatus, under nitrogen at a different scanning rate of 10°C/min, decreased compared to the previous one determined under different conditions and as a precipitate

Thermal properties of PMM4VP32 and its nanocomposites were analyzed by DSC and TGA.

Figure 5 displays thermograms of PMM4VP32 and PMM4VP32/OBT containing 2 and 4% of OBT. Indeed, as shown in Table I that summarizes the T_g of the PMM4VP32 and its corresponding nanocomposites, the T_g of PMM4VP32/OBT (2%) nanocomposite increased significantly by 12°C com-

Table 1. T_g and Thermogravimetric Data of PMM4VP32 and its Nanocomposites Under Nitrogen

Temperature (°C)	PMM4VP32	PMM4VP32/ OBT(2%)	PMM4VP32/ OBT(4%)
T_g	101	113	119
$T_{5\%}$	209	252	225
$T_{50\%}$	315	317	318
$T_{75\%}$	349	382	364
$T_{max.}$	310	309	312
Char at 550°C (%)	11.7	18.2	15.3

pared to its virgin copolymer. An increase of OBT loading to 4% led to higher T_g. Such increase of T_g of nanocomposites with clay loading, attributed to the restricted segmental motions of the intercalated polymer chains within the clay galleries, dominant with this latter nanocomposite as confirmed by TEM, was also reported by several authors.[13,16,29–31]

TGA Analysis. Figure 6 shows the TGA and respective derivative d(TG) curves of PMMA4VP32 copolymer and of its corresponding binary nanocomposites under nitrogen. As also reported in the literature, we have in a previous study observed three steps of degradation with PMMA[18] prepared at room temperature using the same NBO initiator. The PMM4VP32/OBT nanocomposite decomposition appeared slightly different from that of virgin PMM4VP32 and showed in addition to the two stages of decomposition, observed with this later, a shoulder at 280°C attributed to the decomposition of the surfactant. The first stage of decomposition of PMM4VP32, in the 120–245°C region, showed two shoulders at 185 and 211°C and is attributed to the decomposition of weak linkages in the chains. The major decomposition peak of the virgin copolymer, observed in the second stage at 310°C, is due to random scission of polymer main chain. A third step characterized by a weak peak appearing as a shoulder around 394°C for the virgin copolymer was detected from the d(TG) curves. The intensity of this latter decreased and shifted slightly to higher temperatures in presence of OBT as shown with PMM4VP32/OBT nanocomposites.

Table I summarizes the thermogravimetric data of PMM4VP32 and its nanocomposites. A significant increase of 28°C in $T_{d(5\%)}$, considered as a measure of the onset degradation temperature, was observed for PMM4VP32 (2%) as compared to the virgin PMM4VP32. Although no appreciable increase was observed at $T_{d(50\%)}$ (the temperature at which 50% degradation occurred), as illustrated in Figure 6, the nanocomposites exhibited higher resistance to degradation toward the end of thermal decomposition, especially that containing 2% of OBT. Moreover, the char increase which acts as insulator and mass transport barrier, observed with PMM4VP32/OBT nanocomposites at 550°C, also confirmed the enhanced thermal stability of the
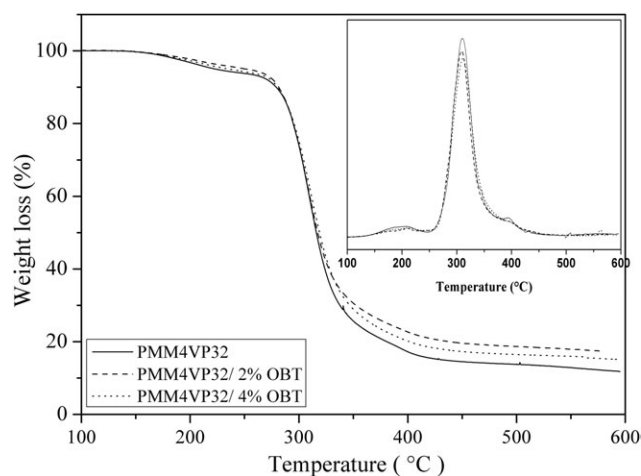

Figure 6. TG and d(TG) curves of PMMA4VP32 copolymer and of its corresponding binary nanocomposites under nitrogen.

elaborated nanocomposites compared to their corresponding virgin PMM4VP32.

The effect of bentonite loading on the morphology and thermal stability of the resulting nanocomposite was also investigated. The thermogravimetric data gathered in Table I were in good agreement with TEM analysis that confirmed a better dispersion of OBT with 2% loading and the presence of more intercalated layers, evidenced by a higher T_g of the nanocomposite prepared with 4% OBT loading and that favored the formation of aggregated tactoids which contribute less to thermal stability.

CONCLUSION

Nanocomposites based on poly(methyl methacrylate-co-4-vinylpyridine) prepared at room temperature, in presence of a neutral Ni(II) α-benzoinoxime complex as initiator were elaborated via solution method using Maghnia bentonite (Algeria) modified with HDAC (OBT) PMM4VP32/OBT (2 and 4%) in THF as the solvent and were characterized by XRD, TEM, DSC, and TGA.

The obtained results showed that mixed exfoliated/intercalated PMM4VP32/OBT nanocomposite of mainly exfoliated structure with a significant increase of 28°C in the onset temperature ($T_{5\%}$) and of enhanced T_g of 12°C as compared to the virgin PMM4VP32 was elaborated at relatively low OBT loading (2%).

An increase of OBT loading from 2 to 4% led to an increase of T_g but to a decrease of T_{onset} of the elaborated PMM4VP32/OBT (4%) containing more intercalated layers as compared to PMM4VP32/OBT (2%).

This study will be extended to the synthesis of such copolymers at a larger scale and to the investigation of the mechanical properties of these nanocomposites.

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REFERENCES

1. Kiliaris, P.; Papaspyrides, C. D. *Prog. Polym. Sci.* **2010**, *35*, 902.

2. Pavlidou, S.; Papaspyrides, C. D. *Prog. Polym. Sci.* **2008**, *33*, 1119.

3. Ray, S. S.; Okamoto, M. *Prog. Polym. Sci.* **2003**, *28*, 1539.

4. Paul, D. R.; Robeson, L. M. *Polymer* **2008**, *49*, 3187.

5. Wilson, R.; Plivelic, T. S.; Aprem, A. S.; Ranganathaiagh, C.; Kumar, S. A.; Thomas, S. *J. Appl. Polym. Sci.* **2012**, *123*, 3806.

6. Habi, A.; Djadoun, S.; Grohens, Y. *J. Appl. Polym. Sci.* **2009**, *114*, 322.

7. Unnikrishnan, L.; Mohanty, S.; Nayak, S. K.; Ali, A. *Mater. Sci. Eng. A* **2011**, *528*, 3943.

8. Wang, H. W.; Chang, K. C.; Chu, H. C. *Polym. Int.* **2005**, *54*, 114.

9. Sivudu, K. S.; Thomas, S.; Shailaja, D. *Appl. Clay Sci.* **2007**, *37*, 185.

10. Zha, W.; Han, C. D.; Han, S. H.; Lee, D. H.; Kim, J. K.; Guo, M.; Rinaldi, P. L. *Polym. J.* **2009**, *50*, 2411.

11. Jeon, H. S.; Rameshwaram, J. K.; Kimb, G.; Weinkaufa, D. H. *Polym. J.* **2003**, *44*, 5749.

12. García N.; Corrales, T.; Guzmán, J.; Tiemblo, P. *Polym. Degrad. Stab.* **2007**, *92*, 635.

13. Cui, L.; Tarte, N. H.; Woo, S. I. *J. Appl. Polym. Sci.* **2008**, *110*, 784.

14. Nikolaidis, A. K.; Achilias, D. S.; Karayannidis, G. P. *Eur. Polym. J.* **2012**, *48*, 240.

15. Lerari, D.; Peeterbroeck, S.; Benali, S.; Benaboura, A.; Dubois, P. *Polym. Int.* **2010**, *59*, 71.

16. Oral, A.; Tasdelen, M. A.; Demirel, A. L.; Yagci, Y. *Polym. J.* **2009**, *50*, 3905.

17. Tiwari, R. R.; Natarajan, U. *J. Appl. Polym. Sci.* **2007**, *105*, 2433.

18. Ouaad, K.; Djadoun, S.; Ferfera-Harrar, H.; Sbirrazzuoli, N.; Vincent, L. *J. Appl. Polym. Sci.* **2011**, *119*, 3227.

19. Harrar-Ferfera, H. *J. Appl. Polym. Sci.* **2008**, *107*, 3963.

20. Salahuddin, N. *J. Appl. Polym. Sci.* **2007**, *104*, 3317.

21. Fournaris, K. G.; Boukos, N.; Petridis, D. *Appl. Clay. Sci.* **2001**, *19*, 77.

22. Fournaris, K. G.; Karakassides, M. A.; Petridis, D. *Chem. Mater* **1999**, *11*, 2372.

23. Hassanein, M.; El-Hamshary, H.; Salahuddin, N.; Abu-El-Fotoh, A. *J. Mol. Catal. A: Chem.* **2005**, *234*, 45.

24. Rajesh; Ahuja, T.; Kumar, D. *Sens. Actuators B* **2009**, *136*, 275.

25. Hank, Z.; Boutamine, S.; Meklati, M.; Vittori, O. *Synth. React. Inorg. Met. Org. Chem.* **1997**, *27*, 1315.

26. Stadtmueller, L. M.; Ratinac, K. R.; Ringer, S. P. *Polym. J.* **2005**, *46*, 9574.

27. Huskic, M.; Žagar, E.; Žigon, M. *Eur. Polym. J.* **2012**, *48*, 1555.

28. Tabitiang, A.; Lumlong, S.; Venables, R. A. *Eur. Polym. J.* **2000**, *36*, 2559.

29. Hwu, J. M.; Jiang, G. J.; Gao, Z. M.; Xie, W.; Pan, W. P. *J. Appl. Polym. Sci.* **2002**, *83*, 1702.

30. Huskic, M.; Zigon, M. *Eur. Polym. J.* **2007**, *43*, 4891.

31. Xu, Y.; Brittain, J.; Xue, C.; Eby, R. K. *Polym. J.* **2004**, *45*, 3735.