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Polymer–clay nanocomposites: exfoliation of organophilic montmorillonite nanolayers in polystyrene

X. Fu, S. Qutubuddin*

Department of Chemical Engineering, Case Western Reserve University, Cleveland, OH 44106, USA

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Abstract

A polymerizable cationic surfactant, vinylbenzyldimethyldodecylammonium chloride (VDAC) was synthesized for functionalization of montmorillonite (MMT) and preparation of exfoliated polystyrene–clay nanocomposites. Organophilic MMT was prepared by cationic exchange between inorganic ions of MMT and ammonium cations of VDAC in an aqueous medium. Dispersions of intercalated clay (VDAC–MMT) in styrene monomer formed gels. Shear thinning behavior of the gels was observed via rheological measurements. Polystyrene–clay nanocomposites were prepared by free radical polymerization of styrene containing dispersed organophilic MMT. Exfoliation of MMT in polystyrene matrix was achieved as revealed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The exfoliated nanocomposites have higher dynamic modulus and higher decomposition temperature than pure polystyrene. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Montmorillonite; Polystyrene; Nanocomposites and nanolayers

1. Introduction

Polymer composite materials are used widely in diverse applications such as transportation vehicles, construction materials, electronics and sporting goods and consumer products. The properties of polymer composites are affected greatly by the dimensions and microstructure of the dispersed phase. Polymer nanocomposites are a new class of materials with at least one ultrafine phase dimension, typically a few nanometers. Nanocomposites possess unique properties that are not shared by conventional composites primarily because of large interfacial area per unit volume. Polymer–clay nanocomposites can improve dramatically the mechanical reinforcement and high temperature durability [1–6], provide enhanced barrier properties [5,7] and reduce flammability [1]. Polymer–clay nanocomposites were first synthesized by a Toyota research group [2–3]. Individual layers (about 1 nm thickness) of clay particles were exfoliated in a polymer matrix (nylon-6) as revealed by X-ray diffraction (XRD) and transmission electron microscope (TEM).

The dispersion of clay particles in a monomer or polymer matrix can result in the formation of three types of composite materials [8]. The first type is conventional composites that contain clay tactoids with the layers aggregated in an un-intercalated face-to-face form. In this case, the clay tactoids are dispersed simply as a segregated phase resulting in poor mechanical properties of the composite material. The second type is intercalated polymer–clay nanocomposites, which are formed by the insertion of one or more molecular layers of polymer into the clay host galleries. The last type is exfoliated polymer–clay nanocomposites, characterized by low clay content, a monolithic structure, and a separation between clay nanolayers that depend on the polymer content of the composites. Exfoliated polymer–clay nanocomposites are especially desirable for improved properties because of the homogeneous dispersion of clay and huge interfacial area between polymer and clay.

Intercalated polystyrene–clay nanocomposites have been prepared by several researchers. Kato et al. [9] reported the intercalation of polystyrene in stearyltrimethylammonium cation exchanged montmorillonite (MMT). Akelah and Moet [10,11] prepared intercalated polystyrene–clay nanocomposites using an organic solvent (acetonitrile). The sodium ions of MMT were ion exchanged with vinylbenzyltrimethylammonium. Intercalated polystyrene–clay nanocomposites with the largest basal spacing of 2.45 nm were obtained. There was no characterization of mechanical and

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* Corresponding author. Tel.: +1-216-368-4182; fax: +1-216-368-3016.
E-mail address: szq@po.cwru.edu (S. Qutubuddin).

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thermal properties for these intercalated nanocomposites. Recently, Doh and Cho [12] reported the synthesis of intercalated polystyrene–MMT nanocomposites by in situ polymerization of styrene containing dispersed organophilic MMT. They found that polystyrene–clay nanocomposites exhibited higher thermal stability compared with pure polystyrene (PS) or PS–pristine–MMT composites. The PS–clay nanocomposites with organophilic MMT containing benzyl-unit similar to styrene exhibited a decomposition temperature higher than other PS–organophilic MMT nanocomposites. Giannelis [1] developed a new approach called polymer melt intercalation to fabricate polymer–clay nanocomposites. Intercalated PS–clay nanocomposites were also prepared by this technique [13].

The preparation of exfoliated polystyrene nanocomposites using functionalized MMT was reported in previous short communications [14,15]. Details of the synthesis and characterization of exfoliated polystyrene–clay nanocomposites are presented in the present work. A polymerizable cationic surfactant, vinylbenzyldimethyldodecylammonium chloride (VDAC) was synthesized for the preparation of exfoliated nanocomposites. The nanocomposites were characterized using XRD, TEM, dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials

The montmorillonite (MMT) powders were provided by Southern Clay Products Inc. under the trade names of Mineral Colloid BP and Bentolite L, which contain exchangeable cations of primarily Na^+ and Ca^{2+}, respectively. Mineral Colloid BP (Na-MMT) is a fine powder with an average particle size of 75 μm in the dry state, and a cation exchange capacity (CEC) of 90 mEq/100 g. Bentolite L (Ca-MMT) powder has an average particle size of 15 μm and a CEC of 80 mEq/100 g. Dimethyldodecylamine, diethyl ether, ethyl acetate, styrene and vinylbenzyl chloride containing 500 ppm tert-butylcatechol and 500 ppm nitroparaffin inhibitors were purchased from Aldrich Chemical Company. Styrene was purified by distillation under reduced pressure at 30°C. The free radical initiator, 2,2-azobis-isobutyronitrile (AIBN), was obtained from Du Pont and purified by recrystallization twice from methanol.

VDAC was prepared by the reaction of vinylbenzyl chloride with dimethyldodecylamine (one half stoichiometric excess) in diethyl ether at ambient temperature for 72 h. The precipitate was filtered and washed with diethyl ether and dried under vacuum. The product was a white powder. Samples for NMR spectra were recrystallized twice from ethyl acetate.

2.2. Copolymerization of styrene–VDAC monomers

VDAC was polymerized in acetonitrile. Styrene and VDAC were copolymerized at different molar ratios by bulk polymerization. Styrene and VDAC were also copolymerized with different feed compositions in acetonitrile solution. AIBN was used as a free radical initiator. All samples were polymerized at 60°C for 72 h. For solution polymerization, the product was poured into a large excess of diethyl ether after reaction, filtered and dried under vacuum. The yield and VDAC content in the copolymers were determined by ^1H NMR.

2.3. Preparation of VDAC functionalized MMT

Organophilic MMT was prepared by cationic exchange between Na^+ or Ca^{+2} in MMT galleries and VDAC cations in an aqueous solution. 2.5 g of MMT was suspended in 250 ml of distilled water. An aqueous solution of 3 mmole VDAC was added gradually. After stirring for 3 h at ambient temperature, the exchanged clay was filtered and washed with distilled water until no chloride ion was detected with 0.1 $AgNO_3$ solution. It was then dried in a vacuum oven at room temperature. The organophilic clay was ground with a mortar and a pestle, and particles with the size less than 65 μm were collected for the synthesis of nanocomposites.

2.4. Synthesis of polystyrene–MMT nanocomposites

The desired amount of VDAC functionalized MMT was dispersed in styrene monomer. The mixture was stirred by vortex and sonication for 4 h. Then, 0.5 wt.% (based on styrene) of initiator AIBN was added to the dispersion. The samples were purged with nitrogen for 15 min, and polymerized in an oil bath at 60°C for at least 48 h to obtain polystyrene–clay nanocomposites.

2.5. Characterization of nanocomposites

^1H NMR spectra were recorded on a GEM 200 MHz spectrometer. The samples were dissolved in $CDCl_3$. The viscosity was measured on a Carrimed CSL-rheometer with cone plate geometry. XRD patterns of polystyrene–clay nanocomposites were obtained by using a Phillips XRG 3100 X-ray generator equipped with a Ni-filtered CuKα (1.5418 Å) source that was connected to a Phillips APD 3520 type PW 1710 diffractometer controller. All samples were dried in a vacuum oven for at least 24 h before XRD measurements. The microstructure of polystyrene–clay nanocomposites was examined by TEM. Samples were cut to 60 nm thick sections with a diamond knife.

Dynamic mechanical properties were measured using a dynamic mechanical analyzer (Perkin–Elmer DMA 7) with a three-point bend fixture. The DMA specimens ($1 \times 2.5 \times 20\ mm^3$) were cut from the center of the samples. A temperature sweep at 5°C min^{-1} from -25 to 100°C at a frequency of 1 Hz was used to determine the dynamic storage modulus G' and the tan δ. The value of dynamic storage modulus G' is very close to the flexural modulus as measured by ASTM D-790. The ratio of the loss modulus

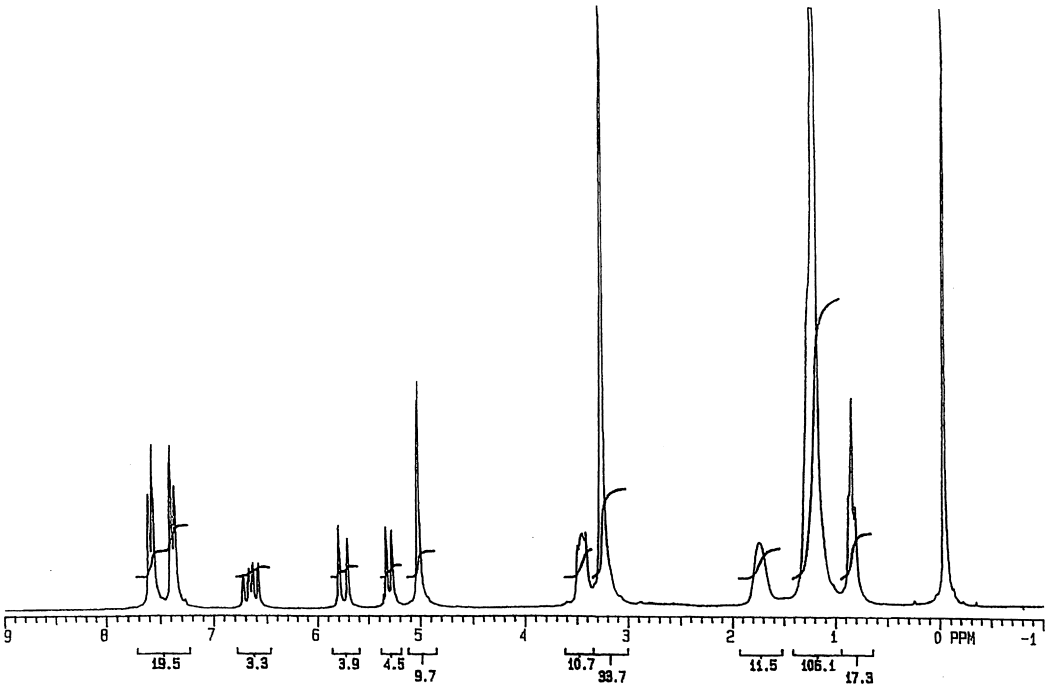


Fig. 1. ^{1}H NMR spectrum of VDAC (in $CDCl_3$).

(G'') to the storage modulus (G') is known as a mechanical loss factor (tan δ). Thermogravimetric analysis was performed with a Du Pont thermogravimetric analyzer. Samples of 20 mg masses were heated to 600°C at a heating rate of 20°C/min under nitrogen atmosphere.

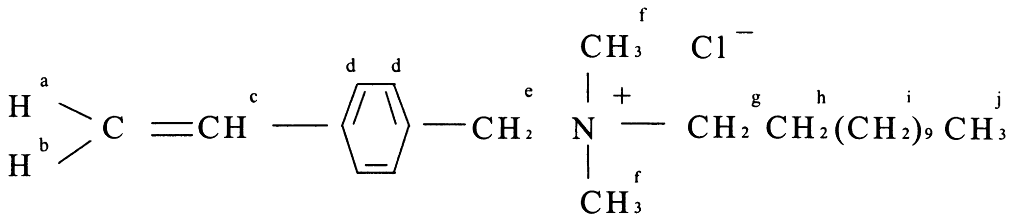
3. Results and discussion

3.1. Synthesis of VDAC and copolymerization with styrene

Functionalization of clay by a cationic surfactant plays a critical role in the preparation of exfoliated polymer–clay nanocomposites. The modified organophilic clay should have strong interaction with a specific monomer or polymer, and should improve the interfacial properties between the organic and inorganic phases of the nanocomposites. Therefore, the first goal of this work was to synthesize a cationic surfactant containing a polymerizable aromatic group that has good affinity with styrene and use it to functionalize MMT for the preparation of exfoliated polystyrene–clay nanocomposites.

The synthesized monomeric surfactant, VDAC, is insoluble in nonpolar solvents such as aliphatic hydrocarbons, diethyl ether, but soluble in carbon tetrachloride, benzene and styrene. It is readily soluble in polar solvents such as

Table 1
NMR spectral data of quaternary monomer VDAC



Compound	Chemical shifts (ppm)									
	H^a	H^b	H^c	H^d	H^e	H^f	H^g	H^h	H^i	H^j
VBC	5.25	5.75	6.70	7.35	4.55	–	–	–	–	–
DDA						2.18		–	1.24	0.85
VDAC	5.30	5.75	6.70	7.50	5.02	3.24	3.45	1.75	1.20	0.90

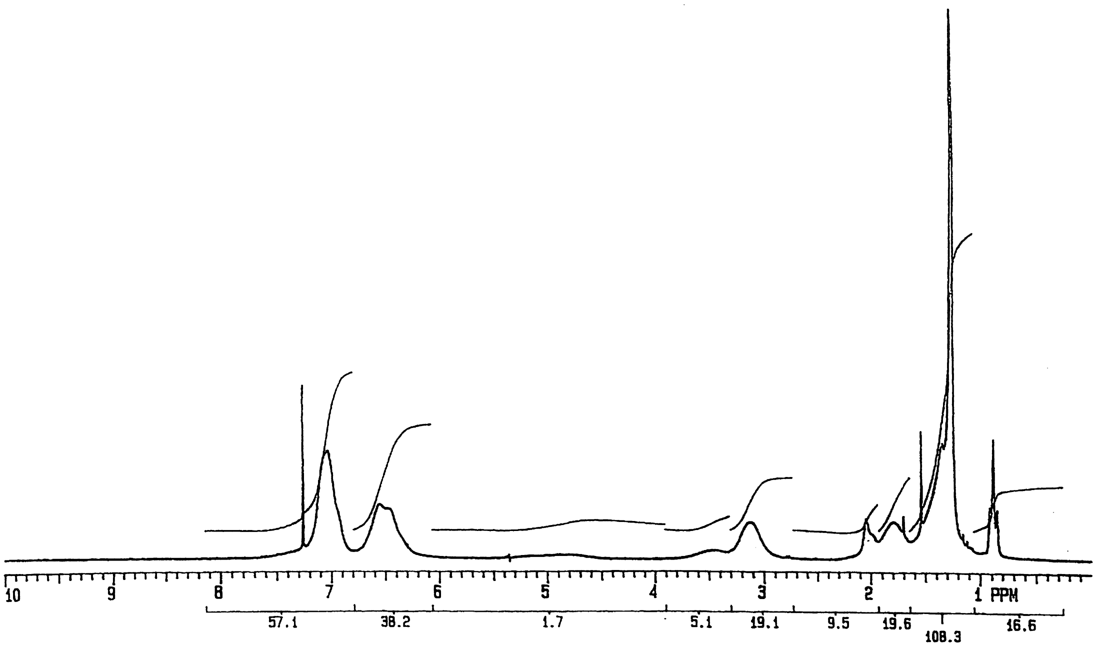


Fig. 2. ^{1}H NMR spectrum of poly(styrene–VDAC) copolymer (in $CDCl_3$).

water, alcohol, acetone and acetonitrile. The NMR spectrum of VDAC is shown in Fig. 1 and the spectral data of reactants are listed in Table 1. Compared to vinylbenzyl chloride (VBC), the methylene (H^e) protons of VDAC near the quaternary ammonium group are shifted downfield from 4.55 [16] to 5.02. The two methyl protons (H^f) near the quaternary ammonium group are also shifted downfield from 2.18 of dimethyldodecylamine (DDA) to 3.24, and methylene (H^g) near the quaternary ammonium group appears as a shoulder of the two methyl protons. Apparently, these shifts are caused by the cationic character of the nitrogen in VDAC.

VDAC can homopolymerize as well as copolymerize with monomers like styrene in an organic medium, e.g. acetonitrile. There was significant increase of the solution viscosity after polymerization. Fig. 2 shows the ^{1}H NMR spectrum of VDAC–styrene copolymer obtained by bulk polymerization. The initial molar ratio of styrene to VDAC was 4:1. The loss of vinyl protons in NMR spectrum indicates complete copolymerization of styrene with VDAC. The calculated molar ratio between styrene and VDAC content of the copolymer is about 3.5:1 based on the integration of benzyl (H^d) protons and the end methyl (H^j) protons of the long alkyl chain. Detailed characterization of poly(VDAC–styrene) copolymer will be described elsewhere.

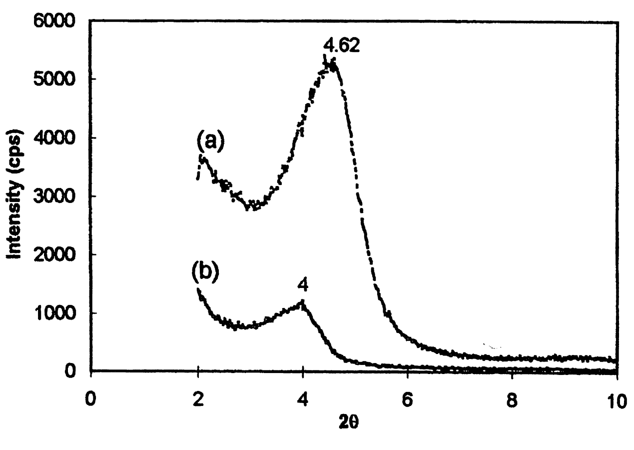


Fig. 3. XRD patterns of: (a) VDAC–NaMMT; and (b)VDAC–CaMMT.

3.2. Functionalization of MMT by VDAC

The crystal structure of MMT consists of two-dimensional layers formed by fusing two silica tetrahedral sheets to an edge-shared octahedral sheet of aluminum hydroxide. Stacking of the layers of clay particles are held by weak dipolar or van der Waals forces [17]. The surface of the pristine clay is hydrophilic. The small inorganic cations such as Na^+, Ca^{+2} can be exchanged by organic cations [18,19]. After cation exchange by a surfactant, the clay surface becomes hydrophobic, The resulting organoclay is dispersed easily in organic media. Fig. 3 shows typical XRD patterns of VDAC–NaMMT and VDAC–CaMMT. The silicate layer (001) reflection has peaks at $2\theta = 4.62°$ and $2\theta = 4°$ for VDAC–NaMMT and VDAC–CaMMT, respectively. The d_{001} spacing was calculated from peak positions using Bragg's law: $d = \lambda/(2 \sin \theta)$, where λ is the X-ray wavelength (1.5418 Å). The d_{001} spacing of vacuum dried pristine NaMMT was 0.99 nm, while that of pristine CaMMT was 1.32 nm. The d_{001} spacing value of pristine NaMMT is the same as documented in literature [18]. In the ion exchange process, VDAC cations intercalated into the interlayer space, replacing the Na^+ or Ca^{+2} cations.

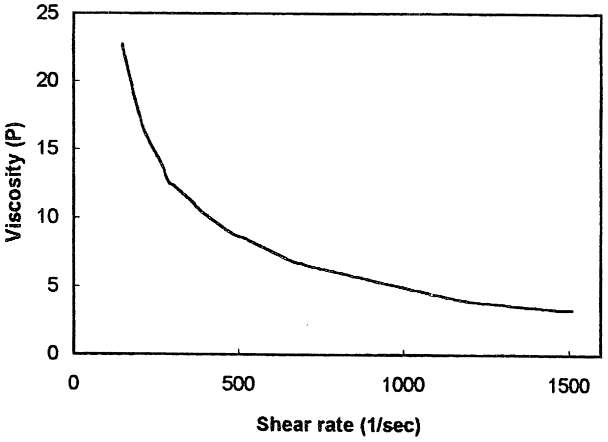


Fig. 4. The relationship between viscosity and shear rate of 3.6 wt.%VDAC–NaMMT.

After the cation exchange, the d_{001} space increased to 1.92 nm for NaMMT and 2.22 nm for CaMMT in dry state. TGA was used to determine the total amount of VDAC adsorbed by clay particles. For all samples of VDAC functionalized MMT, the amount of adsorbed VDAC is higher than 90% of the CEC (90 mEq/100 g for NaMMT and 80 m Eq/100 g for CaMMT).

3.3. Characterization of polystyrene–clay nanocomposites

The synthesis of nanocomposites involved the dispersion of organophilic MMT in the monomer and swelling the clay with stirring for several hours. After adding the desired amount of VDAC–MMT (less than 10 wt.%) to styrene and mixing by vortex or sonication, the viscosity of the dispersion increased dramatically within a few minutes resulting in a gel. Fig. 4 shows strong shear thinning behavior of a styrene–clay dispersion containing 3.5 wt.% VDAC–MMT. The gels exhibit an yield stress. Messersmith and Giannelis [5] found that dispersions of 10 wt.% or more organoclay in epoxy resin resulted in strong gel formation during sonication. Organoclays are well known for use as rheological control agents in organic systems such as paints, cosmetics, and greases [20,21]. The viscosity increase and gelation by organophilic clay dispersed in organic media has been attributed to the expansion and delamination of clay layers and structure formation between the layers due to strong hydrogen bond interactions at the edge-to-edge and edge-to-face contacts [21].

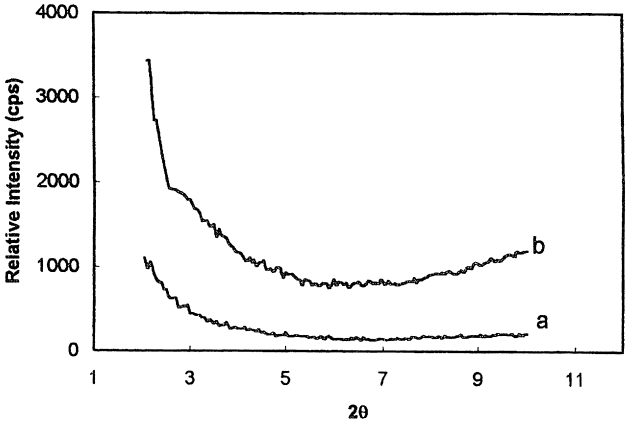


Fig. 5. XRD patterns of polystyrene–clay nanocomposites: (a) 5.6 wt.% VDAC–NaMMT; and (b) 5.6 wt.% VDAC–CaMMT.

XRD analysis is a powerful tool for examining the crystal structure of polymer–clay nanocomposites [1–7]. Fig. 5 shows typical XRD patterns of PS–VDAC–MMT nanocomposites. There is no characteristic MMT peak in the XRD pattern for PS–clay nanocomposite containing 5.6 wt.% VDAC–MMT. This result indicates the exfoliation of VDAC–MMT into nanolayers in the polymer matrix. The exfoliation of the clay layers was further confirmed by using TEM. Fig. 6 shows TEM micrographs of PS–MMT nanocomposites containing 5.6 wt.% VDAC–NaMMT and 5.6 wt.% VDAC–CaMMT. The dark lines in the figure correspond to the silicate nanolayers. Micron sized clay tactoids do not exist in the nanocomposite because of swelling and expansion in styrene, and further exfoliation during stirring and polymerization. Thus, the MMT is dispersed as nanolayers in the polystyrene matrix. The orientation of the exfoliated MMT reflects the initial stacking arrangement of the layers of pristine clay particles. The exfoliation of MMT in polystyrene matrix may be attributed to the strong interaction between styrene and VDAC–MMT, as evident from the sharp viscosity increase.

Attempts to prepare PS nanocomposites by bulk polymerization of styrene containing stearyltrimethylammonium [9], or tallow alkyl benzyl ammonium [12] cation exchanged MMT resulted in only intercalated PS–clay nanocomposites. Other cationic surfactants including octadecylamine, hexadecyltrimethylammonium bromide, and benzalkonium chloride were also examined for preparing PS–clay nanocomposites by bulk polymerization. Such modification with non-polymerizable surfactant resulted in intercalated rather than exfoliated polystyrene–clay nanocomposites. Washburn capillary rise [22] and rheological measurements were used to examine the wettability and swelling kinetics of different organophilic clays by styrene. The results suggest that VDAC–MMT has stronger interaction and better swelling ability in styrene than other surfactant intercalated clays [23].

The thermal decomposition behavior of PS and PS–VDAC–MMT nanocomposite is shown in Fig. 7. The onset degradation temperature of the nanocomposite was higher than PS. The nanocomposite has higher thermal stability compared to PS. This may result from the interaction between organic and inorganic phases and copolymerization between styrene and VDAC–MMT. Similar results of higher thermal decomposition temperature of intercalated polystyrene–clay nanocomposites with organoclay containing benzyl unit were reported by Doh and Cho [12].

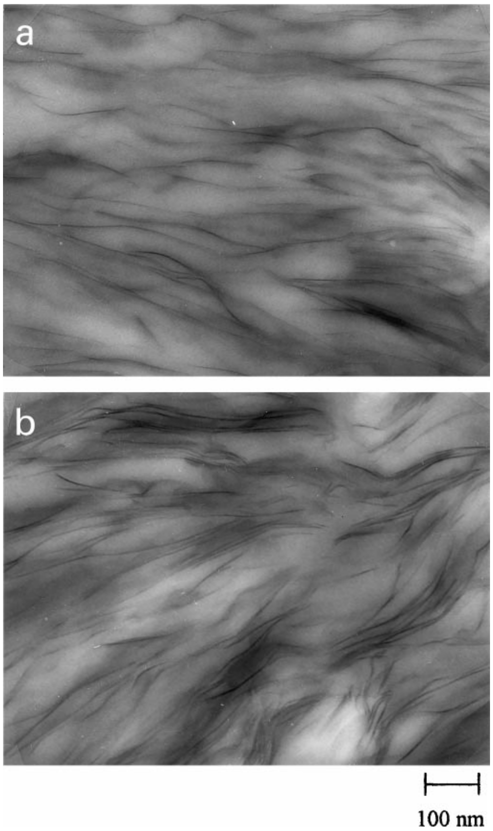


Fig. 6. TEM micrographs of polystyrene–clay nanocomposites: (a) 5.6 wt.% VDAC–NaMMT; and (b) 5.6 wt.% VDAC–CaMMT.

Fig. 8 shows DMA results of polystyrene and PS–VDAC–MMT nanocomposites at different clay loadings. The dynamic modulus increased with MMT loading. The glass transition temperature (T_g) of polystyrene matrix decreased slightly with increasing MMT loading. The T_g of polystyrene nanocomposite containing 7.6% VDAC–MMT was 94°C. The apparent decrease may be attributed to the high viscosity of organophilic MMT–styrene dispersion that affects the diffusion of initiator molecules and chain propagation during polymerization. GPC measurements indicated that as the clay loading increased, the polystyrene molecular weight decreased. The Toyota group [2] also found a decrease in the molecular weight of nylon-6 with increasing MMT loading. Further investigation on the effect of loading on the thermal and mechanical properties of the nanocomposite is in progress.

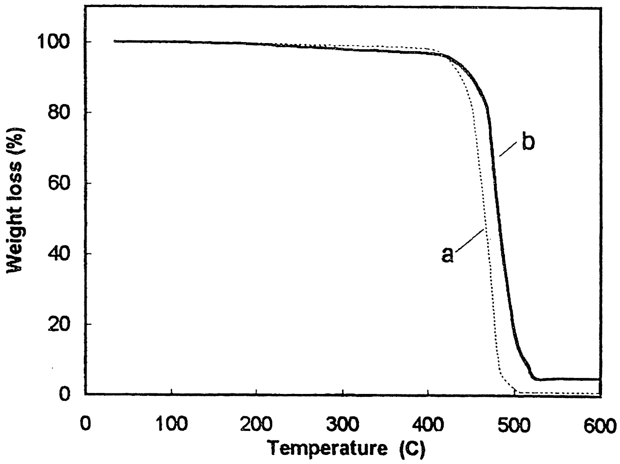


Fig. 7. TGA thermograms of weight loss versus temperature: (a) pure PS; and (b) Nanocomposite containing 5.6 wt.% VDAC–NaMMT.

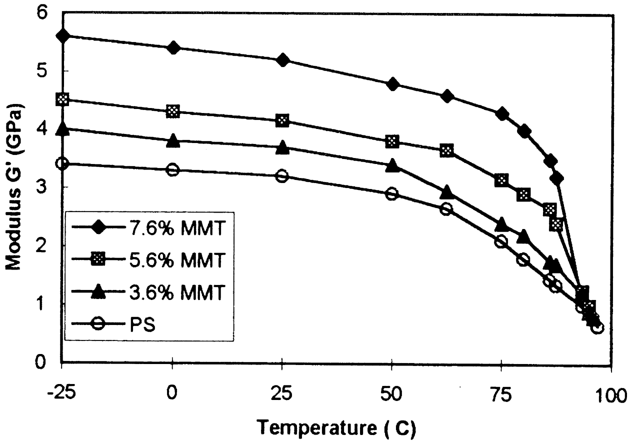


Fig. 8. DMA scans of pure polystyrene and polystyrene–clay nanocomposites.

4. Conclusions

VDAC, a cationic surfactant with a polymerizable group was synthesized for the preparation of exfoliated polystyrene–clay nanocomposites. This surfactant copolymerizes with styrene. VDAC functionalized MMT has strong swelling ability and forms a viscous gel in styrene. The gels exhibit yield stress and shear thinning behavior. Exfoliated polystyrene nanocomposites were successfully synthesized by bulk polymerization using functionalized forms of both NaMMT and CaMMT. PS–VDAC–MMT nanocomposites show a higher thermal degradation temperature than pure polystyrene. The nanocomposites exhibit a higher dynamic modulus with increased loading of VDAC–MMT in polystyrene.

Acknowledgements

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