

Encapsulation of Clay by Ad-Miniemulsion Polymerization: The Influence of Clay Size and Modifier Reactivity on Latex Morphology and Physical Properties

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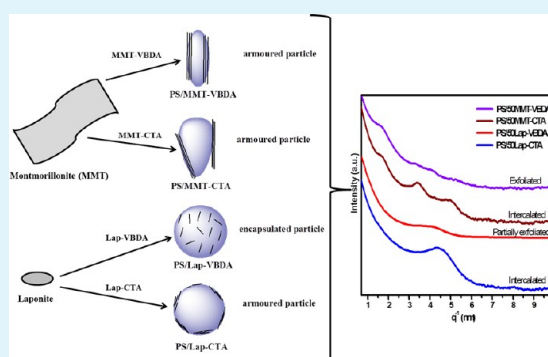
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S Supporting Information

ABSTRACT: The influence of clay platelet size and type of organic modifier (reactive or nonreactive) on highly filled hybrid latex morphology and physical properties of the resultant polymer/clay nanocomposites (PCNs) were investigated. The hybrid latexes, containing clay loadings between 30 and 50 wt % clay, were prepared using ad-mini-emulsion polymerization. These materials have potential use in the packaging and coating industry since clay platelets are well-known for barrier property improvements. Comparative studies on the use of montmorillonite (MMT), a large clay platelet (average size: 50–500 nm), and Laponite (Lap), small-sized clay platelets (average size: 25–40 nm), were conducted. Two different clay modifiers were used to modify the clays, i.e., a conventional nonreactive modifier (cetyltrimethylammonium bromide (CTAB)) and a reactive modifier (vinylbenzyl dodecyl dimethyl ammonium chloride (VBDAC)). Transmission electron microscopy (TEM) imaging of the hybrid latexes clearly showed strong morphological dependency on both the type of modifier and the clay platelet size. Furthermore, TEM together with small-angle X-ray scattering (SAXS) showed that the extent of clay exfoliation was strongly dependent on the reactivity of the clay modifier, irrespective of the clay platelet size. Both the type of modifier and clay platelets size were found to have an influence on different physical properties of the resultant PCNs. The influence of clay size was clearly indicated by storage modulus and thermal stability behaviors, while that of the clay modifier was indicated by the T_g . Lap-based PCNs exhibited constant or increasing storage modulus and no change in thermal stability with increasing clay content, while MMT-based PCNs showed a decreasing trend in both storage modulus and thermal stability. PCNs based on clay modified with CTAB showed a decreasing T_g with increasing clay content, while those based on clay modified with VBDAC showed an increasing trend. It was concluded that the clay platelet size and the type of modifier play a crucial part of both the latex morphology and the physical properties of the resultant PCNs.

KEYWORDS: hybrid latex, polymer/clay nanocomposite, thermomechanical properties, cossonation miniemulsion, high clay content



1. INTRODUCTION

Incorporation of clay in polymers has been found to result in materials with desirable properties, and such materials have been at the forefront of many research efforts in the past two decades.^{1–10} One of the prerequisites toward the preparation of polymer clay nanocomposites (PCNs) is the modification of clay platelets. This can be achieved using either surface modification or edge modification of the platelet via three different methods, namely, cationic exchange surface modification,^{11–13} edge modification,^{14,15} and adsorption surface modification.^{10,16,17} Edge modification involves modification of clay edges using compounds that can covalently bond with the hydroxyl groups found on clay edges. On the other hand, adsorption surface modification involves the use of molecules that adsorb into the clay galleries via interactions such as hydrogen bonding, van der Waals forces, or dipole–dipole

interactions. Organic cationic compounds, such as quaternary alkyl ammonium compounds, can also be used to replace the inorganic cations found in the clay galleries in a process called cationic exchange surface modification. The reason behind modification of clay platelets is to improve their compatibility with hydrophobic monomers and/or polymers. Organic compounds that can be used for clay modifications can be classified as reactive or nonreactive modifiers. Nonreactive modifiers are those that do not participate in the polymerization reaction, e.g., quaternary alkyl ammonium compounds. On the other hand, reactive modifiers are those that can participate in the polymerization process either as initiators,

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inisurfs,^{18,19} or comonomers (surfmers).^{11,20,21} The use of nonreactive modifiers for clay modification prior to incorporation in polymers is widely reported.^{11,20–24}

Once the clay has been modified, different polymerization methods can be used to prepare the PCNs, and these include melt intercalation and in situ intercalation polymerization. Melt intercalation involves blending of clay platelets with a molten polymer under high shear. On the other hand, in situ intercalation involves dispersion of clay platelets within a monomer prior to polymerization. PCN is therefore obtained upon polymerization of the monomer in the presence of the clay platelets. In situ intercalation is a versatile approach offering better control of morphology of the PCNs than any other method. The in situ intercalation method affords the preparation of PCNs using most of the available polymerization methods. In situ intercalation polymerization has therefore been employed in heterogeneous polymerization methods like emulsion and miniemulsion polymerizations to prepare latexes of various morphologies.^{9,15,25,26} As such, there has been a growing interest in highly filled inorganic–organic hybrid latex materials prepared by the in situ intercalation heterogeneous polymerization methods.

Irrespective of the modification used, the PCN preparation method or polymerization method, it is generally desirable to have the clay platelets fully exfoliated and homogeneously dispersed in the polymer matrix. In low clay content PCNs, exfoliation is understood to be a function of the polymer chains intercalated between the clay platelets. Naturally, clay platelets exist in stacks, called tactoids, which are held together by ionic interactions brought about by counterions that exist in the clay galleries. Exfoliation is therefore a state where the orderly structure of these tactoids is completely disrupted. On the other hand, intercalation is where the spacing between the clay platelets is increased by polymer chains but the orderly nature of the clay tactoids is retained. Polymer chain growth within the clay galleries is understood to play a significant role in bringing about exfoliation.^{5,27–29}

One of the desirable characteristic properties of polymer/clay nanocomposites is their superior barrier properties relative to the parent polymer, making them attractive for packaging and barrier coating applications. Highly filled polymer/clay nanocomposites would be important particularly in barrier coatings. The high clay content has a potential to increase the barrier properties significantly, at the same time reducing material cost since clay is relatively cheap. However, the preparation of highly filled polymer/clay hybrid latexes using conventional methods such as emulsion or miniemulsion remains a challenge. Very limited reports can be found in the literature that discuss the polymer/clay hybrid materials with ≥ 30 wt % clay using miniemulsion or emulsion polymerization. Tong and Deng reported on polymer/clay hybrid materials with up to 30 wt % clay prepared using emulsion polymerization.²¹ They reported that clay encapsulation was dependent on both the clay platelet size and the type of clay modifier used. These findings were in agreement with a summary reported by Moraes et al.³⁰ on morphologies obtainable in an effort to encapsulate different sizes of clay platelets at low clay concentrations, i.e., < 10 wt %. Furthermore, Tong and Deng reported that the use of reactive modifiers facilitates encapsulation better than nonreactive modifiers. Bourgeat-Lami and co-workers,³¹ utilizing a reactive modifier (inisurf) 2,2-azobis(2-methyl propionamide) hydrochloride to modify Laponite, prepared highly filled polymer/clay hybrid latexes. Despite using a small-size clay platelet and

reactive modifier, in the prepared hybrid latexes the clay platelets were predominantly attached on the polymer surfaces rather than encapsulated.

To date, the amount of clay that has been encapsulated in polymer materials by emulsion and miniemulsion still remains low, and similar problems have been encountered with other inorganic particles. It was not until Landfester's group developed the ad-mini-emulsion polymerization that inorganic nanoparticles could be effectively encapsulated at high concentrations such as 40 wt %.^{32,33} The ad-mini-emulsion process is based on stepwise formation of a hybrid miniemulsion which is then polymerized to give the desired hybrid nanoparticles. It involves preparing the inorganic particle suspension and the monomer mini-emulsion separately and then relies on fission/fusion processes to produce the hybrid miniemulsion during cosonication of the two dispersions. However, to the best of our knowledge, the method has not yet been used to prepare polymer/clay hybrid materials encapsulating high clay contents.

The current study focuses mainly on the preparation of highly filled (30–50 wt %) polystyrene/clay hybrid latexes. The study highlights the important techniques and parameters necessary to effectively incorporate high clay content in polymer, a challenge that has been experienced widely in polymer/clay nanocomposite research. The study aims at evaluating the role of clay platelet size and modifier reactivity on the encapsulation of the clay at high clay loadings using the ad-mini-emulsion polymerization technique. The two clays used in this study were montmorillonite (MMT) and Laponite (Lap), which were chosen on the basis of their platelet size difference. Two modifiers were used to modify the clays, i.e., a reactive modifier, a surfmer (vinylbenzyl dodecyltrimethylammonium chloride (VBDAC)), and a nonreactive modifier (cetyltrimethylammonium bromide (CTAB)). The two modifiers were chosen based on their differences in ability to copolymerize with the styrene monomer during the polymerization reaction. VBDAC bears a styrene moiety and, hence, was expected to copolymerize into the polymer chain backbone via the addition polymerization reaction, whereas the CTAB bears no reactive site and, therefore, was not expected to participate in the polymerization reaction. The structures of the two modifiers are given in Figure S1 of the Supporting Information. Furthermore, the study tries to establish correlations between clay platelet size or modifier reactivity and the physical properties of the resultant highly filled PCNs. The physical properties evaluated include thermo-mechanical properties and thermal stability.

2. EXPERIMENTAL SECTION

2.1. Materials. Styrene (99%) was supplied by Sigma Aldrich and was washed with 0.3 M aqueous potassium hydroxide (KOH) solution and then with deionized water. This was followed by distilling the washed styrene at 40 °C under reduced pressure to remove the inhibitor. Azobisisobutyronitrile (AIBN) was supplied by Sigma Aldrich and was purified by recrystallization from methanol before use. Laponite RD (Lap) (25 nm \times 0.92 nm dimensions, CEC of 55 mmol/100 g, *d* spacing of 1.59 nm and an aspect ratio (L/W) of 27:1) was supplied by Rockwood Additives Limited, U.K. Montmorillonite (MMT) (50–500 \times 1 nm dimensions, CEC value of 116 mmol/100 g, *d* spacing of 1.27 nm and L/W ratio of up to 500:1) was supplied by Southern Clay products, a subsidiary of Rockwood Additives (U.K.). Sodium dodecyl sulfate (SDS, 99%), 4-vinylbenzyl chloride (99%), *N,N*-dimethyl dodecylamine (99%), cetyltrimethylammonium bromide (CTAB, 99%), and hexadecane (HD, 99%) were supplied by Sigma

Aldrich and were used as received. Silver nitrate was supplied by Sigma Aldrich and was used as received. VBDAC was synthesized as reported elsewhere.³⁴

2.2. Modification of Clay. Clay (Lap or MMT) (1 wt % relative to water) was dispersed in 1 g/1 dm³ sodium pyrophosphate solution at room temperature, and the dispersion was stirred for 2 h to obtain a clear dispersion. A predetermined amount of modifier (VBDAC or CTAB) equivalent to the 100% CEC of the clay was dissolved in 100 mL of deionized water to produce an aqueous modifier solution. The aqueous modifier solution was added dropwise to the clay dispersion before the mixture was stirred for a further 24 h at room temperature. Table 1 shows the typical formulations used for the modification of the

Table 1. Formulations for the Modification of Lap and MMT

sample	^a clay (g)	Na ₂ P ₂ O ₄ (g)	VBDAC (g)	CTAB (g)	water (mL)
Lap-VBDA	10.0	1.00	0.201	-	1000
Lap-CTA	10.0	1.00	-	0.20	1000
MMT-VBDA	10.0	1.00	0.425	-	1000
MMT-CTA	10.0	1.00	-	0.425	1000

^aLap or MMT.

clay. The modified clay (precipitate) was recovered from the mixture by centrifugation at 2790 relative centrifuge force (RCF) for 60 min. Several washings were done on the obtained modified clay until no free modifier molecules were detected in the supernatant. This was confirmed by the absence of an off-white precipitate upon addition of a few drops of 0.1 M aqueous silver nitrate solution to the supernatant. The amount of modifier grafted onto the clay platelet surfaces was quantitatively determined by TGA. The amount of modifier was found to be 48 mmol/100 g, 50 mmol/100 g, 104 mmol/100 g, and 106 mmol/100 g for Lap-VBDA, Lap-CTA, MMT-VBDA, and MMT-CTA, respectively.

Lap modified with VBDAC and CTAB was labeled Lap-VBDA and Lap-CTA, respectively, and the same applies for MMT-VBDA and MMT-CTA. The amount of modified clay in the pastes was determined by gravimetric and TGA methods. Lap-based pastes contained ~13% modified Lap, while MMT-based paste contained ~25% modified MMT. Refer to Figure S2 of the Supporting Information for the TGA procedure.

2.3. Preparation of Hybrid Latex. Aqueous Modifier Suspension. Aqueous modified clay suspension was prepared using modified clay paste, i.e., wet modified clay recovered soon after washing to remove free surfactant. A predetermined amount of modified clay paste was dispersed in SDS solution and agitated for 2 h. This was followed by exposing the resulting dispersion to sonication for 20 min at 90% amplitude using a Vibra Cell Autotune series 750VCX high

intensity ultrasonic processor (Sonics, U.S.A.). SDS and sonication were used to facilitate stabilization of the modified clay aggregates in the aqueous media. The sonication process breaks down the aggregates into small aggregates, while the SDS molecules stabilize the clay aggregates through tail-to-tail interactions with the modifiers grafted onto the clay platelet surfaces, thus forming ad-micelles.^{35–39}

Monomer Miniemulsion. The monomer miniemulsion was prepared by dispersing styrene, AIBN, and hexadecane in 10 mM SDS solution. The monomer/water ratio was maintained at 3:5, but the volume of this miniemulsion was varied in an effort to maintain the overall solid content of the latex constant. The dispersion was then agitated for 30 min in an ice bath followed by sonication for 2 min in an ice bath at 50% amplitude. The amount of energy exerted on the dispersion during the sonication process was 4 ± 1 kJ. Table 2 summarizes the formulations used for the preparation of hybrid latexes of different clay loadings.

Cosonication and Polymerization. The modified clay dispersion and the styrene miniemulsion were mixed together under vigorous agitation for 30 min in an ice bath. This was followed by sonicating the mixture for 4 min in an ice bath at 50% amplitude (10 ± 2 kJ of energy was exerted). The resultant hybrid miniemulsion was transferred into a three-neck round-bottom flask connected to a condenser and a nitrogen inlet. The hybrid miniemulsion was purged with nitrogen for 30 min. After raising the temperature to 75 °C, polymerization was initiated and allowed to run for 6 h. The resultant hybrid latexes and PCNs were labeled PS/*x*C-S, where PS represents polystyrene, *x* the amount of clay used, C the type of clay incorporated, and S the type of modifier used for clay modification; e.g., PS/30Lap-CTA is PCNs of polystyrene containing 30 wt % Lap modified with CTAB.

2.4. Analytical Techniques. To determine the hybrid latex morphologies, transmission electron microscopy (TEM) was used to evaluate the latexes and the PCNs obtained after drying the latexes. The latex was diluted using deionized water using a 1:10 latex-to-deionized water ratio. A 3 μL aliquot of the diluted latex was transferred by micropipet onto a 300-mesh copper grid.

To establish the extent of clay exfoliation in the polymer matrix, PCNs from dried latexes were embedded in epoxy resin and cured at 60 °C for 24 h. The embedded samples were then ultramicrotomed with a diamond knife using a Reichert Ultracut S ultramicrotome, at room temperature, thus yielding film sections of about 100 nm thick.

In both latex and microtomed film analyses, bright-field TEM images were recorded at 200 kV with a Tecnai G²20 high-resolution TEM (FEI, Netherlands) equipped with LaB₆ filament and a Gatan GIF Tridiem postcolumn energy filter. During analyses, the image contrast was enhanced by inserting an energy filter of 20 eV in the electron beam path to filter out inelastically scattered electrons, which contribute toward background noise in the digitally recorded images.

Thermograms of the dry sample powders were recorded using a Q500 TGA 7 thermogravimetric analyzer (Perkin-Elmer, U.S.A.). The

Table 2. Formulations Used to Prepare PS/Lap and PS/MMT Hybrid Latexes

sample	aqueous clay dispersion			monomer miniemulsion				
	clay (g)	SDS (mM)	water (mL)	styrene (g)	AIBN (g)	HD (g)	SDS (mM)	water (mL)
PS00	-	-	-	10.0	0.20	0.40	10.0	50.0
PS/30Lap-CTA	3.00	20.0	38.4	7.00	0.14	0.28	10.0	11.7
PS/40Lap-CTA	4.00	20.0	40.0	6.00	0.12	0.24	10.0	10.0
PS/50Lap-CTA	5.00	20.0	41.7	5.00	0.10	0.20	10.0	8.30
PS/30Lap-VBDA	3.00	20.0	38.4	7.00	0.14	0.28	10.0	11.7
PS/40Lap-VBDA	4.00	20.0	40.0	6.00	0.12	0.24	10.0	10.0
PS/50Lap-VBDA	5.00	20.0	41.7	5.00	0.10	0.20	10.0	8.30
PS/30MMT-CTA	3.00	30.0	88.4	7.00	0.14	0.28	5.00	11.7
PS/40MMT-CTA	4.00	30.0	90.0	6.00	0.12	0.24	5.00	10.0
PS/50MMT-CTA	5.00	30.0	91.7	5.00	0.10	0.20	5.00	8.30
PS/30MMT-VBDA	3.00	30.0	88.4	7.00	0.14	0.28	5.00	11.7
PS/40MMT-VBDA	4.00	30.0	90.0	6.00	0.12	0.24	5.00	10.0
PS/50MMT-VBDA	5.00	30.0	91.7	5.00	0.10	0.20	5.00	8.30

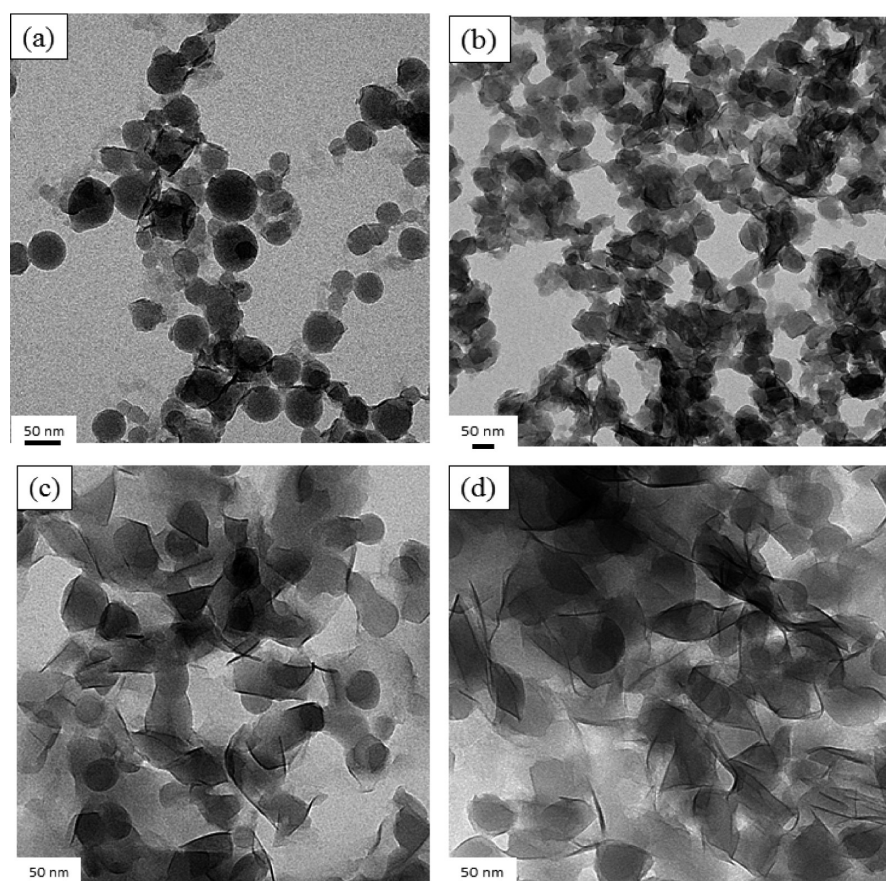


Figure 1. TEM images of (a) PS/50Lap-CTA, (b) PS/50Lap-VBDA, (c) PS/50MMT-CTA, and (d) PS/50MMT-VBDA (scale bar: 50 nm).

experiments were carried out under a nitrogen atmosphere, at a flow rate of 5 mL/min. The temperature was increased from 25 to 590 °C, at a heating rate of 15 °C/min.

Dynamic mechanical analysis (DMA), to determine the storage modulus (G'), loss modulus (G''), and $\tan(\delta)$ of the PCNs, was carried out using a Physica MCR 501 (Anton Paar, Germany) in oscillatory mode, from 150 to 20 °C, at a cooling rate of -4 °C/min, using a 25 mm diameter plate geometry. All tests were done under 0.1% deformation and 15 N normal force, at a frequency of 1 Hz. Prior to the analysis, samples were molded into disk-shaped films by compression at 150 °C. The thickness of all samples was in the range 0.8–1.0 mm.

The glass transition temperatures of PS and its PCNs were determined by DSC. The analyses were conducted on a Q100 DSC system (TA Instruments, U.S.A), calibrated with indium metal according to standard procedures. Heating and cooling rates were maintained at 10 °C/min. The samples were first subjected to a heating ramp up to 200 °C, after which the temperature was kept isothermally at 200 °C for 5 min to remove thermal history. The cooling cycle, from 200 to 20 °C, followed the isothermal stage from which data were recorded.

The dispersion of the clay platelets was analyzed using small-angle X-ray scattering (SAXS). SAXS experiments were performed with an in-house setup of the Laboratoire Charles Coulomb, "Réseau X et gamma", Université Montpellier 2, France. A high-brightness, low-power X-ray tube, coupled with aspheric multilayer optic (GeniX^{3D} from Xenocs), was employed. It delivers an ultralow divergent beam (0.5 mrad). Scatterless slits were used to give a clean 0.8 mm beam diameter (35 Mphotons/s) at the sample. Using a transmission configuration, the scattered intensity was measured by a Schneider 2D image plate detector prototype, at a distance of 1.9 m from the sample for SAXS configuration. All intensities were corrected by transmission, and the empty cell contribution was subtracted.

3. RESULTS AND DISCUSSION

The hybrid materials showed high conversions ($\geq 90\%$) in the ad-miniemulsion polymerization with limited deviation from the neat polymer. The incorporation of Lap and MMT afforded stable hybrid latexes with very low coagulation levels ($< 5\%$) at 20% and 10% total solid content, respectively. This was attributed mainly to the differences in clay sizes. The type of modifier was found to have no influence on the total solid content achievable. The solid content achievable after modification with the two modifiers remained fairly constant for both PS/Lap and PS/MMT PCNs.

3.1. Morphological Properties. Figure 1 shows the morphologies of Lap and MMT based hybrid latexes. PS/Lap-CTA PCNs exhibited predominantly armored particles, where clay platelet stacks were adhered onto the polymer particle surface, as shown in Figure 1(a). On the other hand, PS/Lap-VBDA PCNs exhibited nanoparticles with predominantly encapsulated morphology, as shown in Figure 1(b). It appears that no significant amount of clay platelet stacks was observed outside the hybrid particles. However, there were insignificant differences observed between TEM latex images of PS/MMT-CTA and PS/MMT-VBDA. Irrespective of the modifier used, MMT-based hybrids exhibited armored particle morphology (see Figure 1(c) and (d)). MMT platelet stacks adhered onto the polymer particle surfaces were clearly visible from both PS/MMT-CTA and PS/MMT-VBDA latex images.

MMT platelets appeared too big to encapsulate, and both normal TEM and high-resolution TEM (HRTEM) were used in an effort to establish the number of polymer particles per clay stack. Figure 2 shows low magnification TEM and

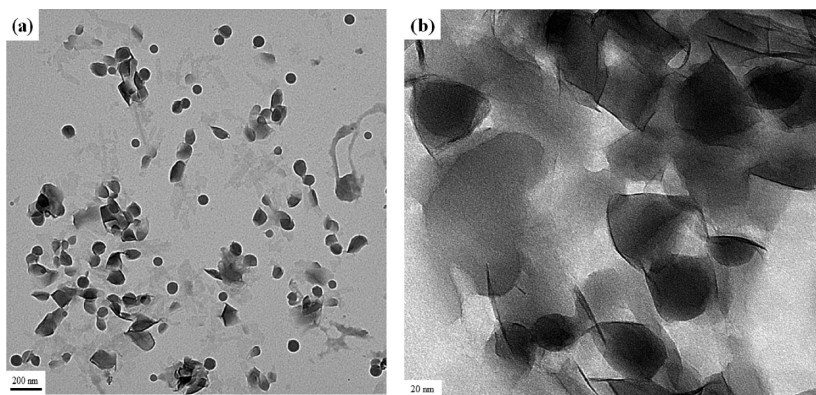


Figure 2. Low-magnification TEM image (200 nm) and HRTEM image (20 nm) of PS/Lap-VBDA nanocomposite.

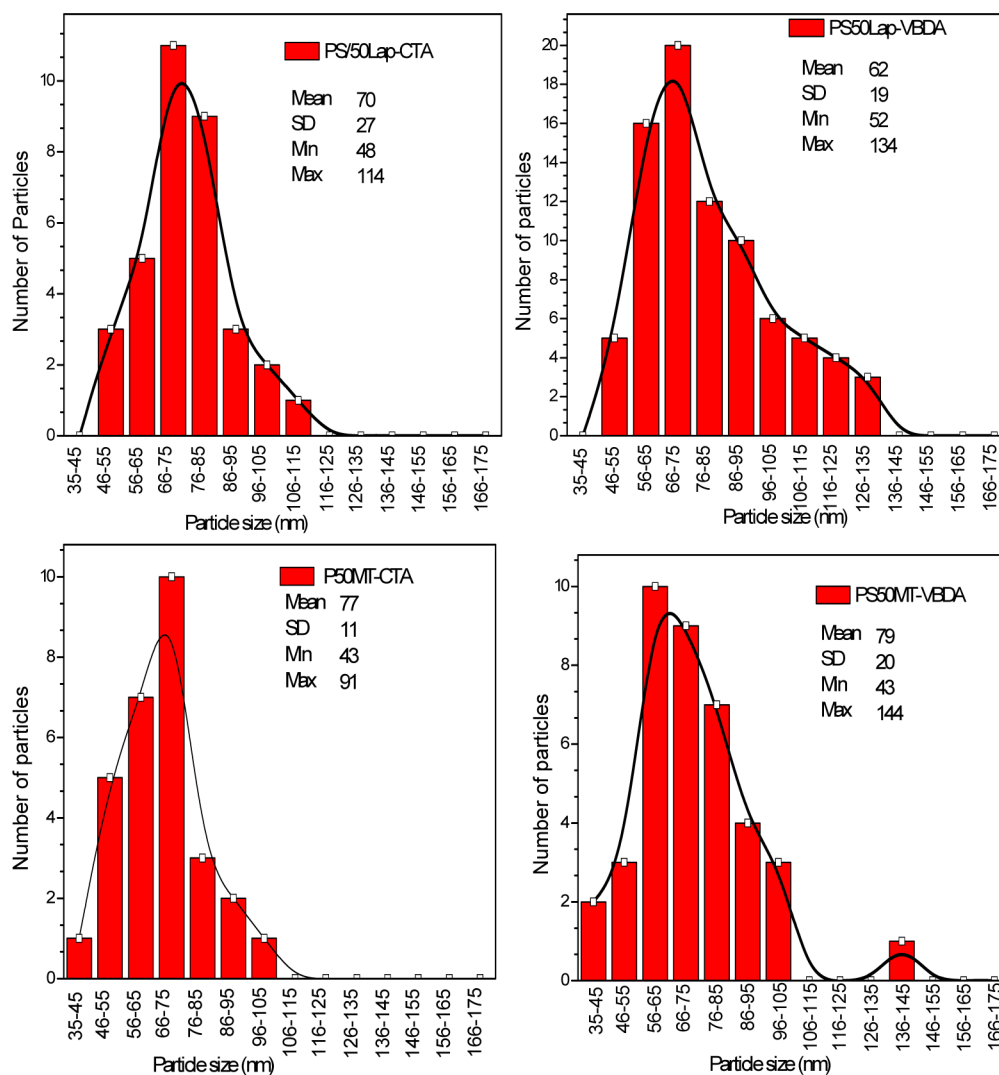


Figure 3. Particle size distributions of the different latexes as estimated from TEM images: PS/50Lap-CTA, PS/50Lap-VBDA, PS/50MT-CTA, and PS/50MT-VBDA.

HRTEM images of MMT-based PCNs. In less aggregated regions, it was observed that there was predominantly one polymer particle per platelet. However, in the aggregated areas one could not tell the number of polymer particles per clay stack.

The reactive modifier (VBDAC) improved monomer/clay compatibility as compared to the nonreactive modifier

(CTAB). This was evident from the formation of a homogeneous paste upon dispersing Lap-VBDA in styrene,^{28,29} whereas clear phase separation could be observed in styrene/Lap-CTA dispersion. This is indicative of the fact that modification of clay with VBDAC improves the wettability of clay by the monomers where CTAB could not afford this

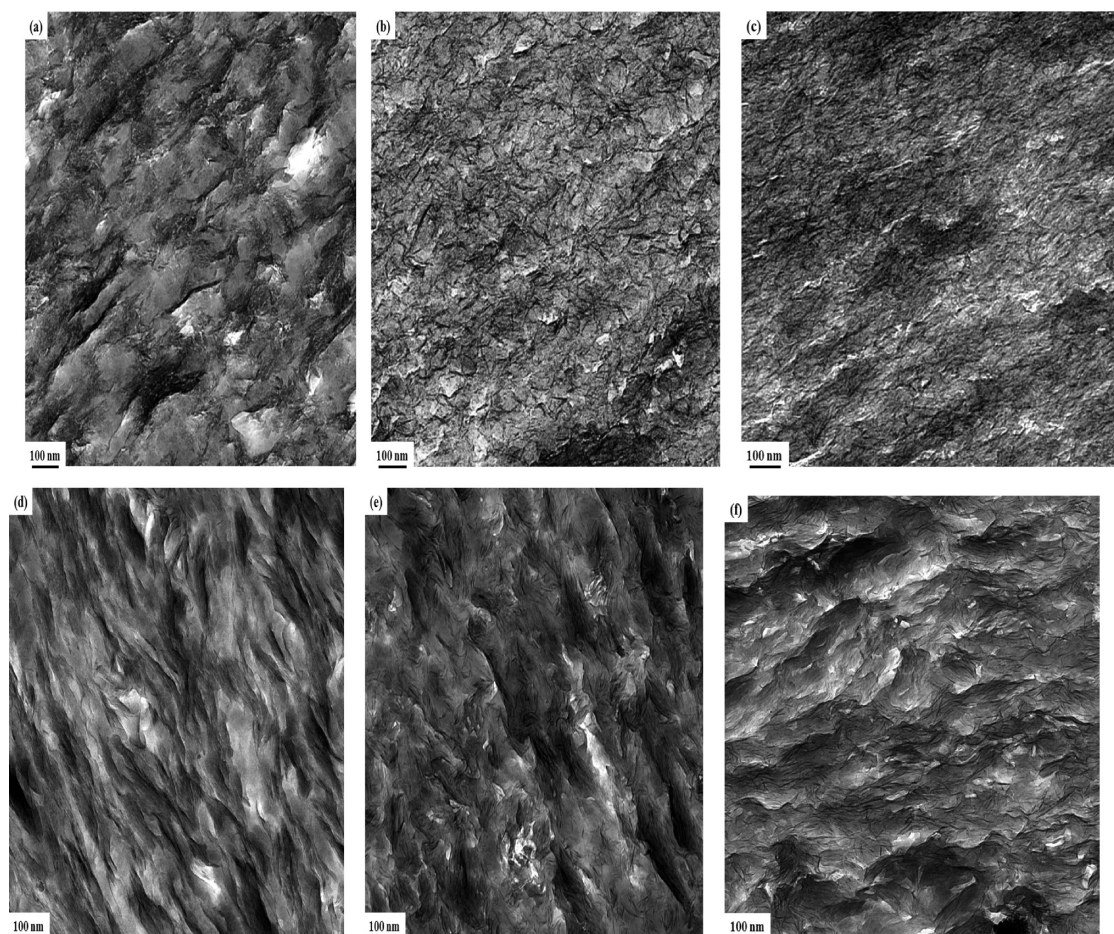


Figure 4. TEM images of microtomed samples: (a) PS/50Lap-VBDA control, (b) PS/Lap-CTA, (c) PS/50Lap-VBDA, (d) PS/50MMT-VBDA control, (e) PS/30MMT-CTA; and (f) PS/30MMT-VBDA (scale bar: 50 nm).

benefit. Furthermore, the reactive modifier facilitated encapsulation by copolymerizing into the polystyrene backbone.

However, the size of the clay platelet was found to have a dominating effect over modifier reactivity. The same reactive modifier that facilitated encapsulation of a small-sized clay appeared to ineffectively encapsulate large clay platelets, according to TEM images of the latexes. It was therefore concluded that a modifier that facilitates compatibility between the clay and monomer is a prerequisite for the effective encapsulation of the clay platelets. However, encapsulation is ineffective if the clay platelet dimensions are equivalent to or greater than the monomer droplets, as was observed with MMT. According to estimations from TEM images, the average MMT platelet stack length (75 nm) was greater or comparable to the average polymer particle size (56–80 nm in diameter). These findings were in agreement with those reported for low clay content PCNs.³⁰

Figure 3 shows the statistical average particle size distributions of the different latexes as estimated from TEM images.

These estimations were made mainly from individual particles with well-defined edges and shape. Therefore, those particles obscured by aggregation and clay clusters were not included in the estimations because their exact dimensions could not be established. As a result, this affected the estimations in MMT-based latexes because a larger number of particles were omitted in the estimations because they were

obscured in polymer/clay clusters. However, the average polymer particle size of PS/MMT-based latexes was consistent with the average MMT platelet length (as estimated from TEM images), indicating that the polymer particle size was largely governed by the clay platelet length.

The dried latexes obtained after casting the hybrid latexes into an aluminum pan were microtomed into 100 nm thin film samples. The extent of clay platelet delamination within these microtomed film samples was evaluated using TEM. Figure 4 shows the TEM images of PS/Lap and PS/MMT PCNs, together with their respective control samples (PS/50Lap-VBDA and PS/50MMT-VBDA blends). The control samples were prepared by blending the polystyrene latex and clay-VBDA dispersion using a 1:1 ratio to obtain a 50% clay nanocomposite, before drying and microtoming the blend. The influence of the ad-mini-emulsion method was clearly visible. The control samples exhibited clear phase separation between the clay aggregates and the polymer matrix. Clay platelet distribution within the nanocomposite improved with the use of ad-mini-emulsion method. PS/Lap-CTA PCN films, shown in Figure 4(b), exhibited a cellular structured morphology, similar to those reported for Pickering stabilization.^{9,40–42} The cellular structure morphology was attributed to the restriction of interdiffusion at the particle interface by the clay platelets adhered onto the polymer particle.^{40,43,44} However, PS/Lap-VBDA PCNs (see Figure 4(c)) exhibited homogeneous distribution of the clay platelets within the microtomed

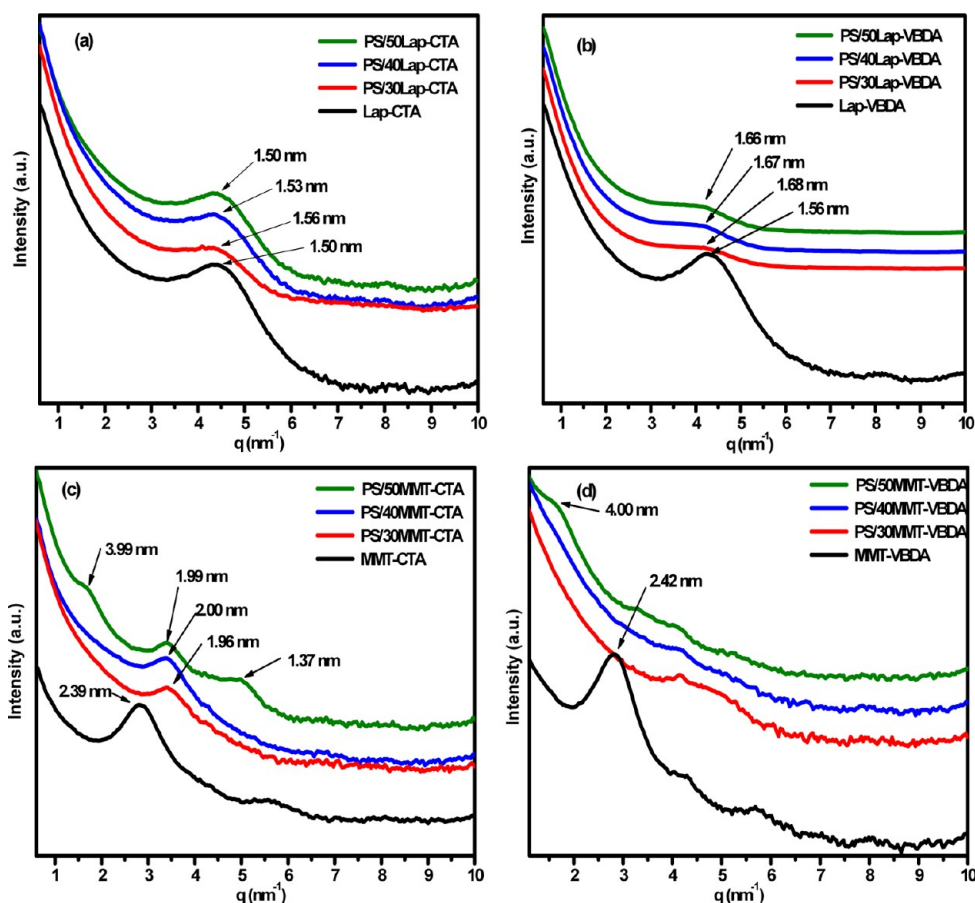


Figure 5. SAXS profiles of (a) PS/Lap-CTA, (b) PS/Lap-VBDA, (c) PS/MMT-CTA, and (d) PS/MMT-VBDA.

samples. This was considered as an indication that the clay platelets were efficiently encapsulated and hence could not restrict interdiffusion at the particle interface. On the basis of these results, it can be argued that blending, ad-mini-emulsion polymerization using nonreactive modifier, and ad-mini-emulsion polymerization using reactive modifier yield a phase-separated nanocomposite, PCN with cellular structure morphology, and PCN with homogeneous clay distribution, respectively. The homogeneous distribution in PS/Lap-VBDA was attributed to the predominant encapsulated morphology in the latex.

The MMT-based PCNs also showed a morphological transition from the blend (control sample) through to the PCNs prepared by ad-mini-emulsion using a reactive modifier. However, the morphological differences observed in the PS/MMT series were not as pronounced as those observed in PS/Lap PCNs. This was probably due to the higher encapsulation efficiency in PS/Lap PCNs than PS/MMT PCNs. For clarity, images shown in Figure 4 were reproduced and enlarged in Figure S3 of the Supporting Information. Similar to PS/Lap PCNs, this result was an indication that the participation of the modifier in the polymerization process facilitated the exfoliation of the clay platelets and hence the homogenization of the clay platelets within the polymer matrix. Similar results showing differences between the extent of exfoliation as a result of using reactive and nonreactive clay modifier have been reported for low clay content PCNs.²⁹ As such, this homogeneous distribution of clay could be indicative of a predominantly encapsulated latex morphology. PS/MMT-VBDA exhibited homogeneous distribution of clay within the film with limited

aggregation even at higher clay loadings (see Figure S4 of Supporting Information).

On the basis of these results, it was concluded that the effective encapsulation of clay at higher loadings using ad-mini-emulsion polymerization can be effectively achieved by choosing a clay platelet of smaller dimensions, relative to the polymer particles and a reactive modifier that improve monomer/clay compatibility. These findings were in agreement with those reported for low clay content PCNs.²¹

Studies on the delamination of the clay platelets within the polymer matrix were further conducted using SAXS to complement the TEM results. It is possible to evaluate the extent of clay platelet delamination and affinity between the polymer chains and the clay based on the changes in SAXS profiles. In the literature, the widening of scattering peak and/or the lowering in scattering peak intensity is generally regarded as an indication for intercalation of polymer chains within the interlayer gallery. Changes in the d -spacing of clay platelets are calculated using the equation $d = 2\pi/q$, where q is a wave vector. PCNs with fully exfoliated clay platelets do not show any scattering peak due to the disruption of the orderly nature of clay platelets.^{45,46} The SAXS scattering patterns of PS/Lap-CTA, PS/Lap-VBDA, PS/MMT-CTA, and PS/MMT-VBDA are shown in Figure 5. The SAXS patterns of PS/Lap-CTA show a scattering peak whose intensity and position were independent of clay content.

The calculated d -spacings of these PS/Lap-CTA PCNs were found to be relatively constant irrespective of clay content (see Figure 5(a)). Interestingly, there was no significant difference between the d -spacing of the PS/Lap-CTA and that of Lap-

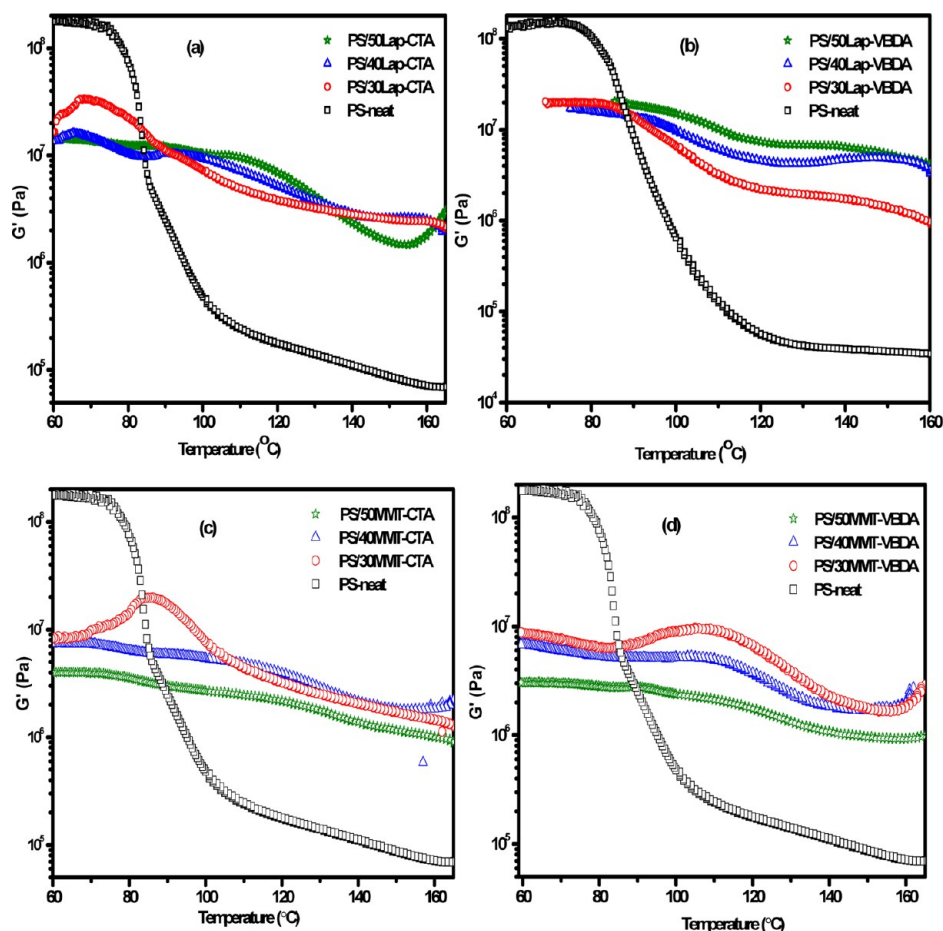


Figure 6. Storage modulus curves of (a) PS/Lap-CTA, (b) PS/Lap-VBDA, (c) PS/MMT-CTA, and (d) PS/MMT-VBDA PCNs.

CTA. Similar results were obtained for PS/MMT-CTA PCNs, shown in Figure 5(c).

However, when clay modified with VBDAC was used, partially and fully exfoliated PCNs were obtained. PS/Lap-VBDA PCNs showed broad scattering peaks with very low intensity, and the calculated d -spacings were found to be larger than those of PS/Lap-CTA (see Figure 5(b)). This is an indication that the PCNs were partially exfoliated. From Figure 5(d), no scattering peak was observed in PS/MMT-VBDA PCNs, a fully exfoliated morphology, except for the PS/50MMT-VBDA sample which showed a scattering peak at very low q values, corresponding to a d -spacing of 4.00 nm. The morphological differences observed between PCNs prepared from clay modified with CTAB and VBDAC were attributed to the difference in reactivity between the two modifiers. It is generally accepted that the growth of polymer chains inside the clay galleries generates pressure onto the platelets, thus bringing about exfoliation.⁴⁷ At the same time, thermodynamic compatibility of the polymer/monomer with the modified clay is required to allow efficient exfoliation of clay platelets.^{28,29,48}

3.2. Thermo-Mechanical Analysis. Figure 6 shows the storage modulus (G') of the different PCNs as a function of temperature. Generally, all PCNs had much higher G' values compared to the neat polymer, irrespective of the clay or the modifier used, especially in the rubbery region. This is in agreement with other literature reports where enhancement in G' values has been observed with the incorporation of clay.^{4,8,11,41,49–52} Such behavior could be attributed to polymer–clay interactions which bring about restriction on

polymer chain mobility.^{11,51} However, the dependency behavior of G' on clay content was found to be strongly influenced by both the clay size and the type of modifier. Figure 6(a) shows that Lap-CTA exhibited fairly constant G' values irrespective of clay content. Lap-VBDA-based PCNs exhibited a monotonic increase in G' with increasing clay in the rubbery regions while remaining fairly constant in the glassy region. PS/MMT-CTA and PS/MMT-VBDA PCNs exhibited a monotonic decrease in storage modulus with increasing clay content, irrespective of the clay modifier used. The result was surprising for PS/MMT-VBDA PCNs which exhibited exfoliated morphology. Furthermore, strong polymer/clay interactions were expected in these PCNs due to the copolymerization of VBDA into the main polymer chain. However, for PS/MMT-CTA and PS/Lap-CTA PCNs the observed G' behavior with increasing clay content was attributed to the nonreactive nature of CTAB. Furthermore, these PCNs exhibited intercalated morphology irrespective of clay content, as was established by SAXS. Intercalated morphology reduces the effective surface area of clay platelets, thus reducing polymer/clay interaction. As such the enhancement in G' was compromised. Notably, the conventional glassy phase to rubbery phase step was significantly diminished by the high clay loadings incorporated. This was attributed to the high clay loadings used in the study. Both the neat clay and the modified clay were found to exhibit no transition step

Figure 7 shows the temperature dependency of the damping factor of the PCNs. These highly filled PCNs generally

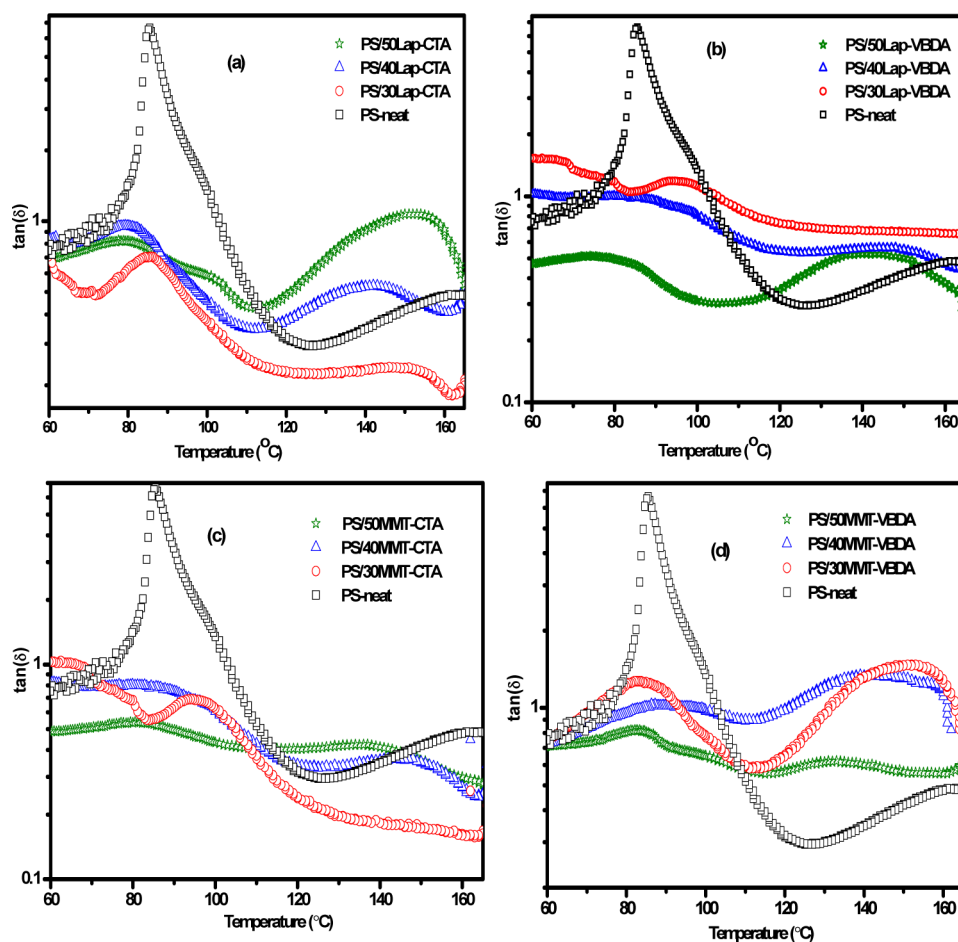


Figure 7. $\tan(\delta)$ peaks of (a) PS/Lap-CTA; (b) PS/Lap-VBDA; (c) PS/MMT-CTA; and (d) PS/MMT-VBDA.

exhibited two $\tan(\delta)$ peaks, irrespective of the clay or the modifier used.

The first peak, around 85 °C, was attributed to T_g , while the second peak, above 100 °C, was associated with flow relaxation of untethered polymer chains intercalated between the clay platelets.⁵³ In all PCNs, the $\tan(\delta)$ peak associated with T_g decreased in intensity and became broader with increasing clay content. This was attributed to the reduced chain mobility in the PCNs brought about by the incorporation of clay platelets.^{52,54} No direct correlation could be established between the damping factor and neither clay type nor type of modifier used. The results show that the amount of clay platelets had a dominating effect on the damping factor. It is possible that any effect on $\tan(\delta)$ peak imparted by the reactivity of the modifier was nullified by the ultrahigh clay loadings employed in this study. The glass transition temperature (T_g) discussed in the current study was determined using differential scanning calorimetry (DSC). Figure 8 shows the DSC profiles of PS/Lap and PS/MMT PCNs, and Table 3 summarizes the T_g values of the different PCNs.

The T_g of both PS/Lap and PS/MMT PCNs was found to depend heavily on the type of modifier used to modify the clay. PS/Lap-VBDA and PS/MMT-VBDA PCNs showed an increasing T_g value, while PS/Lap-CTA and PS/MMT-CTA PCNs showed a decrease in T_g values, with increasing clay content.

This was attributed to the strong polymer-to-clay interactions brought about by the polymerizable VBDA molecules

compared to the nonpolymerizable CTA molecules. The incorporation of VBDA onto the main polymer chain promoted polymer–clay interactions thus restricting long-range molecular motions. The results indicate that the reactive modifier enhanced the polymer–clay interactions, hence an increase in T_g with increasing clay content. On the other hand, the nonreactive modifier could be acting as a plasticizer, resulting in a decrease in T_g with increasing clay content. This effect was observed in both Lap- and MMT-based PCNs. No particular changes in T_g could be directly attributed to the difference in clay size.

3.3. Thermal Decomposition. The thermal decomposition of the PCNs was determined by monitoring the onset of thermal degradation of the thermograms of the PCNs. The thermograms of both PS/Lap and PS/MMT PCNs are shown in Figure 9.

It is well documented, especially for low clay content PCNs (<10 wt %), that the clay-filled polymer exhibited superior thermal stability properties compared to the corresponding neat polymer. This is due to clay acting as a mass transport barrier and insulator between the polymer and the decomposition zone. Furthermore, it creates a tortuous path for the gaseous products of decomposition.^{11,18,19,22,55,56} However, it has been reported that in PCNs there is a threshold clay content value beyond which either no thermal stability improvement or a negative effect on thermal stability is observed.^{54,55} On the basis of the tortuous path effect, one would expect clay platelets with high aspect ratio, e.g., MMT, to

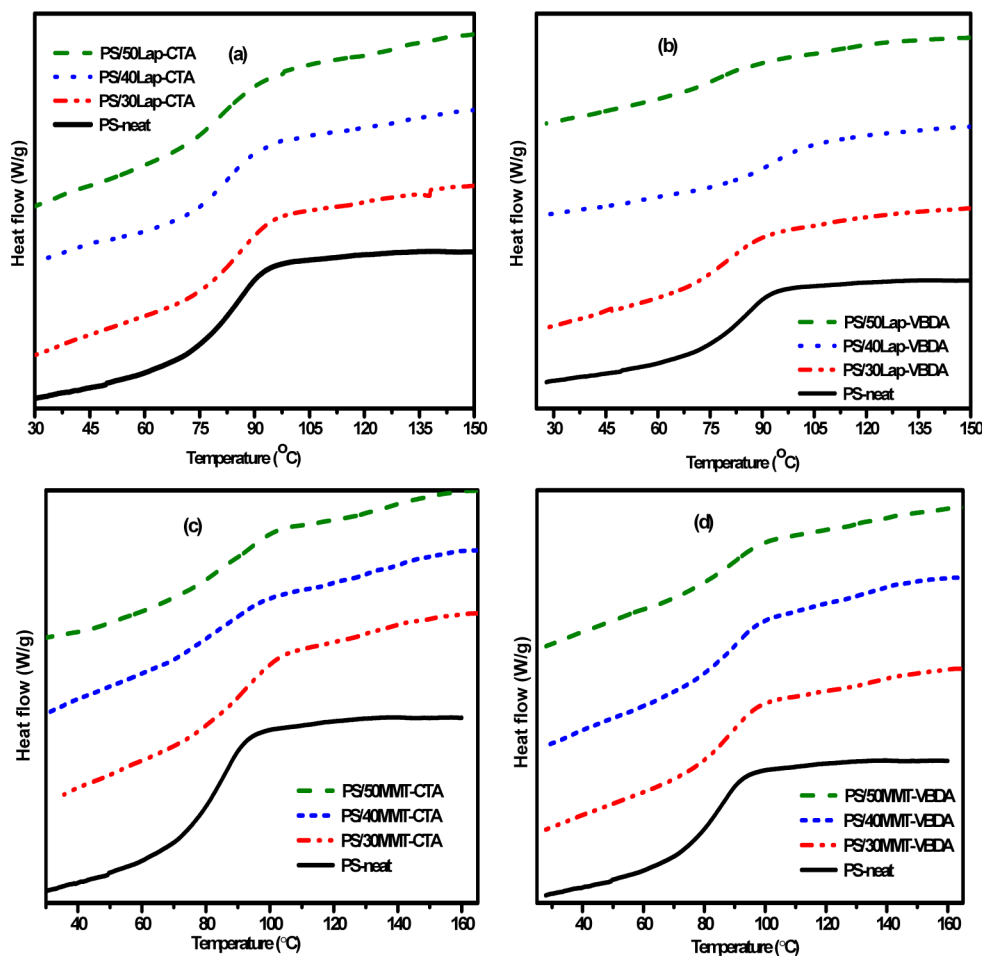


Figure 8. DSC profiles of (a) PS/Lap-CTA; (b) PS/Lap-VBDA; (c) PS/MMT-CTA; and (d) PS/MMT-VBDA.

Table 3. Summary of T_g Values of Highly Filled PS/Lap and PS/MMT PCNs

sample	clay content (wt %)	T_g
PS	-	85
PS/Lap-CTA	30	86
	40	83
	50	82
PS/Lap-VBDA	30	85
	40	94
	50	98
PS/MMT-CTA	30	94
	40	92
	50	92
PS/MMT-VBDA	30	90
	40	92
	50	94

improve thermal stability more significantly than Lap. Surprisingly, in the current study PS/MMT PCNs exhibited lower onset temperatures of decomposition than the neat PS, irrespective of the modifier used. PS/Lap PCNs did not show any change in the onset temperature of decomposition, irrespective of the type of modifier used. Indeed the clay platelet had an influence on the thermal stability of the materials, but the effect was not in line with the expectation. The result shows that there are other factors influencing the thermal stability of the PCNs besides the clay surface

dimensions and morphology. It has been reported that factors such as polymer decomposition, modifier decomposition, and reactivity of metals on clay platelets all influence the thermal stability of the PCNs.¹³ Results obtained in this study appear to suggest that the MMT platelets acted as a catalyst for PS chain decomposition. This may be associated with the higher impurities in MMT (natural clay) than in Lap (synthetic clay) since all other factors were similar between PS/MMT and PS/Lap PCNs.

4. CONCLUSION

The cosonication (ad-mini-emulsion) polymerization method was found to be an effective way to prepare highly filled polymer/clay hybrid latexes (30–50 wt % clay). Monomer/clay compatibility, modifier reactivity, and clay platelet size were found to influence the effective encapsulation of clay platelet size with the polymer particles. The use of a reactive modifier facilitated the exfoliation of the clay platelets and their subsequent homogeneous distribution with the polymer matrix, irrespective of clay platelet size. The use of a nonreactive modifier resulted in predominantly intercalated PCNs, while the use of a reactive modifier resulted in partially to fully exfoliated PCNs. As such, the influence of clay size and modifier properties was evident in the physical properties of the resultant PCNs. A storage modulus of PS/Lap PCNs made from hybrid latex with encapsulated morphology showed a monotonic increase with increasing clay content. PS/MMT PCNs showed a decreasing storage modulus with increasing

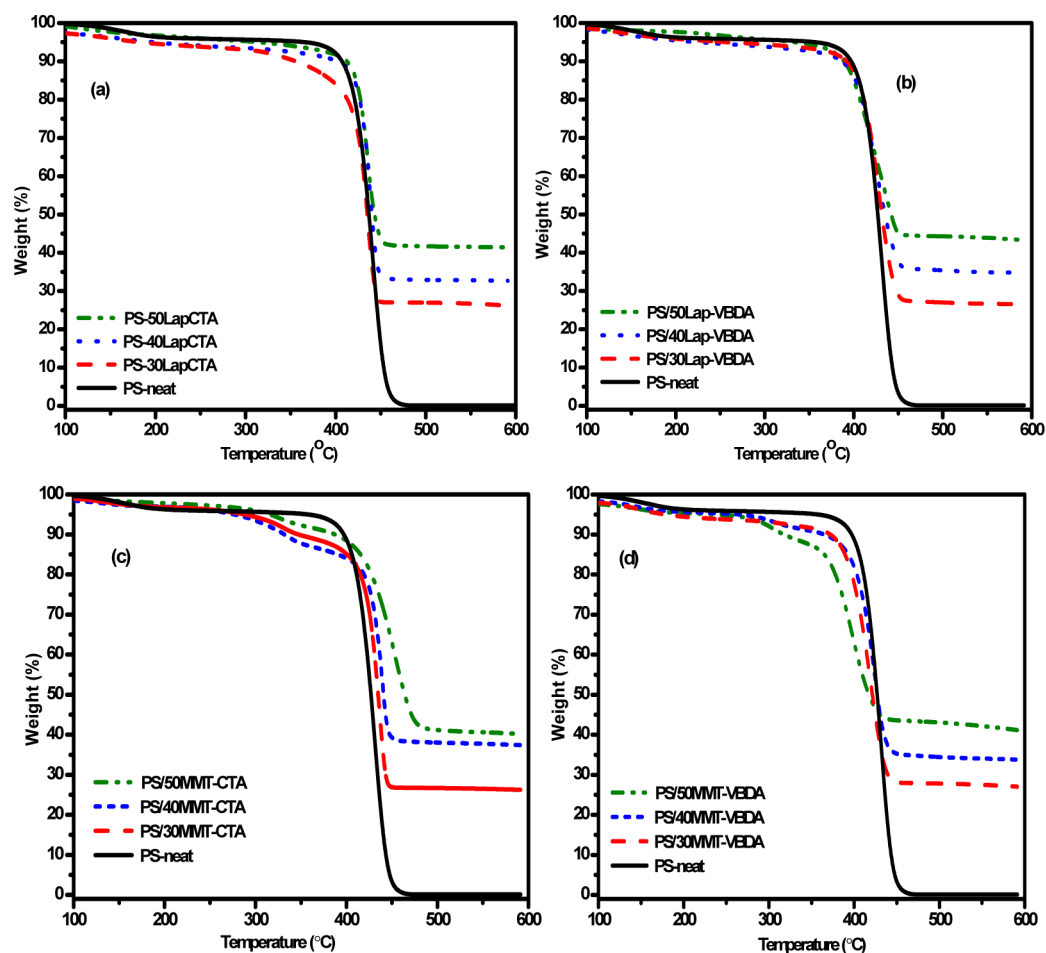


Figure 9. Thermogravimetric thermograms of: (a) PS/Lap-CTA; (b) PS/Lap-VBDA; (c) PSMMT-CTA; and (d) PSMMT-VBDA.

clay content, irrespective of the morphological structure of these PCNs. PCNs based on a reactive modifier showed higher T_g values than those based on a nonreactive modifier. This showed that the polymer–clay interaction effect plays a crucial role in restricting polymer chain mobility. The thermal stability of the PCNs was mainly dependent on the morphological structure of the PCNs which was influenced by the clay size. In conclusion, it was found that even at these high clay concentrations the nature of the modifier and the size of clay platelet influence significantly both the morphology and eventually the properties of the PCNs.

■ ASSOCIATED CONTENT

Supporting Information

The structure of the modifiers used for clay modification, the outline on the procedure followed to quantify the amount of modified clay in modified clay pastes, and TEM images of the different PCNs produced after drying the hybrid latex based on different clays employed in the study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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