

Highly Filled Water Based Polymer/Clay Hybrid Latexes

by

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*Dissertation presented for the degree of Doctor of
Philosophy in Polymer Science in the Faculty of Science at
Stellenbosch University*



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December 2012

Declaration

I, the undersigned, hereby declare that the work contained in this thesis is my own work and that I have not previously in its entirety or in part submitted it at any university for a degree.

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December 2012

Abstract

The use of co-sonication (ad-mini-emulsion) polymerisation for the preparation of highly filled polymer/clay hybrid latexes is described. Laponite (Lap) content levels in the range of 10–50 wt% were effectively encapsulated in both polystyrene (PS) and polystyrene-co-butyl acrylate nanoparticles (PSBA). The latex and film morphological features of these highly filled hybrid materials were evaluated using both transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS). PS/Lap latexes exhibited mixed particle morphologies from armoured particles at low clay content (10 wt%) to encapsulated particles at high clay content (50 wt%). However, PSBA/Lap hybrid latexes exhibited predominantly crumpled particle morphologies through the clay content studied. The resultant polymer/clay nanocomposites (PCNs) of PS/Lap and PSBA/Lap exhibited either partially or fully exfoliated structures. It was found that generally these PCNs exhibited superior properties than the neat polymers except for thermal stability properties. As much as 5000% storage modulus improvement was observed for both PS/Lap and PSBA/Lap relative to the neat polymers. The T_g of PSBA/Lap showed a 14 °C shift towards higher temperature. Rheology tests showed that the resultant PCNs exhibited solid-like viscoelastic behaviour. The encapsulation of montmorillonite clay (MMT) using the ad-mini-emulsion procedure was found to be ineffective. The MMT platelets remained adhered onto the polymer particles surfaces. Ineffective encapsulation of MMT platelets was attributed to their dimensions which were either large or equal to those of the polymer particles. Despite the ineffective encapsulation, the MMT platelets were completely exfoliated within the final PCNs as shown by both SAXS and TEM.

Overall, the ad-mini-emulsion was found to be an effective method for the preparation of highly filled water based polymer/clay hybrid latexes. However, the clay encapsulation in polymer particles and the extent of clay exfoliation were found to be dependent on clay dimensions relative to the polymer particles, monomer/clay compatibility and clay modifier reactivity. It was found that clay dimensions and use of clay modifier that improve monomer/clay compatibility enhances encapsulation. On the other hand, the modifier reactivity influenced the extent of clay exfoliation in the final PCN, irrespective of clay encapsulation in the polymer particles. These findings were based on comparative studies conducted on the use of Lap versus MMT and non-reactive modifier versus reactive modifier during ad-mini-emulsion polymerisation.

Opsomming

Die gebruik van mede-sonikasie (ad-miniemulsie) polimerisasie vir die voorbereiding van die hoogsge vulde polimeer/klei hibriedlatekse word beskryf. Laponiet (Lap) vlakke in hoeveelhede van 10-50 gew% is effektief ge-inkapsuleer in beide polistireen (PS) en polistireen-ko-butielakrylaat nanopartikels (PSBA). Die morfologiese eienskappe van die latekse en films van hierdie hoogsge vulde hibried materiale is geëvalueer deur beide transmissie-elektronmikroskopie (TEM) en klein-hoek X-straal-verstrooiing (SAXS). PS/Lap latekse het gemengde partikel morfologieë getoon, bv. vanaf gepantserde partikels by lae kleihoeveelhede (10 gew%) tot ge-inkapsuleerde partikels by hoë kleihoeveelhede (50 gew%). Daarteenoor het PSBA/Lap hibriedlatekse 'n oorwegend verkreukelde partikelmorfologie getoon vir die reeks kleihoeveelhede wat bestudeer is. Die gevolglike polimeer/klei nanokomposiete (PKNs) van PS/Lap en PSBA/Lap het, óf gedeeltelike, óf ten volle geëksfolieerde strukture getoon. Oor die algemeen is bevind dat hierdie PKNs beter eienskappe as die suiwer polimere getoon het, behalwe vir die termiese stabiliteit eienskappe. Verbeteringe van soveel as 5000% in die stoormodulus is waargeneem vir beide PS/Lap en PSBA/Lap met betrekking tot die suiwer polimere. Die T_g van PSBA/Lap het 'n 14°C verskuiwing na 'n hoër temperatuur getoon. Reologiese toetse het getoon dat die gevolglike PKNs vastestofagtige visko-elastiese gedrag getoon het. Die inkapsulering van montmorilonietklei (MMT), deur middel van die ad-miniemulsieproses, was ondoeltreffend. Die MMT plaatjies het agtergebly op die oppervlakte van die polimeerpartikel. Oneffektiewe inkapsulering van MMT plaatjies is toegeskryf aan hul grootte, wat óf groter, óf gelyk was aan dié van die polimeerpartikels. Ten spyte van die oneffektiewe inkapsulering was al die MMT plaatjies in die finale PKNs geëksfolieer soos deur beide SAXS en TEM aangedui.

Oor die algemeen is bevind dat ad-miniemulsie 'n effektiewe metode is vir die voorbereiding van hoogsge vulde waterbasis polimeer/klei hibriedlatekse. Daar is egter bevind dat klei inkapsulering in polimeerpartikels asook die omvang van klei eksfoliëring, afhanklik is van die klei afmetings in verhouding tot die polimeerpartikels, monomeer/klei verenigbaarheid en die reaktiwiteit van die kleiwysiger. Daar is bevind dat die klei afmetings en die gebruik van 'n kleiwysiger wat die monomeer/klei verenigbaarheid verbeter, inkapsulering bevorder. Aan die ander kant het die reaktiwiteit van die kleiwysiger die omvang van klei eksfoliëring in die finale PKNs beïnvloed, ongeag van klei inkapsulering in die polimeerpartikels. Hierdie bevindings is gebaseer op vergelykende studies van die gebruik van Lap teenoor MMT en nie-reaktiewe wysiger teenoor reaktiewe wysiger gedurende ad-miniemulsiepolimerisasie

Acknowledgements

To God the Father, my Saviour and King Jesus Christ and the Holy Spirit, be glory forever.

By God's grace I found Grace, my motivator and comforter. Thanks for being here at such a time.

I would like to extent my special gratitude to my promoters, Prof H. Pasch and Dr. P. C. Hartmann, for all the guidance and support. Furthermore my colleagues in the research group of Prof Pasch.

I would also want to thank all the members of the Division of Polymer Science especially Dr Margie Hurndall, Mrs Erinda Cooper, Mrs Aneli Fourie, Mr Deon Koen, Mr Jim Motshweni and Mr Calvin Maart. And also the whole Chemistry and Polymer Science Department.

Thanks to all those who helped with the analyses, Elsa Malherbe for NMR analysis, Illana Bergh for PAS-FTIR, Mahommed Jaffer for TEM, Phillipe Dieudonne for SAXS.

To my inspiration, my mum, and my challengers, my siblings, Erosi, Jakwi and Joboko and those that supported me from the beginning, Mr/Mrs Zengeni (Byo), Mr/Mrs Kapofu (Byo), Mrs Zengeni (Mtre), Mr/Mrs Maraire, thank you all.

Finally, for feeding me during my study period, I would like to thank Mpact paper and Harry Crossley Foundation.

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List of Abbreviations

AIBA	2,2-azobis(2-methylpropionamide)
AIBN	azobisisobutyronitrile
AMPS	2-acrylamido-2-methyl-1-propanesulphonic acid
CB	carbon black
CEC	cationic exchange capacity
CEP	conventional emulsion polymerisation
CMC	critical micelle concentration
CTAB	cetyl trimethylammonium bromide
CTAC	cetyltrimethylammonium chloride
DLS	dynamic light scattering
DMA	dynamic mechanical analysis
DSC	differential scanning calorimetry
FFF	field flow fractionation
FTIR	fourier transform infrared
HD	hexadecane
KOH	potassium hydroxide
Lap	laponite
Lap-CTA	laponite modified with cetyl trimethylammonium bromide
Lap-VBDA	laponite modified with vinylbenzyl dodecyldimethylammonium chloride
LVE	linear viscoelastic range
MEHQ	monomethyl ether hydroquinone
MMT	montmorillonite
MMT-CTA	montmorillonite modified with cetyl trimethylammonium bromide

MMT-VBDA	montmorillonite modified with vinylbenzyl dodecyl dimethyl ammonium chloride
NMR	nuclear magnetic resonance
PCN	polymer/clay nanocomposite
PGMA	polyglycidyl methyl methacrylate
PMMA	poly(methyl methacrylate)
PS	polystyrene
PS/Lap	polystyrene/laponite nanocomposite
PS/MMT	polystyrene/montmorillonite nanocomposite
PSBA	poly(styrene-co-butyl acrylate)
PSBA/Lap	poly(styrene-co-butyl acrylate)/laponite nanocomposite
PSD	particle size distribution
RCF	relative centrifugal force
RAFT	reversible addition-fragmentation chain transfer
SAXS	small angle X-ray scattering
SDS	sodium dodecyl sulphate
TEM	transmission electron microscope
T _g	glass transition temperature
TGA	thermogravimetric analysis
TMS	tetramethylsilane
THF	tetrahydrofuran
US	ultrasonication
VBDAC	vinylbenzyl dodecyl dimethyl ammonium chloride
WAXS	wide angle X-ray scattering

List of Symbols

d	clay platelet interlayer distance
T_{60}	temperature at 40% weight loss
T_{onset}	Onset temperature of decomposition
$T_{\text{ROI-onset}}$	Onset temperature of decomposition of polymer recovered by reverse ion exchange
λ	wavelength of the X-ray
θ	diffraction angle
ω	angular frequency
G'	storage modulus
G''	loss modulus
η^*	complex viscosity
q	wave vector
γ_L	LVE limiting value

Chapter 1

Introduction and Objectives

1.1 Introduction

Organic/inorganic hybrid materials, blends of organic polymeric materials and inorganic particles, have received substantial attention in recent years due to their wide applications resulting from the properties imparted to the hybrid material by the inorganic particles. One of the reasons for the inclusion of nanoparticles in polymers is to enhance polymers' physical properties such as chemical resistance, thermal stability, barrier properties and mechanical properties. Some of the nanoparticles studied to date include nanofibres, silica,^{1,2} titanium dioxide,³ graphite⁴ and clay^{5,6}. The incorporation of clay platelets in polymers yields polymer/clay nanocomposites (PCNs).

PCNs were discovered in the early 1990s and they have become an area of both academic and industrial interest to date.⁷⁻²¹ PCNs are produced by finely dispersing clay platelets in the polymer matrix. They have been found to exhibit improved properties when compared to their parent neat polymers due to the strong interaction between the polymer matrix and clay platelets. However, the clay platelets being hydrophilic in nature cannot be easily dispersed in most polymers, which are usually hydrophobic in nature. There is need to modify the clay to enhance compatibility between the clay platelets and the polymer chains. Methods such as ion exchange,^{22,23} adsorption^{24,25} and sonication²⁶ have been used to achieve this goal. PCNs have been found to exhibit superior properties compared to their corresponding neat polymers even at very low clay content, such as 1 wt%. As such, the majority of the studies on PCNs to date have been focused mainly on low clay content PCNs, typically below 10 wt%. Only a limited number of reports on PCNs with more than 10 wt% clay can be found in the open literature.

Water based organic/inorganic hybrid materials have become the focal point of nanocomposite research in recent times due to their environmental friendliness. As such heterogeneous polymerisation methods (e.g. emulsion and miniemulsion) have become the main choice for hybrid materials preparation. Most inorganic particles used for polymer reinforcement, including clay, are hydrophilic in nature, making it challenging to successfully encapsulate them into non-polar polymer particles. The encapsulation of inorganic particles in polymer particles via heterogeneous polymerisation methods is currently under

investigation by various research groups.^{1,27-32} Latex instability and viscosity increase limit the amount of clay platelets that can be incorporated in the polymer particles using emulsion and miniemulsion polymerisation. Effective encapsulation has been reported with less than 10 wt% clay content. To date, highly filled PCNs whose clay is not necessarily encapsulated have been reported,³³⁻³⁵ on the other hand, successful encapsulation has been limited to low clay contents, typically well below 10 wt%.³⁶⁻³⁸ There remains therefore a challenge to prepare water based PCNs encapsulating high clay contents, typically above 10 wt%.

A similar challenge was experienced with other nanoparticles such as magnetite, silica, and even carbon black but has been overcome by the ad-mini-emulsion (co-sonication) polymerisation method developed in the group of Landfester.^{31,39,40} The method is based on the separate preparation of the monomer and the nanoparticle dispersions. The two are then mixed and co-sonicated to yield a hybrid miniemulsion, generated by merging dislike particles upon collision. These hybrid particles then produce inorganic/organic hybrid material upon polymerisation. Using such a method, both carbon black and magnetite particles of up to 40 wt% weight fraction have been successfully encapsulated in polymer particles. The work presented in this dissertation involves the encapsulation of high contents of clay platelets in polymer particles using ad-mini-emulsion to prepare highly filled water based PCNs.

1.2 Aims and objectives

The main aim of the current study was to prepare highly filled water based PCNs using the ad-mini-emulsion polymerisation method. Montmorillonite (MMT) and Laponite (Lap) clays were chosen for the study with polystyrene and styrene/butyl acrylate copolymers being the polymers of choice.

The objectives of this study were to:

- a) Synthesise water based polymer/clay hybrid materials with as high as 50 wt% clay weight fraction using the ad-mini-emulsion polymerisation method and then:
 - Determine the characteristic properties of the hybrid materials in terms of monomer-to-polymer conversion, particle sizes of the latex.
 - Establish the latex and film morphological properties of the hybrid materials.

- Evaluate and compare the use of different clays (large-sized vs small-sized) and different clay modifiers (reactive vs non-reactive) on the encapsulation of high clay content (> 30 wt%) and the physical properties of the resultant hybrids.
- b) Study the physical properties of the hybrid materials and evaluate how the incorporation of high clay content and dispersion impacts:
- Thermal stability
 - Thermomechanical properties, i.e. damping factor and storage modulus
 - Melt-state linear viscoelastic properties
 - Water vapour sorption properties

1.3 Thesis layout

A short introduction and the objectives of the study are described in Chapter 1.

The theoretical background to this work is presented in Chapter 2. It includes a brief definition of PCNs, their preparation and characterisation. The chapter also gives a background on miniemulsion and ad-miniemulsion polymerisation methods. Lastly it encompasses what has been reported in literature as far as encapsulation of clay platelets is concerned.

Chapter 3 focuses on the preparation of aqueous organolaponite dispersions which are the pre-requisite for the ad-miniemulsion polymerisation. Here the effect of stabilising surfactant, sodium dodecyl sulphate (SDS), sonication and total solids content, on the particle sizes of organolaponite dispersions are discussed. The particle sizes of the dispersions were monitored using DLS to establish conditions (SDS concentration and sonication time) which give the smallest particle size.

Chapter 4 describes the synthesis and characterisation of polystyrene/Laponite (PS/Lap) and poly(styrene-co-butyl acrylate)/Laponite (PSBA/Lap) based hybrid latexes with different Lap contents up to 50 wt%. Syntheses were carried out using ad-miniemulsion polymerisation. The morphological characteristics of these PCNs were confirmed by small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). Other characteristics of the hybrid materials such as copolymer composition, particle size, conversion and molecular weight were also investigated.

The physical properties of the PCNs obtained from the latexes described in Chapter 4 are described in Chapter 5. This chapter describes properties such as thermal stability, thermo-mechanical properties and the melt-state linear viscoelastic properties of hybrid materials.

Chapter 6 describes polystyrene/montmorillonite (PS/MMT) based hybrid latexes prepared using ad-mini-emulsion polymerisation method. The chapter details the feasibility and limitation associated with encapsulation of MMT using ad-mini-emulsion. Furthermore, thermo-mechanical and thermal stability properties of the PS/MMT PCNs are included.

The influence of clay platelet dimensions and clay modifiers (reactive or non-reactive) on encapsulation of high clay contents in polystyrene using the ad-mini-emulsion polymerisation is described in Chapter 7. Results described in this chapter focused on highly filled hybrid materials (30–50 wt% clay) obtained using Lap and MMT. The chapter mainly focuses on comparisons made on latex morphology and physical properties of materials obtained by the use of the two different clays and the two different clay modifiers.

Finally, Chapter 8 summarises the main conclusions of this study, and suggestions for future research are given.

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Chapter 2

Historical Background

2.1 Hybrid nanoparticles

2.1.1 Polymer/inorganic hybrid nanomaterials

Polymer/inorganic hybrid nanomaterials also known as organic/inorganic hybrid nanomaterials are polymers incorporating inorganic materials. Many inorganic particles have been incorporated into polymeric materials and such particles include silica,^{1,2} titanium dioxide,³ graphite,⁴ magnetite particles,⁵⁻⁷ carbon black,^{8,9} and clay platelets.¹⁰⁻¹² The reasons for the incorporation of inorganic materials in polymers include; protecting the encapsulated material, protecting the environment from the encapsulated material and improving the polymers' physical properties. Hybrid materials, especially those with improved physical properties have a wide range of applications, including packaging, biomedical, engineering, and pharmaceutical. The applications are mainly dependent on the properties imparted to the polymer by the inorganic material used. For example, magnetite filled polymers have potential biomedical applications due to their superparamagnetic and biocompatibility properties.¹³ Clay filled polymers are used for packaging applications due to the ability of clay platelets to reduce gas permeation through polymers. The main reason for the incorporation of clay in polymers is to improve the properties of the polymers. As such, polymer/clay nanocomposites (PCNs) have been extensively studied in the last two decades.

2.1.2 Polymer/clay nanocomposites

PCNs are polymeric materials that are reinforced with clay platelets, hence they fall in the category of filled polymeric materials. They are termed nanocomposites because the reinforcing clays used have dimensions in the nanometer level. Clay naturally exists as sheets stacked together, known as tactoids, whose dimensions are in the micron level. Polymer chains can penetrate into the interlayer spaces between the clay tactoids leaving clay platelets finely dispersed in the polymer matrix, to yield PCNs. However, these tactoids may not be fully separated and this results in the formation of microcomposites. As such PCNs are normally classified into three general groups, i.e. microcomposites, intercalated nanocomposites and exfoliated nanocomposites depending on the extent of tactoid exfoliation.

PCNs have been found to exhibit enhanced physical properties as compared to their corresponding neat polymer counterparts, as well as to conventional microcomposites. Since PCNs' discovery in the early 1990s,¹⁴⁻¹⁶ it was found that a small fraction of these nano-platelets (as low as 1 wt%) can cause significant improvement in physical properties. Because of these observed enhanced physical properties, PCNs have found wide applications, replacing both neat polymers and polymers filled with micro-fillers. Some of the applications of PCNs include packaging films¹⁷ due to their excellent barrier properties, flame retardants due to their high thermal stability^{18,19} and engineering plastics because they have enhanced mechanical properties, e.g. high storage moduli and tensile strengths.^{20,21} They can also be produced as water based latex via heterogeneous polymerisation methods,²²⁻²⁵ hence they can be used in coatings applications.

2.2 Clay platelets nanofillers

2.2.1 Chemistry of clay

Clays generally fall into two families, the 2:1 phyllosilicates (swellable clay) and the 1:1 phyllosilicate (non-swellable clay). Fig. 2.1 shows the general structure of the swellable clays.^{11,26}

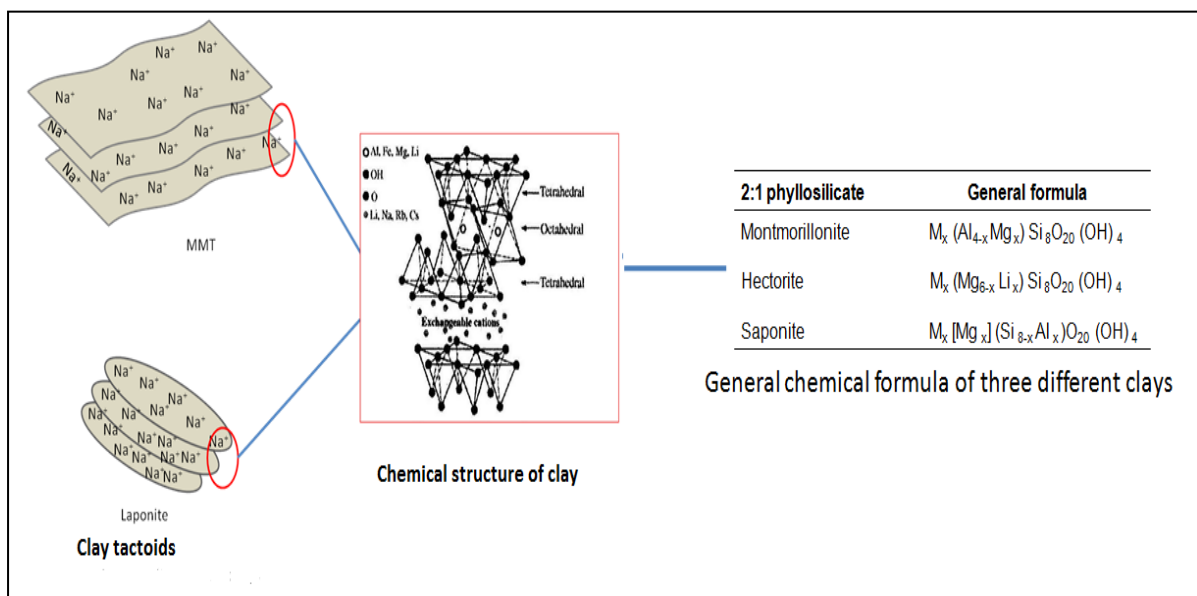


Fig. 2.1: General structure and chemistry of swellable clays (MMT and Laponite).

In their natural state the clay platelets exist in stacks being held by electrostatic forces existing between adjacent plates. Each platelet is composed of three sheets, a central sheet of magnesium atoms octahedral coordinated with oxygen atoms and hydroxyl groups

sandwiched between two tetrahedral silica sheets. Isomorphic substitution of some of the magnesium atoms with lithium atoms in the central sheet and the presence of vacant positions results in a partial negative charge to the platelet surfaces. This negative charge is counter balanced by sodium cations adsorbed at the surfaces. Furthermore, the sodium cations are responsible for the electrostatic forces holding adjacent plates together because they are shared between adjacent platelets.

Clays used in the preparation of PCNs belong to the swellable family and the non-swellable clays are not as equally important. This is mainly due to the relatively weak forces holding the tactoids together allowing the clays to easily swell in solvents like water. The swellable clay family comprises of smectites, vermiculites and mica clays and the smectite group consists of clays such as montmorillonite, saponite and hectorite. Of all the smectite clays, the use of montmorillonite for PCNs preparation exceeds all the other clays in the group. Bentonite and saponite are other naturally occurring clays that have been used in polymer clay nanocomposites. Besides the naturally occurring clays, there are commercially available organically modified clays such as Cloisite. These commercial clays do not require pre-modification like the natural clays. Moreover synthetic clays such as Laponite are also available.

Laponite (Lap) platelets are disc shaped measuring 25 nm in length and 0.92 nm in thickness, as shown in Fig. 2.1 with cationic exchange capacity of 50–55 mmol/100g.²⁷⁻³² Unlike natural clay, Lap has a narrow platelet size distribution and smaller particle sizes. Lap fully disperses in water to produce clear dispersions at low concentrations, typically below 2 wt%. At high concentrations, above 2 wt%, Lap forms a highly viscous gel due to edge/surface electrostatic interactions of the Lap platelets arranging into a so called “house of cards”. However gel formation can be eliminated by the use of a peptising agent, e.g. tetrasodium pyrophosphate, allowing to inverse the positive charge of the clays’ edges into an overall negative charge hence inhibiting the edge-to-face electrostatic interaction.

2.2.2 Clay modification

Clay can be used to reinforce polymers in their natural state but commonly they are incorporated in polymers after modification. The modification process involves the grafting of organic molecules onto the clay platelets so as to improve compatibility between the clay and polymer chains. In its natural state, swellable clay is generally hydrophilic making it incompatible with hydrophobic polymers. Secondly, in its natural state, the interlayer

distance between the clay platelets is too small to allow penetration of polymer chains between clay platelets. Thirdly, when employing in-situ intercalation polymerisation techniques, the hydrophilic nature of clay limits the wettability of clay platelets by the hydrophobic organic monomer. These drawbacks make it necessary to modify the clay platelets prior to using them in preparing PCNs. This modification process promotes strong interactions between the clay platelets and the polymer chains of the PCN. The modification of clay is generally done by either the substitution of inorganic cations present on the clay surfaces or by functionalization of the hydroxyl groups found on the edges. The modification of clays therefore targets either the edges (edge modification) or the surfaces (surface modification) of the clay platelets. The resultant modified clay, sometimes referred to as organosilicate or organoclay, can be used in the preparation of PCNs irrespective of the method of preparation,³³⁻⁴⁰ although unmodified clays can also be used in PCN preparations.⁴¹

2.2.2.1 Edge modification

This method involves modification of clay platelets using compounds that can covalently react with the hydroxyl groups found on the edges of the platelets and the commonly used compounds are silanes and titanates.^{30,42,43} Armoured particles, where the clay platelets are not encapsulated in the polymer particles but found at the particle/continuous phase interface, were reportedly prepared with clay modified using this method.⁴⁴ Voorn *et al.*,⁴³ using the edge modification process, obtained encapsulated polystyrene/Lap latexes with effective encapsulation of the Lap in the polymer particles. However, within the same latex different particle morphologies were reported, ranging from spherical through to snowman morphologies and the amount of Lap encapsulated remained relatively low, that is below 5 wt% relative to the polymer.

2.2.2.2 Surface modification

Surface modification can be achieved via cationic exchange or adsorption. Ion exchange surface modification involves cationic organic compounds (often cationic surfactants) which are able to substitute the inorganic cationic ions in the clay interlayer spaces, such as quaternary alkyl ammonium⁴⁵ and alkyl phosphonium cationic compounds.⁴⁵ These cationic surfactants facilitate the expansion of the interlayer spaces and promote intercalation of the polymer chains in the clay galleries. In this study, surfactants used for clay modification will be referred to as modifiers, in order to differentiate them from the surfactants used for

mini-emulsion stabilisation. Although the use of short chain cationic modifiers is not popular, Tong *et al.*³⁹ reported the use of short reactive cationic modifier (surfmers) to obtain nanocomposites with high clay content encapsulated in the polymer particles. Reactive modifiers can take part in the polymerisation process as initiators (inisurfs),^{25,37,38} monomeric modifiers (surfmers)^{36,39,46,47} or transfer agents (transurfs). Conventional modifiers that do not take part in the polymerisation process are consequently classified as non-reactive modifiers as they only serve to render the clay platelets surface more hydrophobic. The advantage of reactive modifiers over non-reactive modifiers is that by taking part in the polymerisation process the reactive modifiers can enhance clay dispersion in the polymer and promote interaction between the polymer and clay platelets.

On the other hand, surface modification by adsorption involves the use of molecules that can adsorb on the clay surfaces, e.g. 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS),^{23,48-52} without necessarily exchanging the inorganic cations. This method involves interactions such as hydrogen bonding and Van der Waals forces between the clay platelets and the modifiers. This method led to PCNs with as high as 20 wt% clay content.^{48,50}

Surface modification and edge modification can be used simultaneously in the modification of clay, and this method can be termed dual modification, combined modification or double modification. Dual modification has been reported before, where the dual modified clay was melt blended with poly(L-lactide).⁵³ The extent of exfoliation was reported to be enhanced when the double modified clay was used, as a result of increased epoxy groups. The epoxy groups were part of the silane molecule used for edge modification. Chen *et al.*^{53,54} and Effenberger *et al.*⁵⁵ modified montmorillonite (MMT) with dual modification using a silane molecule and an amino acid. The dual modified MMT was used in in-situ emulsion polymerisation with polymethyl methacrylate (PMMA) and polyglycidyl methyl methacrylate (PGMA) to yield PCNs with up to 20 wt% clay.⁵⁵

2.3 Preparation and characterisation of PCNs

2.3.1 Methods of PCNs preparation

Different methods can be employed in the synthesis of PCNs ranging from blending of polymer chains and clay platelets to in-situ intercalative polymerisation, where monomers are polymerised in the presence of the clay. Synthetic methods for PCNs include melt blending, solution blending, intercalation by sonication, and in-situ intercalation.

2.3.1.1 Melt blending

This is one of the oldest techniques used in the preparation of PCNs. Melt intercalation is particularly popular in industry as it is compatible with industrial processes such as injection, blow moulding and extrusion. In this method the polymer in its molten state is blended with unmodified or pre-modified clay. This is usually done under high shear in order to promote penetration of polymeric chains inside the clay galleries. However this method often yields microcomposites rather than nanocomposites because it is difficult for the polymer chains to penetrate the confined clay galleries and the modifier used for clay modification may decompose under the applied heat causing the clay gallery distance to significantly decrease during the process. Despite these draw backs, this method has been used in many instances for preparation of PCNs,⁵⁶⁻⁶² and has been utilised industrially more than any other method.

2.3.1.2 Solution blending

The silicate layers are swollen in a compatible solvent. The resulting dispersion is then mixed with the polymer or a prepolymer and the polymer diffuses into the silicate galleries displacing the solvent. PCNs can only be formed when the solvent molecules in the galleries are successfully substituted by the polymer molecules.⁶³ Here a negative Gibbs free energy difference between the solvent intercalated platelets and the polymer matrix is required. For the polymer chains in solution to adsorb into the galleries, the driving force comes from the entropy gained by desorption of the solvent molecules which compensates for the decreased entropy of the confined chains. The major disadvantage of this method is the use of harsh solvents which are usually not environmentally friendly.

2.3.1.3 Intercalation by sonication

Although not popular, this method utilises the energy provided by the sonicator to overcome the forces holding the platelets together. The sonicator provides sufficiently high ultrasound energy and there is a negative pressure in the liquid as it tears.⁶⁴ This energy breaks down the tactoids, allowing the polymer chains to intercalate inside the clay galleries. At the same time heat energy is produced which can be used to thermally initiate polymerisation unwillingly.

2.3.1.4 In-situ intercalation polymerisation

In-situ intercalation refers to the intercalation of polymer chains inside the clay galleries during polymerisation of monomer. Unlike with other techniques such as solution blending and melt intercalation, where the polymer is synthesised separately before it is blended with clay, with the in-situ intercalation technique the monomers are firstly intercalated inside clay

galleries, from where polymerisation is initiated. This results in polymer chains growing from inside the clay galleries, thus expanding the galleries and facilitating the exfoliation of the clay tactoids. This technique has received considerable attention in the academic research of PCNs because it allows in depth study of the PCN synthesis, e.g. the study on polymerisation parameters⁶⁵, it is applicable to most polymerisation processes which are utilised in academic research. In-situ intercalation also allows easier manipulation of the resulting PCN as compared to the other preparation methods. Although exfoliated structures can be obtained using other preparation methods the manipulation of PCN morphology using these methods is difficult. Since in-situ intercalation polymerisation is compatible with heterogeneous polymerisation processes such as emulsion, suspension and miniemulsion polymerisation, it is possible to control and manipulate the latex morphologies as well. As such different morphological features have been reported with this method ranging from highly exfoliated morphology for PCN films to sophisticated latex structures such as armoured particles,^{66,67} clay encapsulating polymer particles^{38,39} and cellular arranged particle/clay structures.⁶⁸

2.3.2 Characterisation of PCNs

2.3.2.1 Polymer chain analysis

The molecular weight of any polymeric material plays an important role on its overall physical properties hence the need to evaluate molecular weight characteristics of different PCNs. The use of size exclusion chromatography (SEC) remains the routine form of analysis for molecular weights of the materials. In PCNs the presence of clay platelets can affect both the molecular weight and the molecular weight distribution of the polymer chains. However, the presence of clay platelets may complicate the measurements of molecular weight using SEC.

2.3.2.2 PCN latex characterisation

For PCNs prepared via heterogeneous polymerisation methods, the evaluation of the latex particle size is important because the particle size and the morphology of the latex play an important role in the application of the latex. The presence of clay platelets has been found to affect particle sizes and size distributions of the PCN latex.^{38,69} The common methods for particle size analysis are dynamic light scattering (DLS) and TEM, with TEM being equally important when it comes to the morphological characterisation of these latex particles.^{6,43} However, it is difficult to quantify the amount of clay platelets encapsulated in the polymer

particles using these techniques. Field flow fractionation (FFF) is another interesting method that has the ability to fractionate particles according to size.^{70,71}

2.3.2.3 PCN morphological property characterisation

Morphological properties are generally described by the way in which clay platelets are dispersed in the polymer matrix. When using in-situ intercalation heterogeneous polymerisation methods the location of the clay platelets relative to the polymer particles is also considered as morphological feature of the PCNs. These morphological properties play an important role in the observed enhancement in physical properties of the resultant PCN material. Techniques such as X-ray diffraction (XRD) and transmission electron microscopy (TEM) are commonly used to evaluate the morphological features of PCNs. TEM provides a pictorial view of the PCN film or latex. Fig. 2.2 shows a typical TEM image of a microtomed poly(acrylonitrile-co-methyl acrylate) nanocomposite film containing 7 wt% montmorillonite clay.⁷² The clay platelets are viewed as dark stripes while the polymer material is viewed as clear areas. The contrast between the clay platelets and the polymer particles provides a visual clue that the PCN has a partially exfoliated morphology. However, TEM suffers from a major drawback that the sample used in the analysis is not truly representative of the whole sample. Despite this drawback TEM still remains one of the most commonly used techniques to evaluate the morphological structure of PCNs mainly as a complementary technique to XRD studies. Although TEM has been successfully used in analysing PCN films and latexes with armoured and cellular structured particle morphologies, it may be limited when analysing latexes with encapsulated morphologies. This is because polymer particles cannot transmit light. This problem has been overcome by the use of high resolution TEM (HRTEM) or cryo-TEM.

XRD on the other hand is used to assess the extent of exfoliation of the clay tactoids by analysing the Bragg diffraction peaks of the clays before and after incorporation in the polymer matrix. Use of the Bragg's law allows for the determination of the interlayer distance between platelets.

$$n\lambda = 2d \sin\theta \quad 2.1$$

Where: n is the order of interference, λ is the wavelength of the X-ray, d is the interlayer distance and θ is the measured diffraction angle.

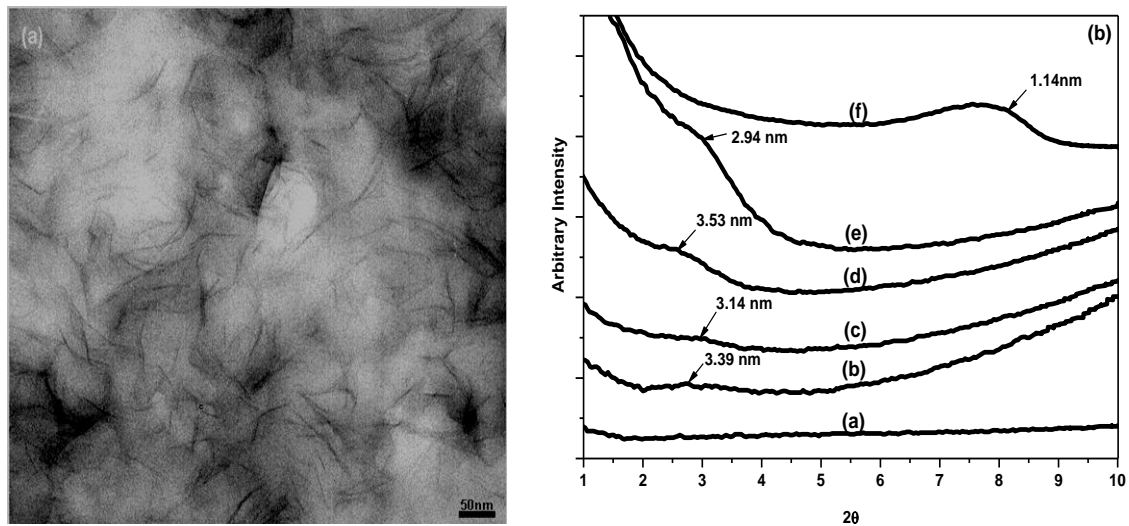


Fig. 2.2: (a) TEM image of partially exfoliated poly(AN-co-MA)/7 wt% clay nanocomposite and (b) SAXS diffractograms of: (a) neat poly(acrylonitrile-co-methyl acrylate), (b) poly(acrylonitrile-co-methyl acrylate)/1 wt% clay, (c) poly(acrylonitrile-co-methyl acrylate)/3 wt% clay, (d) poly(acrylonitrile-co-methyl acrylate)/5 wt% clay, (e) poly(acrylonitrile-co-methyl acrylate)/7 wt% clay, (f) pristine clay.

XRD analysis is commonly employed on PCN films and powders, with both wide angle (WAXS) and small angle X-ray scattering (SAXS) being conventionally used. Fig. 2.2(b) shows typical SAXS diffractograms of poly(acrylonitrile-co-methyl acrylate)/clay nanocomposites.⁷²

The shift in the Bragg peak from higher to lower angles is attributed to the exfoliation of the clay tactoids and calculations using the Bragg law showed that the interlayer distance increased in the PCNs relative to the pristine clay. XRD, however, doesn't give any information about the location of clay platelets relative to polymer particles.

2.3.2.4 PCN physical properties characterisation

Thermo-mechanical properties

These are obtained from the material's response to cyclic deformation as a function of temperature as measured by dynamic mechanical analysis (DMA). Molecular motions and relaxations taking place during the analysis are measured and results such as storage modulus and glass transition temperature (T_g) are obtained. The thermo-mechanical properties are closely related to the processing and end use of PCNs. The incorporation of clay has been reported to enhance thermo-mechanical properties of PCNs relative to their respective neat polymers, such enhancements including the increased storage modulus and T_g .^{15,51,61,73-75}

These are caused by the strong interactions taking place between clay platelets and polymer chains. This means that the thermo-mechanical properties are affected by the clay dispersion in the polymer matrix.

Rheological properties

These properties give information on the time dependent shear behaviour of materials. Oscillatory tests are done at varying strain frequency whilst the strain amplitude is kept constant so that the long term shear behaviour is simulated by the slow movements at low frequency and the short term behaviour is simulated by the rapid movements at high frequency. Fig. 2.3 shows the angular frequency of poly(acrylonitrile-co-methyl acrylate) and its PCNs.⁷²

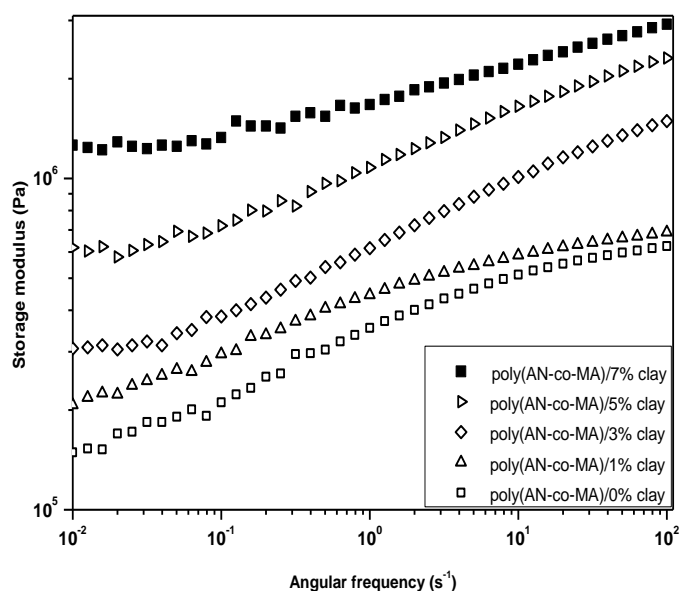


Fig. 2.3: Storage modulus of poly(acrylonitrile-co-methyl acrylate) and its PCNs as a function of angular frequency.

Because these analyses are done in the molten state of the material, rheological properties can be directly related to the processability of the material in question. Lotti *et al.*⁷⁶ evaluated the elastic properties of polyethylene nanocomposites in relation to the processes such as blow moulding and extrusion. When compared to their respective neat polymer, PCNs exhibit different melt properties, e.g. early shear thinning,⁷⁷ enhanced elastic modulus⁷⁶ and higher shear viscosity.⁷⁸ The ability of clay to align towards the direction of shear has been found to play an important role in the rheological properties of PCNs.⁷⁷ Furthermore, the molten state rheological properties can be correlated to the microstructure of PCNs and a comprehensive study on the relationship between rheological properties and the degree of exfoliation was

conducted by Wagener *et al.*⁷⁹ who reported a strong correlation between morphology and dynamic rheological properties.

Thermal stability

The ability of a material to resist thermal degradation is of paramount importance if the material is to be used in applications such as fire retardants. Thermal stability of PCNs is generally evaluated using thermogravimetric analysis. The decomposition profile is monitored from low temperatures to high temperatures, typically from room temperature to 600 °C. The thermal stability can be deduced by monitoring parameters such as the onset of decomposition whereby a delayed decomposition is considered as an improvement in thermal stability. Generally PCNs exhibit improved thermal stabilities as compared to their corresponding neat polymers,^{19,36,80-82} although there are reports where no improvement has been observed.³⁷ The improvement in thermal stability is attributed to the ability of clay char to act as an insulator between the polymer chains and the decomposition site, as well as the restricted polymer chain mobility due to interactions with the surface of the dispersed clay platelets.³⁶

2.4 Use of miniemulsion polymerisation to encapsulate inorganic particles

2.4.1 Miniemulsion polymerisation

A miniemulsion is a nanometric heterogeneous dispersion containing water, oil, surfactant and co-stabiliser, and prepared under high shear. The high shear, which can be provided by a homogenizer or a sonicator, breaks down the monomer droplets to a size range of 50–500nm. The co-stabiliser, usually a highly water insoluble low molecular weight molecule e.g. hexadecane or cetyl alcohol, helps to retard Oswald ripening. Miniemulsion polymerisation, first reported in the 1970s by Ugelstad⁸³ was developed from the conventional emulsion polymerisation (CEP). Therefore, it resembles the CEP in that they both start with monomer droplets and end up with polymer particles but the mechanism of polymerisation of these two methods is different. During emulsion polymerisation, larger monomer droplets (monomer reservoirs) feed the micelles with monomer, through diffusion across the continuous aqueous media, which eventually become the polymer particles in emulsion. On the contrary, miniemulsion polymerisation takes place in the monomer droplets so that the droplets are converted into polymer particles hence no monomer diffusion is present in miniemulsion. The surfactant concentration used during emulsion polymerisation is always above the

critical micelle concentration (CMC), whereas for miniemulsion the surfactant concentration used is carefully set to a value for which no free micelles exist in the continuous phase.

The polymerisation loci in emulsion polymerisation are the micelles whereas for miniemulsion polymerisation the loci are the monomer droplets. The small size and high specific surface area of monomer droplets in miniemulsion allows the droplets to compete with any remaining micelles for radicals. Furthermore, in a properly formulated miniemulsion, all surfactant molecules are utilized in stabilising the monomer droplets.⁸⁴ Consequently droplet nucleation becomes the dominating nucleation mechanism in miniemulsion polymerisation contrary to homogeneous and micellar nucleation mechanisms of CEP.⁸⁵ Since monomer droplets are converted into polymer particles, it is theoretically possible to achieve a one-to-one copy of monomer droplets to polymer particles with miniemulsion polymerisation.⁸⁶ Because of this, miniemulsion polymerisation has become increasingly popular in the preparation of organic-inorganic hybrids.^{1,5,8,22,24,38,39,87-94} Once the inorganic particle is dispersed in the monomer, it will be incorporated inside polymer particle during polymerisation.

2.4.2 Encapsulation of inorganic particles using miniemulsion polymerisation

Encapsulation entails the inclusion of one component into another. For hybrid materials such as those produced by miniemulsion, the inorganic material is generally incorporated into the organic polymer particle. The encapsulation of materials such as liquids and inorganic particles into polymeric particles has found a wide range of applications such as in controlled drug targeting,⁹⁵ coatings,⁹⁶ tissue engineering as well as in mechanical and electrical devices.⁹⁷ These interesting applications have led to a major focus on the study on these encapsulated materials. Miniemulsion polymerisation has become one of the most useful methods in the preparation of these hybrid materials due to its advantages over the other heterogeneous polymerisation methods. Using miniemulsion polymerisation, homogeneous distribution of the encapsulated component can be achieved relatively easy.^{1,6} Also using admixemulsion technique, which is a modified miniemulsion polymerisation method, it is possible to encapsulate high contents of inorganic particles in polymeric particles, an achievement that is difficult to attain with the other heterogeneous polymerisation techniques. Although organic pigments and liquids can be encapsulated in polymeric shells,⁹¹ these materials will not be discussed in the current study, which focuses on the encapsulation of inorganic nanoparticles, in particular clay platelets. Many inorganic nanoparticles used to

date for the preparation of hybrid nanoparticles include carbon black,⁸ silica,¹ magnetite,^{5-7,98} gold nanoparticles, nanorods⁹⁹ and clay platelets.^{22,38,43} Using miniemulsion polymerisation, two preparation routes can be followed, one that involves direct miniemulsion and another method that involves co-sonication, also known as ad-miniemulsion polymerisation.

2.4.2.1 Direct miniemulsion polymerisation

Particles to be encapsulated are dispersed in the monomer phase prior to emulsification. This requires that the particles be hydrophobic in order to be compatible with the hydrophobic monomer. Therefore hydrophilic particles such as clay platelets, silica or magnetite particles should be pre-modified using organic modifiers which will help to stabilise the particle in the hydrophobic monomer as well as to facilitate the wetting of these particles by the monomer.⁹¹

A co-stabiliser, which will help to prevent Oswald ripening, is also added to the monomer dispersion containing particles. This dispersion in the monomer phase is then added into an aqueous surfactant solution, ionic or non-ionic, to form a heterogeneous system. The surfactant helps to stabilise the monomer droplets in the aqueous media against flocculation. The resultant dispersion is emulsified before being exposed to ultrasonication (US) for emulsification. A general procedural example is shown in Fig. 2.4. This method has been used extensively in encapsulation of various inorganic particles.^{22,39,87,91,94,100-102} Its limitations include the heterogeneous distribution of the encapsulated particles in the polymer particles, ineffective inorganic particle encapsulation and inability to encapsulate high levels of inorganic particles in the polymer particles.

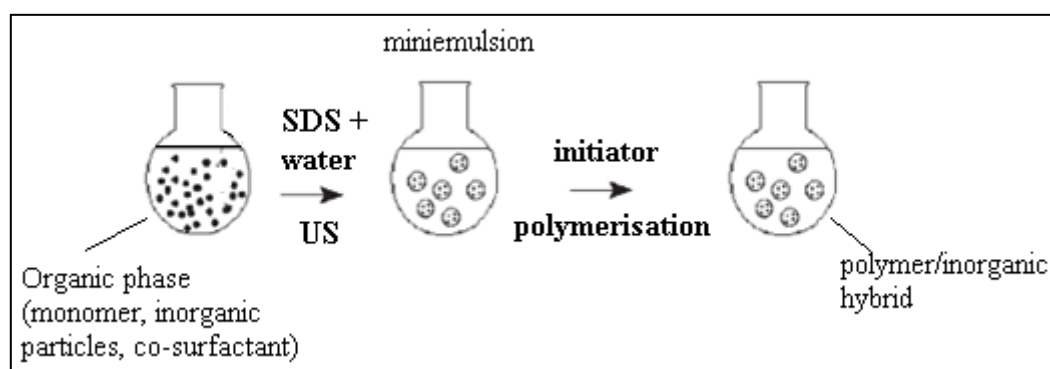


Fig. 2.4: Outlined procedure for the encapsulation by direct miniemulsification

When this method is used to prepare PCNs the amount of clay that can be incorporated remains very low, typically below 5 wt%. This is due to the high viscosity of the monomer/clay dispersion for high clay content (i.e. ≥ 5 wt% clay content). This was overcome by Tong and Deng³⁹ who utilised a small reactive molecule to modify the clay

surfaces and used a small sized clay platelet thus managed to incorporate up to 30 wt% clay in the polymer.

2.4.2.2 Ad-mini-emulsion (Co-sonication) polymerisation

This method was developed by Landfester *et al.*^{6,8} with the desire to produce highly filled polymer particles as well as polymer particles with homogeneously distributed inorganic fillers, goals which could be achieved by neither conventional emulsion polymerisation nor direct mini-emulsion polymerisation. In general this method involves the preparation of two separate dispersions, a monomer mini-emulsion and an inorganic particle dispersion. The two dispersions are then added and co-sonicated forming a hybrid mini-emulsion which is then polymerised. In order to achieve the required final mini-emulsion 2 or 3 steps may be followed as shown by Landfester *et al.*^{6,8} in separate studies.

The first mini-emulsion - the monomer mini-emulsion - is prepared in the conventional mini-emulsion method, i.e. adding monomer, co-stabiliser and surfactant in an aqueous media followed by sonication after the pre-emulsification process. In the second mini-emulsion it is desired that the inorganic nanoparticles be stabilised in the aqueous phase. This is achieved through the use of surfactant that can interact on the water-inorganic particle interface, thus stabilising the particle in the aqueous phase. However with hydrophilic particles, two surfactants may be used. The first surfactant (the modifier) renders the particle surface hydrophobic while the second surfactant stabilises the modified particle in the aqueous phase by preventing flocculation or coagulation of the particles. It is understood that upon the addition of these two mini-emulsions and the subsequent sonication, the fission and fusion process brought by the sonication process will cause the formation of hybrid droplets which are more stable than the aggregates and the liquid droplets. A typical 3 stage ad-mini-emulsion procedure used by Landfester *et al.*⁶ is outlined in Fig. 2.5.

Using ad-mini-emulsion polymerisation Ramirez *et al.*⁶ and Zheng *et al.*⁷ successfully prepared polymer nanospheres with 40 wt% magnetite content. Their aim was to produce aqueous ferrofluids consisting of uniform and stable magnetite polystyrene nanoparticles. In a three stage process, the oleic acid coated magnetite particles were first dispersed in octane and the obtained octane/magnetite dispersion was combined with an aqueous SDS solution. This mixture was then emulsified and heated to evaporate octane leading to an aqueous ferrofluid consisting of SDS encapsulated magnetite particles. In the final stage the magnetite

dispersion and the styrene miniemulsion were co-sonicated and then polymerised yielding highly filled PS nanospheres with uniform encapsulation.

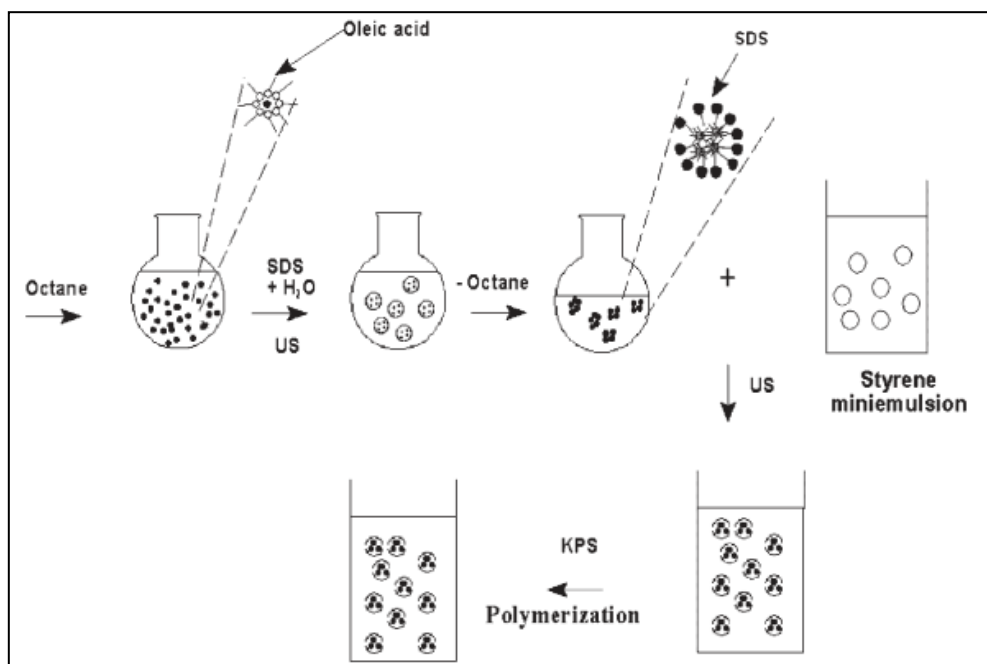


Fig. 2.5: Encapsulation of magnetite particles using co-sonication procedure.⁶

Tiarks *et al.*⁸ co-sonicated carbon black (CB) and styrene miniemulsions to produce carbon black encapsulated nanoparticles. This method allowed them to prepare nanoparticles with up to 40 wt% encapsulated CB. In the first step hydrophobic CB was dispersed in water using a surfactant, and then a monomer miniemulsion was prepared separately and added to the CB dispersion before this mixture was co-sonicated, thus obtaining full encapsulation of the CB in the final polymer particles, which contained up to 40 wt% CB. The controlled fission/fusion process during sonication breaks down the aggregates and liquid droplets so that only hybrid particles composed of CB and monomer remain due to their high stability.

Kim *et al.*⁹² used different methods to encapsulate yttrium oxysulfide and found that mini-emulsification was the most effective method, yielding different morphological structures when the monomer polarity and the sonication time were varied.

Despite the encapsulation success reported so far using ad-mini-emulsion polymerisation, no reports have been found, to the best of our knowledge, where it has been used to encapsulate clay platelets. In the current study the ad-mini-emulsion will be utilised in an effort to prepare polymer nanoparticles with clay content as high as 50 wt% relative to the monomer/polymer.

The resultant materials have potential applications in areas such as coatings and film packaging.

2.5 Highly filled and encapsulated PCNs

2.5.1 Highly filled PCNs

During the early days of PCN discovery significant improvements of material properties were observed even with fairly low clay content, as compared to conventional micro-sized dispersed fillers. Typically, properties such as storage modulus, barrier, and thermal resistance were improved with the addition of as low as 2 wt% clay content to the neat polymer.^{11,16,19,54,103,104} However, interest in the effects of increased clay content grew and endeavours to prepare PCNs with large clay contents increased and to date reports of PCNs with as high as 50 wt% clay content can be found in literature. PCNs containing as high as 70 wt% clay have been prepared via melt blending using organophilic clay,¹⁰⁵⁻¹⁰⁸ however the current study is focused on PCNs prepared via water based polymerisation techniques. Using soap free emulsion polymerisation, Choi *et al.*^{48,50} prepared PCNs of polyacrylonitrile and poly(methyl methacrylate) containing up to 20 wt% montmorillonite clay using AMPS as compatibiliser. These studies however did not characterise the latex morphology of these nanocomposites so that no information on encapsulation could be extracted from these reports. Soap free emulsion was used in the preparation of PCNs of poly(methyl acrylate-co-methyl methacrylate) containing up to 20 wt% MMT. Although the clay was homogeneously distributed within the resultant films, it was reported that the growing polymer particles adhered to the clay surfaces.^{109,110} Polystyrene/Lap PCNs with a clay content of 20 wt% were prepared using emulsion polymerisation.¹¹¹ The Lap was first stirred in peptising agent and cationic modifier solution. To promote attachment of Lap to polystyrene, the macromonomer poly(ethylene oxide) monomethyl ether methacrylate with a molecular weight of 1000 g/mol was added and the functionalised Lap, monomer and initiator were added into a reactor and allowed to polymerise. TEM images showed that the Lap clay platelets were bound on the polymer surfaces resulting in films with cellular structures. The use of this emulsion technique also led to polystyrene/Lap PCNs with up to 50 wt% clay content still exhibiting the cellular structure as a result of Lap adhering to the polymer particle surfaces.^{112,113}

Despite the recent successes enjoyed on the preparation of highly filled nanocomposites via heterogeneous polymerisation methods, encapsulation of high clay content in polymer particles remains a challenge. To date, reports on highly filled PCNs prepared by

heterogeneous methods such as emulsion and miniemulsion have either neglected specifying the location of clay platelets in the latex or have reported platelets being on the polymer particle/water interface.

2.5.2 Encapsulated PCNs

Organic/inorganic hybrids materials have shown potentially crucial applications in areas such as coatings, adhesives, cosmetics, medical diagnosis and treatment, additives for paper and textiles. Reports on effective encapsulation of clay platelets can be found in the open literature, however contrary to high inorganic content encapsulation obtained by spherical particles, the encapsulation of clay platelets is still limited to relatively low clay content with respect to the monomer.

Although Diaconu and co-workers¹¹⁴ managed to synthesise poly(methyl methacrylate-co-butyl acrylate)/clay PCNs with up to 30 % total solids content via miniemulsion polymerisation using Cloisite 15A and Cloisite 30B clays, the clay content in the actual composite did not exceed 5 wt%. Using conventional emulsion and miniemulsion, utilising both the batch and the semi batch processes, they were also able to prepare polymer clay nanocomposites with solids content as high as 45 wt% but the clay content remained as low as 3 wt%. Their work utilised MMT and Cloisite 30B and it was established that the semi batch process afforded PCNs with higher solids content compared to the batch process in both polymerisation processes.¹¹⁵

Bouanani *et al.*²² encapsulated up to 5 wt% MMT clay in poly(trifluoropropylmethyl)siloxane using miniemulsion polymerisation technique. In a typical procedure, clay and cationic/non-ionic surfactant mixture were dispersed in water and after rigorous emulsification the monomer was added followed by sonication to obtain the miniemulsion. Inhomogeneous dispersion and partial encapsulation of clay was observed using this method.

The use of covalently modified Lap and MMT clay platelets in emulsion polymerisation and the preparation of poly(methyl methacrylate) PCNs led to the effective encapsulation of the platelets exhibiting both dumbbell and snowman particle morphology.⁴³ Although they reported up to 75% encapsulation efficiency the total clay encapsulated remained below 5 wt% relative to the monomer content.

Polystyrene/Lap encapsulated hybrid system was developed via miniemulsion polymerisation by Sun *et al.*⁸⁸ containing up to 5 wt% clay content modified by cationic exchange using

alkyl quaternary ammonium modifiers. They followed the direct miniemulsion procedure where the modified Lap was dispersed in organic phase prior to sonication and eventually polymerisation. The fact that the Lap was dispersed in the organic phase limited the amount of clay content that could be dispersed or encapsulated in the monomer due to excessive viscosity increase at clay content beyond 5 wt%. Therefore the resultant encapsulated clay was not found to be different from that obtained using conventional emulsion polymerisation.

Previous work done in our group led to encapsulation of only up to 5 wt% MMT as well. The MMT was modified through cationic exchange using cationic RAFT agents. Using direct miniemulsion polymerisation, the RAFT-modified MMT clay was encapsulated but again the clay content could not be increased beyond 5 wt% due to the instability of the resultant miniemulsion.³⁸ Again, the limitation with regard to the amount of clay encapsulated can be attributed to the viscosity increases beyond 5 wt% clay content.

Tong *et al.*³⁹ reported a series of studies done on the encapsulation of saponite of different sizes using a direct miniemulsion polymerisation procedure similar to the one reported by Sun *et al.*⁸⁸ where the modified clays are dispersed in the organic phase before co-sonication. The miniemulsion polymerisation process was carried out using hexadecane as co-stabiliser, Triton 405 as surfactant and an oil soluble initiator. It was also reported that although modification using long chain cationic modifiers, e.g. CTAB, allowed clay to be well dispersed in the organic phase, the resultant viscosity increased rapidly so that only up to 4% clay content a stable miniemulsion was obtained. From Tong and Deng's findings it is reported that the particle size, particle size distribution and the surface properties of the nanoplatelets play synergistic roles in encapsulation, exfoliation and stability of miniemulsion. With MMT (400 nm average particle size) encapsulation was unsuccessful due to the large size of the platelets as opposed to the monomer droplets, hence could not be encapsulated. This finding is however contrary to other reports where MMT was successfully encapsulated despite its large size. When saponite (200–300nm) was used,^{65,87} a stable dispersion was obtained but the clay adhered onto the polymer latex particles rather than being encapsulated. Using smaller saponite clay platelets (50 nm) and a short reactive cationic modifier to modify the clay, they managed to encapsulate up to 30 wt% saponite. Besides the role played by platelet sizes, it was also found that the modifier chain length also plays a role on encapsulation efficiency.

Moraes *et al.*¹⁰⁰ summarised the possible particle morphologies, based on literature reports, of different PCNs using different clay types, Fig. 2.6. The summarised morphologies were in agreement with Tong's reports where the clay platelet size played a role in the effectiveness of encapsulation and the overall particle morphology.

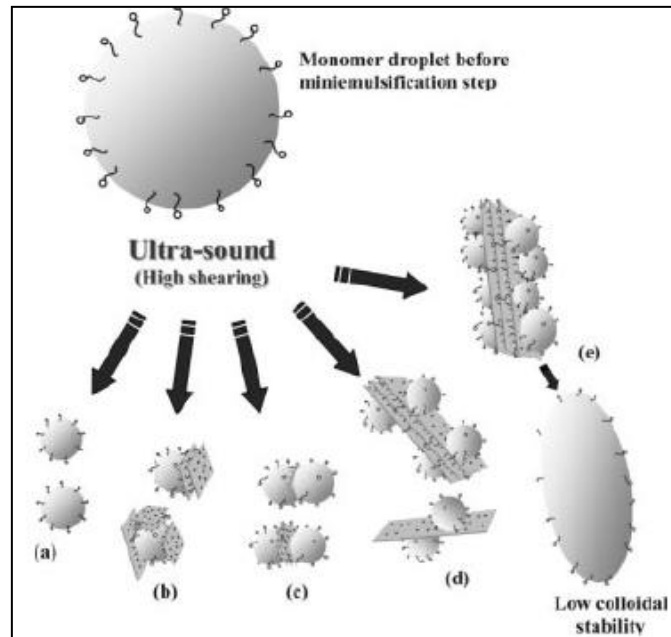


Fig. 2.6: Possible particle morphologies (a) Platelets encapsulated inside the latex,⁶⁵ (b) platelets adsorbed on the latex surface,⁶⁶ (c) dumbbell or snowman like morphology,⁴³ (d) Polymer particles adsorbed on large clay platelets and (e) large platelets encapsulation resulting in colloidal instability.⁸⁷

Recently Leiza *et al.*¹¹⁶ modelled the equilibrium morphology maps of nanodroplets in the presence of nanofillers, taking into consideration both spherical and platelet nanofillers. Using Monte Carlo simulations it was found that in the case of high aspect ratio nanofillers, the compatibility of nanofiller with monomer and aqueous phases, the aspect ratio and the monomer droplet diameter play a crucial role in controlling the polymer particle morphology using miniemulsion polymerisation.

Successful encapsulation of clay is mainly limited to contents not exceeding 5 wt% due to viscosity increase. On the other hand clay nanocomposites containing up to 50 wt% clay content have been produced without necessarily encapsulating the clay platelets inside the polymer particles. To the best of our knowledge only very few reports can be found in the open literature on highly filled encapsulated PCN latexes. The current study aims to

encapsulate high clay contents in polymer particles, in the range of 10–50 wt% clay content, relative to monomer. The current effort utilises ad-mini-emulsion polymerisation, a technique that has been used successfully to encapsulate other inorganic nanoparticles, such as carbon black and magnetite^{6,8,98} when conventional emulsion and direct mini-emulsion encapsulation were unsuccessful.⁹¹

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Chapter 3

Stabilisation of Organolaponite in Aqueous Media Using Anionic Surfactant and Ultrasonication

3.1 Introduction

Clay is one of the many inorganic nanoparticles that are used for the reinforcement of polymers. As such studies on polymer/clay nanocomposites (PCNs) have been a prime area in the last decade.¹⁻¹⁹ Due to its naturally hydrophilic nature clay may require pre-modification using organic molecules to improve its compatibility with hydrophobic polymers and monomers. This modification process can be done through different methods such as ion exchange surface modification or edge modification. Using ion exchange method the inorganic cations that act as counter ions at the clay surfaces are exchanged with organocations such as quaternary alkylammonium compounds. The edge modification involves the use of reactive compounds such as silanes or titanates to covalently bond with the hydroxyl groups found on the platelets edges.^{20,21} Adsorption surface modification makes use of compounds which can adsorb onto the clay surface via interactions such as hydrogen bonding without necessarily substituting the inorganic counter ions.²²⁻²⁴ The modification process renders the clay platelets more organophilic and limits its dispersability in aqueous media. These organoclays are used for the preparation of PCNs using techniques such as melt intercalation, solution polymerisation and in-situ intercalation polymerisation. Using the in-situ intercalation process, the organoclay is dispersed in the monomer prior to polymerisation.²⁵⁻²⁷

During the modification process, the amount of clay modifier required for complete surface modification using ion exchange modification is equivalent to the available exchangeable sites. The excess modifier molecules can facilitate re-dispersion of the organoclay in aqueous media through the formation of a surfactant double layer (admicelle). Using cetyltrimethylammonium chloride (CTAC), Nakamura and Thomas²⁸ studied the surfactant double layers formed on Lap clay surfaces using *pyrene* fluorescence and concluded that the modified Laponite (Lap) re-disperses in excess CTAC concentration due to tail-to-tail interactions of modifier molecules. A similar phenomenon, where Lap first flocculates and then re-disperses in water with increasing CTAC concentration, was reported by Brahim *et al.*²⁹ This was also attributed to the excess CTAC modifier molecules interacting with

molecules grafted on the clay surfaces to form a surfactant bilayer known as an admicelle. This admicelle layer brings about electrostatic stability to the modified clay in water despite the individual platelets being hydrophobic. The use of a second surfactant, different from the clay modifier, has also been reported to facilitate re-dispersion of flocculated organoclays. This results in the formation of a cationic/anionic admicelle layer on the clay surface. Capovilla *et al.*,³⁰ utilised cationic/anionic admicelles using cetylpyridium and sodium dodecyl sulphate (SDS) to re-disperse modified Lap clay platelets in water. Also Brahim *et al.*³¹ utilised the cationic/anionic surfactant combination to re-disperse Lap and proved the formation of admicelles using pyrene fluorescence. Yang *et al.*³² stabilised organo-montmorillonite (MMT) in water by SDS and sonication prior to emulsion polymerisation. The MMT platelets were first modified with non-reactive or reactive cationic modifiers. Besides clay platelets, the same concept has been reported for other nanoparticles surfaces. Meguro *et al.*³³ showed that multiple layers of cationic/anionic surfactants can adsorb on surfaces of α -Fe₂O₃ and TiO₂ as a result of the admicelle layer formation (tail-to-tail interactions) and head-to-head interactions. This shows that stable aqueous organolaponite aqueous dispersions and other nanoparticles can be prepared following the formation of admicelles on their surfaces. However, the particle sizes of these stabilised dispersions were not reported hence it remained an area of investigation.

Bourgeat-Lami and co-workers³⁴ were the first to investigate the particle sizes of modified clays when they monitored the particle sizes of edge-modified Lap as a function of stirring time. Their study involved preparation of aqueous organolaponite dispersions for use in the emulsion polymerisation. The Lap was modified by covalent modification of the Lap edges using mono- and trifunctionalised silane molecules. Although the organolaponite obtained from modification with trifunctionalised silane molecules did not effectively disperse in water, the one obtained from modification with monofunctionalised silane molecules was successfully dispersed in water giving particle sizes of 60–70 nm. In a separate study organolaponite particles modified with cationic initiator 2,2-azobis(2-methylpropionamide) (AIBA) were dispersed in water and stabilised with SDS prior to emulsion polymerisation.³⁵ They reported a decrease in the particles sizes of these organolaponite particles with increasing stirring time. The extent of modification reportedly played an important role in the particle sizes obtained with 50% CEC giving 50 nm particles within 1 day while 200% CEC giving a minimum value of 200 nm after 5 days of agitation. This shows that the fully modified clay platelets strongly interacted with each other so that stirring alone required a

long time in order to break the aggregates. Sonication is usually employed during the preparation of conventional miniemulsions. Sonication time is well known to affect the droplet and polymer particle sizes with a general decrease in droplet or particle size being observed with increasing sonication time.^{36,37}

The current study aims to prepare aqueous organolaponite dispersions for use in the admicelle polymerisation of polymer/Lap hybrid latexes. The approach is to use the admicelle concept to stabilise the hydrophobic organoclays using an anionic surfactant and to break down the organolaponite aggregates using sonication process. The objective of the current study was to establish the conditions (sonication time and SDS concentration) required to achieve the aggregate sizes (average particle size) comparable to miniemulsion monomer droplets, i.e. 50–500 nm.

3.2 Experimental

3.2.1 Materials

Laponite RD (Lap), with 25 nm x 0.92 nm dimensions and CEC of $5.0\text{--}5.5 \times 10^{-5}$ mol/g was supplied by Rockwood Additives Limited, U.K. Cetyltrimethylammonium bromide (CTAB), 4-vinylbenzyl chloride (99%), N,N dimethyldodecylamine (99%), sodium dodecyl sulphate (SDS) and silver nitrate (AgNO_3) were supplied by Sigma Aldrich and were used as received. VBDAC was synthesised using a method reported elsewhere¹⁵ and was confirmed by ^1H NMR (See Appendix 1)

3.2.2 Ion exchange surface modification of Lap clay

Lap (1 wt% relative to water) was dispersed in 1 g/L aqueous solution of sodium pyrophosphate at room temperature and the dispersion was stirred for 2 hr until a clear dispersion was obtained. Modifier (CTAB or VBDAC), equivalent to 100% CEC of the Lap was dissolve in water at room temperature. The resultant aqueous modifier solution was added drop-wise to Lap dispersion and the mixture was stirred for a further 24 hr at room temperature. The obtained white precipitate was recovered by centrifugation at 2900 RCF for 60 min. Several washings were done on the obtained precipitate until no free modifier was detectable using silver nitrate (AgNO_3) test (i.e. precipitate was observed upon the addition of a few drops of 0.1 mol silver nitrate to the supernatant). Powder samples used to evaluate the extent of modifier grafting onto clay platelets were obtained by drying the organolaponite at 45 °C under vacuum.

Fourier transform infrared spectroscopy (FTIR) measurements were conducted on the vacuum dried Lap-VBDA using a 1650 Fourier transform infrared spectrophotometer, (Perkin Elmer, U.S.A). Thirty two scans were recorded for each sample. This was done to qualitatively evaluate the efficiency of the cationic exchange.

Thermograms of the dry sample powder were recorded using Q500 TGA 7 thermogravimetric analyser (Perkin Elmer, U.S.A). The experiments were carried out under a nitrogen atmosphere, at a flow rate of 5 mL/min. The temperature was increased from 25 °C to 590 °C, at a heating rate of 15 °C/min.

3.2.3 Preparation of aqueous organolaponite dispersions

In the preparation of aqueous organolaponite dispersions, the organolaponite (Lap-CTA or Lap-VBDA) paste was used as recovered from the centrifugation process, without prior drying. The amount of the clay in the paste was 15% in both Lap-CTA and Lap-VBDA pastes, as determined by TGA and gravimetric methods. In a typical example, Lap-CTA (1–10 wt% relative to water) was dispersed in aqueous SDS solution of predetermined concentration (0–50 mM). The dispersion was then agitated for 2 hr in order to re-disperse the Lap-CTA. This was followed by sonicating the dispersion for pre-determined time (10–60 min). Studies were conducted to establish how SDS concentration, sonication time and organolaponite content affect the average particle size of the aqueous organolaponite dispersions. The particle sizes were analysed using dynamic light scattering.

A Zetasizer ZS 90 (Malvern Instruments, U.K.) equipped with a 4 mW He-Ne laser, operating at a wavelength of 633.0 nm was used for DLS analysis of the dispersions. The scattered light was detected at an angle of 90°. The final average particle size was obtained from three measurements, each comprising 10–15 sub-runs. The average particle size was calculated using a CONTIN analysis. Prior to the analyses the dispersions were first diluted at a ratio of 15 drops of deionised water per every drop of dispersion.

3.3 Results and Discussion

3.3.1 Laponite modification

The modification of Lap was studied using FTIR and TGA. Fig. 3.1 shows the infrared spectra of Lap, the cationic modifiers and the modified organolaponite. The encircled bands are those that were observed in organolaponite and could be traced to either the modifier or to

unmodified Lap. Asymmetrical and symmetrical vibrations of $-\text{CH}_2-$ of the alkyl chains of CTAB³⁸⁻⁴⁰ at 2929 cm^{-1} and 2852 cm^{-1} appear in the spectra of both Lap-CTA and CTAB. Shifting asymmetric C–H vibrations of the CH_3-N^+ from 1485 cm^{-1} in CTAB to 1477 cm^{-1} in Lap-CTA suggest the attached CTAB to the clay surfaces via its headgroup.⁴⁰ On the other hand the broad band between 3000 cm^{-1} and 3600 cm^{-1} , 1637 cm^{-1} and 980 cm^{-1} could be easily traced to Lap.

For Lap-VBDA the bands at 2926 cm^{-1} , 2854 cm^{-1} and 1475 cm^{-1} can all be traced to the spectra of VBDAC, while those at 3696 cm^{-1} , 1637 cm^{-1} , and 980 cm^{-1} can be traced to the Lap spectrum indicating that VBDAC was also successfully grafted onto the Lap surface in a similar way as CTAB does.

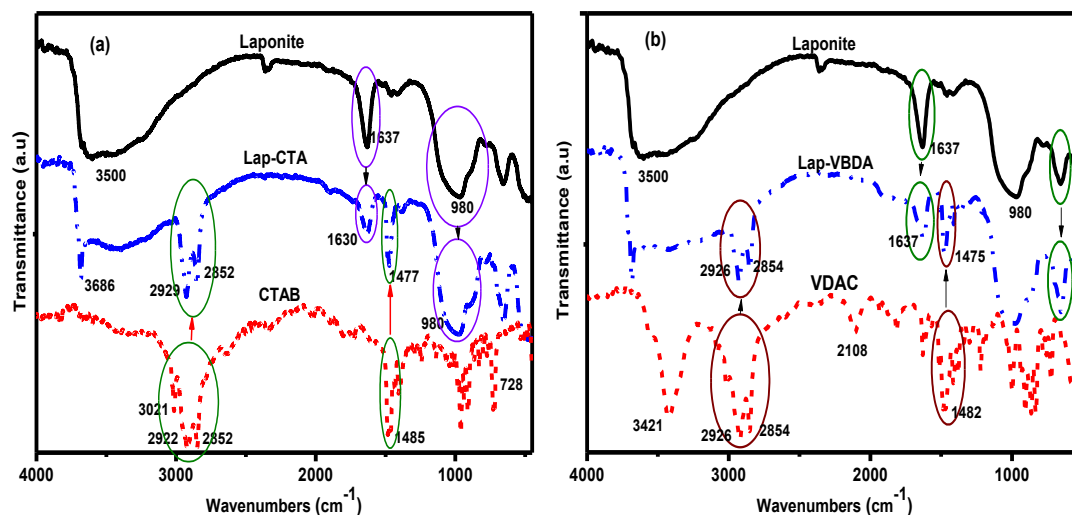


Fig. 3.1: FTIR spectra of; (a) CTAB, Lap modified with CTAB and unmodified Lap and (b) VBDAC, Lap modified with VBDAC and unmodified Lap.

Thermogravimetric analysis was used to quantify the amount of surfactant grafted onto the Lap surface. Fig. 3.2 shows the TGA thermograms of modifiers (inserts), neat Lap and organolaponite modified at 100% CEC. The unmodified Lap thermogram is also characterised by one weight loss step between $70\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$ which is due to the loss of water molecules adsorbed on clay platelets.^{34,41,42} The TGA thermogram of CTAB shown in Fig 3.2(a) (insert) is characterised by one weight loss step between $200\text{ }^{\circ}\text{C}$ and $300\text{ }^{\circ}\text{C}$ with a residual mass of 0.003% at $600\text{ }^{\circ}\text{C}$ which is due to the bulk CTAB decomposition³⁹. The VBDA thermogram, shown in Fig. 3.2(b) (insert), is characterized by two decomposition steps, first between $150\text{--}300\text{ }^{\circ}\text{C}$ due to the decomposition of VBDAC and secondly at $350\text{--}500\text{ }^{\circ}\text{C}$ which was attributed to the decomposition of products of thermally induced auto-polymerisation of VBDAC.

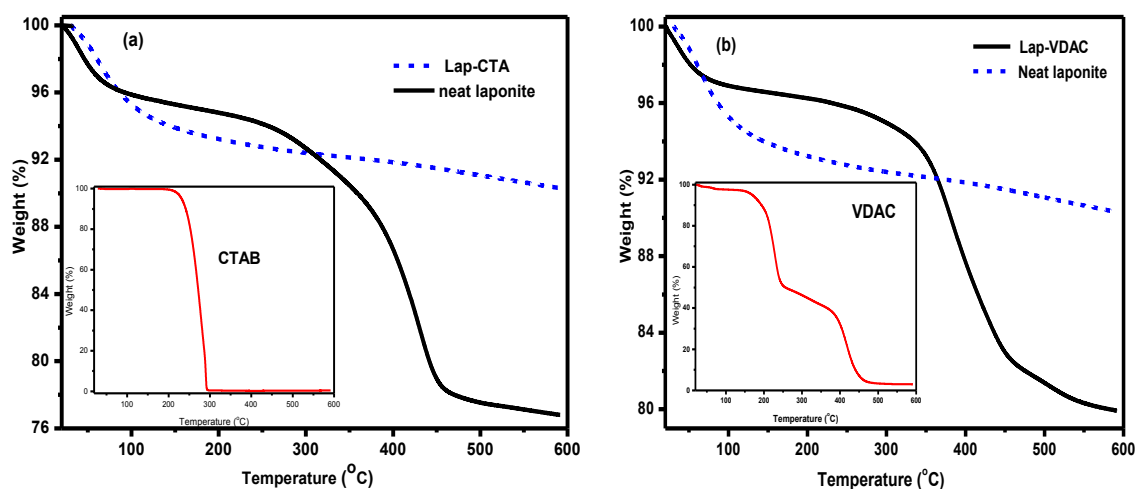


Fig. 3.2: TGA thermograms of cationic modifiers, neat Lap and organolaponite.

Organolaponite thermograms were characterised by two weight loss steps. The first step, below 100 °C, was due to loss of adsorbed water molecules. The second step, observed between 250 °C and 450 °C, was attributed to the decomposition of grafted modifiers. The residual weight differences between 200 °C and 600 °C were used to calculate the amount of modifier grafted on the Lap surfaces using Equation 3.1,⁴³

$$\text{Amount of grafted surfactant} = \frac{\left(\frac{W_{200-600}}{100 - W_{200-600}}\right) \times 100 - W_{\text{lap}}}{M} \quad 3.1$$

where $W_{200-600}$ is the weight loss between 200 °C and 600 °C, W_{lap} is the weight loss of unmodified Lap between 200 °C and 600 °C and M is the molecular weight of modifier.

The calculated amounts of CTA^+ and VBDA^+ in the organolaponites were found to be equivalent to 0.050 mol/100g and 0.048 mol/100g respectively, which accounts for 90% and 83% exchange of the available exchangeable sites, respectively.

3.3.2 Organolaponite aqueous dispersions

Unmodified Lap dispersed well in water and after 30 min of stirring a clear dispersion was obtained. However upon addition of the cationic modifier solution a white precipitate was observed. This was attributed to face-to-face flocculation of clay platelets via tail-to-tail interaction of modifier molecules attached onto the platelets surface.³⁰ Organolaponite obtained after washing off the unattached modifiers could not disperse in water. Sedimentation was observed as shown for sample SD00 in Fig. 3.3(a). Since the same dispersion characteristics were observed for both Lap-CTA and Lap-VBDA, only Lap-CTA dispersions are described in this section. Dispersions sonicated in the absence of SDS re-flocculated within 2 hr of standing.

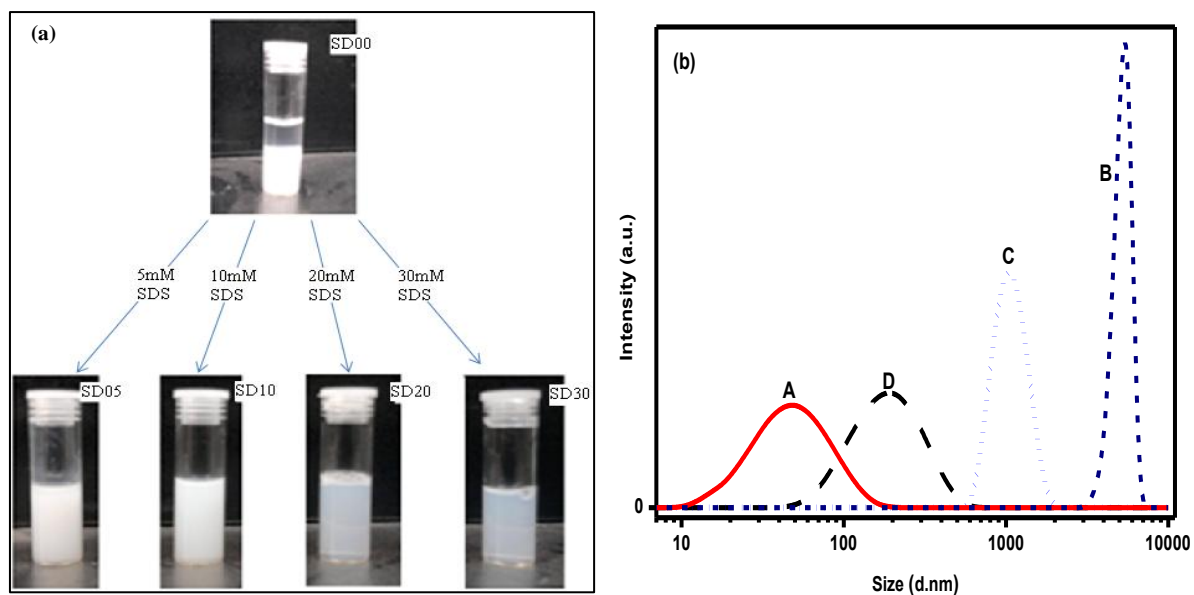


Fig. 3.3: (a) Photographs of organolaponite aqueous dispersion at constant sonication and varying SDS concentration, before sonication and SDS addition (SD00), and after sonication in 5 mM SDS solution (SD05), 10 mM SDS solution (SD10), 20 mM SDS solution (SD20), 30 mM SDS solution (SD30) and (b) The evolution of the particle size distribution of Lap at each step towards stabilisation with SDS; (A) unmodified Lap, (B) Lap-CTA, (C) Lap-CTA in 10 mM SDS solution before sonication, (D) Lap-CTA in 10 mM SDS solution after 10 min ultrasonication.

On the other hand, dispersions prepared in SDS without sonication were fairly stable, showing little sedimentation depending on the time of stirring and SDS concentration. However, dispersions prepared in SDS solutions followed by sonication did not show any sedimentation and were stable for a month. The photographs of these dispersions are shown in Fig. 3.3(a). Below 10 mM highly viscous and opaque dispersion were obtained. Upon increasing the SDS concentration at constant sonication time of 10 min the dispersions' clarity increased. This was attributed to the formation of small aggregates as a result of sonication on which SDS molecules adsorbed forming cationic/anionic admicelle by interacting with the tails of CTA⁺ molecules grafted onto the clay platelet surfaces.^{30,33}

Similar observations were found when the sonication time was varied at constant SDS concentration. Upon increasing the sonication time from 10–60 min at constant SDS concentration, the clarity increased significantly with increasing sonication time. Besides the improved transparency, no sedimentation was observed in all sonicated dispersions. These observations were attributed to the effectiveness of sonication in breaking down the modified clay aggregates into small sizes and the ability of SDS to adsorb at the clay surfaces thus bringing about electrostatic stabilisation as illustrated in Fig. 3.4.

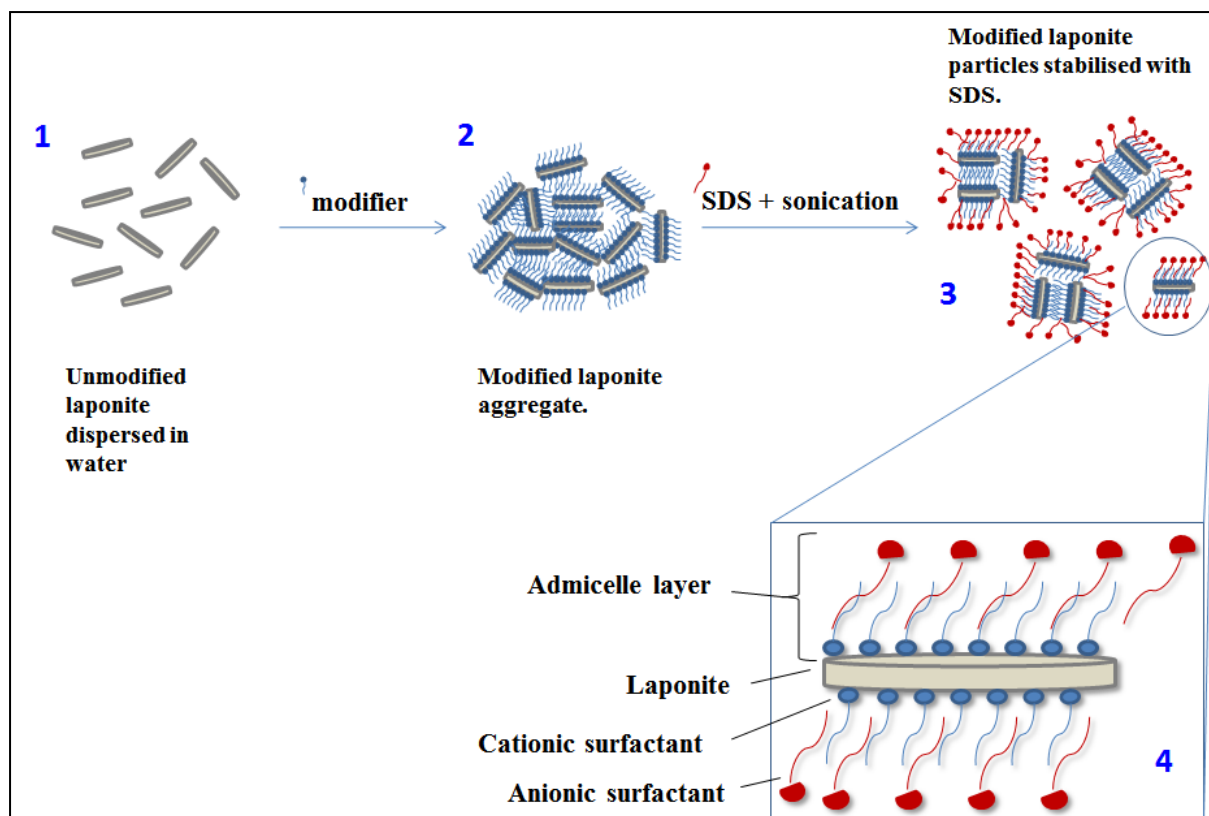


Fig. 3.4: Schematic presentation of the evolution of Lap platelets (1) unmodified Lap, (2) modified Lap, (3) sonicated organolaponite dispersion in SDS solution, (4) Fully exfoliated modified clay platelet stabilised with SDS.

3.3.3 Particle size and particle size distributions of organolaponite dispersions

The results obtained so far suggest a decrease in average particle size of the organolaponite aggregates as a result of sonicating these aggregates in aqueous SDS solution. DLS was therefore used to establish the effect of SDS concentration, sonication time and organolaponite content on average particle size.

3.3.3.1 Particle size evolution

Firstly the average particle size of the dispersions were evaluated from unmodified Lap dispersion through to the stabilised organolaponite dispersions. The particle size distributions of each step of the process are shown in Fig. 3.3(b). This general particle size distribution evolution behaviour was observed for all SDS concentrations studied, the only difference being the particle sizes achieved at each stage after dispersing in SDS solution. Results obtained for Lap-VBDA dispersions showed similar trends to Lap-CTA dispersions, the only difference being the sizes of the particles at each stage especially after the modification of Lap (Table 3.1) and again in this section only Lap-CTA dispersions are discussed.

Before modification, Lap dispersion showed a broad particle size distribution ranging from approximately 15 nm to 110 nm, c.f. peak **A**, Fig. 3.3(b), with an average particle size diameter of 38 nm. Although there still remains a debate on the morphology of Lap in the aqueous phase, it is generally accepted that individual platelets, dimers through to oligomers exist in the aqueous Lap dispersion thus contributing to the broad particle distribution.^{44,45}

Table 3.1: Particle size evolution of Lap-CTA and Lap-VBDA aqueous dispersions

Stage	Lap-CTA	Lap-VBDA
Lap before modification	38 nm	38 nm
Unsonicated organolaponite dispersion	5000 nm	5000 nm
After mechanical stirring	1000 nm	900 nm
After sonication	221 nm	359 nm

After modification with CTAB the unsonicated organolaponite dispersion showed a narrow particle size distribution (PSD), peak **B** of Fig. 3.3(b), with an average particle size diameter of ~5 μm , due to face-to-face aggregation, however reproducibility of this result was poor. Upon dispersing Lap-CTA in 10 mM SDS solution the particle size distribution shifted significantly towards lower values with an average particle size of approximately 1 μm , after 2 hr of mechanical stirring. This was attributed to the formation of a surfactant bilayer on the clay surface (admicelle). An admicelle is a surfactant bilayer on inorganic surfaces with the head groups of the lower layer being adsorbed onto the surface and the head groups of the upper layer pointing towards the aqueous phase^{46,47} illustrated in Fig. 3.4 (**4**). Admicelle formation on clay surfaces is a well-known mechanism causing re-dispersion of organoclays in aqueous media and this can be facilitated by the addition of excess cationic modifier,^{28,29,47} or addition of anionic surfactant to cationic modifier bearing particles.^{30,33}

In the current study it was observed that the particle sizes of these dispersions were relatively large, average particle size was approximately 1 μm after 2 hr of mechanical agitation and their distribution is shown by peak **C**, Fig. 3.3(b). However, sedimentation was observed for this sample after standing for 24 hr. Flocculation decreased with increasing SDS concentration but the average particle size of the unsonicated dispersions remained fairly large compared to the sonicated sample. This indicates that although the second surfactant, SDS, managed to interact with the cationic modifier, CTAB, on the clay surface, it only brought temporary stabilisation to the Lap-CTA aggregates and was ineffective in breaking

down the aggregates to small sizes. The combination of this cationic/anionic admicelle effect and sonication produced stabilised particles with an average size of 221 nm, peak **D**. Broad particle size distribution was also observed for the sonicated dispersions. This could have resulted from different aggregates containing different numbers of platelets. The particle size distribution of sonicated dispersion overlapped with the upper region of the unmodified Lap distribution. This suggested that the process was unable to effectively break down the Lap-CTA aggregates to yield fully exfoliated individual modified clay platelets.

3.3.3.2 Effect of SDS concentration on particle size at constant sonication time and solids content

Initially aqueous organolaponite dispersions with 1 wt% organolaponite were used to evaluate the effect of SDS concentration on average particle size. For Lap-CTA dispersions the average particle size showed a systematic decrease with increasing SDS concentration. Fig. 3.5(a) shows the average particle size of Lap-CTA at different constant sonication times. The tendency of average particle size to decrease with increasing surfactant concentration was also reported by Abismail *et al.*,³⁷ using a non-ionic surfactant.

The average particle size decreased with increasing SDS concentration as seen in Fig. 3.5(a), reaching a constant value from concentrations of 20 mM and higher. For example, the average particle size of Lap-CTA prepared at 10 min sonication decreased from 221 nm in 10 mM SDS solution to 140 nm in 30 mM. No further decrease was observed with further increasing in SDS concentration beyond 30 mM. The decrease in average particle sizes with increasing SDS concentration was attributed to the ability of SDS molecules to adsorb on the modified clay surfaces through Van der Waals attraction with the CTA⁺ molecules attached on the clay surface.^{30,33,48,49} The higher the quantity of SDS molecules available to cover the larger surface area produced by sonication, the lower the average particle sizes of the resulting Lap-CTA dispersion. For lower SDS concentrations, below 10 mM, the interface is not completely covered, therefore, the clay platelets partially aggregate thus giving higher particle sizes.³⁷ On the contrary, the average particle size of Lap-VBDA dispersions decreased until 20 mM before increasing again with further increase in SDS concentration, as shown in Fig. 3.5(b).

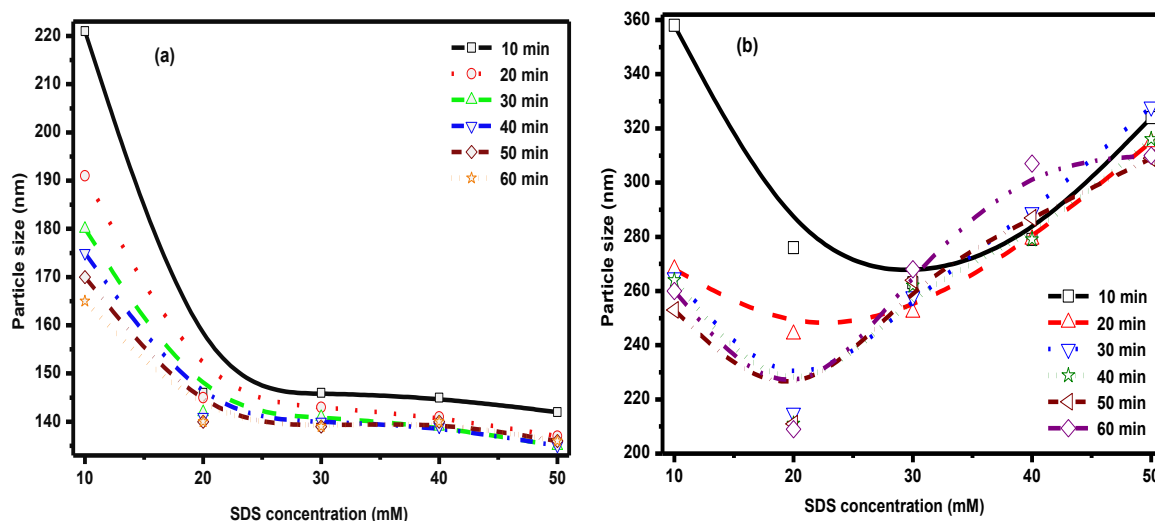


Fig. 3.5: (a) The particle size of Lap-CTA dispersions, (b) The particle size of Lap-VBDA.

The result suggests that there is a threshold SDS concentration beyond which there is a negative effect on reducing the average particle size of the Lap-CTA aggregates. Although the cause of such behaviour could not be conclusively established, it was suggested to be due to formation of clusters of clay aggregates as was reported for carbon nanotubes.⁴⁸

The critical SDS concentration required to achieve the minimum average particle size was taken to be ~20 mM for both Lap-CTA and Lap-VBDA. This estimation method was used after pyrene fluorescence method could not establish the amount of SDS molecules required for admicelle formation.

3.3.3.3 Effect of sonication time at constant SDS concentration and solids content

Fig. 3.6 shows the average particle sizes of the different dispersions as a function of sonication time at different constant SDS concentrations. The average particle size of Lap-CTA decreased with increasing sonication time at low SDS concentrations. However, at higher SDS concentrations the average particle size remained unaffected by the sonication time. The decrease in average particle size due to increased sonication time was attributed to two factors: (i) increased energy exerted on the dispersions with increasing sonication time. The average energy increased from 30 kJ for 10 min sonication to 180 kJ for 60 min sonication; (ii) the volume of the dispersion that passes through the ultrasound region increases with increasing sonication time. The sonifier geometry only allows a small region of the dispersion to be directly affected by the ultrasound waves from the sonication hence more time is required to allow all the vessel volume to pass through the ultrasound region.⁵⁰ Similar decrease in particle sizes with increasing sonication time has been reported in

emulsification processes using sonication although the reports focused on liquid/liquid dispersions^{37,51} rather than solid/liquid dispersions discussed in the current study.

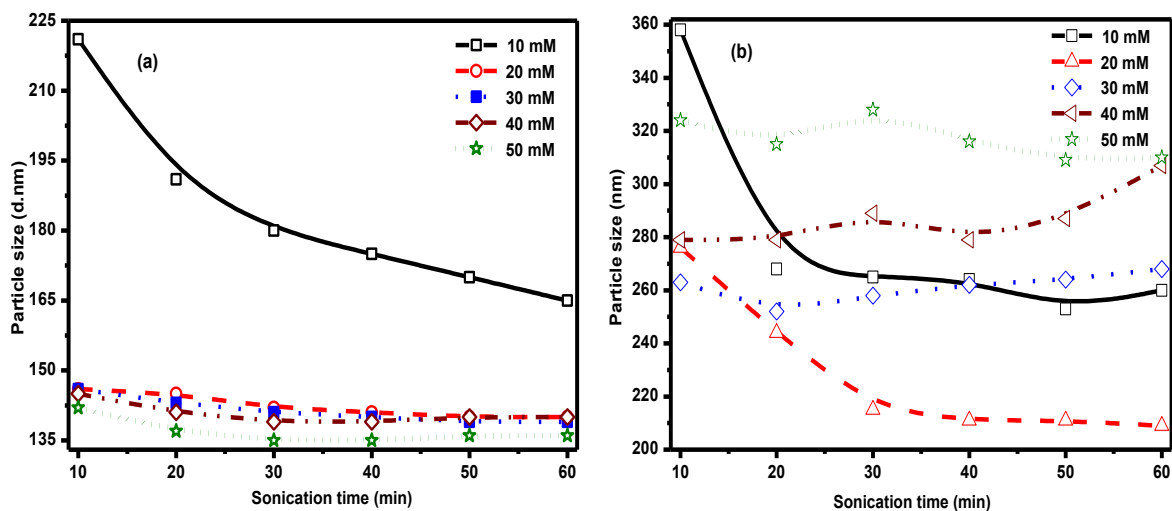


Fig. 3.6: The particle sizes of (a) Lap-CTA dispersions, (b) Lap-VBDA dispersions, of different SDS concentration, as a function of sonication time.

Lap-VBDA dispersions with < 30 mM SDS exhibited a sharp particle size decrease with increasing sonication time. Dispersions prepared in higher SDS concentrations (≥ 30 mM) remain unaffected by sonication time. Although the particle sizes remained constant at each SDS concentration throughout the sonication time range, the average particle size increased with increasing SDS concentration, possibly due to clustering effect, as noted in Section 3.3.3.2.

3.3.3.4 Effect of total solids at constant SDS concentration and sonication time

Results reported so far were based on dispersions with 1 wt% organolaponite content relative to water. In order to understand the role of solids content on the particle sizes of the dispersions, the organolaponite content was varied. Fig. 3.7 shows the effect of solids content on average particle size under various constant SDS concentrations and sonication times. Fig. 3.7(a) shows the variation of particle sizes of Lap-CTA dispersions, prepared with different SDS concentrations, as a function of solids (organolaponite) content. Lap-CTA dispersions showed a linear increase in particle size with increasing solids content at all the SDS concentrations studied. The particle sizes of Lap-CTA increased with increasing solids content at all sonication times used.

On the other hand, Lap-VBDA show a change in behaviour from concave behaviour at lower SDS concentration towards negative linear behaviour at higher SDS concentration as shown

in Fig. 3.7(b). The concave behaviour observed at low SDS concentrations with increasing solids could be due to a combination of two effects. The first is the clustering effect brought about by the excess SDS molecules (micelles) at low solid content. The second is the aggregation of clay platelets with increasing solids content beyond 3 wt% Lap-VBDA due to lack of SDS molecules to stabilise the aggregates. At higher concentrations the aggregation effect is gradually eliminated with increasing the SDS concentration, hence the change in particle behaviour towards linear negative behaviour.

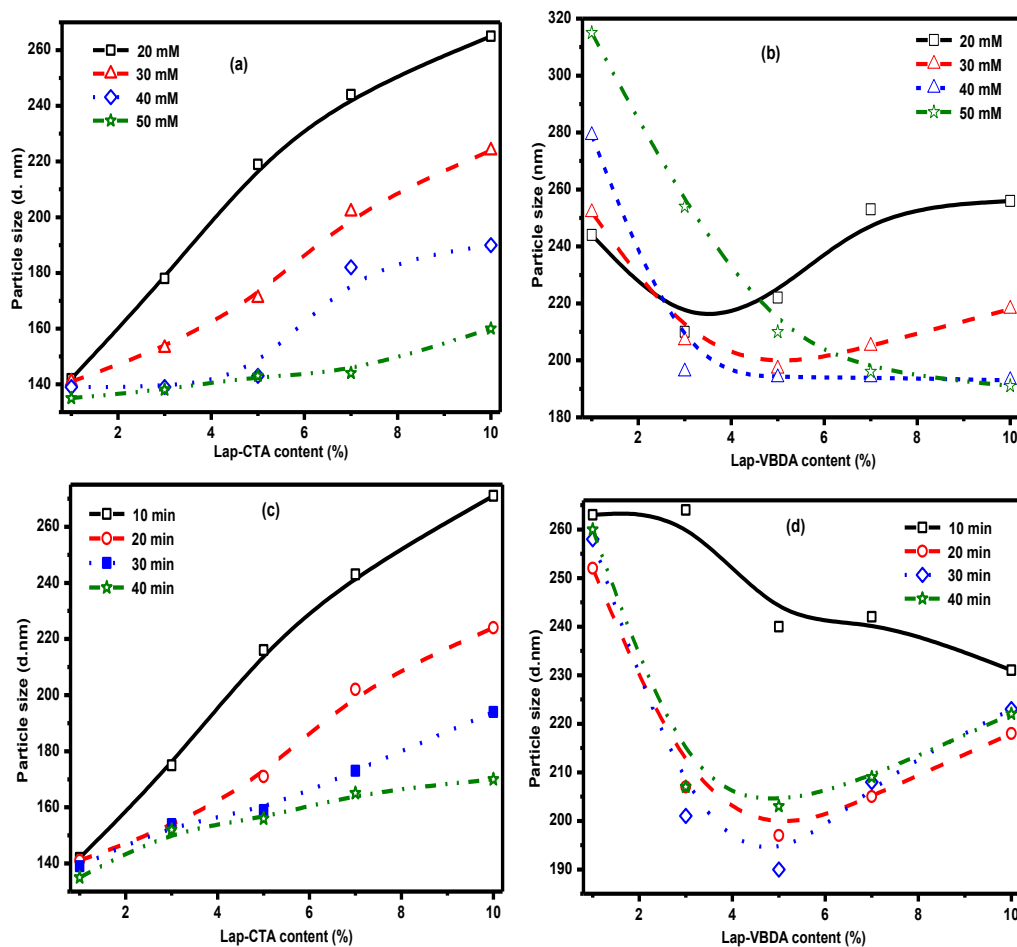


Fig. 3.7: Effect of total solids content on particle sizes of; (a) Lap-CTA dispersions and (b) Lap-VBDA dispersions, using different SDS concentrations at constant sonication time of 20 min and effect of total solids content on particle sizes of (c) Lap-CTA dispersions and (d) Lap-VBDA dispersions, in 30 mM SDS concentrations at different sonication times

To further understand the effect of organolaponite content, the effect of organolaponite content at various constant sonication times were studied. All the dispersions used in this particular study were prepared using an SDS concentration of 30 mM. The average particle sizes resulting for Lap-CTA and Lap-VBDA dispersions as a function of sonication time are

shown in Fig. 3.7(c) and 3.7(d), respectively. The average particle sizes of Lap-CTA dispersions showed a systematic increase with increasing solids content at all sonication times studied. Lap-VBDA again showed surprising and interesting results; at shorter sonication time, i.e. 10 min, the particle sizes decreased with increasing solids content. At higher sonication times, the average particle size exhibited a concave behaviour, where the particle size showed an initial decrease until around 5 wt% solids content. Further increase in solids content beyond 5 wt% was characterised by an increase in average particle size. This was attributed to the conflicting clustering effect and the lack of SDS molecules to stabilise the small particles.

3.4 Conclusion

It was shown that sonication and admicelle formation worked synergistically to break down organolaponite aggregates yielding stable aqueous organolaponite dispersions. The sonication process provides the required energy to break down the clay aggregates. At the same time, SDS molecules provided the electrostatic stabilisation to the newly formed particles through interacting with clay modifier thus forming admicelles on the clay surface. Average particle sizes studies using DLS showed that sonication time, and organoclay content all affect the average particle size of the resultant organolaponite dispersions. At constant sonication time and amplitude, the average particle size decreases exponentially with increasing SDS concentration. A similar decrease in average particle size was observed with increasing sonication time at constant SDS concentration. This was ascribed to an increasing amount of energy being exerted to the dispersion to facilitate the aggregate breakdown. Increasing the Lap-CTA content linearly led to an increase of the average particle size. The average particle sizes as a function of solids content were found to be strongly depended on SDS concentration and sonication time. Although sonication and SDS effectively stabilised organolaponite and reduced the aggregate size, the type of cationic organic surface modifier was also found to affect the average particle size behaviour. Because efforts to quantify the optimum amount required for admicelle formation were unsuccessful, using the concentration at minimum average particle size was chosen for further studies. The sonication time of 20 min was chosen for further studies in order to avoid overheating prior to polymerisation.

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Chapter 4

Polymer/Laponite Hybrid Latexes Prepared Using Ad-mini-emulsion Polymerisation Technique

4.1 Introduction

Polymer/clay nanocomposites (PCNs) have attracted considerable attention over the past two decades. This is mainly due to significant property improvement achieved by the incorporation of clay nano-fillers in the polymer. Most of the PCNs reported to date contain low clay contents; only a limited number of reports can be found in literature dealing with highly filled PCNs, irrespective of the preparation technique or polymerisation method used.¹⁻⁴ Contributing factors to this include the problem of high viscosity associated with the incorporation of large quantities of clay in monomer precursors. Another reason is that only a small amount of clay is generally sufficient to achieve significant property improvement. Choi and co-workers^{5,6} reported PCNs with clay content as high as 20 wt% when they prepared PCNs of polyacrylonitrile and poly(methyl acrylate-*co*-acrylonitrile) via soap-free emulsion polymerisation using montmorillonite (MMT) clay modified with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS). Soap-free emulsion polymerisation was also used by Lee *et al.*⁷ to prepare PCNs of poly(methyl methacrylate-*co*-methyl acrylate)/MMT with up to 20 wt% clay content. Despite the successful preparation of highly filled PCNs, the studies focused mainly on the physical properties of the resultant PCNs without including detailed analysis of the latex morphology. In a series of studies, Bourgeat-Lami and co-workers^{1-3,8} reported highly filled PCNs with up to 50 wt% Laponite (Lap) clay content prepared via emulsion polymerisation. The Lap clay platelets were modified with a macromonomer, poly(ethylene oxide) monomethylether methacrylate with a molar mass of 1000 g/mol. The macromonomer was incorporated to enhance the attachment of Lap clay platelets on the polymer particles to afford PCNs with cellular structured morphology.

The encapsulation of inorganic nano-fillers into organic materials to produce inorganic-organic hybrid nanomaterials has attracted considerable interest in recent years. In order to prepare these materials, heterogeneous polymerisation techniques have been frequently used including dispersion polymerisation,⁹ emulsion polymerisation¹⁰⁻¹⁶ and miniemulsion polymerisation.^{8,17-22} To date, encapsulation of clay has been successfully achieved with low clay content (typically < 10 wt% clay).^{16,19,22-24} In general, ineffective encapsulation of clay

platelets beyond 5 wt% can be attributed to the high viscosity associated with dispersing the clay platelets in the monomer phase and instability of the resultant latex.

Tong and Deng,^{25,26} however, reported the encapsulation of up to 30 wt% clay in polystyrene (PS). In a series of studies they highlighted the importance of parameters such as clay platelet dimensions and the type of modifier when considering encapsulation of clay platelets in polymeric latex particles. When MMT with an average size of 400 nm was used, encapsulation was unsuccessful. However this is contrary to other literature reports, where MMT was effectively encapsulated despite its large size.^{19,22,27} When saponite with an average particle size of 200–300 nm was used stable latexes were obtained, but the clay platelets were adhered onto the particle surfaces. Using small-sized saponite platelets (average size 50 nm), effective encapsulation was obtained with up to 30 wt% clay. Moreover, when a long-chain alkyl quaternary ammonium cation such as cetyltrimethylammonium bromide (CTAB) was used to modify the clay, the resultant organoclay had poor dispersability in monomers such as styrene. High viscosity characterised the monomer/clay dispersion, thus limiting the amount of clay that could be encapsulated to very low contents, *i.e.* < 5 wt%. However, the use of short reactive cationic modifiers improved the amount of clay that could be encapsulated because clay platelets could be dispersed in the organic phase at high concentrations while keeping the viscosity low.

Two miniemulsion polymerisation methods have been reported in literature for the preparation of hybrid nanomaterials, *i.e.* conventional miniemulsion polymerisation^{19,26,28-30} and ad-miniemulsion polymerisation.^{17,31,32} The conventional miniemulsion polymerisation method involves the preparation of a monomer/inorganic particle suspension by dispersing the inorganic particle in the organic phase (monomer, co-stabiliser and initiator), which is then dispersed in an aqueous surfactant solution to form the hybrid miniemulsion by ultrasonication.^{22,28,33} Once the inorganic particles are incorporated in the organic phase they are expected to be effectively encapsulated during polymerisation. The method has been used for encapsulation of a wide range of inorganic nano-fillers, *e.g.* silica,²⁸ magnetite particles,^{31,32,34} titanium dioxide,^{35,36} and clay platelets.^{19,22,26,37} However, it has been widely reported that the method is ineffective for encapsulation of high contents of inorganic nano-fillers. For clay platelets, the amount that can be encapsulated has mainly been limited to < 10 wt% due to increased viscosity of the pre-dispersed organic phase beyond this clay content

and due to latex instability.^{22-24,38} Only Tong and Deng have reported the encapsulation of up to 30 wt% clay using direct miniemulsion polymerisation.²⁶

On the other hand, the co-sonication method (ad-mini-emulsion) involves separate preparation of the two dispersions, i.e. the monomer miniemulsion and the inorganic dispersion. The two dispersions are then mixed together and co-sonicated to produce the final miniemulsion as a result of the fission and fusion processes taking place during co-sonication step. The method was developed by Landfester and co-workers in an attempt to overcome the limitations of direct miniemulsion in as far as encapsulation of high nano-filler content in polymer particles is concerned.^{17,31,34} Using this method, Landfester and co-workers successfully encapsulated up to 40 wt% carbon black²¹ and up to 40 wt% magnetite particles³¹ in PS, an achievement that was not met using direct miniemulsion polymerisation. To the best of our knowledge, this method has not been used to encapsulate clay platelets. Li *et al.*,³⁹ however, utilised an indirect miniemulsion method that resembles ad-mini-emulsion to encapsulate MMT clay in PS. They reported that modified MMT clay platelets were dispersed in SDS solution before the monomer was added to this dispersion. After the addition of the monomer, the mixture was sonicated and polymerised. MMT was modified with a non-reactive cationic modifier, trimethyloctadecyl ammonium chloride. The latex morphology showed particles with clay platelets adhering strongly on the polymer particle surfaces, but not encapsulated. The clay content used in the study was 5 wt%.

The aim of the current study was to prepare highly filled polymer/clay hybrid latexes. The targeted clay content was in the range of 10–50 wt% clay relative to the polymer material. As such, the ad-mini-emulsion was chosen as the method of preparation. Lap clay was chosen for this study due to its small size and narrow particle size distribution. Prior to the polymerisation step, the clay platelets were first modified with vinylbenzyl dodecyl ammonium chloride (VBDAC), a reactive cationic modifier with a polymerisable moiety. The particle size, monomer-to-polymer conversion and morphological features of the hybrid latex and the films obtained from the latex were studied.

4.2 Experimental

4.2.1 Materials

Styrene (99%) and n-butyl acrylate (99%) monomers were supplied by Sigma-Aldrich. Styrene was washed with a 0.3 M potassium hydroxide (KOH) aqueous solution and then

with distilled water. The washed styrene was then distilled at 40 °C under reduced pressure to remove inhibitor. n-Butyl acrylate was passed through a column supplied by Sigma-Aldrich, packed with hydroquinone and monomethyl ether hydroquinone (MEHQ) inhibitor remover. Azobisisobutyronitrile (AIBN) was supplied by Sigma Aldrich and purified by recrystallisation from methanol. Laponite RD (Lap), with 25 nm x 0.92 nm dimensions and CEC of $5.0\text{--}5.5 \times 10^{-5}$ mol/g was supplied by Rockwood Additives Limited, U.K. Sodium dodecyl sulphate (SDS, 99%), 4-vinylbenzyl chloride (99%), N,N dimethyldodecylamine (99%), hexadecane (HD, 99%) and silver nitrate were supplied by Sigma Aldrich and used as received. Vinylbenzyl dodecyl dimethyl ammonium chloride (VBDAC) was synthesised using a method reported elsewhere⁴⁰ and its structure was confirmed by ¹H NMR (see Appendix 1). VBDAC was chosen for this study due to its ability to copolymerise with polystyrene⁴¹ and its compatibility with polystyrene monomer.⁴²

4.2.2 Modification of Laponite RD

The modification of Lap is detailed in Section 3.2.2 and the grafting of the cationic modifier onto the clay platelet surfaces was confirmed by FTIR and TGA as described in Section 3.3.1.

4.2.3 Preparation of polystyrene/Laponite hybrid latexes

4.2.3.1 Aqueous Lap-VBDA dispersion

In a typical procedure, predetermined amount of never-dried Lap-VBDA paste was dispersed in 20 mM aqueous SDS solution and agitated for 2 hr. The resulting dispersion was then exposed to sonication for 20 min at 90% amplitude (exerting 65 ± 5 kJ of energy) using a Vibra Cell Autotune series 750VCX high intensity ultrasonic processor (Sonics, U.S.A.). Formulations used to prepare PS/Lap PCNs hybrid latexes are given in Appendix 2.

4.2.3.2 Monomer miniemulsion

The monomer miniemulsion was prepared by dispersing monomer (styrene or styrene/n-butyl acrylate for PS/Lap and PSBA/Lap hybrids, respectively), AIBN (2 wt% relative to monomer) and hexadecane (4 wt% relative to monomer) in a 10 mM aqueous SDS solution. For PSBA, a 50:50 molar ratio was used between styrene and n-butyl acrylate. The monomer-to-water ratio in the monomer miniemulsion was maintained at 3:5 but the volume of this miniemulsion was varied in an effort to maintain the overall solids content of the latex at 20% and 15% for PS/Lap and PSBA/Lap hybrids, respectively. 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 without the use of pulse. Energy exerted on the solution was 4 kJ.

4.2.3.3 Co-sonication and polymerisation

The Lap-VBDA dispersion and the monomer miniemulsion were mixed together under vigorous agitation for 30 min followed by sonication for 4 min in an ice bath at 50% amplitude, exerting 10 ± 2 kJ of energy. The resultant hybrid miniemulsion was transferred into a three neck round bottom flask connected to a condenser and a nitrogen inlet. The miniemulsion was bubbled with nitrogen for 30 min. After rising the temperature to 75 °C, polymerisation was initiated and allowed to run for 6 hr.

4.2.4 Analyses

4.2.4.1 Transmission electron microscopy

To determine latex's particle size and morphology, the obtained latex was diluted using water at a ratio of 5 drops of water per every drop of latex. A 3 μ L aliquot of the diluted latex was transferred by micropipette onto a 300-mesh copper grid. In order to establish the extent of clay delamination in the PCNs, dried latex samples were embedded in epoxy resin and cured at 60 °C for 24 hr. The embedded samples were then ultra-microtomed with a diamond knife using a Reichert Ultracut S ultra-microtome (Leica, Switzerland) at room temperature, thus yielding film sections of about 100 nm thick. In both 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 post-column energy filter. During analyses, the image contrast was enhanced by inserting an energy filter of 20 eV in the electron beam path in order to filter out inelastically scattered electrons, which contribute towards background noise in the digitally recorded images.

4.2.4.2 Dynamic light scattering

A Zetasizer ZS 90 (Malvern Instruments, U.K.) equipped with a 4 mW He-Ne laser, operating at a wavelength of 633.0 nm was used for DLS analysis of the PCN latex samples. The scattered light was detected at an angle of 90°. The final average particle size was obtained from three measurements, each comprising 10–15 sub-runs. The average particle size was calculated using a CONTIN analysis. Prior to the analyses the hybrid latex samples were first diluted at a ratio of 15 drops of deionised water per every drop of latex.

4.2.4.3 Thermogravimetric analysis

Thermograms of the dry powder samples were recorded using Q500 TGA 7 thermogravimetric analyser (Perkin Elmer, U.S.A). The dry PCN powder samples were obtained by precipitating the hybrid latexes in methanol followed by vacuum drying at 45 °C. The TGA experiments were carried out under a nitrogen atmosphere, at a flow rate of 5 mL/min. The temperature was increased from 25 °C to 590 °C, at a heating rate of 15 °C/min.

4.2.4.4 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) measurements were conducted on the vacuum dried Lap-VBDA using a 1650 Fourier transform infrared spectrophotometer, (Perkin Elmer, U.S.A). Thirty two scans were recorded for each sample. This was done to qualitatively evaluate the efficiency of the clay surface modification by cationic exchange.

4.2.4.5 Small angle X-ray scattering

The dispersion of the clay platelets was analysed 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.

4.3 Results and Discussion**4.3.1 Preparation of hybrid latexes****4.3.1.1 Pre-polymerisation stage**

The pre-polymerisation stage involved the preparation of the Lap-VBDA dispersion, the monomer miniemulsion and then the hybrid miniemulsion. During this stage the particle sizes of the Lap-VBDA dispersion, monomer miniemulsion and the hybrid miniemulsion were monitored using DLS. Fig. 4.1 shows the average particle sizes of Lap-VBDA dispersions and the hybrid miniemulsion as a function of the targeted clay content in the final hybrid latex. The Lap-VBDA content in the aqueous Lap-VBDA dispersions were in the range of 2.9–12 wt% and 2.0–8.8 wt% relative to water for PS/Lap and PSBA/Lap, respectively. The

average particle size of the Lap-VBDA dispersion was found to increase with increasing clay content. The monomer droplet size remained fairly constant (not shown in Fig. 4.1), because all parameters were kept constant, i.e. SDS concentration, monomer/water ratio and sonication time. The average particle size of the hybrid miniemulsion was significantly affected by the average particle size of the Lap-VBDA dispersion. Despite the average monomer droplet size between the monomer miniemulsions used to prepare hybrids of different clay content being fairly constant, the average particle size of the hybrid miniemulsion increases with increasing clay content. The average particle size increase observed for the hybrid miniemulsion followed a fairly similar trend to that of the Lap-VBDA dispersions.

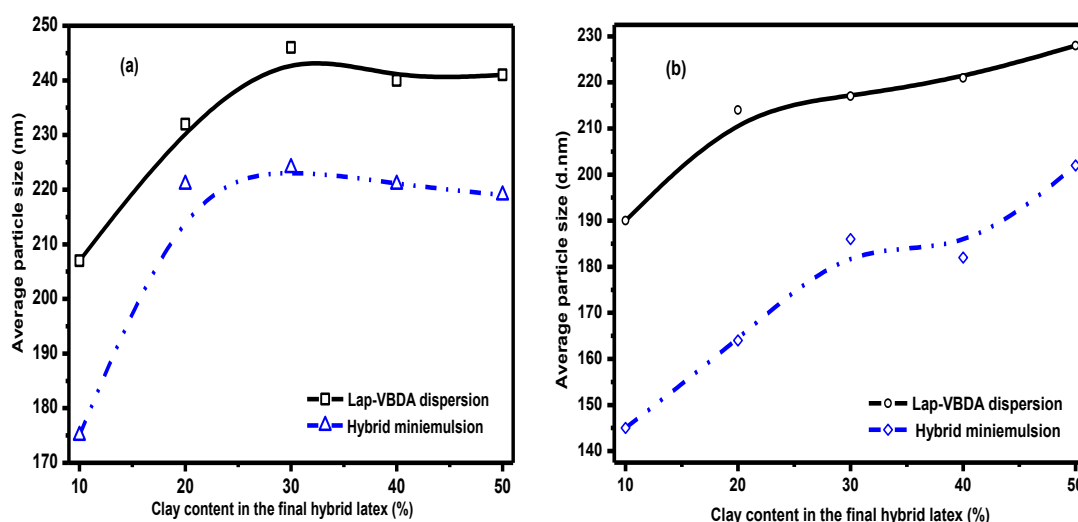


Fig. 4.1: Particle sizes of Lap-VBDA and hybrid miniemulsions used of (a) PS/Lap hybrid latexes and (b) PSBA/Lap hybrid latexes, as a function of targeted clay content in the final hybrid latexes.

4.3.2.2 Polymerisation stage

During polymerisation, the average particle size and the monomer-to-polymer conversion were monitored at pre-determined time intervals. Fig. 4.2 shows the time dependency of average particle size and monomer-to-polymer conversion of PS/Lap and PSBA/Lap hybrid latexes. All samples' average particle sizes followed a similar trend, i.e. the average particle size decreased during the initial stages of polymerisation, i.e. below 1 hr of polymerisation, after which it remained constant through the polymerisation period. This could be due to secondary nucleation or instability of the hybrid droplets.¹⁸ Small particles were observed in all samples by TEM indicating a possibility of secondary nucleation. However, it was also found that the decrease in the average particle size during initial stages of polymerisation was strongly depended on the amount of clay incorporated. The drop decreased with increasing in

clay content. Such changes suggest that the observed drop in average particle size could be due changes in density from the monomer droplets to polymer particles.

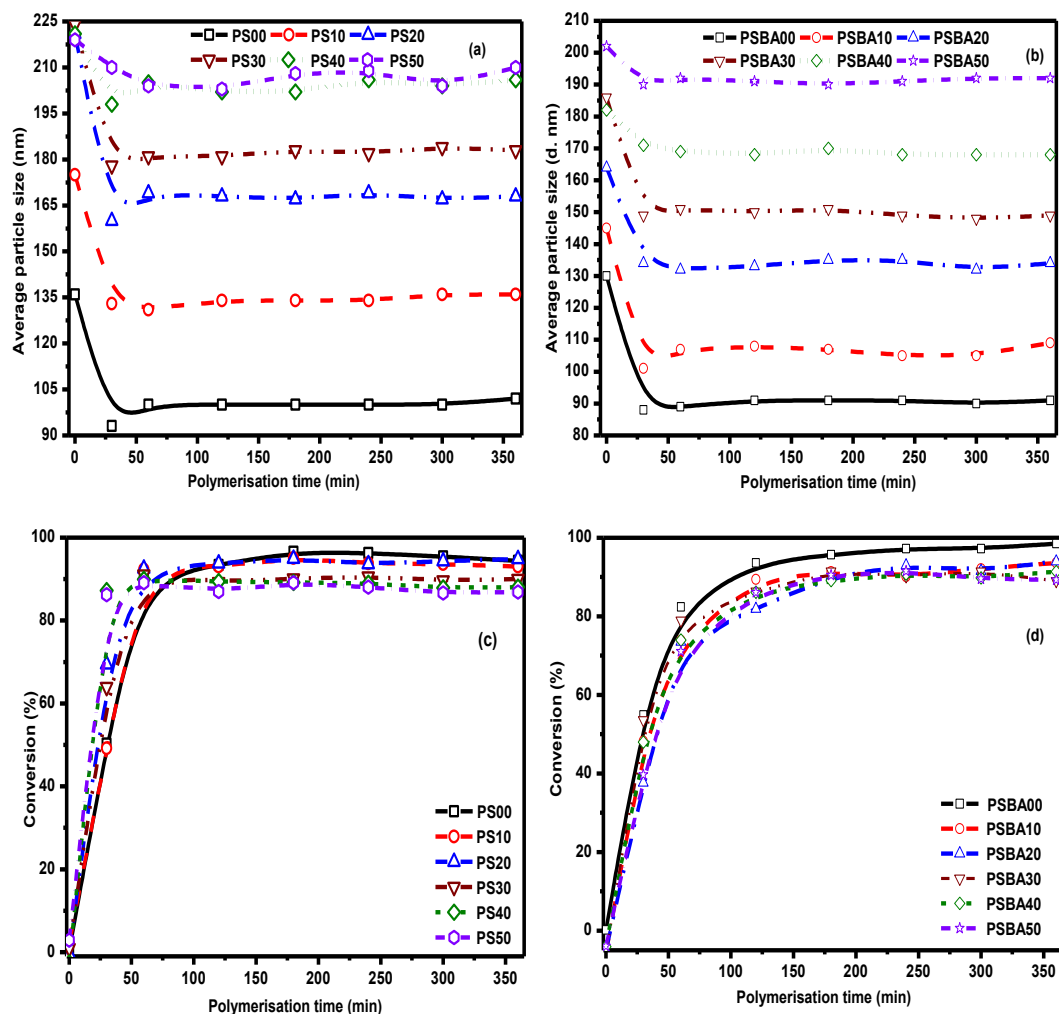


Fig. 4.2: Average particle sizes of (a) PS/Lap hybrid latexes (b) PSBA/Lap hybrid latexes, as a function of polymerisation time, and monomer-to-polymer conversion of (c) PS/Lap hybrid latexes and (d) PSBA/Lap hybrid latexes, as a function of polymerisation time.

The drop in average particle size during the initial stages of polymerisation could also be due to differences in aggregation between the hybrid monomer droplets and polymer hybrid particles during sample preparation prior to analysis. There was a general increase in average particle size at each interval with increasing clay content throughout the polymerisation stage showing that the presence of clay content influenced significantly the average particle size of the hybrid latex. The monomer-to-polymer conversion was monitored gravimetrically during polymerisation and Figs. 4.2 (c) and (d) show the monomer-to-polymer conversion profile of different latexes as a function of time. All samples, in both polymer systems, exhibited higher conversions irrespective of the clay content indicating that the clay content had limited

negative effect on conversion. Only up to 5% decrease in conversion, relative to neat polystyrene, was observed at the highest clay content, i.e. 50 wt% Lap content. The results are in agreement with other researchers' findings who reported limited or no change in conversion with incorporation of clay.^{18,30,43} However, this is contrary to other reports where the incorporation of clay either decreased significantly^{22,25,44,45} or increased the conversion.⁴⁶ Decrease in conversion with increasing clay is usually attributed to a decrease in monomer's translational diffusion as local viscosity increases with increasing conversion in the presence of clay platelets.⁴⁷ In the present study, such effect could have been limited by the compatibility between Lap-VBDA and the monomers. As such, the monomers were pre-intercalated in the platelets interspaces before polymerisation thus promoting radical compartmentalisation at higher clay content hence higher conversions. In case of low clay content PS/Lap PCNs, with clay platelets adhered onto the polymer particles surfaces, higher conversions are due to compartmentalisation inherent to miniulsion polymerisation technique.

4.3.2.3 Post polymerisation

After polymerisation the final average particle size of the hybrid latexes was determined by DLS and TEM and the results are shown in Fig. 4.3. From DLS results the average particle sizes of both PS/Lap and PSBA/Lap hybrid latexes increased with increasing clay content. This could be a result of the following factors: the encapsulation of clay in polymer particles which result in increased average particle size; or aggregated particles which, by DLS, are measured as one particle; or increased particle density as a result of clay encapsulation. DLS measurements are based on correlation measurements related to Brownian motion. Increasing the particle density reduces particle motion hence the analysis may interpret the increased density as an increase in particle size. The particle aggregation and possibly the effect of density were confirmed by TEM results. TEM showed that although the average individual particle size remained fairly constant (~ 80 nm), the particles were aggregated, and aggregation increased with increasing clay content. Average particle size values obtained from TEM were number average particle diameters of 75–100 particles. It is worth noting that at higher clay content, i.e. > 30 wt%, the spherical shape of PS/Lap hybrid particles was distorted by the presence of clay. On the other hand, it was difficult to determine the average particle size for PSBA/Lap hybrid latexes using TEM images due to poor resolution, aggregation of the particles and loss of spherical shape of the hybrid particles.

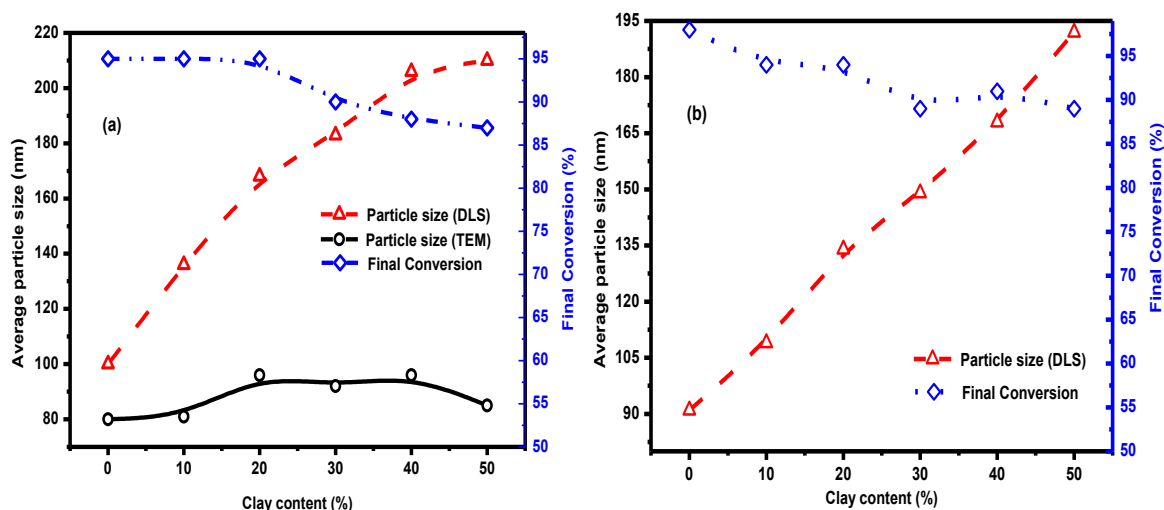


Fig. 4.3: Final average particle sizes determined by DLS (red) and TEM (black) and final conversion (blue) of (a) PS/Lap hybrid latexes and (b) PSBA/Lap hybrid latexes as a function of clay content.

However, DLS measurements showed a general increase in average particle size with increasing clay content. The increase in average particle size observed from DLS measurements as a function of increasing clay content, in both systems, was therefore attributed to increased particles density and particle aggregation which were both enhanced by the presence of clay. Particle aggregation was evident from TEM images (see Fig. 4.4).

4.3.3 Morphological properties

4.3.3.1 Latex morphology

TEM was used to study the morphological structures of the hybrid latexes. Fig. 4.4 shows TEM images of PS/Lap and PSBA/Lap hybrid latexes. The ad-mini-emulsion technique produced stable PS/Lap and PSBA/Lap latexes at 20% and 15% solids content, respectively. Both hybrid latex systems showed only very limited coagulation, not exceeding 5%, even for the highly filled hybrid latexes. TEM is conventionally used to explore the morphology of PCN latexes as the difference in contrast between the polymer and clay platelets giving an indication on both the location and extent of dispersion of the clay platelets in the latex. The particles of neat PS latexes were found to be spherical in shape, as shown in Fig. 4.4(a₁), with an average particle size of ~80 nm (estimated from TEM images). Upon incorporation of 10 wt% clay, mixed particle sizes were observed with smaller particles being dominant (see Fig. 4.4(a₂)). It is also worthwhile to note that the PS10 sample had a multimodal distribution (according to the estimations from TEM images).

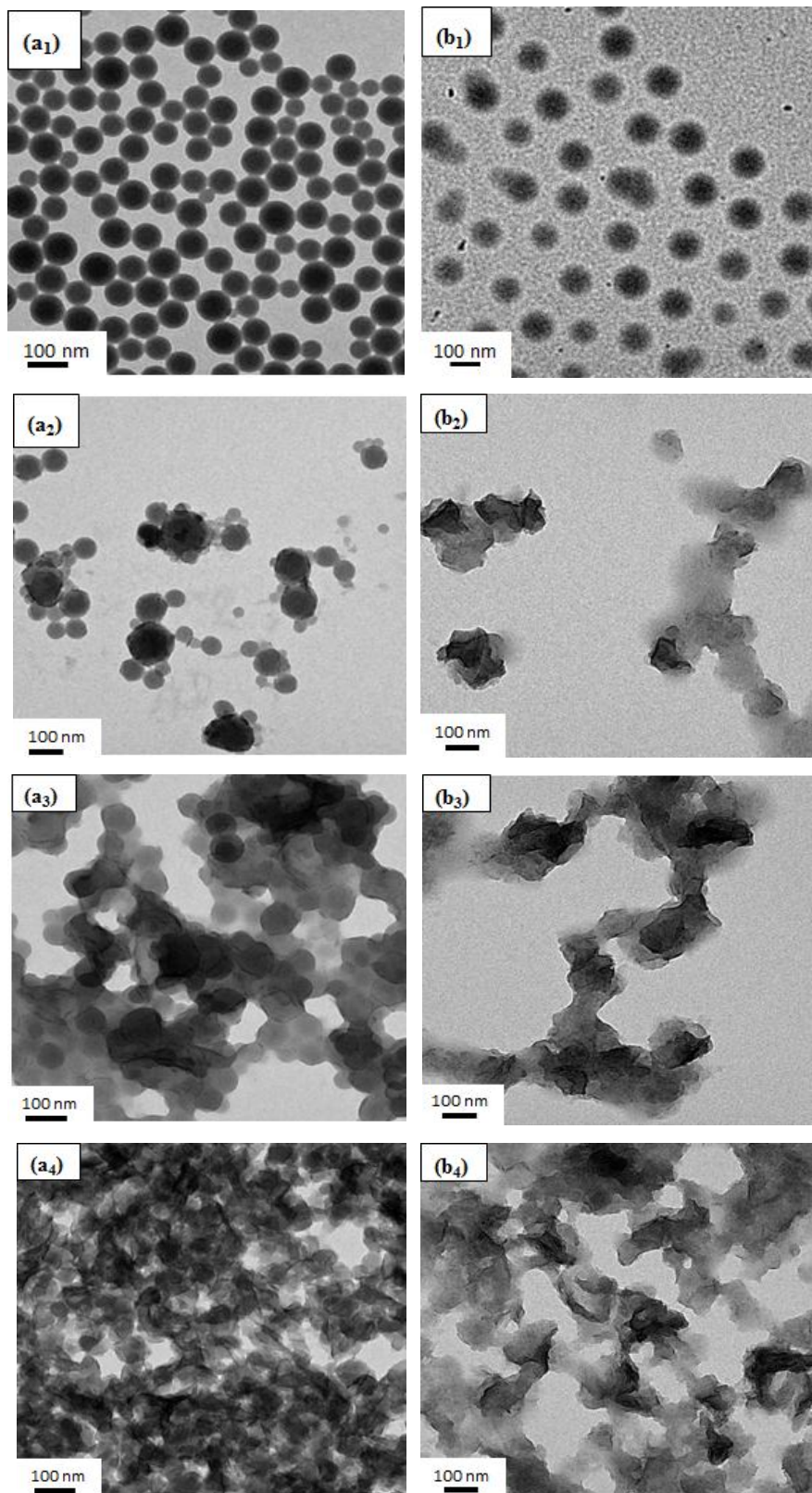


Fig. 4.4: TEM latex images of (a₁) neat PS and its hybrid latexes [(a₂) PS/10 wt% Lap, (a₃) PS/20 wt% Lap, (a₄) PS/50 wt% Lap]; and (b₁) neat PSBA and its hybrid latexes [(b₂) PSBA/10 wt% Lap, (b₃) PSBA/20 wt% Lap, (b₄) PS/50 wt% Lap].

The multimodal distribution composed of smaller particles without clay platelets on the surface (~45 nm), medium sized particles with few clay platelets on the surface (~80 nm) and larger particles incorporating clay platelets both on the surface and encapsulated (~130 nm). When the clay content was increased to 20 wt%, a more even clay platelet distribution in the polymer particles was observed, as seen in Fig. 4.5(a₃). Also the multimodal hybrid particle size distribution seems to disappear despite clay platelets being both encapsulated and attached on the surface. Interestingly, although the polymer particles were substantially aggregated, the individual particles bearing clay platelets were smaller (~ 85 nm) than those observed in latexes with 10 wt% Lap (~130 nm). The distribution of clay platelets in the polymer particles improved with further increase in clay content. TEM pictures show that the polymer particles and the Lap-VBDA effectively merged during the co-sonication step as the amount of clay platelets observed outside polymer particles decreased with increasing clay content. The amount of polymer particles that are completely free of clay was also effectively reduced upon increasing clay content. The polymer particles were found to exhibit mixed morphology, i.e., armoured particles as was obtained with Pickering stabilisation,^{48,49} and encapsulated particles. PS/Lap hybrid particle morphology evolved from predominantly armoured particles at low clay content to predominantly encapsulated particles at high clay content.

When considering the encapsulation of Lap in PSBA, it was found that the spherical shape of neat PSBA (see Fig. 4.4(b₁)) was completely lost upon incorporation of clay even at low clay content. PSBA/Lap hybrid latexes exhibited typical crumbled particle morphology; see Fig. 4.4 (b₂, b₃ and b₄). Crumpled morphology, where the spherical shape of polymer particles is lost, has been reported for polyacrylonitrile particles prepared by heterogeneous polymerisation methods.^{50,51} Polyacrylonitrile is insoluble in its monomer and is highly crystalline, therefore it precipitates out of the monomer droplets during polymerisation. The nanocrystals formed during polymerisation lead to the crumpled morphology. In the current study, the crumpled particle morphology was attributed to the effective encapsulation of rigid clay platelets in the soft copolymer particles. As such, the encapsulation of clay platelets resulted in the loss of spherically shaped particles thus producing the crumpled hybrid nanoparticles. The encapsulation of clay platelets in PSBA polymer particles was facilitated by two factors: firstly, the improved compatibility between Lap-VBDA aggregates and monomer and secondly, the participation of the clay modifier in the polymerisation reaction. Grafting of VBDA⁺ molecules onto Lap surfaces improved the compatibility between the

monomer and the Lap-VBDA, as evidenced from the gel-like paste formed when dried Lap-VBDA was dispersed in the comonomer. The morphological structure of PSBA/Lap hybrid latex remained fairly constant throughout the clay content range studied.

4.3.3.2 Microtomed film morphology

Microtomed film samples of PS/Lap provided evidence for morphological evolution observed in the latexes as well the degree of Lap dispersion within the polymer matrix, as shown in Fig. 4.5. In order to evaluate the degree of clay platelet dispersion within the resultant PCNs, thin films obtained by drying the latex at room temperature followed by microtoming were directly visualised using TEM. Cellular structured morphology was observed for low clay content PS/Lap PCNs (< 30 wt%) which is comparable to morphological structures observed for PCNs produced by Pickering stabilisation.^{1-3,52} The cellular structured morphology is a result of restricted particle inter-diffusion due to clay platelets adhered on the polymer particles.⁵²⁻⁵⁴ However, no cellular structured morphology^{1-3,52} could be observed in high clay content PCNs, an indication that these samples exhibited encapsulated morphology. The high clay content samples exhibited evenly distributed clay platelets throughout the films indicating that the clay platelets were predominantly encapsulated in the polymer particles rather than being adsorbed onto the polymer particle surface of the latex.

PSBA/Lap PCN samples showed similar morphological features throughout the clay content range studied, as shown Fig 4.5 (b₁, b₂, b₃ and b₄). The clay platelets were homogeneously distributed throughout the film. The results indicate that the clay platelets were encapsulated in the polymer particles in the original latex. Had the clay platelets been adhered onto the polymer particle surface, then cellular structured morphology would have been observed as was observed for PS/Lap PCNs.

SAXS studies conducted on the PCNs gave crucial information on the extent of clay delamination of Lap within the polymer material. Fig. 4.6 shows the SAXS spectra of PS/Lap and PSBA/Lap PCNs. The Lap-VBDA exhibited an intense scattering peak whose maximum q value was at 4.36 nm^{-1} , corresponding to d -spacing of 1.44 nm. However, the intensity of the peak decreased significantly in both PCN systems indicating that significant clay delamination took place during the polymerisation process.

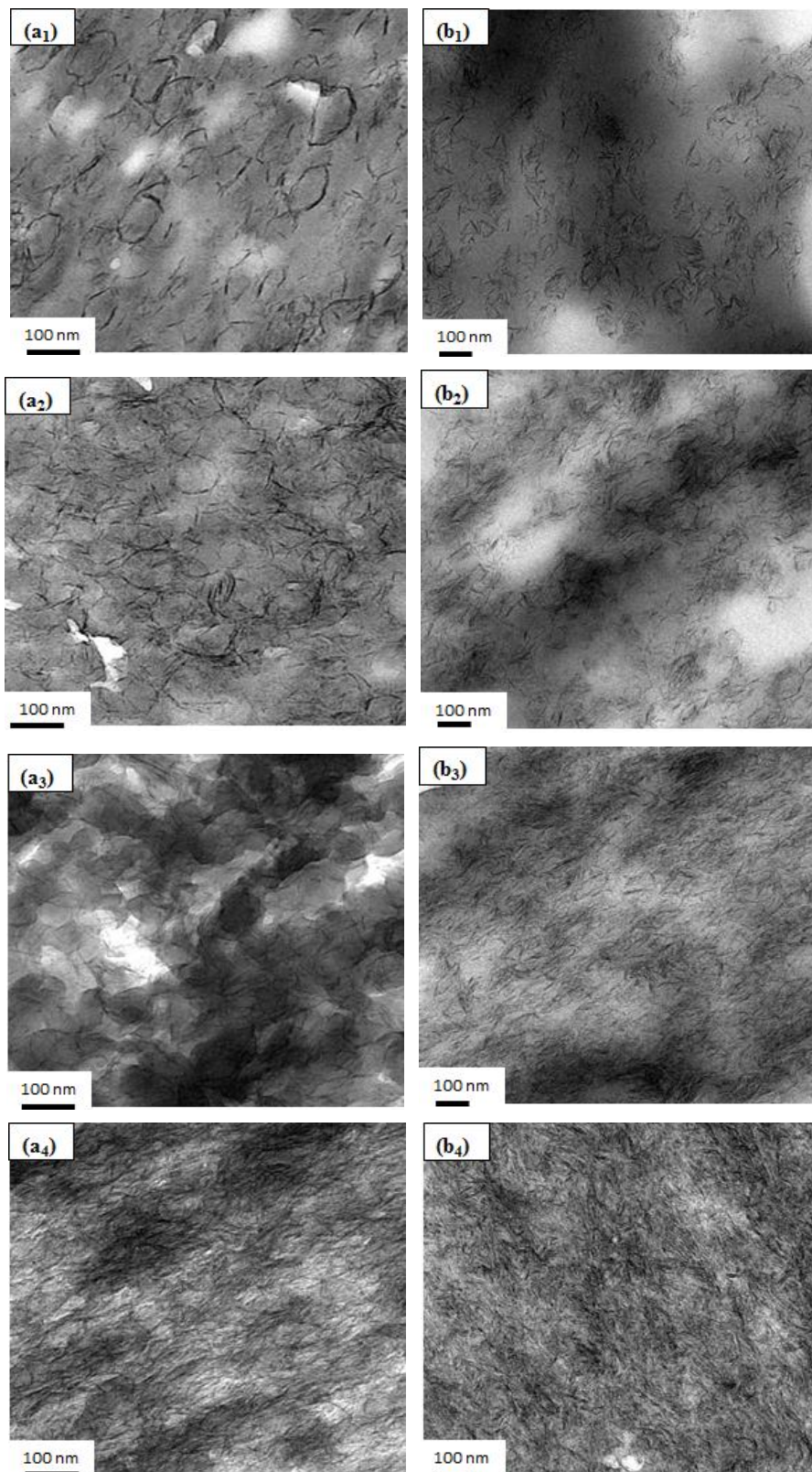


Fig. 4.5: TEM images of microtomed PS/Lap PCN films [(a₁) 10 wt% Lap, (a₂) 20% Lap, (a₃) 30 wt% Lap and (a₄) 50 wt% Lap](Scale bar - 50 nm) and PSBA PCN films [(b₁) 10 wt% Lap, (b₂) 20 wt% Lap, (b₃) 30 wt% Lap, (b₄) 50 wt% Lap (Scale bar - 100nm).

Within the PCN series, the scattering peak intensity increased with increasing clay content but it remained significantly lower than that of Lap-VBDA. This was due to the decreased extent of exfoliation with increasing clay content. As such it was concluded that the morphology of the PCNs moved from fully exfoliated at low clay content towards partially exfoliated at high clay content.

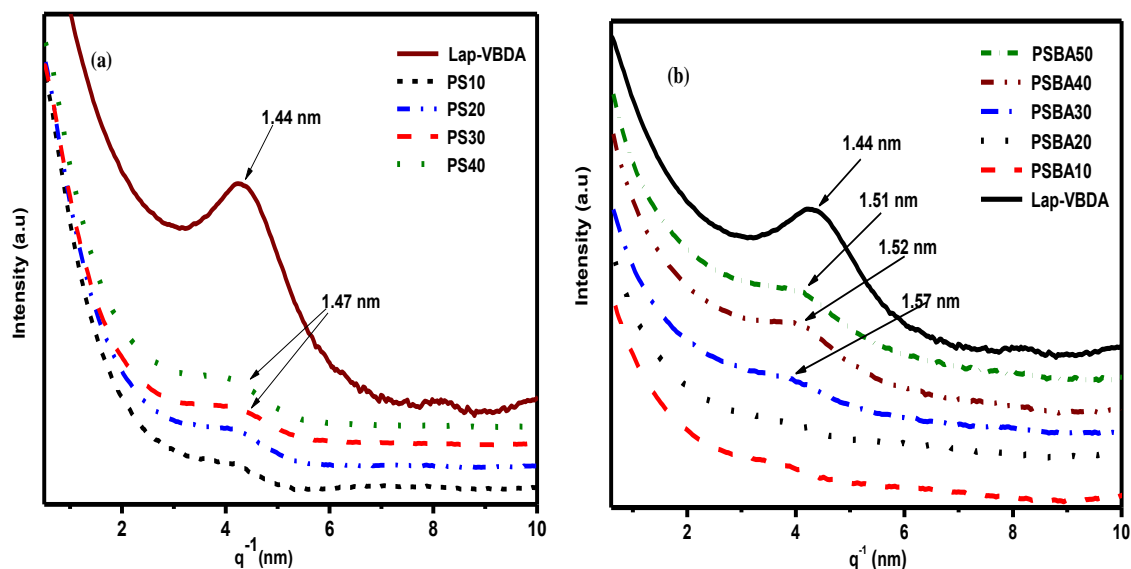


Fig. 4.6: SAXS spectra of different (a) PS/Lap and (b) PSBA/Lap PCNs

4.4 Conclusion

The use of ad-mini-emulsion polymerisation technique was found to be an effective method to prepare PCNs with as high as 50 wt% Lap clay content. The key to this method was found in the use of never-dried modified clay paste rather than the conventional powder form of modified clay. Notably, the method effectively encapsulated ultrahigh clay content, typically > 20 wt%, irrespective of the monomer/polymer used. However, at low clay content encapsulation was dependent on the polymer used, with PS based hybrids exhibiting armoured particle morphology while PSBA based hybrids exhibiting encapsulated morphology. The result suggests that BA could be enhancing monomer/clay interaction by interacting with the hydroxyl groups of the clay platelets. Despite the effective encapsulation and incorporation of clay in large quantities, monomer-to-polymer conversion remained high throughout the clay content range studied. Furthermore, the resultant PCNs exhibited partially exfoliated morphology, irrespective of the clay content.

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Chapter 5**Physical Properties of Polymer/Clay Nanocomposites Prepared by Ad-
miniemulsion Polymerisation****5.1 Introduction**

The incorporation of inorganic materials leads to hybrid materials. The motivation for this approach stems from reasons such as protecting the environment from the encapsulated/incorporated inorganic material, protecting the incorporated material from the environment and property improvement. Interest in polymer clay nanocomposites (PCNs), necessitated by the need to improve properties of polymers grew exponentially within the last twenty years.¹⁻²¹ It was the discovery of superior physical properties of nylon/clay nanocomposites, relative to neat nylon, by the Toyota research group²² in the early 1990s that sparked the growth in PCNs interest among many academic and industrial researchers. Superior properties can be achieved by incorporating as low as 1 wt% clay content in the polymer. Properties that have been investigated include; thermal, dynamic, rheological, flame retardancy and barrier properties. These improvements are generally attributed to the clay's platelet nature and its high aspect ratio.

PCNs have shown superior thermal stability properties over their corresponding neat polymers.^{7,23-27} Such improvement in thermal stability is understood to be a result of the charring effect of clay and delayed diffusing of gaseous products brought about by the tortuous path effect imparted by the platelets.²⁸ Although the extent of clay delamination affects the thermal stability improvement, it remains a debatable comparison between exfoliation and intercalated structure. Some researchers argue that the exfoliated structure affords higher thermal stability improvements than the intercalated structure.^{5,29,30} On the contrary other researchers have reported that the intercalated structure results in higher thermal stability improvement than the exfoliated structure.^{3,28,31} The amount of clay has also been found to contribute to the thermal stability properties. An increasing thermal stability improvement is usually reported with increasing clay content.³¹⁻³³ However, threshold clay content values have also been reported, beyond which either no further improvement or a decrease in thermal stability is actually observed.^{32,34}

The storage modulus, damping factor and glass transition temperature of polymeric materials has been reported to be influenced by the incorporation of clay platelets. The general trend is

that the incorporation of clay platelets in polymeric materials results in increased storage modulus values. Storage modulus improvement is strongly dependent on clay content and polymer-clay interactions. Storage modulus generally increases monotonically with increasing clay content.^{32,35-37} The stronger polymer-clay interactions result in PCNs exhibiting higher storage modulus values compared to the corresponding neat polymer. As such, it would be worthwhile to employ reactive clay modifiers that enhance polymer-clay interactions necessary for storage modulus improvements. Furthermore, complete exfoliation of clay results in large surface area of the clay platelets, thus offering higher storage modulus increase than in intercalated PCN structures.^{5,38} On the other hand there is no general consensus on the effect of clay platelets on glass transition temperature (T_g) of polymers. Some have reported an increasing T_g trend with increasing clay content^{4,6,13,18} while some have reported a decreasing trend in T_g with increasing clay content.^{7,8,39} Still, there are also reports where the T_g of the polymer remains unaffected by the incorporation of the clay platelets.^{15,40} Increase in T_g with incorporation of clay platelets is mainly attributed to the polymer-clay interactions which restrict the long range molecular motions.^{4,6} On the other hand, the decrease in T_g is associated with plasticisation brought about by the clay modifiers used and the low molecular weight polymer chains.⁴¹ The characteristic feature of the damping factor peak of PCNs relative to the neat polymer is a decreasing intensity of the $\tan(\delta)$ peak associated with T_g .^{24,32} Such behaviour has been attributed to the restricted molecular motions due to the presence of the rigid clay platelets.^{24,32} Some researchers have also reported a shifting of the $\tan(\delta)$ peak to higher temperatures, with the incorporation of clay, which can be regarded as an indication of T_g shifting to higher temperatures.^{18,42,43}

The melt flow properties of PCNs have yielded valuable information regarding their time dependence viscoelastic behaviour and the extent of clay dispersion. Melt state frequency sweep measurements provide information on the dependence of properties like storage modulus and complex viscosity on angular frequency. PCNs generally show a typical shear thinning behaviour with increasing angular frequency,^{44,45} as well as monotonic increase in storage modulus with increasing clay content. Such increments in storage modulus values in the molten state indicate a material exhibiting improved processing.⁴⁶ Melt rheology analysis can also be used to evaluate the extent of clay dispersion within the polymer matrix.^{47,48} Furthermore, the storage modulus plots of PCNs may indicate a terminal plateau. Such a plateau is understood to be an indication of percolation threshold clay content. The

percolation threshold is the clay content whereby a 3D network structure begins to form within the materials.^{15,44}

Other properties that have seen improvement as a result of clay incorporation include barrier properties and flame retardancy.³ Clay platelets contribute to flame retardancy improvement in a similar way as discussed for the thermal stability. On the other hand, the impermeable nature of platelets to penetrants and their platelets nature have been attributed to improvements observed in barrier properties. The clay platelets are generally understood to induce a tortuous path effect to the diffusing molecules. This leads to reduced diffusion and permeability coefficients, hence PCNs exhibit better barrier properties than the corresponding neat polymers.⁴⁹⁻⁵⁵

The current study focuses on the evaluation of the physical properties of PCNs (polystyrene/Lap and poly(styrene-co-butyl acrylate)/Lap) prepared via ad-mini-emulsion polymerisation technique as described in Chapter 4. These PCNs are characteristic highly filled PCNs, containing > 10 wt%, thus the current study aims to evaluate the effect of clay content on physical properties at ultrahigh loadings. Properties evaluated in the current study include thermal stability, thermomechanical properties and rheological properties.

5.2 Experimental

5.2.1 Materials

Polystyrene/Laponite (PS/Lap) and poly(styrene-co-butyl acrylate)/Laponite (PSBA/Lap) whose preparation is detailed in Chapter 4 were used in the current study.

5.2.2 Analyses

5.2.2.1 Dynamic mechanical analysis

Dynamic mechanical analysis (DMA), was used to determine the storage modulus (G'), loss modulus (G'') and $\tan(\delta)$ of the PCNs. It was carried out using a Physica MCR 501 rotational rheometer (Anton Paar, Germany) in oscillatory mode. Analyses of PS/Lap and PSBA/Lap were performed in the temperature range from 165 °C to 20 °C and 140 °C to -10 °C, respectively. All tests were conducted under 0.1% deformation and 15 N normal force with an oscillatory frequency of 1 Hz. Prior to the analysis, samples were moulded into disk shaped films by compression at 150 °C and 100 °C for PS/Lap and PSBA/Lap, respectively. However, PSBA00 and PSBA10 were prepared by casting latex onto an aluminium pan. The thickness of all compressed samples was in the range 0.8–1.0 mm.

5.2.2.2 Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to determine the T_g of the PCNs. 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 a standard 10 °C/min. The samples were first subjected to a heating ramp up to 200 °C, after which the temperature was kept isothermal at 200 °C for 5 min to remove thermal history. The cooling cycle from 200 °C to 20 °C for PS/Lap and from 200 °C to -20 °C for PSBA/Lap followed the isothermal stage from which data was recorded.

5.2.2.3 Melt rheology

Frequency sweep measurements were performed using a Physica MCR 501 rotational rheometer (Anton Paar, Germany) in oscillatory mode. The measurements were carried out using an angular frequency range of 300–0.01 s⁻¹. Measurements were conducted at 170 °C under 20 N normal force and at 100 °C under a 10 N normal force for PS/Lap and PSBA/Lap PCNs, respectively. A constant strain of 0.1% and 0.01% was used for PS/Lap and PSBA/Lap PCNs, respectively, which was within their linear viscoelastic (LVE) range. Before conducting the measurements, dried polymer samples were moulded into circular discs by compression at 150 °C and 100 °C for PS/Lap and PSBA/Lap PCNs, respectively. The disc samples were 40 mm in diameter and the sample thickness in the range 0.8–1.2 mm.

5.2.2.4 Thermogravimetric analysis

Thermograms of the dry sample powder were recorded using a Q500 TGA 7 thermogravimetric analyser (Perkin Elmer, U.S.A.). The experiments were carried out under a nitrogen atmosphere. Using a heating rate of 15 °C/min, the temperature was increased from 25 °C to 590 °C.

5.3 Results and Discussion**5.3.2 Thermomechanical properties****5.3.2.1 Storage modulus**

Fig. 5.1 shows the temperature dependence of the storage moduli of PS/Lap and PSBA/Lap PCNs. A monotonic increase in storage modulus was observed for both polymer materials studied with increasing clay content, above T_g . Monotonic increase in storage modulus with the incorporation of clay platelets has been widely reported^{20,21,23,24,35,56,57} and is attributed to strong polymer-clay interactions within the PCN sample.²³ In this study, polymer-clay

interactions were enhanced by the use of a co-polymerisable clay modifier which facilitated crosslinking of polymer chains with clay platelets acting as crosslinking sites. This was evident from the PCNs forming gels in tetrahydrofuran (THF), a conventional solvent for both PS and PSBA. Significant decrease in storage modulus was observed at higher clay content, > 20 wt% for PS/Lap and > 30 wt% for PSBA. PCNs with larger storage modulus increase in the rubbery phase than glassy state have been reported in literature.^{19,21}

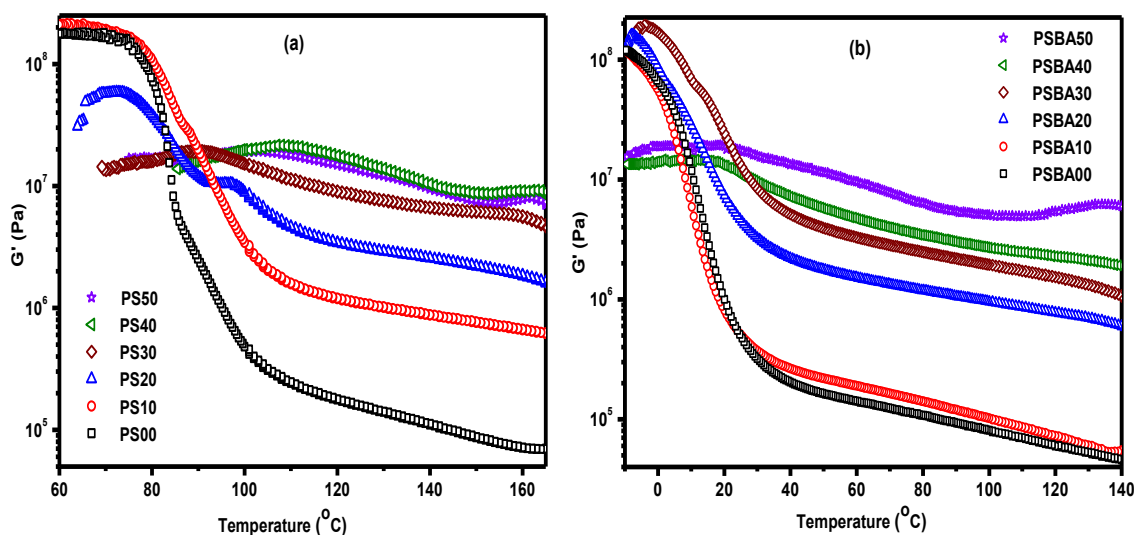


Fig. 5.2: Storage moduli of (a) PS/Lap and (b) PSBA/Lap PCNs.

However, to the best of our knowledge no reports have been made where the storage modulus decreases with clay content in the glassy state for PCNs prepared by conventional free radical polymerisation. The cause of such a decrease is not well understood but could be due to decreasing molecular weight with increasing clay content as was reported from PCNs prepared by controlled free radical polymerisation.^{18,45} In the current study, it was found that the storage modulus of the highly filled PCNs showed a similar trend to that of Lap-VBDA as a function of temperature. Both did not exhibit the typical glass-to-rubbery step that was lost with increasing clay content.

5.3.2.2 Damping factor peak

Fig. 5.3 shows the $\tan(\delta)$ as a function of temperature. The $\tan(\delta)$ plots of PS/Lap PCNs were shifted vertically for clarity's sake. The temperature at the maximum value for the $\tan(\delta)$ peak of PS was found to be 85 °C while that of PSBA was found to be at 17 °C. These peaks are associated with the transition from glassy to rubbery state (T_g) of the polymers. The $\tan(\delta)$ peak intensity decreased with increasing clay content at the same time becoming broader. This is an indication of restricted molecular mobility of the polymer chains.^{24,32} The restricted

molecular mobility could also be accounted for in the observed slight shift of the $\tan(\delta)$ peak to higher temperatures with increasing clay content. The $\tan(\delta)$ peak of PSBA shifted, from 17 °C for the neat copolymer to 21 °C for the PCN with 50 wt% Lap. Interestingly, for both polymer systems the PCNs with high clay content (> 30 wt%) exhibited a second $\tan(\delta)$ peak at temperatures higher than the peak associated with the expected T_g of the polymer matrix. The second $\tan(\delta)$ peak of PSBA/Lap PCNs shifted to higher temperature, at the same time increasing in intensity with increasing clay content. The temperature at the maximum of the second $\tan(\delta)$ was 85 °C and 100 °C for PSBA/40 wt% Lap and PSBA/50 wt% Lap, respectively. The temperature at the maximum of the second $\tan(\delta)$ peak of PS/Lap was ~ 145 °C for both PS/40 wt% Lap and PS/50 wt% Lap. Such a peak has not been reported in low clay PCNs but has been reported in highly filled PCNs^{58,59} and other highly filled inorganic-organic hybrid materials.⁶⁰⁻⁶³

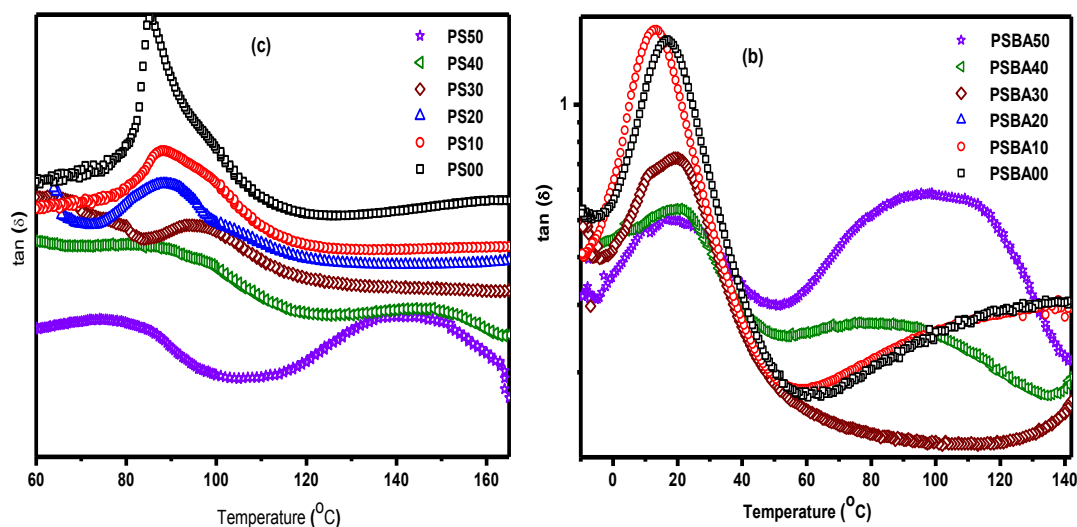


Fig. 5.3: Damping factor profiles of (a) PS/Lap and (b) PSBA/Lap PCNs of varying clay content.

Explanations given in the literature for the second $\tan(\delta)$ peak include melt-like order-disorder transition of adsorbed long alkyl chain of surfactant,⁵⁸ transition of polymer crystallites⁶⁰ and transition of severely mobility-restricted polymer chains near the particles surface.^{62,63} However, recent studies by Robertson and Rackaitis on the transitions in filled polymers showed that the second peak is associated with chain flow relaxation (chain diffusion/reptation)⁶¹ rather than the previously reported causes. These findings are consistent with the current findings and findings reported elsewhere^{21,61} where the second $\tan(\delta)$ peak could not be detected using DSC. As such the second $\tan(\delta)$ peak observed in the current study was attributed to chain flow relaxation of untethered polymer chains intercalated inside the clay galleries.

5.3.2.3 Glass transition temperature

Polymers reinforced with clay have shown different behaviours as far as T_g is concerned. Increase in T_g ,^{4,6,13,18,43,64-66} decrease in T_g ,^{7,8,39} and unchanged T_g ^{15,40} with increasing clay content have all been reported in PCNs. Increase in T_g is associated with increased restrictions in molecular motions due to the strong interactions between polymer chains and clay platelets,^{4,6} while decrease in T_g has been attributed to plasticisation brought by the surfactants.^{41,67} Using DSC measurements, see Fig 5.3, it was found that the T_g of PS/Lap PCNs remained fairly constant at 85 °C with increasing clay content until incorporation of 30 wt% Lap.

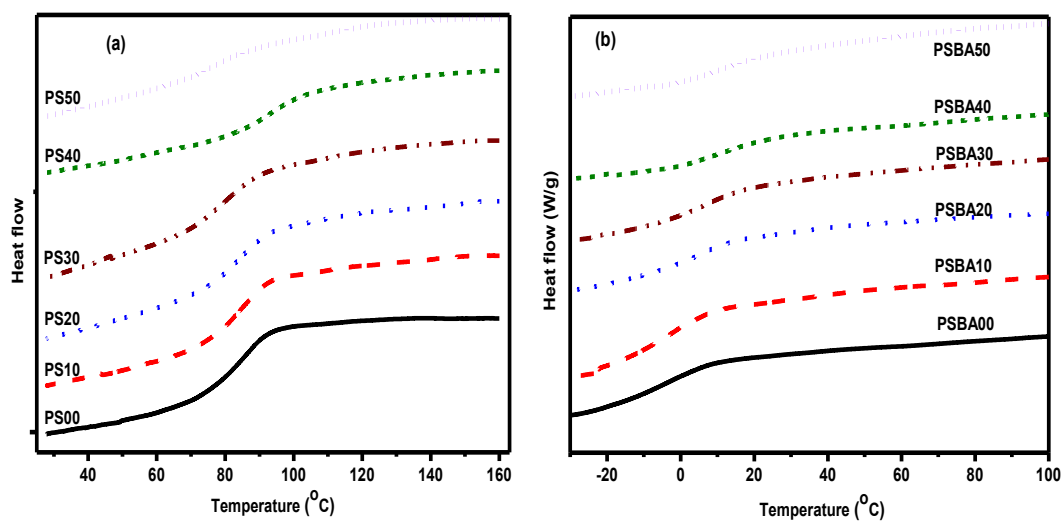


Fig. 5.3: DSC profiles of PS/Lap and PSBA/Lap PCNs of varying clay content.

At higher clay content (≥ 30 wt%), the T_g increased with increasing clay content. The T_g of PS/40 wt% Lap and PS/50 wt% Lap was found to be 94 °C and 98 °C, respectively. This change in behaviour with increasing clay content could be due to contradictory effects between plasticisation by surfactants and short chains and restricted chain mobility as a result of strong polymer-clay interactions. Plasticisation effect therefore dominated in low clay PCNs while restricted chain mobility effect due to polymer-clay interactions dominated in highly filled PCNs. On the other hand, the T_g of PSBA was found to increase with increasing clay content, from -3 °C for the neat PSBA to 11 °C for the PCN with 50 wt% Lap. DSC measurements confirmed that clay incorporation did not have an effect on the copolymerisation of styrene and n-butyl acrylate as one T_g was observed in all the PCN samples studied. ¹H NMR studies showed that the copolymer composition of these PCNs remained fairly constant at 1:1 molar ratio, in agreement with the feed ratio used. (See Appendix 3)

5.3.3 Melt-state linear viscoelastic properties

5.3.3.1 Amplitude sweep

Amplitude sweep test was performed in order to determine the limit of the linear viscoelastic (LVE) range of the PCN samples.⁶⁸ Within the LVE range, the G' values of the material remain constant. Beyond the LVE range, the structural integrity of the material is affected by the irreversible chain scissions taking place, leading to a sudden drop in storage modulus. Fig. 5.4(a) shows the amplitude sweeps of the PS/Lap and PSBA/Lap PCNs.

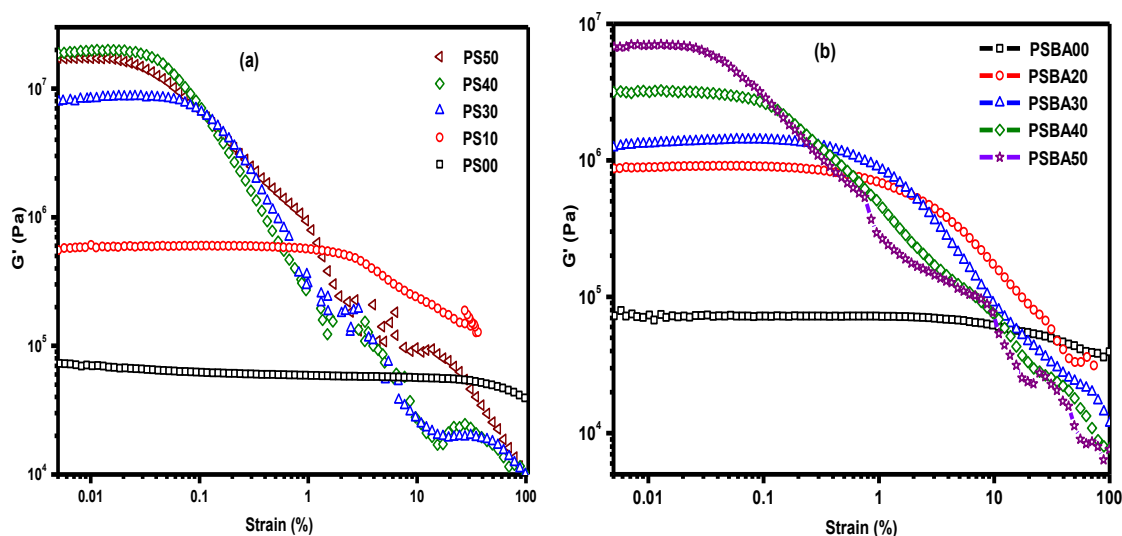


Fig. 5.4: Dynamic storage modulus (G') of (a) PS/Lap PCNs and (b) PSBA/Lap PCNs.

It was found that the LVE limiting value (γ_L) decreased with increasing clay content. For PSBA/Lap PCNs, the γ_L decreased from 4.5% for the neat copolymer to 0.3%, 0.2%, 0.08% and 0.03% amplitude strain for PCNs with 20 wt%, 30 wt%, 40 wt% and 50 wt% Lap content, respectively. At the same time monotonic increase in G' with increasing clay content was observed in both polymer systems. This was consistent with the increase in G' observed under the dynamic mechanical analysis. Such increase in G' values with increasing clay content has been reported for low clay content PCNs and is attributed to polymer-clay interaction.^{44,69,70}

5.3.3.2 Frequency sweep

This is an oscillatory test with variable frequency and constant strain (within the LVE range) which is used to examine the time dependent viscoelastic behaviour of a material.⁶⁸ The high frequencies simulate the short term viscoelastic behaviour while the low frequencies simulate the long term viscoelastic behaviour of the material. The frequency sweep measurements of

all samples were conducted using 0.1% and 0.01% strain at temperature of 150 °C and 100 °C for PS/Lap and PSBA/Lap, respectively. Fig 5.5 shows the angular frequency dependency of the complex viscosity (η^*) of both PS/Lap and PSBA/Lap.

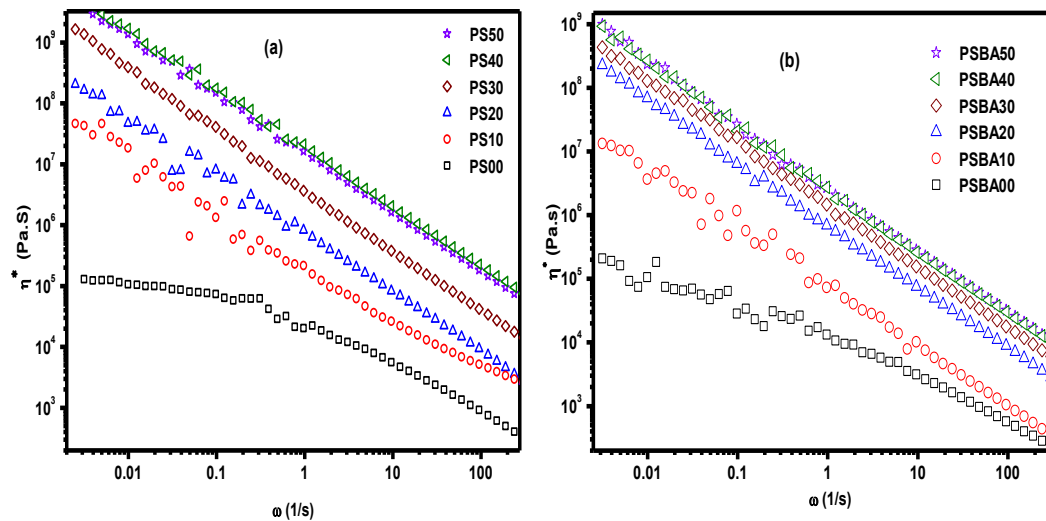


Fig. 5.5: Complex viscosity of (a) PS/Lap PCNs and (b) PSBA/Lap PCNs, as a function of angular frequency.

In both polymer systems, shear thinning behaviour was observed among the samples, as η^* decreased with increasing angular frequency. The shear thinning behaviour increased with increasing clay content. Similar results have also been reported for low clay content PCNs.^{44,45} In the current study, no onset of shear thinning could be observed among the PCNs and the shear thinning behaviour was attributed to the clay's ability to align in the direction of shear with increasing shear.⁷¹⁻⁷⁴ From this finding it can be said that irrespective of the clay content the clay platelets have the ability to align in the direction of shear with increasing shear. Furthermore, it was found that η^* increased monotonically with increasing clay content which could be attributed to enhanced polymer-clay interactions.

Fig. 5.6 shows logarithmic plots of storage and loss moduli of PS/Lap and PSBA/Lap PCNs as a function of angular frequency (ω). The storage modulus of the neat PS and PSBA showed a steady increase with increasing angular frequency. However, all the PCNs exhibited an almost constant G' throughout the frequency range studied due to enhanced polymer-clay interactions thus enhancing material stiffness. The G' values were found to increase monotonically with increasing clay content throughout the angular frequency range as has also been reported for low clay content PCNs.^{44,48,66,74,75}

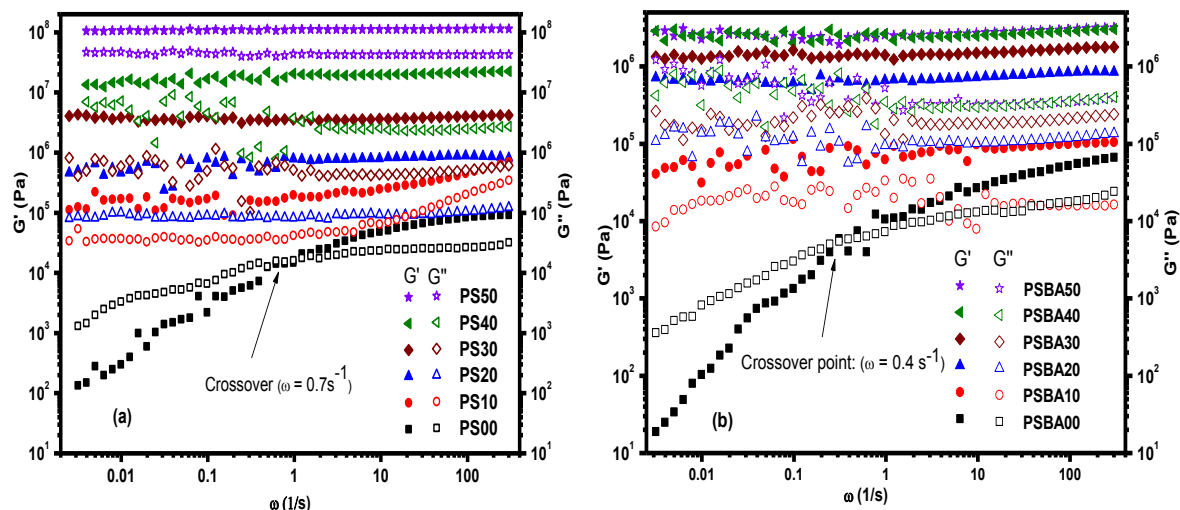


Fig. 5.6: Logarithmic plots of storage and loss moduli of (a) PS/Lap PCNs and (b) PSBA/Lap PCNs as a function of angular frequency.

Usually, for low clay content PCNs (< 10 wt%), there is a clay content value (the percolation threshold value) above which G' values exhibit a plateau at low angular frequency. Such a plateau is attributed to formation of a 3-D network structure as a result of the formation of a percolated microstructure.^{46,48,70,72,76} The constant storage modulus values obtained in the current study showed that the clay content in all PCN samples was above the threshold value. This means the high clay content PCNs acted like solid-like viscoelastic materials throughout the frequency range studied.²⁴

Comparing the G' and G'' values, the neat polymers were found to exhibit a crossover point (where $G' = G''$) at $\omega = 0.7 \text{ s}^{-1}$ and 0.4 s^{-1} for PS/Lap and PSBA/Lap, respectively. Above the crossover point, $G' > G''$, whereas below the crossover frequency, $G' < G''$. This shows that the material shifted from solid-like viscoelastic behaviour at high frequencies to liquid-like viscoelastic behaviour at low frequency.^{45,72} The PCNs, on the other hand, were found to exhibit no crossover point, with G' being higher than G'' . The values for G' and G'' running parallel to each other throughout the frequency range studied is a result of the stiffness imparted into the materials by the crosslinking effect of the clay platelets.^{45,68} This indicates that the PCNs of both polymer systems exhibited solid-like viscoelastic properties through the angular frequency studied.

5.3.4 Thermal stability

Fig. 5.7 shows the TGA thermograms of PS/Lap and PSBA/Lap PCNs. The graphs show the decomposition behaviour of the materials as temperature increased from 100 °C to 590 °C.

The increase in residual weight at 590 °C of the bulk PCNs with increasing clay content was consistent with the amount of clay added during preparation of the latexes, indicating that the PCN preparation method effectively facilitated the incorporation of clay in the polymer. However, as indicated in Table 5.1 the clay content determined by TGA was found to be slightly lower than the nominal clay content.

Table 5.1: Summary of physical properties of PS/Lap and PSBA/Lap PCNs

Sample	Clay content (%)		Thermal characteristics			Thermomechanical properties	
	Nominal	Actual ^(a)	T _{onset} ^(b) (°C)	T ₆₀ ^(c) (°C)	T _{ROI-onset} ^(d) (°C)	G' (GPa) ^(e)	T _g (°C) ^(f)
PS00	-	-	405	418	401	0.11	85.0
PS10	10.0	10.4	412	428	403	0.89	85.0
PS20	20.0	20.3	408	424	403	2.56	85.0
PS30	30.0	27.3	407	426	404	6.57	85.0
PS40	40.0	35.4	408	426	405	9.50	94.0
PS50	50.0	43.4	408	431	402	10.5	98.0
PSBA00	-	-	389	405	390	0.09	-3.00
PSBA10	10.0	11.0	390	405	389	0.10	-2.00
PSBA20	20.0	23.0	369	395	388	0.94	6.00
PSBA30	30.0	26.0	369	395	390	1.90	9.00
PSBA40	40.0	39.7	368	395	389	2.60	12.0
PSBA50	50.0	48.3	369	403	391	5.00	11.0

^(a)Residual weight at 590 °C, ^(b)Onset temperature of decomposition, ^(c)Temperature at 40% weight loss, ^(d)Onset temperature of degradation of polymer recovered by reverse ion exchange, ^(e)Storage modulus at 140 °C and 100 °C for PS/Lap and PSBA/Lap respectively, ^(f)From DSC.

Such differences could be due to the inherent error in the estimation of the clay content in Lap-VBDA paste used in the early stages of the preparation. Regarding thermal stability, the clay platelets act as a mass transport barriers and insulators between the polymer and the decomposing zone and secondly create a tortuous path for the gaseous products of the decomposition.^{6,28} Based on the onset temperature of decomposition and temperature at 40% residual weight (T₆₀), no thermal stability improvement was observed for PS/Lap PCNs

relative to the neat PS. However, a slight decrease in onset temperature of decomposition was observed for PSBA PCNs with more than 20 wt% Lap.

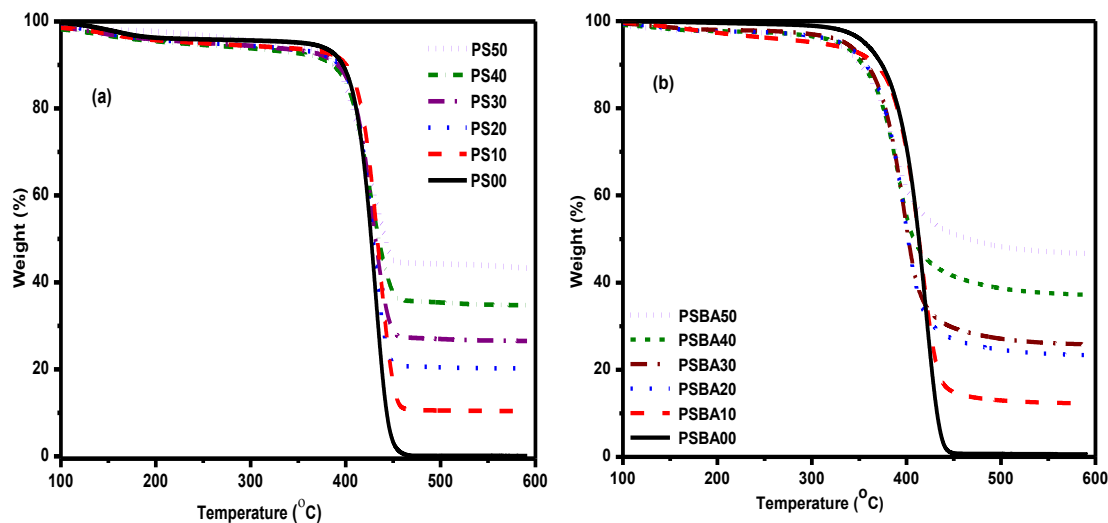


Fig. 5.7: TGA Thermograms of (a) PS/Lap PCNs and (b) PSBA/Lap PCNs.

No change in thermal stability was observed between thermograms of PS recovered from the PCNs by reverse ion exchange, (see Appendix 4) however the decomposition step around 200 °C observed in these thermograms was attributed to the decomposition of alkyl chain branches from the VBDA copolymerised in polystyrene backbone. As such this decomposition step increased with increasing clay content, an indication that the alkyl branches increased with increasing clay content

5.4 Conclusion

The highly filled PCNs prepared by the ad-mini-emulsion polymerisation technique generally exhibited superior physical properties over their corresponding neat polymers. The enhanced polymer-clay interactions brought about by the use of a polymerisable modifier contributed significantly to the properties improvement observed in PCNs relative to neat polymers. As much as 5000% increase in storage modulus was observed in PCNs with the highest clay content relative to the neat polymer. Furthermore, a general increase in T_g with increasing clay content, due to reduced molecular mobility of polymer chains, was observed. The reduced molecular mobility was also evident from the decrease in intensity of the $\tan(\delta)$ peak associated with T_g as a function of clay content. The highly filled PCNs (> 30 wt% Lap) exhibited an additional $\tan(\delta)$ peak as a result of the flow relaxation of untethered polymer chains intercalated within the clay galleries. The high clay content together with enhanced polymer-clay interaction resulted in PCNs exhibited typical solid-like viscoelastic properties

as evidenced from linear viscoelastic melt-rheology tests. Storage modulus values remained higher than the loss modulus values through the angular frequency range studied. Melt rheology tests also showed that the clay platelets are able to align in the direction of shear with increasing shear, even at high clay content. This was confirmed by the shear thinning behaviour of the PCNs as a function of increasing angular frequency. However, the incorporation of clay in polymer at such high concentrations did not improve the thermal stability of the material. This was indicated by the unchanging onset temperature of decomposition, irrespective of increasing clay content.

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Chapter 6

Water Based Polystyrene/MMT Nanocomposites Prepared by Ad-miniemulsion Polymerisation

6.1 Introduction

Montmorillonite (MMT) is natural clay belonging to the smectite group of clays. It remains one of the predominantly used clay in reinforcing a wide range of polymers.¹⁻¹⁴ Because of its platelet structure, MMT has a high aspect ratio, as such PCN materials made from this clay exhibit superior properties than the corresponding neat polymer. This has contributed to its extensive use in PCN preparation. Another contributing factor to its use is its lower cost compared to synthetic clay such as Laponite (Lap). Methods such as melt intercalation, solution and in-situ intercalative polymerisation can be used to incorporate MMT and other clay types in polymeric materials. The in-situ intercalative polymerisation is a versatile technique that is compatible with most of the available polymerisation methods. The use of the in-situ intercalative technique in heterogeneous polymerisation methods such as emulsion or miniemulsion allows for the preparation of polymer/clay hybrid latexes.

Despite its extensive use, incorporation of high MMT contents in polymer materials using direct miniemulsion polymerisation remains a challenge due to its large size. The encapsulation of MMT remains limited below 5 wt% clay content.¹⁵⁻¹⁷ Tong and Deng demonstrated that the size of clay platelets plays an important role in its encapsulation.^{18,19} They reported that MMT could not be effectively encapsulated in polymer particles using conventional miniemulsion technique due to its large size but saponite of small size was effectively encapsulated. Moraes *et al.*²⁰ summarized the possible latex morphologies attainable when clays of different sizes are encapsulated in polymer particles using miniemulsion. They reported that the MMT clay platelets result in unstable latex and their encapsulation in the polymer particles is largely ineffective.

In Chapter 4 the encapsulation of Lap clay using a modified miniemulsion polymerisation method (ad-miniemulsion) was described. It was demonstrated that the ad-miniemulsion polymerisation method can be used effectively to incorporate and encapsulate up to 50 wt% Lap in both PS and PSBA polymer particles. The current study aims at extending the use of ad-miniemulsion polymerisation in an effort to incorporate MMT platelets in polystyrene particles. A relatively similar procedure as the one used for PS/Lap hybrid latexes (refer to

Chapter 4) was followed in this study. The objective of the current study was to incorporate high MMT contents in PS particles and study the latex morphology, platelet delamination and the physical properties of resultant PCNs relative to the neat polymer.

6.2 Experimental

6.2.1 Materials

Styrene (99%) was supplied by Sigma-Aldrich and was washed with 0.3 M potassium hydroxide (KOH) aqueous solution. The washed styrene was then washed with deionised water, followed by distillation at 40 °C under reduced pressure to remove the inhibitor. Azobisisobutyronitrile (AIBN) was supplied by Sigma-Aldrich and purified by recrystallisation from methanol. Montmorillonite (MMT), with 116 mequiv/100g CEC was supplied by Rockwood Additives Limited, U.K. Sodium dodecyl sulphate (SDS, 99%), 4-vinylbenzyl chloride (99%), N,N dimethyldodecylamine (99%), hexadecane (HD, 99%) and silver nitrate were supplied by Sigma-Aldrich and were used as received. Vinylbenzyl dodecyl dimethyl ammonium chloride (VBDAC) was synthesised using a method reported elsewhere²¹ and its structure was confirmed by ¹H NMR (see Appendix 1). VBDAC was chosen for this study due to its ability to copolymerise with styrene²² and its ability to improve compatibility between the styrene monomer and the modified clay.²³

6.2.2 Preparation of polystyrene/MMT hybrids

The hybrid latexes were prepared using ad-mini emulsion polymerisation as has been detailed in Chapter 4. The monomer mini emulsion formulation used in this study was similar to the one used for Laponite (Lap) based PCNs (refer to Section 4.2.3.2). However, for the MMT dispersion 30 mM SDS solution and 20 min sonication were used. Although the overall formulation and procedure used in this study was similar to that of Lap based PCNs, the total solids content for the MMT based PCNs was 10% (see Appendix 2 for the formulations of PS/MMT hybrids).

6.2.3 Analyses

The latex and film morphologies of the PCNs were analysed using TEM and SAXS. The procedures for these analyses were outlined in Sections 4.2.4.1 and 4.2.4.5, respectively. The extent of modification was qualitatively evaluated using FTIR and the amount of grafted modifier was quantitatively determined using TGA. TGA was also used to evaluate the thermal stability and to quantify the amount of clay incorporated in the hybrid latexes. The

PCNs' thermomechanical properties were determined by dynamic mechanical analysis whereas the T_g was determined using DSC. The conditions of analyses used in this study were similar to those of PS/Lap PCNs. The procedures for the analyses were outlined in Sections 5.2.2.1 – 5.2.2.4.

6.3 Results and discussion

6.3.1 Modification of MMT

The modification of MMT with VBDA was qualitatively confirmed by FTIR and the amount of grafted VBDA was quantified using TGA. Fig. 6.1 shows the FTIR spectra and the TGA thermograms of the unmodified MMT, MMT modified with VBDA (MMT-VBDA) and VBDA.

The FTIR spectrum of MMT-VBDA shows bands which could be traced to both MMT and VBDA. The MMT-VBDA bands at 3600, 1641, 1469 and 1040 cm^{-1} corresponded to bands from MMT while those at 2925, 2852 and 1469 cm^{-1} could be traced to VBDA. This qualitatively confirmed that the VBDA⁺ molecules were successfully grafted onto the clay platelets. In order to complement the FTIR results, TGA was used to quantify the amount of VBDA⁺ grafted onto the clay platelets using Equation 3.1 (refer to Section 3.3.1). The amount of the grafted modifier was found to be 0.104 mol/100g which is equivalent to 85% of the available exchangeable sites of MMT. Given that the VBDAC is cationic in nature, it is reasonable to consider the modifier as being attached to the clay surfaces via the cationic headgroup, based on the FTIR and TGA results.

Figure 6.1(c) shows the SAXS spectra of MMT and the corresponding MMT-VBDA (before and after drying). As expected, the grafting of VBDA⁺ onto MMT surfaces caused an increase in the d-spacing of MMT from 1.25 nm to 2.94 nm before drying the MMT-VBDA. Upon drying the MMT-VBDA, it was found that the d-spacing decreased from 2.94 to 2.22 nm. This indicates that the water molecules trapped between the modified clay platelets after centrifugation were responsible for the larger d-spacing of the wet MMT-VBDA compared to the dried MMT-VBDA. Therefore, desorption of water molecules by vacuum drying resulted in the observed decrease in d-spacing values upon drying the MMT-VBDA. Stable latexes could be obtained using wet MMT-VBDA instead of using the dried MMT-VBDA. This was attributed to the ease with which wet MMT-VBDA aggregates were broken down into smaller aggregates by the sonication process. It was suggested that the trapped water

molecules weakened the face-to-face attraction between the MMT platelets of wet MMT-VBDA.

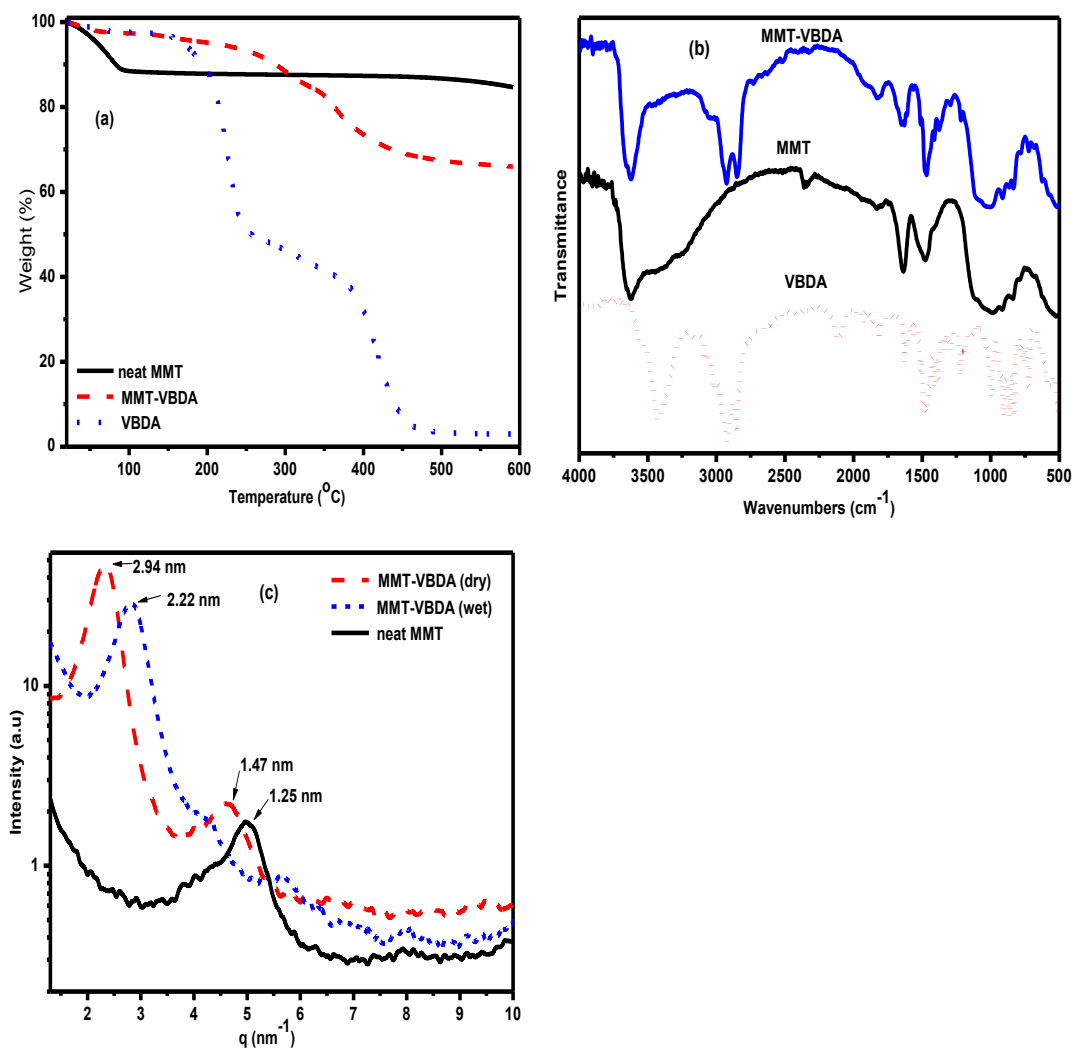


Fig. 6.1: (a) TGA thermograms and (b) FTIR spectra of MMT, VBDA and modified MMT and (c) the SAXS profile of MMT, MMT-VBDA paste, MMT-VBDA dried powder.

6.3.2 Polystyrene/MMT hybrid latex

The monomer-to-polymer conversion of PS/MMT hybrids was monitored as a function of polymerisation time using gravimetric method. Although a decrease in conversion was observed upon the incorporation of clay, conversion remained high (> 80%) throughout the clay content range. The decrease in conversion observed in hybrid latexes relative to the neat polymer could be due to a decrease in monomer translational diffusion as a result of increased local viscosity with increasing conversion.²⁴ The decrease in conversion with the incorporation of clay content was in agreement with other literature reports.^{17,18,25,26} The relatively high conversion observed in the current study could be attributed to possible radical and monomer compartmentalisation within the clay platelets galleries. At the same time,

compatibility between the modified clay and the monomer facilitated intercalation of monomer in clay galleries. The average polymer particle size, determined from TEM images, was found to increase with increasing clay content. However, the average particle sizes of hybrid materials remained lower than that of the neat PS. The increasing particle size was attributed to decreasing free SDS molecules as increasing clay concentration adsorbed SDS during the formation of the admicelle layer.

Table 6.1: Characteristic properties of the PSMMT/hybrid latexes of different clay content

Sample	Conversion	Particle size ^(a)	Clay content ^(b)	Latex morphology
PS00	95	80	0.0	-
PS10MMT	90	55	12	Armoured
PS20MMT	89	55	17	Armoured
PS30MMT	88	66	27	Armoured
PS40MMT	86	70	34	Armoured
PS50MMT	88	75	41	Armoured

^(a)Estimated from TEM images, ^(b)Residual weight at 590 °C

6.3.3 Morphological properties

Fig. 6.2 shows the TEM images of PS/MMT hybrid latexes of varying MMT content. Neat PS and low clay content PCNs, < 30 wt%, exhibited predominantly spherical nanoparticles. The TEM images showed that the MMT platelets of the hybrid latexes were predominantly adhered onto the polymer particles surfaces rather than being encapsulated. At higher MMT content (> 20 wt%) the spherical shape of PS particles was gradually lost with increasing MMT content, refer to Appendix 5 for the low magnification TEM images. Highly filled hybrid latexes exhibited non-spherical armoured particle morphology. It appears this change in particle shape was influenced by the clay platelets adhered onto the particles surface.

Based on estimations from TEM images, the average particle sizes of PS10MMT and PS20MMT hybrid latexes were found to be ~55 nm, which was lower than that of neat PS (80 nm). This was attributed mainly to the differences in SDS concentrations between neat PS (10 mM) and the hybrid latexes (30 mM). The higher SDS concentration used in hybrid latexes was intended to stabilise the MMT-VBDA aqueous dispersion. Separate tests on conditions necessary to stabilise MMT-VBDA dispersion showed that 30 mM concentration

was the minimal concentration that could stabilise the MMT-VBDA dispersion in order to obtain a stable PS50MMT hybrid.

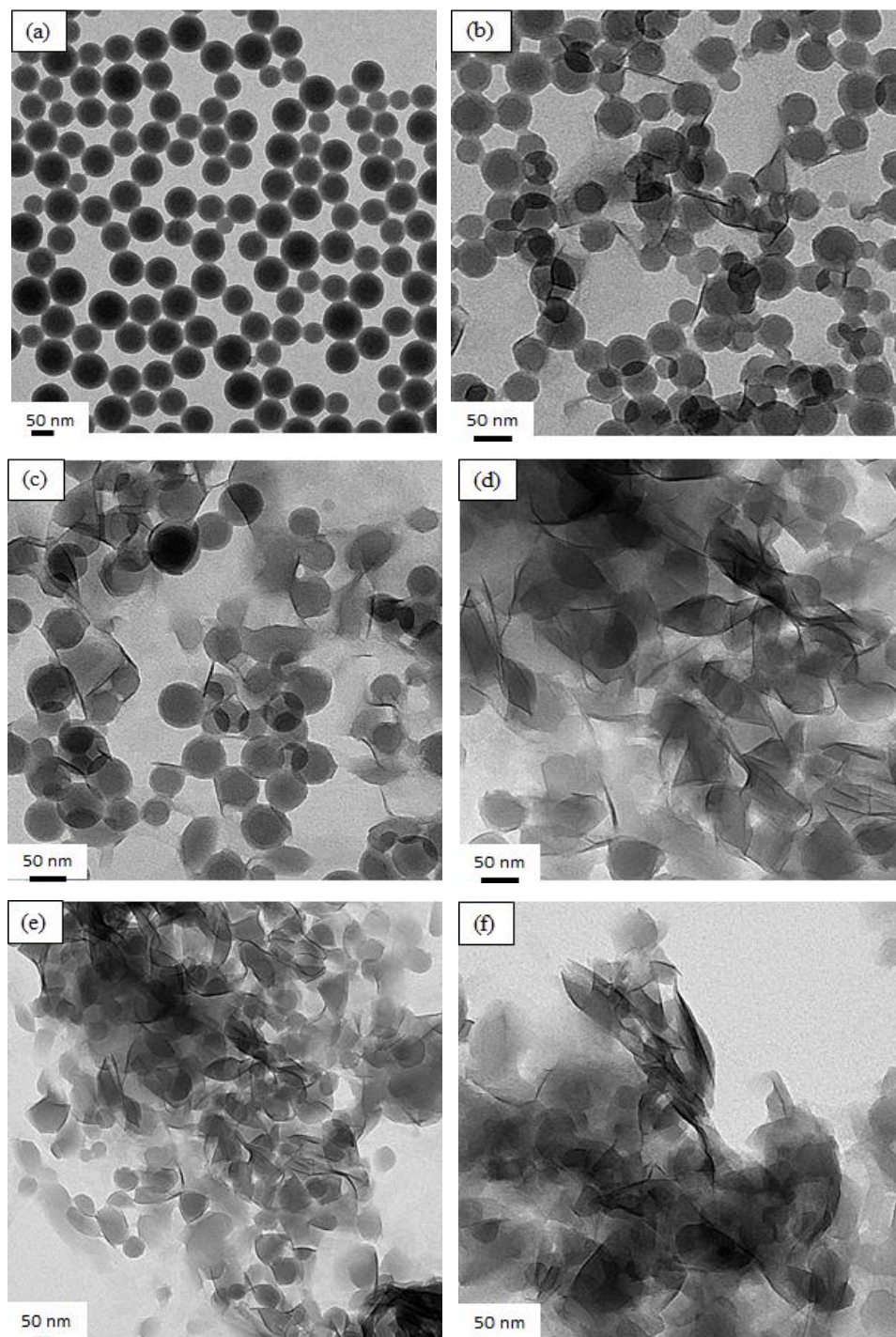


Fig. 6.2 TEM images of latexes of PS/MMT PCNs of different clay content, (a) PS, (b) PS/10MMT, (c) PS/20MMT, (d) PS/30MMT, (e) PS/40MMT and (f) PS/50MMT.

However, the observed increase in particles size with increasing clay content suggests that free SDS molecules were present at low clay content and their concentration decreased with increasing clay content. The decreasing SDS concentration can be attributed to admicelle

formation on modified clay surfaces. The average particles sizes of polymer particles during miniemulsion or emulsion polymerisation are usually affected by the concentration of SDS.²⁷ A systematic increase in average particle size of the latexes with increasing MMT content from 55 nm for PS/10MMT to 75 nm for PS/50MMT was observed.

Despite the increasing average particle size with increasing clay content, the clay platelets remained attached onto polymer particle surfaces throughout the clay content range studied. The ineffective encapsulation of MMT observed in this study could be a result of the larger platelet dimensions of the MMT clay compared to the polymer particles. The average platelet length was found to be ~80 nm, which was always greater than the average polymer particles (55–75 nm, depending on clay content). This finding is in agreement with other literature reports where the clay platelet dimensions were reportedly found to affect the effective encapsulation and latex morphology.^{18,20} At the same time, significant aggregation was evident from the TEM image with increasing MMT content. This was evident from the TEM images and was attributed to ineffective breakdown of MMT-VBDA aggregates during the preparation of MMT-VBDA aqueous dispersion. Despite the particle aggregation observed and the ineffective encapsulation, no sedimentation was observed in PS/MMT hybrid latexes. Furthermore, the coagulum in these latexes remained less than 10%, an indication that the latexes were stable.

TEM was also used to study the distribution of the clay platelets within the polymer/clay nanocomposite. The PS/MMT hybrid latexes were first dried at room temperature. The dried latex samples were embedded in epoxy resin before microtoming them into 100 nm thick slices which were imaged using TEM. Fig. 6.4 shows the TEM images with PS/MMT PCNs of varying clay content. Delaminated clay platelets showed that insignificant platelet aggregation of tactoids was observed in these samples. Only at very high clay content (i.e. 50 wt%) could uneven distribution (platelet aggregation) be observed. Although the armoured particle morphology was the predominant latex morphology of these materials, no cellular structured morphology was observed in the films. The cellular structured morphology is typical for films obtained from latexes exhibiting armoured nanoparticles.²⁸⁻³¹ The homogeneous distribution of MMT platelets within the material was in agreement with previous reports on PCNs obtained from clay modified with VBDAC.^{22,23,32-34} The use of a polymerisable modifier, VBDAC, which results in improved compatibility between MMT-

VBDA and styrene monomer promotes intercalation of the monomer within the platelet galleries prior to polymerisation.

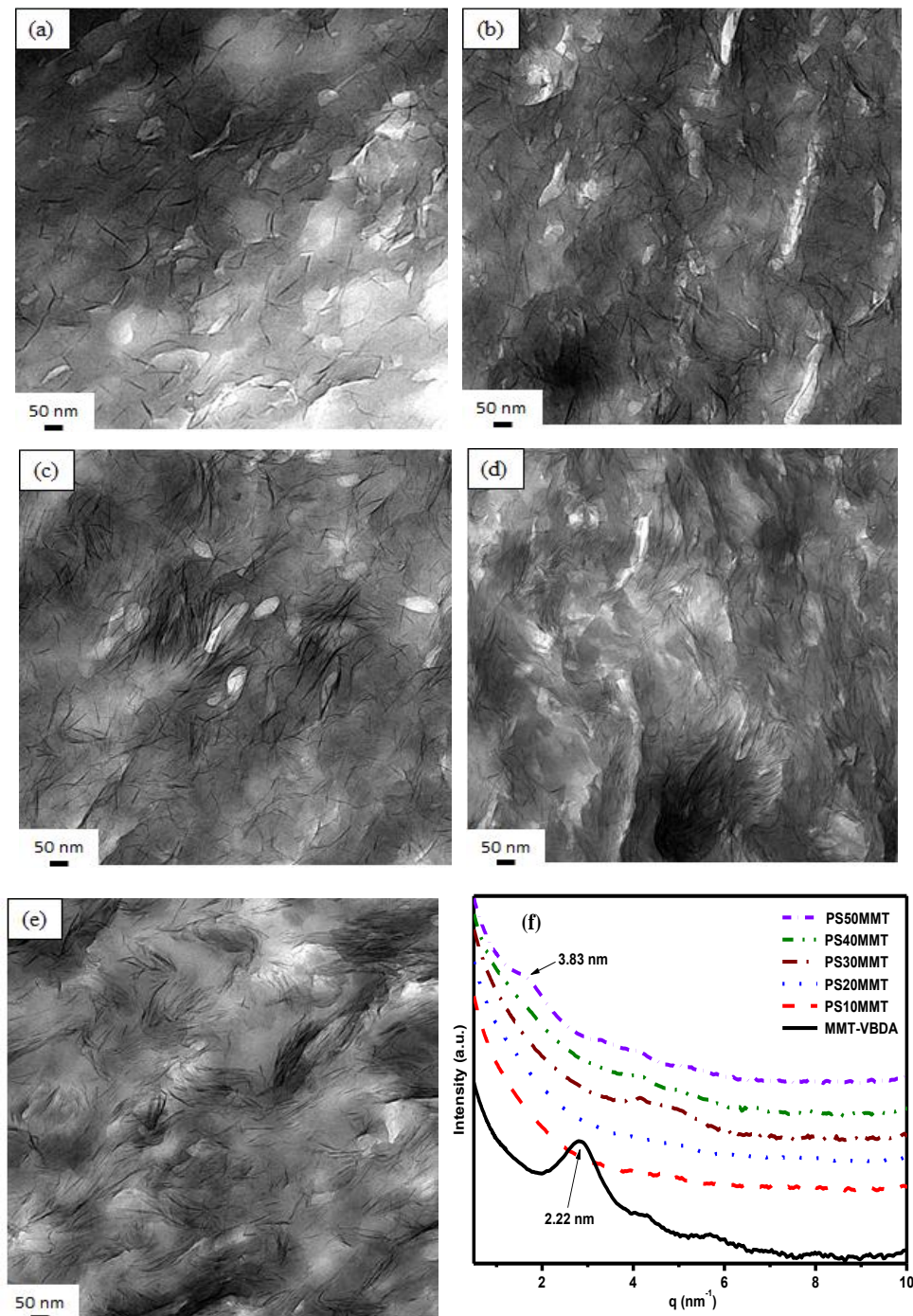


Fig. 6.3: TEM images of microtomed film samples of PS/MMT PCNs of different clay content, (a) PS/10MMT, (b) PS/20MMT, (c) PS/30MMT, (d) PS/40MMT, (e) PS/50MMT, (f) The scattering intensity plot of MMT-VBDA and PS/MMT PCNs of varying clay content.

Upon polymerisation the polymer chains grew from within the clay galleries resulting in gallery expansion hence clay exfoliation. It is the exfoliation of clay platelets that resulted in the observed homogeneous distribution of clay platelets.

SAXS was used to further elucidate the extent of MMT delamination in the polystyrene matrix as a complementary method to TEM. Fig. 6.3(f) shows the plot of scattering intensity of the different PS/MMT PCNs. The MMT-VBDA exhibited a scattering peak at q value of 2.8 nm^{-1} (corresponding to a d -spacing of 2.22 nm). However, no scattering peaks could be observed on the intensity plots of all the PCNs. This is an indication that the clay platelets were fully exfoliated within the polymer matrix, except for PS/50MMT. PS/50MMT exhibited a q value of 1.64 ($d = 3.83$) indicating that at ultrahigh clay content, the platelets were only partially exfoliated. The result was consistent with the TEM image results (Fig 6.3(e)) which showed that at high clay content, the platelets were aggregated within the polymer matrix.

6.3.4 Physical properties

Fig. 6.4 shows the storage modulus and damping factor plots of PCNs as a function of temperature. Similar to results obtained with Lap, storage modulus dependency on clay content was different between the glassy region and the rubbery state

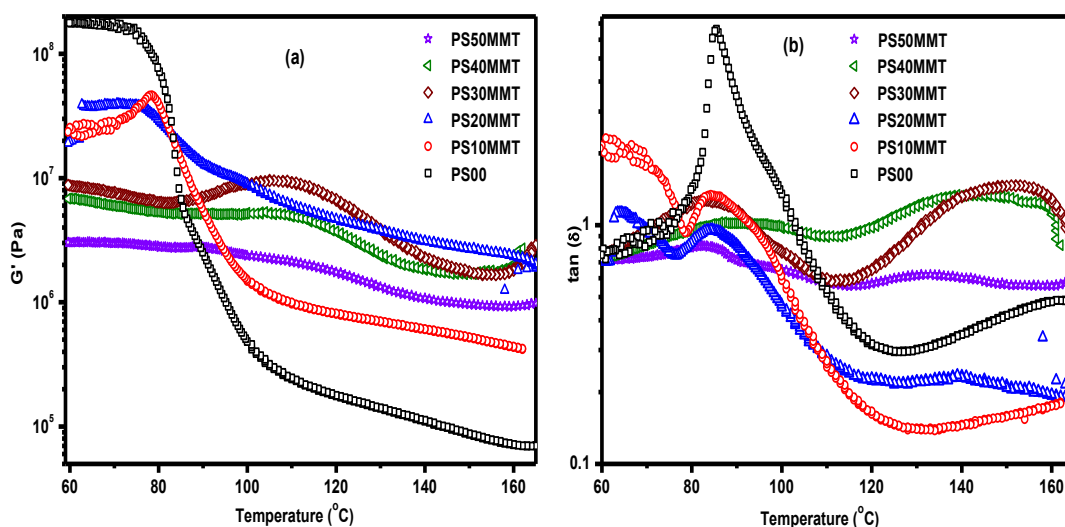


Fig. 6.4: (a) loss moduli, (b) storage moduli and (c) $\tan(\delta)$ peaks of polystyrene and its MMT based nanocomposites

. In the rubbery region, the storage modulus increased with increasing clay content until 30 wt% clay content followed by a decrease with further increase in clay content. This trend was contrary to that of PS/Lap PCNs (see Section 5.3.2.1) which showed a monotonic increase in

storage modulus with increasing clay content throughout the clay content range. For the conventional low clay content PCNs (i.e. < 10 wt%), monotonic increase in storage modulus is usually associated with strong polymer-clay interactions.³⁵⁻³⁸ This was attributed to strong interaction between the clay platelets and polymer chains with increasing clay content. Furthermore, a gradual decrease in the glassy-to-rubbery transition step with increasing clay content was observed in PS/MMT PCNs. The storage modulus of highly filled PCNs remained fairly constant throughout the temperature range studied. On the other hand, the glassy state was characterised by a monotonic decrease in storage modulus with increasing clay content.

Typical of filled polymers, the intensity of the $\tan(\delta)$ peak associated with T_g decreased in intensity and became broader with increasing clay content.^{39,40} The temperature at maximum $\tan(\delta)$ peak remained fairly constant at 85 °C throughout the clay content range studied. This gave an indication that the T_g was not affected by the incorporation of clay. However studies on T_g using DSC (c.f. Fig. 6.5(a)) showed that the T_g increased from 85 °C to 94 °C with incorporation of 10 wt% clay and then decreased with further increase in clay content. The T_g values of the PS/MMT PCNs are given in Table 6.2. Despite the decrease in T_g within the PCN series, the T_g of the PCNs remained higher than that of the neat polymer. The highly filled PCNs exhibited a second $\tan(\delta)$ peak whose maximum was around 150 °C, similar to highly filled PS/Lap PCNs. However, the intensity of the second $\tan(\delta)$ peak of PS/MMT decreased with increasing clay content (see Fig. 6.4(b)). This was opposite of Lap based PCNs which showed an increase in intensity of the second peak with increasing clay content. This second $\tan(\delta)$ peak was associated with chain flow relaxation of untethered polymer chains intercalated within the clay galleries.⁴¹ The decrease observed in PS/MMT PCNs could therefore be associated to a decreasing number of untethered polymer chains as clay content increased. The higher aspect ratio of MMT compared to that of Lap could result in more polymer chains being tethered onto the clay platelets in PS/MMT PCNs than in PS/Lap PCNs.

Fig 6.5(b) shows the thermal decomposition profiles of PS/MMT PCNs as a function of temperature. Generally the onset temperature of decomposition shifted towards lower temperatures with the increasing clay content, except for PS10MMT which showed a shift towards higher temperatures. Similarly, the temperature at 40% weight loss (T_{60}) decreased with increasing clay content, see Table 6.2. According to these findings, it can be said that the

thermal stability of the PCNs decreased with increasing clay content, with PS30MMT, PS40MMT and PS50MMT actually exhibiting poor thermal stability properties compared to the neat polymer.

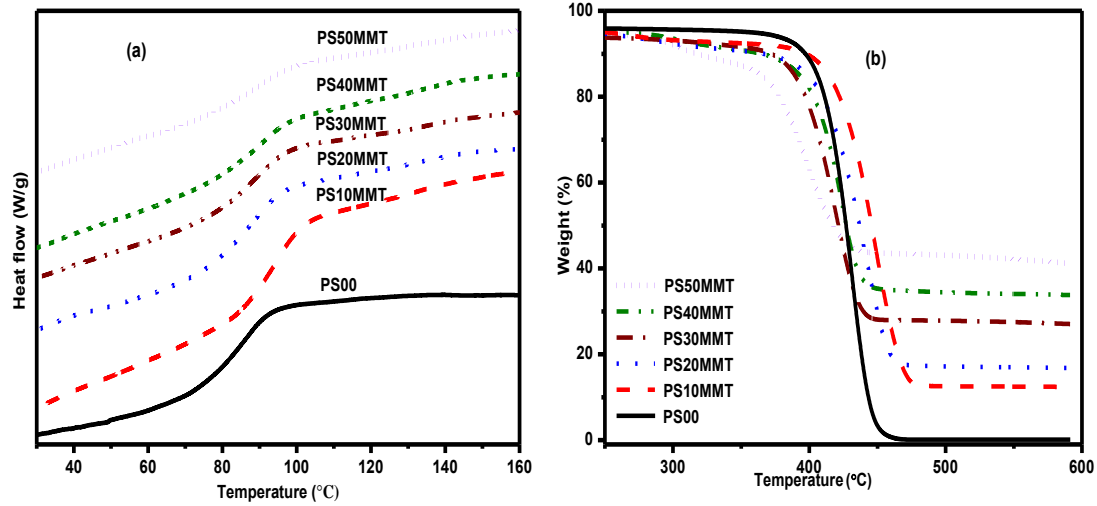


Fig. 6.5: (a) DSC profiles and (b) thermal decomposition profiles of polystyrene and its MMT based nanocomposites as a function of temperature.

The 10 wt% clay content seems to be the threshold value for improving the thermal stability. Similar findings were reported by our group where a decrease in thermal stability was observed beyond 10 wt% clay content.⁴²

Table 6.2: Thermomechanical and thermal stability values of PS/MMT PCNs of varying clay content

Sample	Storage modulus		^(c) T _g °C	Thermal decomposition		
	^(a) G' ₇₀ (MPa)	^(b) G' ₁₄₀ (MPa)		^(d) T _{onset} (°C)	^(e) T ₆₀ (°C)	^(f) T ₅₉₀ (°C)
PS00	169	0.11	85	405	418	0.03
PS10MMT	24.0	0.63	94	418	441	12
PS20MMT	40.0	3.09	90	411	430	17
PS30MMT	7.63	2.38	90	391	421	27
PS40MMT	6.30	1.88	92	400	414	34
PS50MMT	2.88	1.08	84	374	402	41

^(a)G' value at 70 °C, a temperature below T_g, ^(b)G' value at 140 °C, a temperature above T_g, ^(c)taken from DSC measurements, ^(d)Onset temperature of decomposition, ^(e)temperature at 40% weight loss, ^(f)Residual weight at 590 °C.

The decreasing thermal stability with increasing clay content within the PCN range could be attributed to changing the morphological structure with increasing clay content. Generally microcomposites and intercalated PCNs have been reported to exhibit poorer thermal stability than exfoliated PCNs,^{8,43,44} although some intercalated PCNs have been found to have superior thermal stability over exfoliated PCNs.⁴⁵⁻⁴⁷ Furthermore, this could be due to clay platelets acting as catalysts for the decomposition process of PS chains.

6.4 Conclusion

Highly filled PS/MMT hybrid latexes were successfully prepared using the ad-mini-emulsion. However, the MMT platelets remained adhered onto the polymer particles rather than being encapsulated mainly due to their large size relative to the polymer particles. Significant particle aggregation was observed in PS/MMT latex samples. As a result stable hybrid latexes with up to 50 wt% clay could only be obtained at total solids content not exceeding 10%. The conversion remained high despite the high MMT content incorporated, possibly due to compartmentalisation effects. Both the T_g and storage modulus increased with incorporation of clay, however the T_g of high MMT content PCNs (> 10 wt%) had lower T_g values than lower MMT content PCN (PS10MMT). MMT contents of 10 wt% appear to be the threshold content for increasing thermal stability and T_g . Significant improvement was observed with the incorporation of 10 wt% MMT. Typical of highly filled PCNs, the high MMT content PCNs exhibited an additional $\tan(\delta)$ peak at high temperature which is associated with flow relaxation of chains intercalated between the clay platelets. Interestingly, the intensity of the second $\tan(\delta)$ peak decreased with increasing clay content above 30 wt%, an indication of possible increase in tethered polymer chains.

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Chapter 7

Encapsulation of Clay by Ad-mini-emulsion Polymerisation: The Influence of Clay Dimensions and Modifier on Latex Morphology and Physical Properties

7.1 Introduction

Incorporation of clay in polymers yields polymer/clay nanocomposites and these materials have been at the forefront of many research efforts in the past two decades.¹⁻¹⁰ The clay platelets may be used in their natural state or may be pre-modified using organic molecules prior to preparation of polymer clay nanocomposite (PCN). The modification can be achieved using 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 platelet edges. On the other hand, adsorption surface modification involves the use of organic 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 substitute 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 monomer and/or polymer. Organic compounds that can be used for clay modifications can be classified as reactive or non-reactive modifiers. Non-reactive modifiers are those that do not participate in the polymerisation reaction, e.g. quaternary alkyl ammonium compounds. The use of non-reactive modifiers for clay modification prior to incorporation in polymers has been widely reported.^{11,18-22} On the other hand, reactive modifiers are those that can participate in the polymerisation process either as initiators, inisurfs,^{23,24} or as comonomer, surfmers.^{11,19,20}

Once the clay has been modified, different polymerisation methods can be used to prepare the PCNs and among them is the in-situ intercalative polymerisation method. The in-situ intercalation method is a versatile approach offering better control on morphology of the PCNs than any other method. In situ intercalation polymerisation has been employed in heterogeneous polymerisation methods like emulsion and mini-emulsion to prepare latexes of various morphologies.^{9,15,25,26} As such, there has been a growing interest in highly filled

Chapter 7 Influence of Clay Dimensions and Type of Modifier on Encapsulation

inorganic-organic hybrid latexes materials prepared by the in situ intercalation heterogeneous polymerisation methods. However, the preparation of highly filled polymer/clay hybrid latexes using conventional methods such as emulsion or miniemulsion remains a challenge. Only few reports can be found in literature that deal with polymer/clay hybrid materials with ≥ 30 wt% clay using miniemulsion or emulsion polymerisation. Tong and Deng reported on polymer/clay hybrid materials containing up to 30 wt% clay prepared using emulsion polymerisation.²⁰ They reported that clay encapsulation was dependent on both the clay platelet size and the type of clay modifier used. Their findings were in agreement with observations made by Moraes *et al.*²⁷ on low clay content (< 10 wt%) polymer/clay hybrid latex morphologies produced using clay platelets of different sizes of clay platelets. Furthermore, Tong and Deng reported that the use of reactive modifiers facilitate more efficient encapsulation than non-reactive modifiers. Bourgeat-Lami and co-workers²⁸ utilising a reactive modifier (inisurf) 2,2-azobis(2-methyl propionamide) hydrochloride to modify Laponite (Lap), prepared highly filled polymer/clay hybrid latexes. Despite using a small-sized clay platelet and reactive modifier, they reported hybrid latexes exhibiting clay platelets predominantly adhered onto the polymer particle surface rather than being encapsulated.

To date, the maximum amount of clay which can be encapsulated in polymer materials by emulsion and miniemulsion still remains relatively low. To overcome such a problem, Landfester's group developed the ad-mini-emulsion polymerisation method aiming to effectively encapsulate high inorganic filler content in polymer particles.^{29,30} The ad-mini-emulsion process is based on step wise formation of a hybrid miniemulsion which is then polymerised to give the desired hybrid nanoparticles. The current study is a follow up study to studies reported from Chapter 4 through to Chapter 6. This study focused mainly on the highly filled PCNs (30–50 wt% clay) prepared by the ad-mini-emulsion polymerisation method. The aims of the current study were to evaluate the effects of clay platelet dimensions (size) and modifier reactivity on the hybrid latex morphology and the properties of the resultant PCNs. The two clays used in this study were (MMT) and Lap, which were chosen on the basis of their platelet size differences. The two modifiers used to modify the clays were VBDAC, a reactive modifier (surfmex) and Cetyltrimethylammonium bromide (CTAB), a non-reactive modifier.

7.2 Experimental

7.2.1 Materials

Styrene (99%) was supplied by Sigma Aldrich and was washed with 0.3 M aqueous potassium hydroxide (KOH) solution and then with deionised water. This was followed by distilling the washed styrene at 40 °C under reduced pressure to remove inhibitor. Azobisisobutyronitrile (AIBN) was supplied by Sigma Aldrich and was purified by recrystallisation from methanol before use. Laponite RD (Lap), with 25 nm x 0.92 nm dimensions and CEC of $5.0\text{--}5.5 \times 10^{-5}$ mol/g was supplied by Rockwood Additives Limited, U.K. Montmorillonite (MMT), with CEC value of 116 meq/100 g was supplied by Southern Clay products, a subsidiary of Rockwood Additives (U.K.). Cetyltrimethylammonium chloride (CTAB, 99%), Sodium dodecyl sulphate (SDS, 99%), 4-vinylbenzyl chloride (99%), N, N dimethyldodecylamine (99%) and hexadecane (HD, 99%) and silver nitrate were supplied by Sigma Aldrich and were used as received. VBDAC was synthesised as reported elsewhere.³¹

7.2.2 Modification of clay

The clay modification procedure was detailed in Section 3.3.2.

7.2.3 Preparation of hybrid latex

The hybrid latexes were prepared using ad-miniemulsion polymerisation method, following a procedure described in Section 4.2.3. The detailed formulations are given in Appendix 2. The resultant hybrid latexes and PCNs were labelled PS/xC-S [PS representing polystyrene, x representing the amount of clay incorporated, C representing the type of clay incorporated and S representing the type of modifier used for clay modification]. For example PS/30Lap-CTA was a PCN of polystyrene containing 30 wt% Lap modified with CTAB.

7.2.4 Analytical Techniques

The latexes and film morphology of the PCNs were analysed using TEM. Clay delamination within the polymer matrix was analysed using SAXS. The extent of modification was qualitatively confirmed by FTIR and the amount of grafted modifier was quantitatively determined using TGA. TGA was also used to evaluate the thermal stability and to quantify the amount of clay in the PCNs. The PCNs' thermomechanical properties were determined by DMA. The T_g of the PCNs was determined using DSC. The detail for these procedures were similar to those reported in section 5.2.4 Conditions similar to those used for PS/Lap PCNs were used in the current study.

7.3 Results and Discussion

The hybrid latexes showed high conversions ($\geq 80\%$) 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 solids content, for PS/Lap and PS/MMT PCNS respectively. The observed differences in solids content were attributed mainly to the differences in clay sizes. The type of modifier was found to have no influence on the total solids content achievable. Table 7.1 summaries the latex properties of the different highly filled hybrid materials prepared using the ad-mini-emulsion polymerisation.

Table 7.1: Latex characteristics of PS/Lap-CTA, PS/Lap-VBDA, PS/MMT-CTA and PS/MMT-VBDA highly filled hybrid nanocomposites.

Sample	Clay content (wt%)	TSC (%)	Final conversion (%)	Particle size ^(a) (nm)
PS	0	20	95	80
PS/Lap-CTA	30	20	91	56
	40	20	91	58
	50	20	90	64
PS/Lap-VBDA	30	20	90	92
	40	20	88	96
	50	20	87	87
PS/MMT-CTA	30	10	90	52
	40	10	91	56
	50	10	90	— ^(b)
PS/MMT-VBDA	30	10	88	66
	40	10	86	70
	50	10	88	75

^(a)Average particle size diameter determined from TEM images, ^(b)Could not be determined due to particle clustering.

7.3.1 Morphological properties

Fig. 7.1 shows the TEM images of PS/Lap and PS/MMT hybrid latexes. PS/Lap-CTA PCNs exhibited predominantly armoured particle morphology, as shown in Fig. 7.1(a). On the other hand, PS/Lap-VBDA latexes exhibited nanoparticles with predominantly encapsulated morphology, as shown in Fig. 7.1(b).

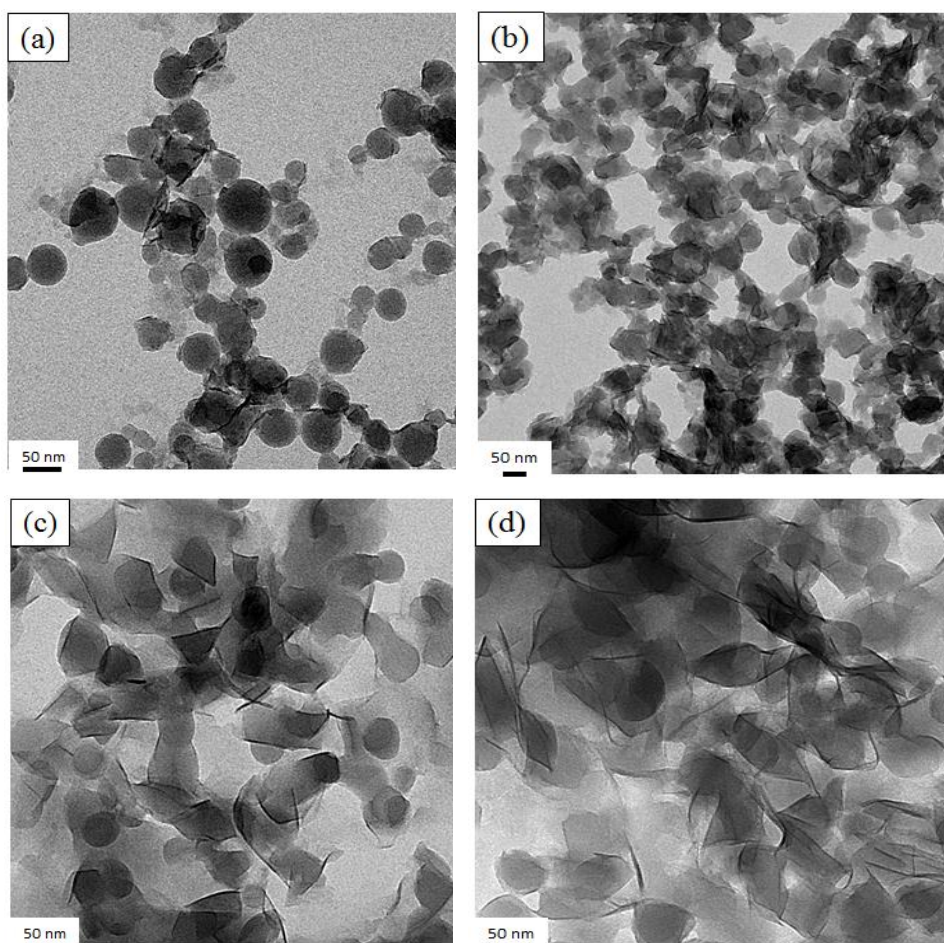


Fig. 7.1: TEM images of (a) PS/50Lap-CTA, (b) PS/50Lap-VBDA, (c) PS/50MMT-CTA and (d) PS/50MMT-VBDA (Scale bar: 50 nm).

No clay platelet stacks were observed outside the hybrid particles in PS/Lap-VBDA latexes. However, no significant morphological differences were visible between TEM latex images of PS/MMT-CTA and PS/MMT-VBDA. They both exhibited armoured particle morphology irrespective of the clay modifier used, as seen from Fig. 7.1(c) and (d). MMT platelet stacks were visible on the polymer particle surface of both PS/MMT-CTA and PS/MMT-VBDA latex TEM images. These results indicate that both the type of modifier and the size of the clay platelet affected the hybrid nanoparticle morphology. The use of a reactive modifier (VBDAC) was considered to have improved monomer/clay compatibility, whereas the non-reactive modifier (CTAB) did not. This was evident from the formation of a homogeneous paste upon dispersing the Lap-VBDA in styrene,^{32,33} whereas a clear phase separation was observed in an attempt to disperse Lap-CTA in styrene. Furthermore, it was postulated that the reactive modifier facilitated encapsulation by copolymerising with styrene into the polystyrene backbone. However, the size of the clay platelet was found to have a dominating effect on particle morphology over the modifier's reactivity. This conclusion was reached

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considering that the same reactive modifier that facilitated encapsulation of Lap appeared ineffective in facilitating the encapsulation of MMT. According to size estimations made from TEM images, the average MMT platelet stack length (80 nm) was greater or comparable to the average polymer particle size (65–75 nm in diameter) of the hybrid latexes.

Dried PCN samples obtained by casting the hybrid latexes into an aluminium pan at room temperature were microtomed into 100 nm thick film samples. These samples were used to evaluate the extent of clay platelet delamination using TEM. Fig. 7.2 shows the TEM images of PS/Lap and PS/MMT PCNs, from which the influence of clay platelet size and the type of modifier on clay delamination are clearly evident. PS/Lap-CTA PCN films, shown in Fig. 7.2(a), exhibited a cellular structured morphology, similar to that of PCNs prepared using Pickering stabilisation.^{9,34-36} The cellular structure morphology was attributed to the restriction of polymer particle inter-diffusion by the clay platelets adhered onto the polymer particle surface.^{34,37,38} However, PS/Lap-VBDA PCNs (see Fig. 7.2(b)) exhibited homogeneous distribution of the clay platelets within the sample. This was considered as an indication of clay platelets being efficiently encapsulated into the hybrid polymer particles in the original latex, prior to film formation. The encapsulated platelets could not restrict polymer particle inter-diffusion. Despite the PS/MMT hybrid latexes exhibiting armoured particle morphology, their microtomed samples did not exhibit the cellular structured morphology, Fig. 7.2(c) and (d). Instead the clay platelets were distributed within the sample. However, the extent of clay aggregation appears to be influenced by the type of modifier used to modify the clay.

PS/MMT-CTA PCNs were characterised by clay aggregation (Fig. 7.2(c)), indicating limited delamination of the clay platelets. On the contrary, PS/MMT-VBDA PCNs (Fig. 7.2(d)) exhibited homogeneous distribution of clay within the film with limited aggregation even at 40 and 50 wt% clay content. This shows that the use of VBDA facilitated the delamination of clay platelets within the polymer matrix. Similar results where the extent of clay delamination has been found to be influenced by type of modifier have been reported elsewhere.³³ It was therefore postulated that the prepolymerisation intercalation of monomer, the inter-platelet chain growth and the copolymerisation of VBDA⁺ promoted greater platelet exfoliation than when CTAB was used as clay modifier. These findings were in agreement with those reported for low clay content PCNs.²⁷ It was therefore concluded that a modifier that facilitates compatibility between the clay and monomer is a prerequisite for the effective

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encapsulation of the clay platelets. However, encapsulation may become ineffective if the clay platelet dimensions are equivalent or greater than the monomer droplets, as was observed with MMT.

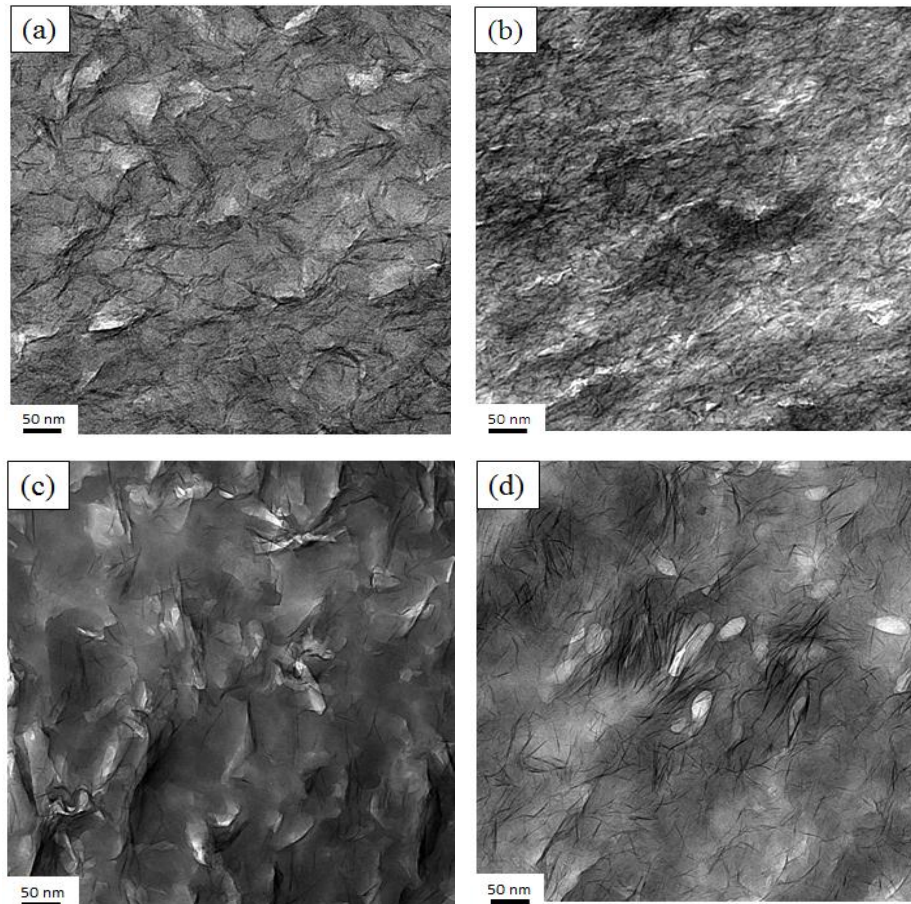


Fig. 7.2: TEM images of microtomed samples; (a) PS/50Lap-CTA, (b) PS/50Lap-VBDA, (c) PS/30MMT-CTA and (d) PS/30MMT-VBDA (Scale bar: 50 nm).

Studies on the delamination of the clay platelets within the polymer matrix were further conducted using SAXS to complement the TEM results. In SAXS diffractograms, the widening and the lowering in intensity of the scattering peak 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 original state of clay platelets.^{39,40} The SAXS scattering patterns of PS/Lap-CTA, PS/Lap-VBDA, PS/MMT-CTA and PS/MMT-VBDA as a function of the wave vector are shown in Fig. 7.3.

The SAXS patterns of PS/Lap-CTA show a scattering peak whose intensity and position was independent of clay content. The calculated d-spacing of these PS/Lap-CTA PCNs were found to be relative constant irrespective of clay content, see Fig. 7.3(a). Interestingly, there was no significant difference between the d-spacing of the PS/Lap-CTA and Lap-CTA. Similar results were obtained for PS/MMT-CTA PCNs, as shown in Fig. 7.3(c). The absence of any change in scattering pattern between Lap-CTA and the PS/Lap-CTA PCNs can be taken as an indication that insignificant amount of polymer chains were intercalated into the clay galleries to cause any significant d-spacing expansion.

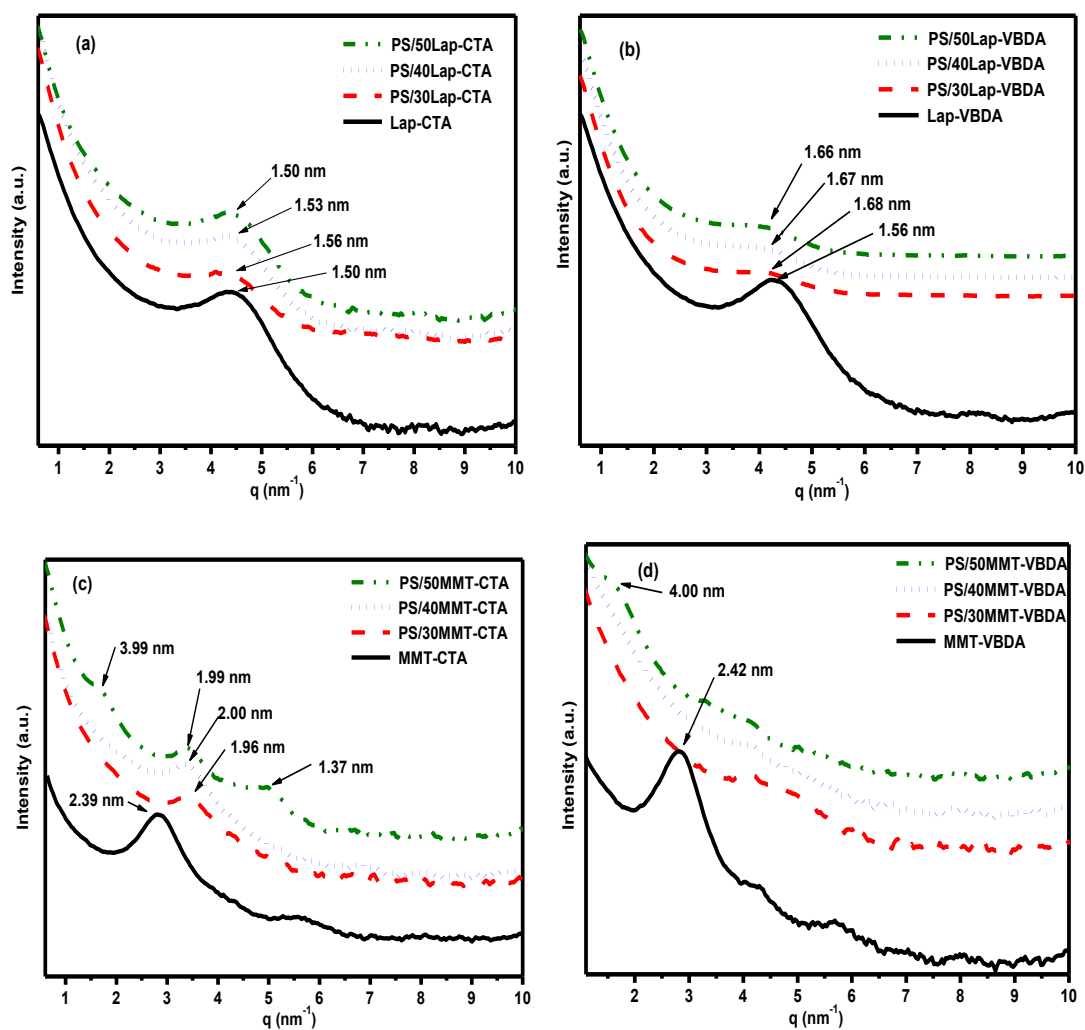


Fig. 7.3: SAXS profiles of (a) PS/Lap-CTA and (b) PS/Lap-VBDA, (c) PS/MMT-CTA and (d) PS/MMT-VBDA.

This was attributed to the lack of pre-polymerisation monomer intercalation into clay galleries as a result of poor compatibility between Lap-CTA and styrene monomer. Therefore, it can be said that no interruption of the orderly nature of the clay platelets took

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place when CTAB was used as the clay modifier. However, when clay modified with VBDAC was used, partially or fully exfoliated PCNs were obtained. PS/Lap-VBDA PCNs showed broad scattering peak with very low peak intensity. The calculated d-spacing of PS/Lap-VBDA PCNs were found to be larger than those of both Lap-CTA and PS/Lap-CTA (Fig. 7.3(b)). This is an indication that the PCNs were partially exfoliated. Fig 7.3(d) shows that PS-MMT-VBDA PCNs exhibited no scattering peak which is an indication of fully exfoliated morphology, except for PS/50MMT-VBDA. The PS/50MMT-VBDA sample exhibited a scattering peak at very low q values, corresponding to a d-spacing of 3.83 nm. The morphological differences observed between PCNs prepared with 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.⁴¹ At the same time, thermodynamic compatibility of polymer or monomer with the modified clay is required to allow efficient exfoliation of clay platelets.^{32,33,42} VBDAC provided both clay/monomer thermodynamic compatibility and participated in the polymerisation process thus allowing polymer chains to grow within the clay galleries resulting in clay exfoliation.

7.3.2 Physical properties

Fig. 7.4 shows the storage modulus (G') of the different PCNs as a function of temperature. Generally, all PCNs exhibited much higher G' values as compared to neat PS, irrespective of the clay or the modifier used, in the rubbery region. Enhancement in storage modulus values has been widely reported with the incorporation of clay platelets in polymeric materials.^{4,8,11,35,43-46} Such behaviour was attributed to polymer-clay interactions which bring about restriction on polymer chains mobility.^{11,45} Fig. 7.4(a) shows that PS/Lap-CTA exhibited fairly constant G' values irrespective of clay content. PS/Lap-VBDA based PCNs exhibited monotonic increase in G' with increasing clay content 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. 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 copolymerisation of VBDA into the main polymer chain and the higher aspect ratio of the MMT platelets. For PS/MMT-CTA and PS/Lap-CTA PCNs the observed G' behaviour with increasing clay content was attributed to morphological structure of the PCNs. These PCNs exhibited intercalated morphology irrespective of clay content, as was established by SAXS.

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The intercalated morphology reduces the effective surface area of clay platelets thus reducing polymer-clay interactions. As such, the expected enhancement in G' with increasing clay content could not be observed. Notably, the conventional glassy-to-rubbery step was significantly lowered by the high clay content incorporated. Both the neat clay and the modified clay were found to exhibit no glassy-to-rubbery transition step.

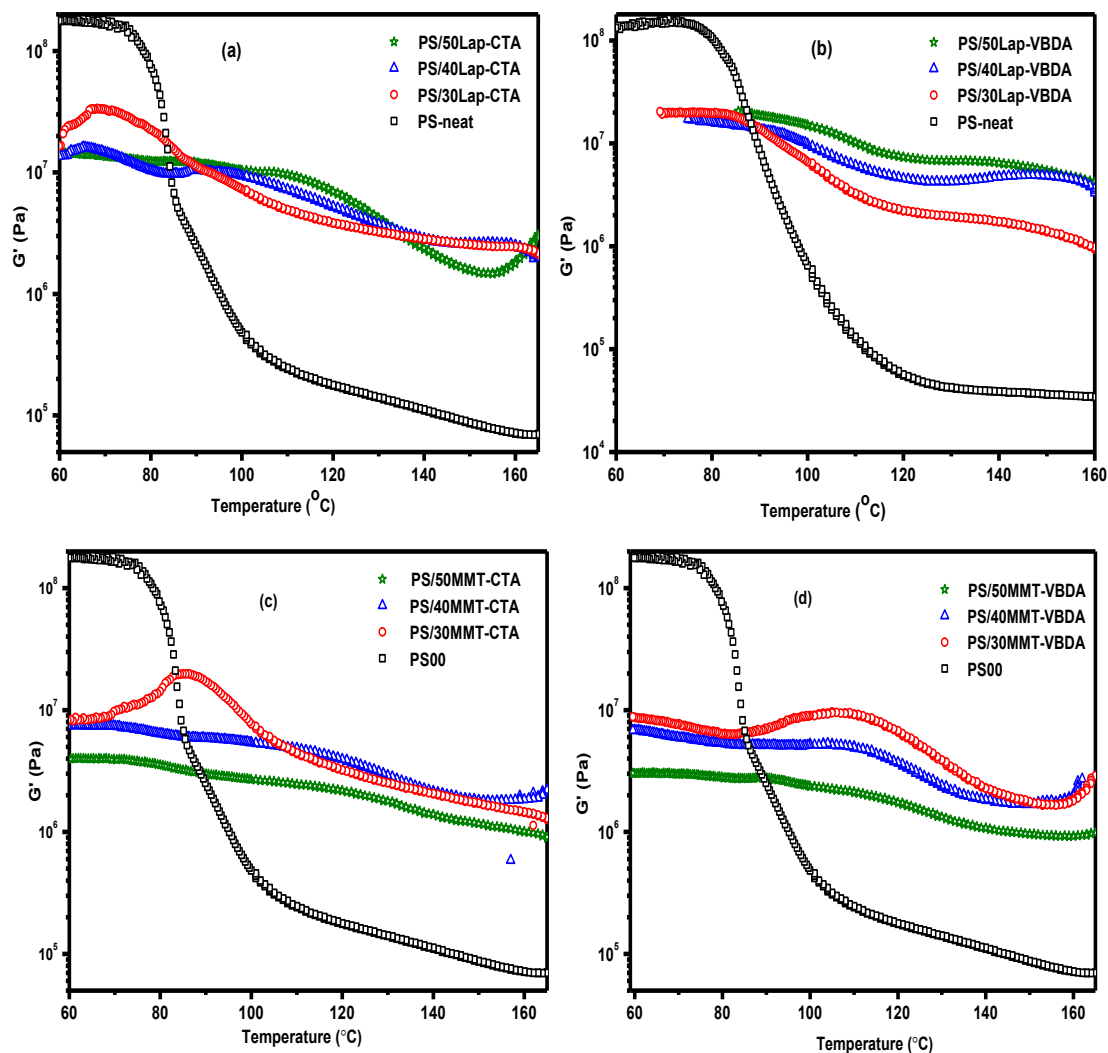


Fig. 7.4: Storage modulus curves of; (a) PS/Lap-CTA, (b) PS/Lap-VBDA, (c) PS/MMT-CTA, (d) PS/MMT-VBDA PCNs.

Fig. 7.5 shows the temperature dependency of damping factor ($\tan(\delta)$) of the PCNs. These highly filled PCNs generally 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.⁴⁷ 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.^{46,48} No direct

correlation could be established between $\tan(\delta)$ peak and either the clay platelet dimensions nor type of modifier used. The results show that the amount of clay platelets had a dominating effect on the damping factor. A possible hypothesis is that any effect on $\tan(\delta)$ peak imparted by the reactivity of the modifier was nullified by the ultrahigh clay content employed in this study. Due to the difficulty in determining the glass transition temperature (T_g) of the PCNs from DMA, T_g was determined by differential scanning calorimetry (DSC).

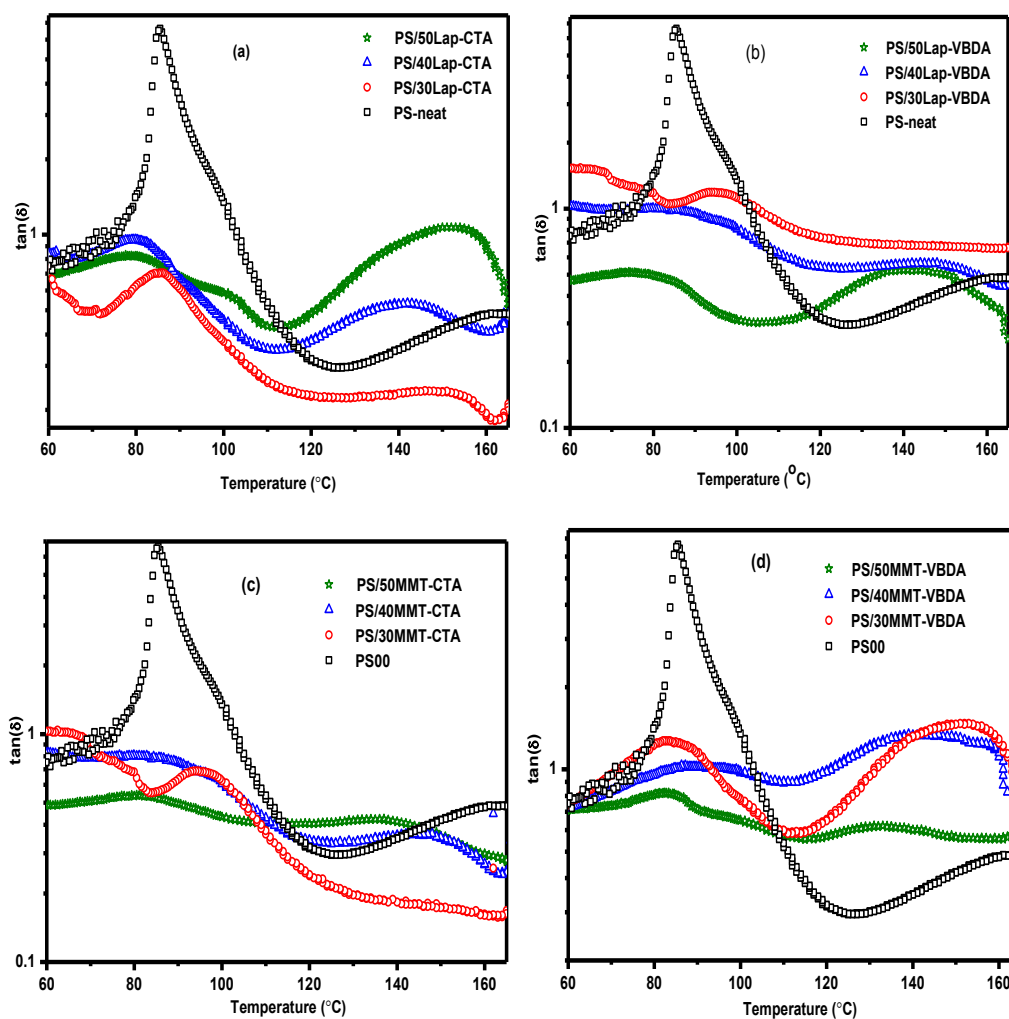


Fig. 7.5: *Tan (δ) peaks of; (a) PS/Lap-CTA, (b) PS/Lap-VBDA, (c) PS/MMT-CTA, and (d) PS/MMT-VBDA.*

Fig. 7.6 shows the DSC profiles of PS/Lap and PS/MMT PCNs and the corresponding data values are summarised in Table 7.2. The T_g was found to depend heavily on the type of modifier used. When clay was modified with non-reactive modifier, the T_g values of the resultant PCNs exhibited a decreasing trend with increasing clay content. The T_g values of PS/40Lap-CTA and PS/50Lap-CTA were found to be actually lower than that of the neat PS. On the other hand, the T_g of PS/MMT-CTA remained higher than the neat PS, despite the

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decreasing trend. Using clay modified with reactive modifier, the T_g of the resultant PCNs increased monotonically with increasing clay content. This was attributed to the strong polymer-to-clay interactions brought about by the copolymerisable VBDA⁺ molecules compared to the non-polymerisable CTA⁺ molecules. The incorporation of VBDA⁺ onto the main polymer chain promoted polymer-clay interactions thus restricting long range molecular motions. No particular changes in T_g could be directly attributed to the difference in clay size.

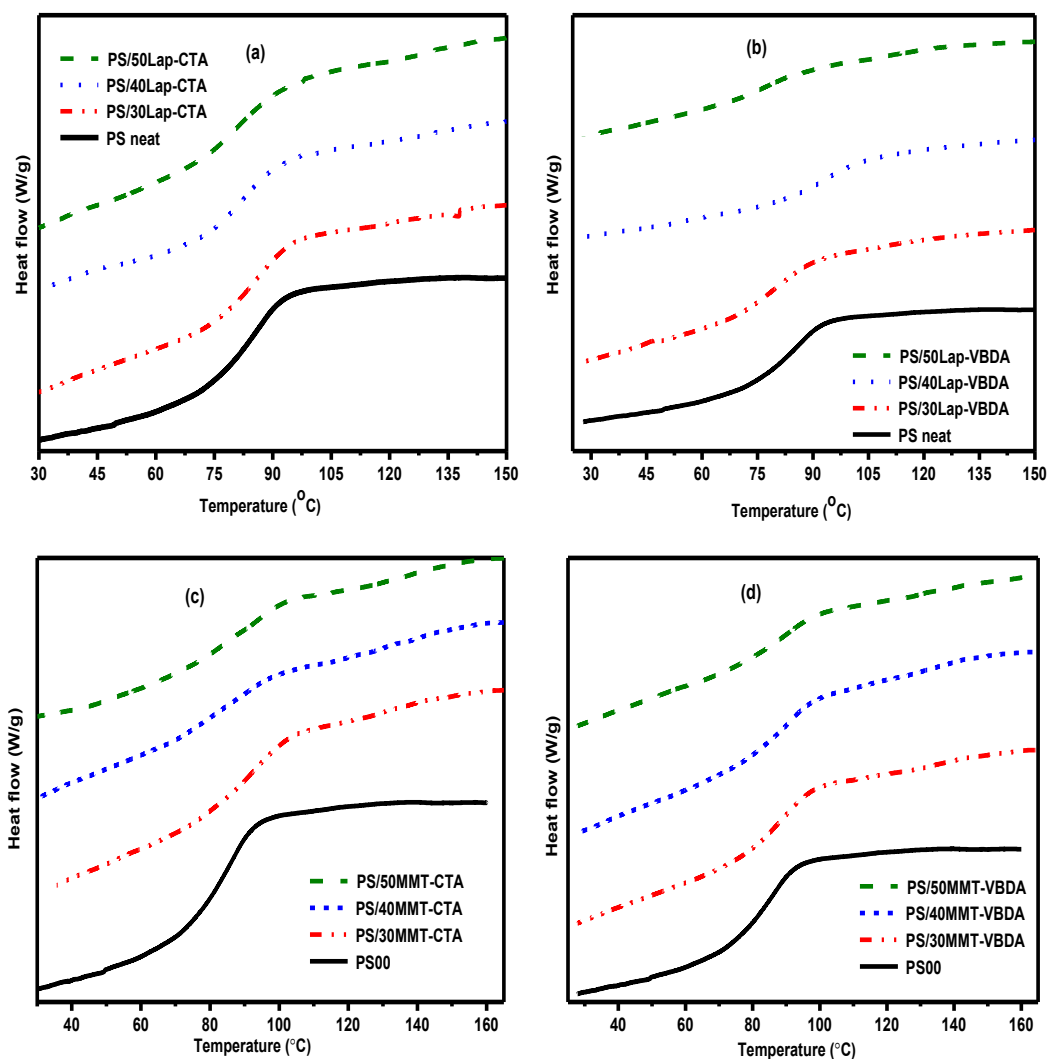


Fig. 7.6: DSC profiles of (a) PS/Lap-CTA, (b) PS/Lap-VBDA, (c) PS/MMT-CTA and (d) PS/MMT-VBDA.

The thermal decomposition of the PCNs was determined by monitoring the onset of thermal degradation from the thermograms of the PCNs. The thermograms of both PS/Lap and PS/MMT PCNs are shown in Fig. 7.7. It is well documented, especially for low clay content PCNs (< 10 wt%), that PCNs exhibit superior thermal stability properties as compared to the corresponding neat polymers. This is due to clay acting as a mass transport barrier and heat

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insulator between the polymer and the decomposition zone. Furthermore, it creates a tortuous path for the gaseous products of decomposition.^{11,18,23,24,49,50}

Table 7.2: Summary of the physical properties of highly filled PS/Lap and PS/MMT PCNs

Sample	Clay content (wt%)	Thermomechanical properties					Thermal stability		
		G' (GPa)		Tan(δ) (°C)		T _g ^(e)	T _{onset} ^(f)	T ₆₀ ^(g)	W _R ^(h)
		< T _g ^(a)	> T _g ^(b)	T _{max1} ^(c)	T _{max2} ^(d)	(°C)	(°C)	(°C)	%
PS	0	16.9	0.11	85	-	85	405	418	0.03
PS/Lap-CTA	30	3.37	2.88	85	-	86	405	433	26
	40	1.54	2.88	81	140	83	412	436	35
	50	1.38	2.43	79	152	82	409	436	42
PS/Lap-VBDA	30	2.05	6.57	97	-	85	407	426	27
	40	-	9.50	87	145	94	408	426	35
	50	-	10.5	78	145	98	408	431	43
PS/MMT-CTA	30	9.84	2.00	97	-	94	307	432	26
	40	7.80	2.09	89	148	92	309	437	28
	50	4.04	1.37	82	137	92	309	443	41
PS/MMT-VBDA	30	7.63	2.38	85	151	90	391	421	27
	40	6.30	1.88	90	138	92	400	414	34
	50	2.88	1.08	84	132	94	374	402	41

^(a)G' value at 70 °C, a temperature below T_g, ^(b)G' value at 140 °C, a temperature above T_g, ^(c)temperature at the maximum tan(δ) peak associated with T_g, ^(d)temperature at the maximum of the second tan(δ) peak, ^(e)taken from DSC measurements, ^(f)Onset temperature of decomposition, ^(g)temperature at 40% weight loss, ^(h)Residual weight at 590 °C.

However, it has also been reported that there is a clay content threshold value beyond which either no thermal stability improvement or a negative effect on thermal stability takes place.^{48,49} Based on the tortuous path effect, one would expect that the incorporation of high content, highly exfoliated clay platelets with high aspect ratio, e.g. MMT, in polymers would improve thermal stability significantly. Surprisingly, in the current study PS/MMT PCNs exhibited lower onset temperatures of decomposition than the neat PS, irrespective of the modifier used. Indeed the clay platelet had an influence on the thermal stability of the materials, but the effect was not with the line of expected results. The result shows that there

are other factors influencing the thermal stability of the PCNs besides the clay surface dimensions and morphology.

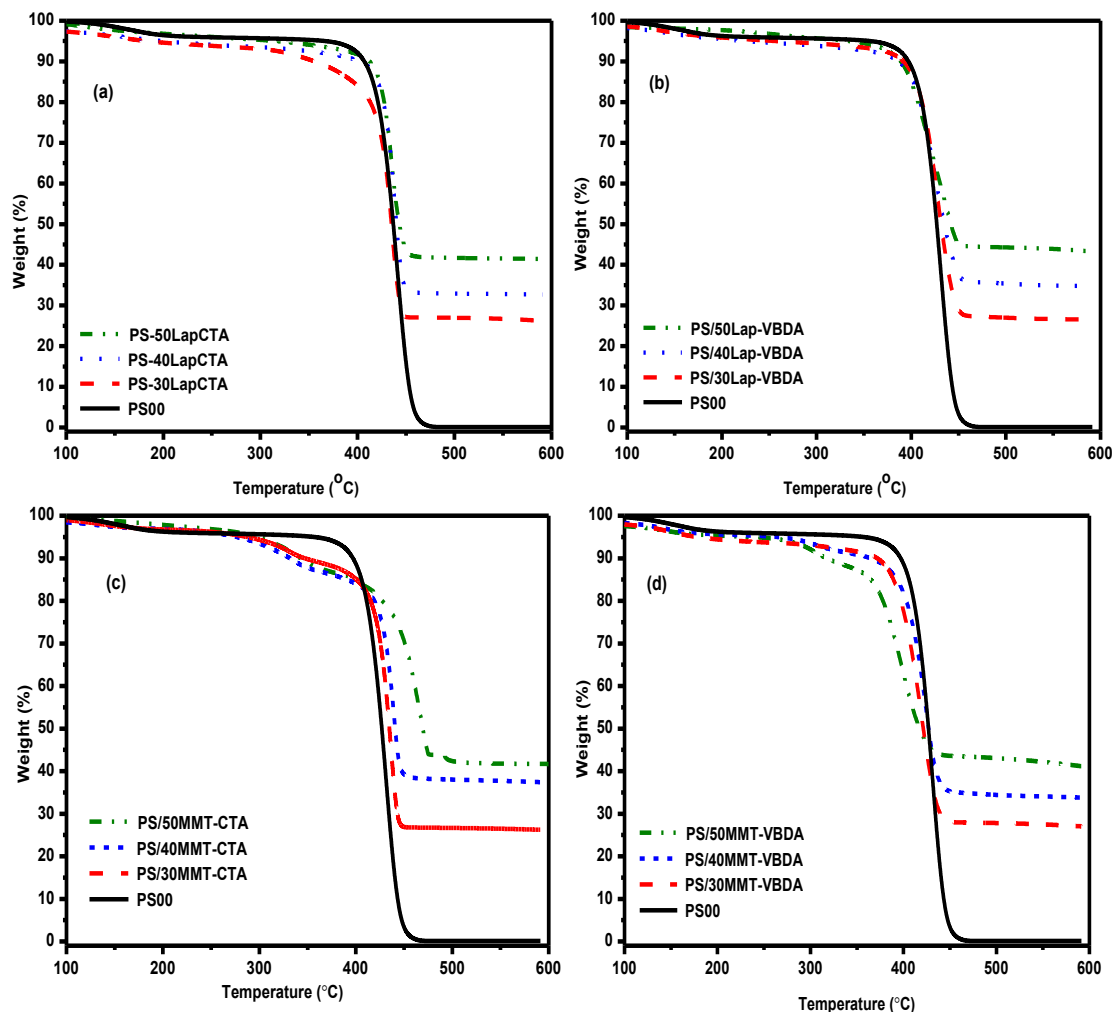


Fig. 7.7: TGA thermograms of (a) PS/Lap-CTA, (b) PS/Lap-VBDA, (c) PS/MMT-CTA and (d) PS/MMT-VBDA.

It has been reported that factors such as polymer decomposition, modifier decomposition, reactivity of metal ions on clay platelets may all influence the thermal stability of the PCNs.¹³ Results obtained in this study appear to suggest that the MMT platelets acted as catalyst for PS chains decomposition.

7.4 Conclusion

Clay platelet dimensions and modifier reactivity were both found to influence the encapsulation and exfoliation of clay platelets within the highly filled PS/clay hybrid latexes. Monomer/clay compatibility and modifier reactivity were found to be a pre-requisite for effective encapsulation provided the clay platelets are smaller than the monomer droplets.

Irrespective of clay platelet size, platelet exfoliation was found to be dependent on the reactivity of the modifier. The use of non-reactive modifier resulted in predominantly intercalated PCNs whilst the use of reactive modifier resulted in partially to fully exfoliated PCNs. As such, the influence of clay platelet size and modifier properties was evident in the physical properties of the resultant PCNs. Storage moduli of PS/Lap-VBDA PCNs films showed a monotonic increase with increasing clay content in the rubbery region. Contrarily, PS/MMT PCNs showed a decreasing storage modulus with increasing clay content, irrespective of the morphological structure of the PCNs. PCNs based on reactive modifier exhibited higher T_g values than those based on non-reactive modifier. This showed that the degree of polymer-clay interaction 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 itself influenced by the dimensions of the clay platelets used. 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.

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Chapter 8

Conclusions and Recommendations

8.1 Conclusions

Highly filled polymer/clay hybrid latexes, incorporating as much as 50 wt% clay platelets were effectively prepared. It was demonstrated that the ad-miniemulsion polymerisation method is an efficient method to prepare these highly filled hybrid latexes. The key to the successful incorporation of high clay content in polymer particles without compromising latex stability was found in the use of wet modified clay rather than the conventional dried powder. Studies on PS/Lap and PSBA/Lap hybrids showed that the latex morphology was influenced by the polymer material used. PSBA/Lap exhibited predominantly crumpled particles with encapsulated morphology. On the other hand, the latex morphology of PS/Lap hybrids evolved from armoured particle morphology to encapsulated morphology with increasing clay content. Both TEM and SAXS analysis showed that in both PS/Lap PCNs and PSBA/Lap, the clay platelets were well distributed into the polymer material with morphologies ranging from partially to fully exfoliated.

Notable changes in the properties of the highly filled PCNs relative to the neat polymer include the large increase in storage modulus values, shifting of T_g towards higher temperature, and characteristic solid-like viscoelastic behaviour. Significant increase in storage modulus values was observed in both PS/Lap and PSBA/Lap where up to 5000% increase was observed at the highest clay content. A 9 °C and a 14 °C shift towards higher temperature was observed between neat polymer and the PCN with the highest clay content, in PS/Lap and PSBA/Lap hybrids, respectively. The incorporation of clay platelets in both PS and PSBA was found to result in restricted polymer chain mobility as evident from the decreasing intensity of the $\tan(\delta)$ peak associated with T_g . Furthermore, a characteristic second $\tan(\delta)$ peak was observed at a temperature far above the T_g . This was attributed to the chain flow relaxation on untethered polymer chains intercalated in the clay galleries. Rheological studies in the melt state showed that the materials exhibited solid-like viscoelastic behaviour as $G' > G''$ throughout the angular frequency range studied. The ability of clay to align in the direction of shear at such high clay content was evident from the shear thinning behaviour observed in the PCNs with increasing angular frequency. Despite the

improvements observed in other properties, the thermal stability of the PCNs remained relatively unchanged.

Following the success on polymer/Lap hybrid latexes, studies on PS/MMT showed that stable PS/MMT could only be achieved upon reaching a compromise between the total solids content of the final latex and the clay content. Stable highly filled latexes (50 wt% clay) could only be obtained with solids content not exceeding 10%. The monomer-to-polymer conversion in these hybrid materials remained high (> 80%) but lower than conversions achieved for neat polymers. However, the clay platelets remained adhered onto the polymer particle surfaces. This was attributed to the clay platelet dimensions being larger or equal to the polymer particle dimensions. Despite the visibly ineffective encapsulation in the latex polymer particles, the resultant dried PCNs exhibited a fully exfoliated microstructural morphology. The monotonic increase in storage modulus reached a peak at 30 wt% MMT content beyond which it decreased with increasing clay content. Similar to polymer/Lap PCNs, PS/MMT exhibited a decreasing $\tan(\delta)$ peak intensity with increasing clay content. At the same time, a second $\tan(\delta)$ peak was observed in highly filled PCNs (30–50 wt%) at temperatures far above the T_g . The second $\tan(\delta)$ peak surprisingly decreased in intensity with increasing clay content. The thermal stability of the PCNs obtained decreased with increasing clay content, with highly filled PCNs exhibiting poorer thermal stability properties than the neat PS. This was possibly due to clay platelets acting as catalysts for the decomposition of the polymer chains.

Both clay platelets dimensions relative to the polymer particle size and the reactivity of the clay modifier were found to influence latex morphology and extent of clay delamination of highly filled PS/clay nanocomposites. It was found that clay platelets whose size is smaller than the polymer particles could be easily encapsulated if they are modified by a reactive modifier. However, the same clay platelets could not be encapsulated if modified with a non-reactive modifier. On the other hand, clay platelets whose length was larger or equal to the polymer particle size could not be effectively encapsulated, irrespective of the type of modifier used (reactive or non-reactive). The extent of clay delamination was found to be highly dependent on the type of clay modifier. Reactive modifier yielded partial to full exfoliation of clay platelets whereas only intercalated PCNs could be obtained when non-reactive modifier was used, irrespective of the clay platelets dimensions.

Overall the prerequisites for effective encapsulation and exfoliation of high clay content using the ad-miniemulsion polymerisation were considered to be: the use of modifier that provides monomer/clay thermodynamic compatibility, use of reactive modifier which would participate in the polymerisation process, use of clay platelets whose dimensions are smaller than the monomer droplets.

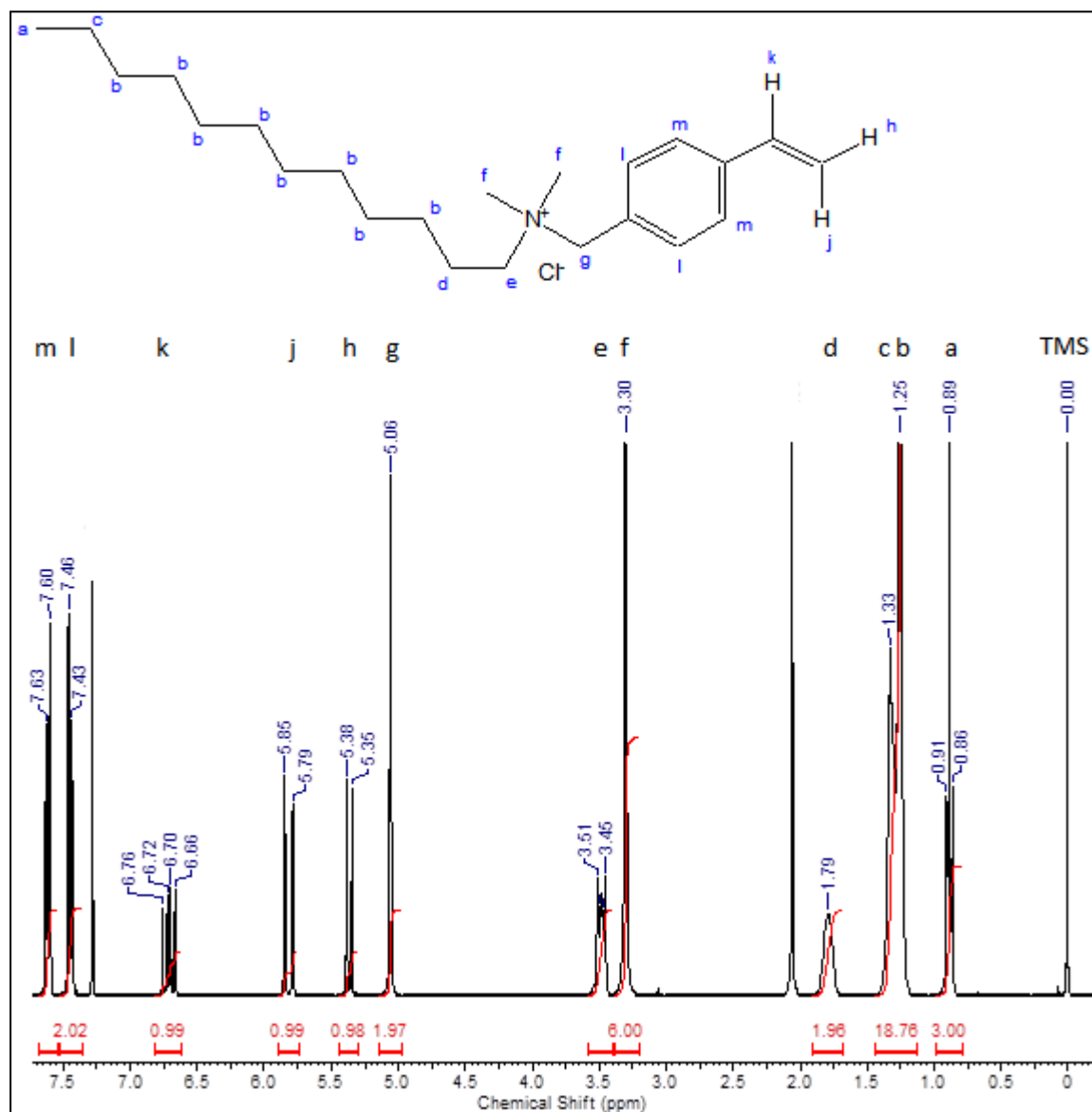
8.2 Recommendations for future work

Clay platelets are well known for their ability to improve the barrier properties of polymeric materials. The platelets are generally impermeable to the diffusing molecules and hence they induce a tortuous path, thereby reducing both the diffusion and permeability coefficients of the material. It is therefore worthwhile to evaluate the barrier properties of the highly filled latexes prepared in this study. These materials would be expected to exhibit high improvements in barrier properties due to the presence of high clay content.

It is worthwhile to extend the study to the use of other reactive clay modifiers such as inisurfs which promote surface initiated polymerisation. The study would help to elaborate the value of different reactive modifiers on encapsulation and clay exfoliation.

The effect of the alkyl chain length of the reactive modifier could be crucial for the effective encapsulation of MMT platelets. It is therefore recommended to evaluate the use of MMT modified with reactive modifiers with varying alkyl chain lengths.

It is recommended to study the effect of varying the copolymer composition of poly(styrene-co-butyl acrylate) on clay encapsulation and the properties of the final PCNs and latexes.

Appendix 1: ^1H NMR Spectrum of VBDAC

Appendix 2: Master Table for the Formulations for all the Hybrid Materials

Sample	^(a) Aqueous clay dispersion				Monomer miniemulsion					^(b) TSC
	^(c) Modified clay (g)	SDS (g)	Water (g)	^(d) SC (%)	^(e) Monomer (g)	AIBN (g)	HD (g)	SDS (g)	Water (g)	
PS00	-	-	-	-	10.0	0.20	0.40	0.1440	50.0	20.0
PS10	1.00	0.202	35.0	2.86	9.00	0.18	0.36	0.0430	15.0	20.0
PS20	2.00	0.212	36.7	5.45	8.00	0.16	0.32	0.0380	13.3	20.0
PS30	3.00	0.221	38.4	7.81	7.00	0.14	0.28	0.0330	11.7	20.0
PS40	4.00	0.230	40.0	10.0	6.00	0.12	0.24	0.0290	10.0	20.0
PS50	5.00	0.241	41.7	12.0	5.00	0.10	0.20	0.0240	8.30	20.0
PSBA00	-	-	-	-	10.0	0.20	0.40	0.1440	66.5	15.0
PSBA10	1.00	0.288	50.0	2.00	9.00	0.18	0.36	0.0430	15.0	15.0
PSBA20	2.00	0.298	51.7	3.86	8.00	0.16	0.32	0.0380	13.3	15.0
PSBA30	3.00	0.308	53.4	5.61	7.00	0.14	0.28	0.0330	11.7	15.0
PSBA40	4.00	0.317	55.0	7.27	6.00	0.12	0.24	0.0290	10.0	15.0
PSBA50	5.00	0.327	56.7	8.81	5.00	0.10	0.20	0.0240	8.30	15.0
PS10MMT	1.00	0.735	85.0	1.18	9.00	0.18	0.36	0.0430	15.0	10.0
PS20MMT	2.00	0.750	86.7	2.31	8.00	0.16	0.32	0.0380	13.3	10.0
PS30MMT	3.00	0.765	88.4	3.39	7.00	0.14	0.28	0.0330	11.7	10.0
PS40MMT	4.00	0.779	90.0	4.44	6.00	0.12	0.24	0.0290	10.0	10.0
PS50MMT	5.00	0.793	91.7	5.50	5.00	0.10	0.20	0.0240	8.30	10.0
PS/30Lap-CTA	3.00	0.221	38.4	7.81	7.00	0.14	0.28	0.0330	11.7	20.0

PS/40Lap-CTA	4.00	0.230	40.0	10.0	6.00	0.12	0.24	0.0290	10.0	20.0
PS/50Lap-CTA	5.00	0.241	41.7	12.0	5.00	0.10	0.20	0.0240	8.30	20.0
PS/30MMT-CTA	3.00	0.765	88.4	3.39	7.00	0.14	0.28	0.0330	11.7	10.0
PS/40MMT-CTA	4.00	0.779	90.0	4.44	6.00	0.12	0.24	0.0290	10.0	10.0
PS/50MMT-CTA	5.00	0.793	91.7	5.50	5.00	0.10	0.20	0.0240	8.30	10.0

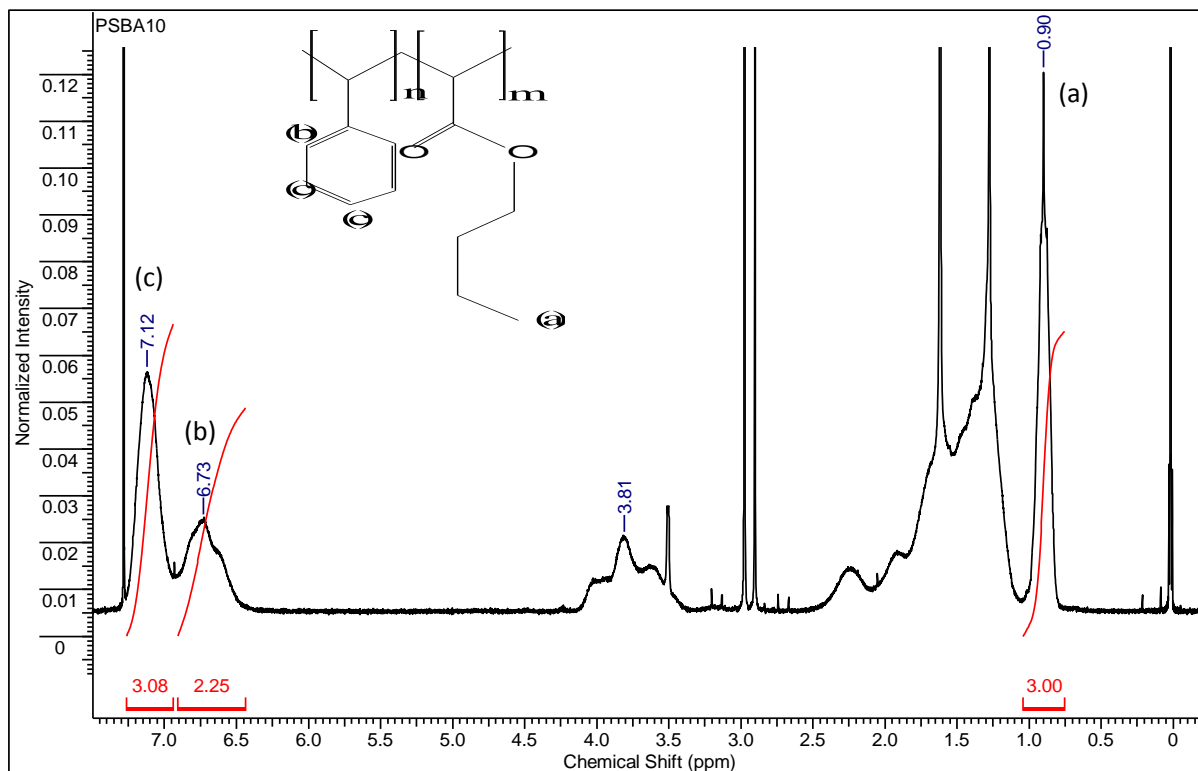
^(a) Dispersion of modified clay (Lap-VBDA, Lap-CTA, MMT-VBDA or MMT-CTA)

^(b) Total solids content in the final latex

^(c) Lap-VBDA, Lap-CTA, MMT-VBDA or MMT-CTA

^(d) Solids content in the modified clay dispersion (clay content (wt%) in the dispersion)

^(e) Styrene or Styrene/n-Butyl acrylate

Appendix 3: ^1H NMR Spectra of PSBA10

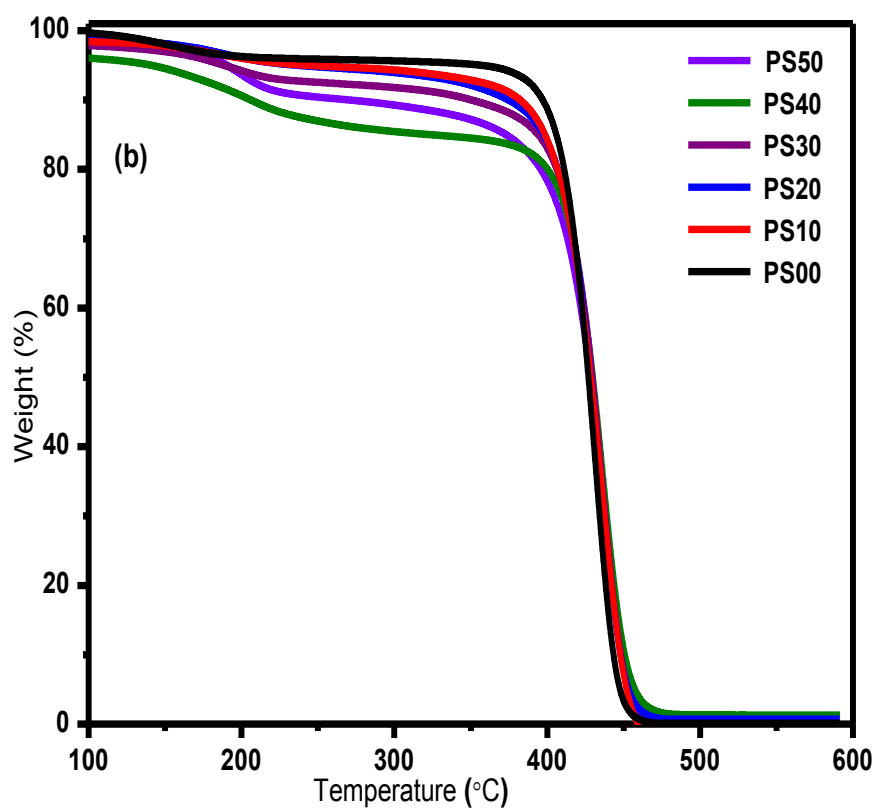
The styrene to butyl acrylate ratio was calculated using the equation:

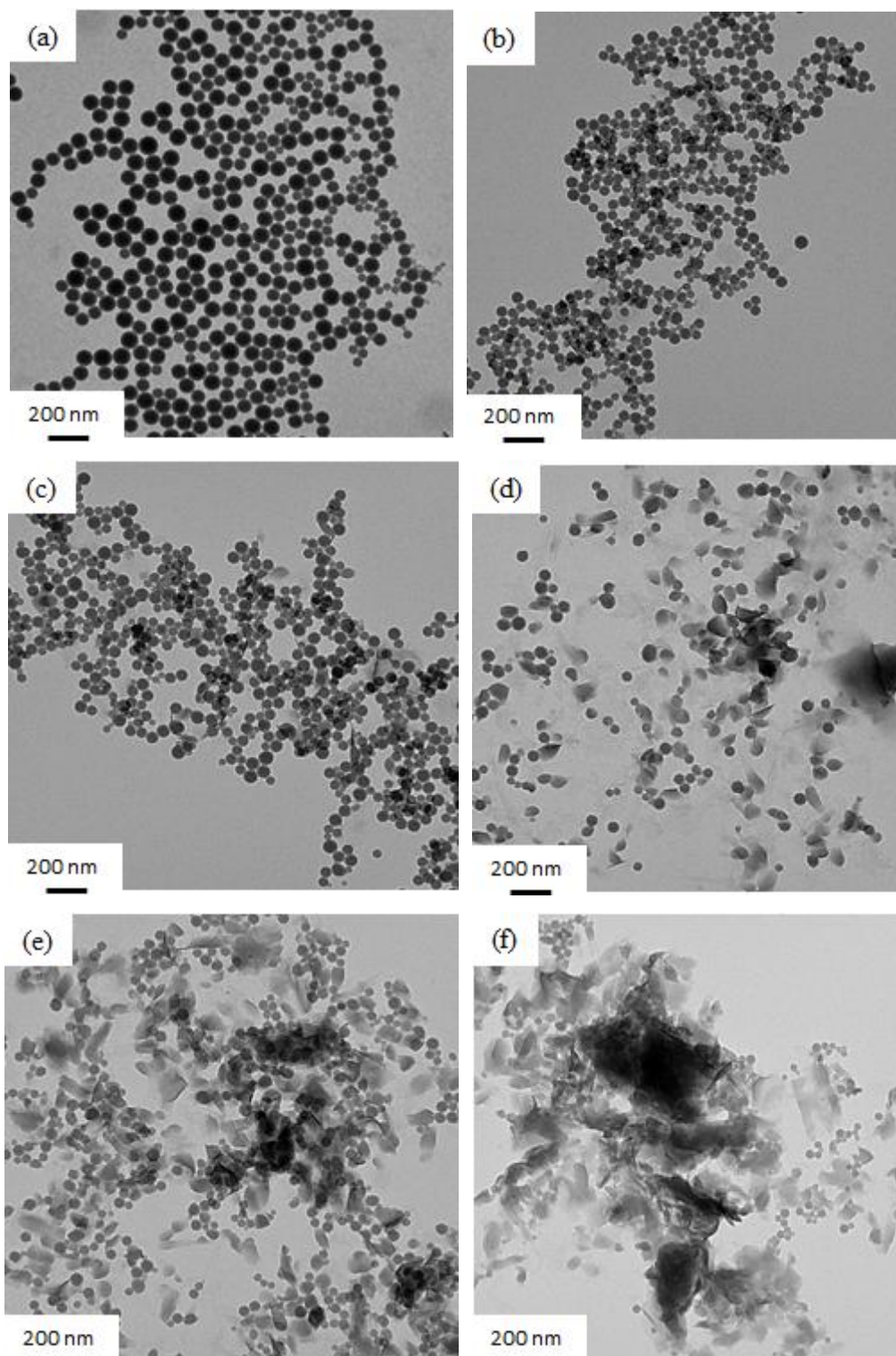
$$R = \frac{3(A_b + A_c)}{5A_a}$$

Where A_a , A_b and A_c denote areas of peaks in the spectrum labelled (a), (b) and (c), respectively.

The ratio of the PSBA sample with different clay content are given in Table A1

Sample	Sty/BA ratio
PSBA	1.04
PSBA10	1.06
PSBA20	1.10
PSBA30	1.04
PSBA40	1.05
PSBA50	1.06

Appendix 4: TGA thermograms of PS/Lap After Reverse Ion Exchange

Appendix 5: TEM Images of PS/MMT at Low Magnification

(a) *PS*, (b) *PS10MMT*, (c) *PS20MMT*, (d) *PS30MMT*, (e) *PS40MMT*, (f) *PS50MMT*

Appendix 6: Research Output

Articles

1. **Eddson Zengeni**, Patrice C. Hartmann, Harald Pasch: Crumpled highly filled poly(styrene-co-butyl acrylate)/clay hybrid latex nanoparticles, **Composite Science and Technology 2012**, *submitted*.
2. **Eddson Zengeni**, Patrice C. Hartmann, Harald Pasch: Encapsulation of clay by ad-miniemulsion polymerisation: The influence of clay size and modifier reactivity on latex morphology and physical properties, **ACS Applied Materials and Interfaces 2012**, *accepted*.
3. **Eddson Zengeni**, Patrice C. Hartmann, Harald Pasch: Highly filled polystyrene/Laponite hybrid nanoparticles prepared using the ad-miniemulsion polymerisation technique, **Macromolecular Chemistry and Physics 2012**, *accepted*.
4. **Eddson Zengeni**, Patrice C. Hartmann, Ronald D. Sanderson, Peter E. Mallon; Poly(acrylonitrile-co-methyl acrylate) copolymers: Correlation between copolymer composition and structural properties determined by positron annihilation spectroscopy, **Journal of Applied Polymer Science 2011**, 119, 1060–1066.*
5. **Eddson Zengeni**, Patrice C. Hartmann, Ronald D. Sanderson: Rheological properties of poly(acrylonitrile-co-methyl acrylate)/clay nanocomposites prepared via emulsion polymerisation, **Polymer composites 2010**, 32, 59-66.*

Book chapter/s

1. **Eddson Zengeni**, Austin Samakande, Patrice C. Hartmann: Polymer-clay nanocomposites prepared in miniemulsion via RAFT process, **RSC Nanoscience and Nanotechnology 2011, Vol 16: Polymer nanocomposites by Emulsion and Suspension**, Royal Society of Chemistry, 244–268.*

**Not part of the current research project*