Polymer Bulletin

Synthesis of poly(methylmethacrylate)/montmorillonite nanocomposites via in situ intercalative suspension and emulsion polymerization

Hisham Essawy (✉), Ahmed Badran, Ahmed Youssef,
Abu El-Fetoh Abd El-Hakim

Polymers and Pigments Department, National Research Center, 12311 Dokki-Cairo-Egypt

Summary

Na-montmorillonite (MMT) with cation exchange capacity (CEC) of 90 mEq/100g was converted to MMT-CTAB and MMT-CPC forms by the intercalation of Cetyltrimethylammonium bromide (CTAB) and Cetylpyridinium chloride (CPC), respectively. The intercalation of these surfactants onto the basal space of the montmorillonite was evidenced by fourier transform infrared spectroscopy (FTIR) and x-ray diffraction (XRD). The intercalation of the CPC expanded the basal space from 12.19 A^o to 21.47 A^o while in case of CTAB it was expanded to 19.35 A^o only. The (MMT-CPC) was subsequently used as a host for the preparation of PMMA nanocomposites via intercalative suspension and emulsion polymerization of methylmethacrylate (MMA) using benzoyl peroxide (BPO) and potassium persulphate (PPS) individually and simultaneously. The use of BPO and PPS together invoked better exfoliation but the yield did not change appreciably in comparison with using either of the initiators alone. Different structures were obtained with the variation of the preparation conditions; exfoliated and intercalated nanocomposites which were characterized by XRD, transmission electron microscope (TEM), thermal gravimetric analysis (TGA), and differential scanning calorimeter (DSC). The resultant nanocomposites exhibited improved thermal stability relative to the equivalent macrocomposites. No glass transition temperature (Tg) could be detected for the prepared nanocomposites which was assumed to result from the restricted molecular motion of the polymer chains.

Introduction

The need for a material which posses unique properties that can not be attained by conventional polymer composites or even by its individuals focused the light on a new class of materials called nanocomposites. Polymer nanocomposites are normal composites with the difference that they have at least one phase in the nanometer range and this was found to be the key for a dramatical improvement in the mechanical properties, and enhanced thermal and dimensional stability [1,2]. In the recent years a great number of polymer clay nanocomposites were created. The polymers used included polyamides [3], polymethylmethacrylates [4], and polystyrene [1] while the most frequently clay used for this category of materials was

montmorillonite because it can be easily intercalated with different kinds of modifiers [5]. In all cases and as a preliminary step [5,7], the layered silicate (clay) must be converted to organic modified silicate by cation exchanging the sodium or the calcium with an organic modifier. There are two idealized polymer clay nanocomposites; intercalated and exfoliated ones [6]. In the case of the exfoliated nanocomposites, the silicate layers of the clay became completely separated into individual layers of the nanometer range. These layers are uniformly dispersed in the polymer phase. On the other hand, extended polymer chains are intercalated between the silicate layers causing only expansion to the original silicate layers. There is no corresponding general method for the preparation of dispersed nanocomposites. The best way to achieve a control over the polymerization process inside the basal space of the layered silicate is a living polymerization method [8], however, most such methods, for example, group transfer and ionic polymerizations, are sensitive to moisture and minute impurities and therefore will be difficult to perform inside the silicate host that typically contains water of hydration and trace impurities, especially in the case of naturally occurring silicates. In contrast, radical polymerization can tolerate water, air, and some impurities and is applicable to a broad spectrum of monomers [9]. Li and coworkers [4] prepared successfully PMMA-montmorillonite nanocomposites via in situ intercalative polymerization and got different structures; partially exfoliated and partially intercalated with higher glass transition temperatures with the variation of the preparation conditions. The thermal stability and the mechanical properties were notably improved by the presence of the nanometric silicate layers. The same nanocomposite were prepared by Lee and Jang [10] under similar reaction conditions with the difference that the emulsion polymerization was employed in the surrounding phase of the montmorillonite with the aid of sodium lauryl sulphate and no change in the glass transition temperature was observed, nevertheless, both the thermal stability and tensile properties were substantially enhanced. Huang and Brittain [5] claimed the preparation of PMMA-layered silicate nanocomposite by in situ suspension polymerization and emulsion polymerization and the analysis showed that the samples from the emulsion and suspension were consisted with an exfoliated structure and displayed glass transition temperatures that are up to 15 ^{o}C higher and thermal degradation temperatures that are up to 60 ^{o}C higher in comparison with the PMMA macrocomposites. In the work done by Dietsche et al. [11] Poly(methylmethacrylate-co-dodecylmethacrylate) nanocomposite was prepared after rendering the layered silicate hydrophobic by cation exchange with N,N,N,N-dioctadecyldimethylammonium cation which enhanced the compatibility towards the dodecylmethacrylate via hydrophobic interactions. Exfoliation was improved by means of 5 and 10 wt.% dodecylmethacrylate addition to afford translucent reinforced acrylic nanocomposites. In this work, exfoliated poly(methylmethacrylate) nanocomposites based on organomontmorillonite (MMT-CPC) are aimed under different experimental conditions via intercalative suspension and emulsion polymerization.

Experimental

Materials

Sodium montmorillonite (MMT) with cation exchange capacity (CEC) of 90 mEq/100 g, under trade name Mineral colloid BP, was purchased from Southern Clay Products

Inc. Cetyltrimethylammonium bromide (CTAB) was provided by Merck, Darmstadt, Germany and Cetylpyridinium chloride (CPC) was obtained from BDH laboratory, Poole, England. Benzoyl peroxide, BPO (Acros, Belgium) and Potassium persulphate, PPS (SRI, Mumbai-India) were used. Methylmethacrylate, from Aldrich was purified by distillation under reduced pressure before use.

Methods

Organophilization of the montmorillonite

The montmorillonite was dispersed in water containing the required amount of the cationic surfactant, CTAB or CPC, which cause complete cation exchange, at room temperature then the temperature was increased to 80 ^{o}C under vigorous stirring for 4 h. The weight ratio of the montmorillonite/water was 1/50. The clay was separated by filtration and washed several times with distilled water before vacuum dried at 60 ^{o}C for 24 h. Complete cation exchange was confirmed on the filtrate by the addition of $AgNO_3$. Finally the clay was grinded with a mortar and a pestle into fine powder. The abbreviations, MMT-CTAB and MMT-CPC refer to the treated montmorillonite with the corresponding cationic surfactants, respectively.

In situ intercalative polymerization

The benzoyl peroxide (BPO) was dissolved in the monomer phase and the montmorillonite was let to swell in the monomer phase for 10 min afterwards the mixture was dispersed in an aqueous phase and the polymerization was carried out under stirring at 80 ^{o}C for 4-8 h (suspension polymerization). In some cases, potassium persulphate (PPS) as initiator was dissolved in the aqueous phase and used instead of the benzoyl peroxide (emulsion polymerization).

Characterizations

The FTIR Spectra were recorded on a Nexus 821 spectrophotometer, Medison, USA. XRD patterns of the PMMA-montmorillonite nanocomposites were carried out on a Diano X-ray diffractometer using CoKα radiation source energized at 45 KV. The microstructure of the samples was examined for very dilute suspensions of the corresponding nanocomposites in chloroform using a Zeiss transmission electron microscope (TEM), Germany with operating voltage 60 KV. The thermal stability was measured on a thermal gravimetric analyzer (TGA), Perkin Elmer using about 20 mg of the samples at a heating rate of 10 ^{o}C /min. in nitrogen atmosphere. Differential scanning calorimeter (DSC), Perkin Elmer with a heating rate of 10 ^{o}C /min. in nitrogen atmosphere was used for the determination of the glass transition temperatures.

Results and discussion

The concept of conducting the polymerization process in the basal space of the clay which is of nanometric range, is based on initiating many growing polymer chains

inside this very confined space which might at least expand this space (intercalation) and at best exfoliate the ordered layered structure of the clay into individual layers dispersed in the polymer phase under the stress of the chains crowding. This is assumed to cause utmost homogeneity and remarkable improvement in the thermal stability and mechanical properties [4]. Of great importance to convert the clay to the organophilic form by substituting the Na^+ with an organic cation. This organic cation may be in the form of monomer, initiator or surfactant as in our case (CPC or CTAB) and this will increase the affinity of the clay to the organic phase and provoke maximum swelling in the monomer due to the penetration of the monomer onto the basal space where it can interact inside with the fixed surfactant molecules by hydrophobic-hydrophobic and van der-waal interaction forces. The intercalation of the CPC and CTAB was proved by the recorded FTIR spectra (not shown). In addition to the characteristic peaks of the montmorillonite, 3630, 1050 and the broad band (400-600) cm^{-1}, which are ascribed to the OH stretching of the lattice water, Si-O and Al-O stretching, and Si-O bending, respectively, some new bands appeared in the case of MMT-CPC, 1450 cm^{-1} (-CH$_2$), 3070 cm^{-1} (-CH aromatic) while in the case of CTAB new bands at 1375 cm^{-1} (-CH$_3$), 2900 cm^{-1} (-CH aliphatic) emerged. This was evidenced as well from the x ray pattern shown in Fig. 1. It is obvious that CPC can expand the basal space of montmorillonite more effectively than CTAB. Also, the XRD profile clearly shows that different basal spacings are arranged in a random fashion in the case of CPC compared with CTAB which is likely to afford easier exfoliation upon conducting the in-situ polymerization and for this CPC was chosen for the completion of the work in this study. Several reaction conditions were tried in order to optimize the different parameters of the polymerization process that provide enhanced properties if employed.
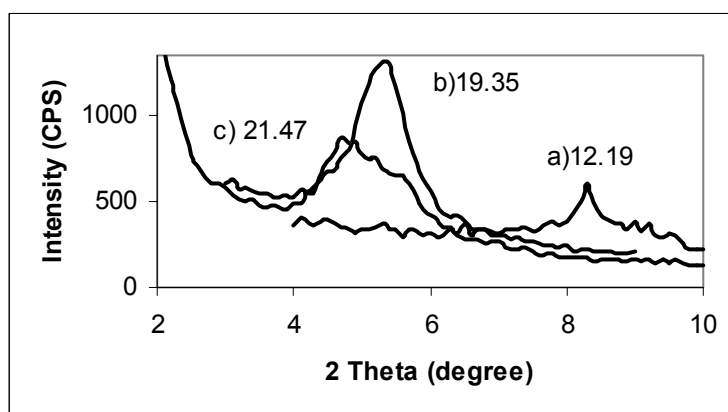

Fig.1. XRD of : a) MMT   b)MMT-CTAB   c)MMT-CPC

Fig.2 displays XRD of MMT-CPC after conducting the polymerization for 4 h at 80 °C using different concentrations of BPO as initiator and we found, while full exfoliation took place at the higher concentrations of the initiator (1.4 and 2.1×10^{-3} mol/l) and the layers became distorted in the polymer matrix as shown in Fig.6a, the average basal spacings of the MMT-CPC remained nearly unchanged upon using very low concentration of BPO, 2.1×10^{-4} mol/l in the polymerization process which leads only

to 15 % yield of PMMA and therefore weakly intercalated nanocomposite since the clay tactoids are still remaining, Fig. 6b. This can be explained on the basis of the work done by many researchers [11,12,13] who confirmed the necessity of the presence of tethered polymer chains that can hinder the aggregation of the silicate layers and help preserve the expanded structure.
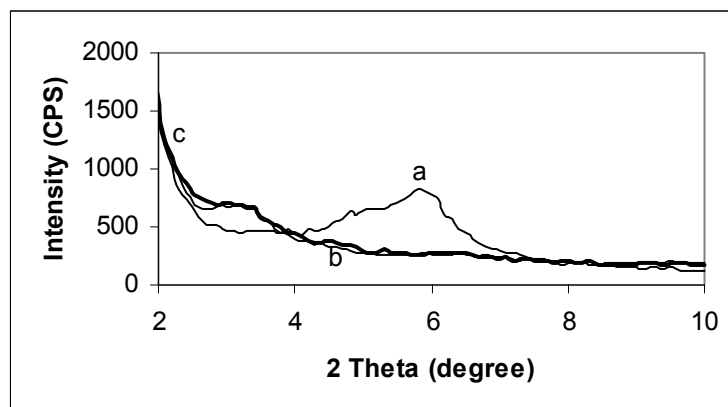

Fig.2. XRD of PMMA nanocomposites prepared by suspension polymerization for 4 hours with 10 wt% MMT-CPC using different concentrations of BPO
  a) 2.1×10^{-4} mol/l   b)1.4×10^{-3} mol/l   c) 2.1×10^{-3} mol/l

The impact of the reaction time on the microstructure of the resulting PMMA nanocomposite was also investigated and revealed in Fig.3, 4-8 hours were quite enough for defoliating the layers into finely dispersed layers in the PMMA phase and this can be confirmed by the phase image taken using TEM (Fig. 6c,d).
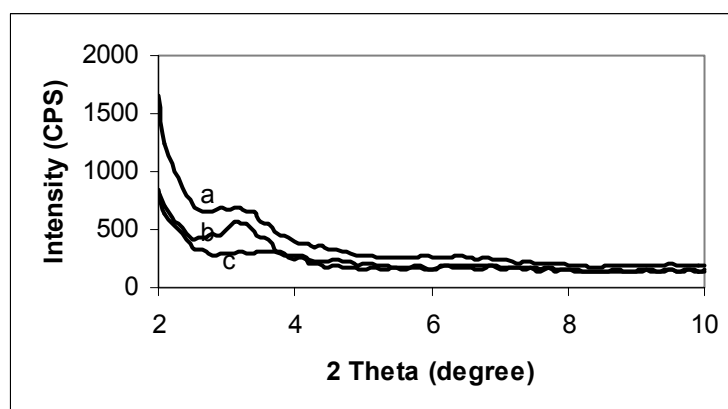

Fig.3. XRD of PMMA nanocomposites prepared by suspension polymerization with 10 wt% MMT-CPC and 1.4×10^{-3} mol/l of BPO at different reaction times
            a) 4h   b) 6h   c) 8h

Interestingly, it was found that potassium persulphate (PPS) can be applied as initiator from the aqueous phase not only for the untreated montmorillonite but also this was

extended to the montmorillonite organophilized with CPC. The XRD shown in Fig. 4 indicated the formation of intercalated nanocomposite with basal space of 17 A^o and this was seconded by the presence of the clay aggregates shown in Fig. 6e, whereas in the latter case the resultant nanocomposite exhibited exfoliated structure.
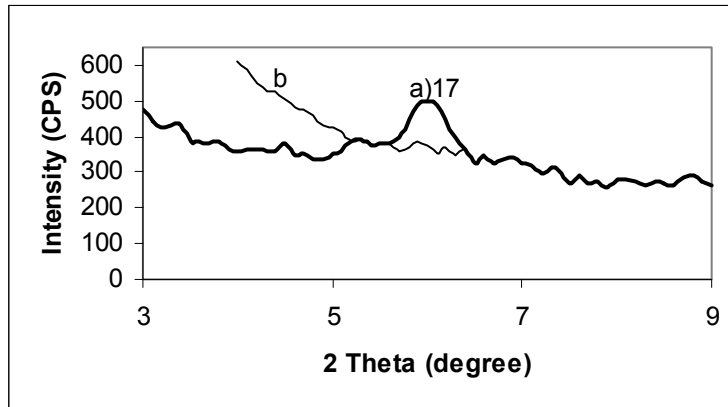

Fig.4. XRD of PMMA nanocomposites prepared by emulsion polymerization for 4 hours with 10 wt% MMT using PPS as initiator
 a)MMT and 18.5×10^{-4} mol/l of initiator   b)MMT-CPC and 13×10^{-4} mol/l of initiator
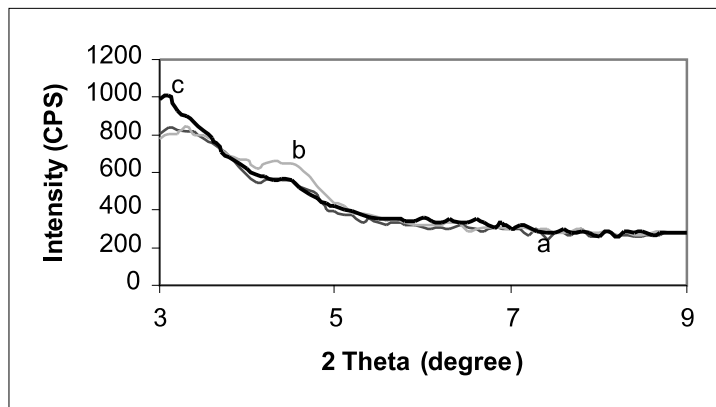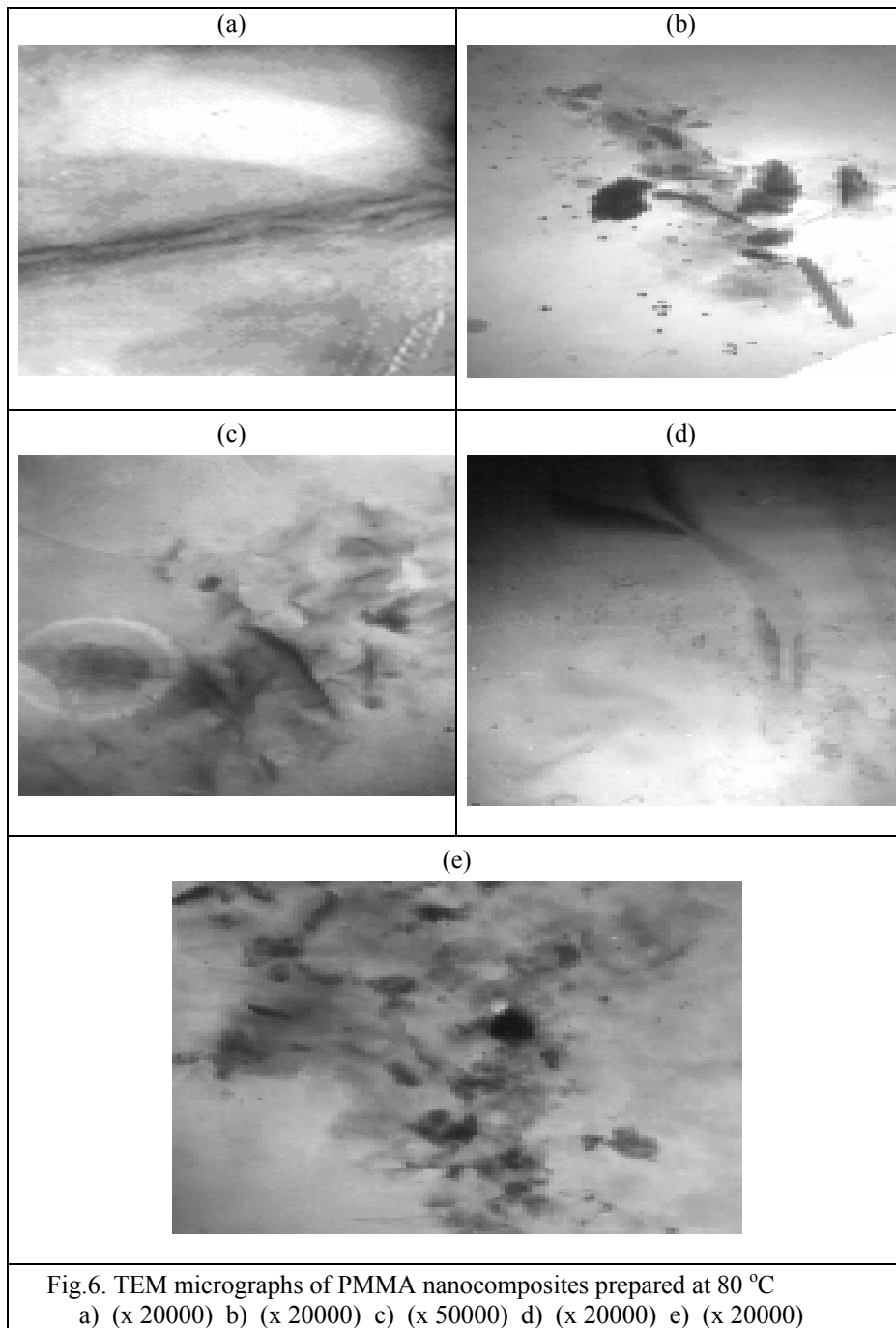

Fig.5. XRD of PMMA nanocomposites prepared by free radical polymerization for 4 hours with 10 wt% MMT-CPC using BPO (1.4×10^{-3} mol/l) and different concentrations of PPS, simultaneously
 a) 7.5×10^{-4} mol/l of PPS   b) 13×10^{-4} mol/l of PPS c) 18.5×10^{-4} mol/l of PPS

15

Fig.6. TEM micrographs of PMMA nanocomposites prepared at 80 °C
a) (x 20000) b) (x 20000) c) (x 50000) d) (x 20000) e) (x 20000)

The thermal stability of the prepared nanocomposites was investigated and shown in Fig 7. It was reported elsewhere [5] that the PMMA macrocomposites with the

unmodified montmorillonite exhibited 20% weight loss at 279 ^{o}C and the nanocomposites prepared in the study of this group showed increase in the decomposition temperature for 20% weight loss by 15-50 ^{o}C. Since this group followed very similar pathway as in our case for the synthesis of the PMMA montmorillonite nanocomposites, it was very interesting for us to perform the same comparison where we found our samples showing 10-87 ^{o}C higher thermal degradation temperatures in comparison with the PMMA-montmorillonite macrocomposites for the same weight loss (Fig. 7) which can be attributed to the improved interaction between the PMMA and clay after the pretreatment of the clay with CPC. The DSC scans of the prepared nanocomposites did not show any transitions and no Tg was observed. This is assumed to the restricted molecular motion of the PMMA chains in the very confined basal space in the case of intercalated nanocomposites or the strong interaction forces between the dispersed silicate layers and the surrounding polymer phase where exfoliation exists. The same trend was found by Lee and Jang [10] for PMMA-montmorillonite nanocomposites prepared under non intercalative emulsion polymerization.
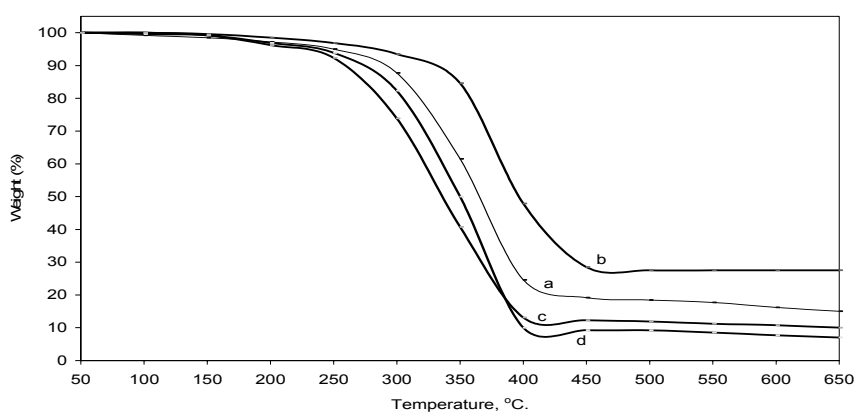

Fig. 7. TGA of PMMA nanocomposites prepared at 80 ^{o}C
a) after 4h using 2.1x10^{-3} mol/l BPO , b) after 4h using 1.4x10^{-3} mol/l BPO
c) after 6h using 1.4x10^{-3} mol/l BPO , d) after 8h using 1.4x10^{-3} mol/l BPO

Conclusions

Cetylpyridinium chloride (CPC) and Cetyltrimethylammonium bromide (CTAB) can be used as intercalative modifiers for Na-montmorillonite (MMT). CPC has more expanding ability and the basal spacings are arranged in a random fashion. In situ intercalative polymerization can be conducted in the basal space after the intercalation of the cationic surfactants in the basal space of the MMT. At low initiator concentration of BPO (2.1x10^{-4} mol/l), weakly intercalated structure can be obtained while higher concentrations of the initiator led to exfoliated nanocomposites after 4 hours of the polymerization at 80 ^{o}C. Potassium persulphate could be used as water soluble initiator with both the MMT and with the MMT-CPC where intercalated nanocomposite with basal space of 17 ^{o}A was obtained in the former case while in the latter case exfoliation took place and this is applicable only with the monomers that

are partially soluble in water as with MMA. The use of BPO and PPS together can invoke better exfoliation but it is not advantageous to the yield in comparison with using either of the initiators alone. The strong interaction between the clay and the polymer phase can restrict the molecular motion of the polymer chains and improve the thermal stability of the resultant composites.

References

1. Fu X, Qutubuddin S (2001) Polymer 42:807.
2. Xie W, Hwu JM, Jiang GJ (2003) Polym. Eng. Sci. 43:214.
3. Liu L, Qi z, Zhu X (1999) J. Appl. Polym. Sci. 71:1133.
4. Li Y, Zhao B, Xie S, Zhang S (2003) Polymer International 52:892.
5. Huan X, Brittain WJ (2001) Macromolecules 34:3255
6. Alexandre M, Dubois P (2000) Mater. Sci. Eng. R: Reports 28:1.
7. White JL, Sasaki A (2004) J. Appl. Polym. Sci. 91:1951.
8. Weimer MW, Chen H, Giannelis EP, Sogah DY (1999) J. Amer. Chem. Soc. 121:1615.
9. Puts RD, Sogah DY (1996) Macromolecules 29:3323.
10. Lee DC, Jang LW (1996) J. Appl. Polym. Sci. 61:1117.
11. Dietsche F, Muelhaupt R (1999) Polymer Bulletin 43:395.
12. Ginzburg VV, Singh C, Balazs A C (2000) Macromolecules 33:1089.
13. Okada A, Usuki A (1995) Mater. Sci. Eng. C3:109.