Nanoclay-Modified Polyisoprene Latexes for Reinforcing Natural Rubber Thin Films

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Thesis Title Nanoclay-Modified Polyisoprene Latexes for Reinforcing Natural Rubber Thin Films
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ABSTRACT

Nanoclay-modified polyisoprene latexes were prepared and then used as a reinforcing component in natural rubber (NR) thin films. The synthesizing efficiency of three emulsion polymerization techniques was first compared so that an adequate technique could be selected for further investigations. Results demonstrate that starve-fed emulsion (SFE) polymerization is the most appropriate synthesizing method compared to conventional and mini-emulsion techniques i.e. batch process. This is attributed to the SFE provides a smaller average polymer particle size which in turn results in a greater polymerization locus, promoting the reaction rate. The addition of organo-nanoclay during synthesizing polyisoprene significantly lessens polymerization efficiency because the nanoclay has a potential to suppress nucleation process of the reaction. It also intervenes stabilizing efficiency of the surfactant – SDS or sodium dodecyl sulfate, giving enlarged average sizes of the polymer particles suspended in the latexes. TEM images show that nanoclay particles are attached on and/or inserted in the polymer particles. XRD and thermal (DSC and TGA) analyses were employed to assess the d-spacing of nanoclay structure in NR nanocomposite films, respectively. Based on the overall results, 5 wt% of nanoclay relative to the monomer content utilized to alter polyisoprene during emulsion polymerization is an optimum amount since the silicate plates of nanoclay in the composite exhibit the largest d-spacing which maximizes the extent of immobilized polymer constituent, giving the highest mechanical properties to the films. The excessive amounts of nanoclay used, i.e. 7 and 10 wt% relative to the monomer content, reduce the reinforcing power due to re-agglomeration effect. Investigation of the influence of Clay-PIP contents on properties of NR thin films reveals that there are three crucial parameters affecting reinforcement mechanism of the composites: 1) nanoclay, 2) molecular characteristics of polyisoprene and 3) material heterogeneity. These influencing factors play a competitive role on reinforcement efficacy in the system. The best possible formulation for a NR thin film based on Clay-PIP as a reinforcing component is NR/Clay-PIP at 90/10 phr using the Clay-PIP containing 5 wt% of nanoclay relative to the monomer content.

Keywords: Nanocomposite, Elastomer; Latex, Filler, Reinforcement

ชื่อวิทยานิพนธ์ น้ำยางพอลิไอโซพรีนดัดแปรด้วยนาโนเคลย์เพื่อใช้เสริมแรงฟิล์มบางจากยางธรรมชาติ
ผู้เขียน นายเจษฎาภรณ์ ช่วยแท่น
สาขาวิชา วิทยาศาสตร์และเทคโนโลยีพอลิเมอร์
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บทคัดย่อ

งานวิจัยนี้ศึกษาการสังเคราะห์น้ำยางพอลิไอโซพรีนดัดแปรด้วยนาโนเคลย์ (Clay-PIP) เพื่อใช้เป็นสารเสริมแรงในฟิล์มบางจากยางธรรมชาติ โดยใช้กระบวนการพอลิเมอไรเซชันแบบอิมัลชันที่ต่างกัน 3 เทคนิค จากนั้นเปรียบเทียบผลการสังเคราะห์เพื่อคัดเลือกเทคนิคที่เหมาะสม ผลการทดลองพบว่า การสังเคราะห์ด้วยวิธีสตาร์ฟเฟดอิมัลชัน (SFE) เป็นวิธีการที่เหมาะสมที่สุด เมื่อเทียบกับเทคนิคแบบปกติ (CE) และแบบมินิอิมัลชัน (ME) โดยระบบ SFE สามารถควบคุมขนาดอนุภาคของมอนอเมอร์ให้มีขนาดเล็ก ทำให้มีพื้นที่ผิวในการเกิดปฏิกิริยาพอลิเมอร์ไรเซชันมากขึ้น และส่งผลให้อัตราการเกิดปฏิกิริยามากขึ้น เมื่อเติมนาโนเคลย์ในระหว่างการสังเคราะห์พอลิไอโซพรีนพบว่า ประสิทธิภาพของปฏิกิริยาพอลิเมอร์ไรเซชันลดลงอย่างมีนัยสำคัญ เนื่องจากนาโนเคลย์มีผลในการยับยั้งกระบวนการเกิดนิวเคลียสของพอลิเมอร์ในช่วงเริ่มปฏิกิริยา และยังรบกวนประสิทธิภาพของสารเพิ่มความเสถียรชนิดโซเดียมโดเดซิลซัลเฟต (SDS) ส่งผลให้อนุภาคของพอลิเมอร์มีขนาดใหญ่ขึ้น ภาพทางสัณฐานวิทยาจากเทคนิค TEM แสดงให้เห็นอนุภาคนาโนเคลย์เกาะติดบนผิวและแทรกเข้าอยู่ในอนุภาคพอลิเมอร์ที่สังเคราะห์ได้ นอกจากนี้ได้วิเคราะห์โครงสร้างผลึกด้วยเทคนิค XRD เพื่อตรวจสอบระยะห่างของแผ่นซิลิเกตในโครงสร้างของนาโนเคลย์ที่กระจายอยู่ในวัฏภาคของพอลิเมอร์ และวิเคราะห์สมบัติเชิงความร้อนด้วยเทคนิค DSC และ TGA เพื่อตรวจสอบอันตรกิริยาระหว่างนาโนเคลย์และพอลิเมอร์ ผลการวิเคราะห์พบว่า การเติมนาโนเคลย์ 5 % โดยน้ำหนักของมอนอเมอร์ ในระหว่างกระบวนการพอลิเมอไรเซชันเป็นปริมาณที่เหมาะสมที่สุด เนื่องจากแผ่นซิลิเกตของนาโนเคลย์กระจายตัวในพอลิเมอร์ได้ดี ส่งผลให้ฟิล์มยางมีสมบัติเชิงกลสูง เมื่อเติมนาโนเคลย์ในปริมาณที่มากเกินไปที่ 7 และ 10 % โดยน้ำหนักของมอนอเมอร์ ส่งผลให้ประสิทธิภาพการเสริมแรงลดลงเนื่องจากการรวมตัวกันเป็นกลุ่มก้อนของอนุภาคนาโนเคลย์ จากผลการทดลองในงานวิจัยนี้สามารถสรุปได้ว่า การเสริมแรงของน้ำยางไอโซพรีนดัดแปรด้วยนาโนเคลย์ในฟิล์มบางจากยางธรรมชาติ มีปัจจัยที่ส่งผลต่อกลไกการ

เสริมแรงที่สำคัญ ได้แก่ นาโนเคลย์ โครงสร้างโมเลกุลของพอลิไอโซพรีน และความเข้ากันได้ของน้ำยางไอโซพรีนดัดแปรและน้ำยางธรรมชาติ สำหรับอัตราส่วนที่เหมาะสมที่สุดในการเตรียมฟิล์มบางจากยางธรรมชาติ คือ สูตรยางที่ใช้น้ำยางธรรมชาติผสมกับน้ำยางไอโซพรีนดัดแปรที่ 90 ต่อ 10 ส่วนโดยน้ำหนัก คิดจากน้ำหนักแห้ง โดยใช้น้ำยางไอโซพรีนดัดแปรที่มีนาโนเคลย์ 5 % โดยน้ำหนักของมอนอเมอร์

คำสำคัญ: พอลิเมอร์ น้ำยาง ยางธรรมชาติ สารตัวเติม การเสริมแรง

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Jadsadaporn Chouytan

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
BR	Butadiene rubber
CE	Conventional emulsion polymerization
CEC	Cation exchange capacity
CMC	Critical micelle concentration
Clay	Nanoclay
Clay-PIP	Nanoclay-modified polyisoprene
DSC	Differential scanning calorimeter
DTG	Derivative thermogravimetric analysis
DI water	Deionized water
IP monomer	Isoprene monomer
K	Empirical parameter related to the free volume in the sample
k_p	Rate coefficient of the propagation process
LPSA	Laser particle size analyzer
N_A	Avogadro's constant
N_c	Particle number concentration
NR	Natural rubber
NRL	Natural rubber latex
NR/Clay-PIP	Natural rubber reinforced with nanoclay-modified polyisoprene
ME	Miniemulsion polymerization
MMT	Montmorillonite
M_p	Initial mass of polymer per unit
MWD	Molecular weight distributions
PIP	Polyisoprene
phr	Part per hundred rubber
$\mathrm{R_p}$	Rate of polymerization

LIST OF ABBREVIATIONS (continued)

SFE	Starve-fed emulsion polymerization
SBR	Styrene butadiene rubber
TEM	Transmission electron microscopy
T_d	Decomposition temperature
T_g	Glass transition temperature
$T_{g,\infty}$	Maximum T_g at a theoretical infinite molecular weight
TGA	Thermal gravimetric analysis
TSC	Total solid content
XRD	X-ray Diffractometer
ΔC_p	Heat capacity
[M]	Monomer concentration

CHAPTER 1

INTRODUCTION

1.1 Background and rationale

Natural rubber (NR) is a renewable polymeric material which is derived from Para rubber trees. A variety of products available in our daily life are made from or composed of NR, such as tires (for passenger cars, trucks and airplanes), engineering goods (for instance, building- and bridge-bearing pads), shoes, gloves, condoms, rubber bands, medical devices, etc. Key factors influencing processibility of rubber compounds and overall properties of the final products include rubber formulations, processing techniques, as well as product designs. Besides these three factors, the production cost is one of the most important industrial requirements which need to be minimized.

Rubber articles produced from latexes are mostly available in the products of condoms and gloves. These rubber thin film-based products have continually been improved in order to fulfill the utmost requirements of the users. The preferred properties of these products include strength, modulus and elongability. In addition, there has been an attempt to reduce the thickness of the films while maintaining overall properties. It is agreeable that the products with a thinner thickness give better touch sensitivity to the users. Super thin-wall condoms provide the users with a better feeling upon utilizing. While surgery gloves with a very thin thickness make the users or surgeons more confident. The accuracy of surgical operations is highly important for operated patients. Mistakes and inconveniences during a surgical process are, in most cases, caused by poor touch sensitivity. This can occur, in particular, when doctors or their assistants pick surgical tools, medicines or patient’s organs. However, thin film-based rubber products have, in general, poorer mechanical properties than that of the thicker ones. Therefore, it becomes a challenge that an appropriate method used to reduce the thickness of the rubber films while maintaining processing and mechanical properties needs to be explored.

In the rubber industry, the technology of reinforcing fillers is practically crucial and useful for enhancing product performance, especially mechanical properties. Several types and grades of active fillers have been developed such as carbon black: the classical one, silica and various nanofillers. However, the addition of these fillers into rubber compounds faces some difficulties, e.g. dispersibility of the fillers as they are, by nature, in the form of clusters or bundles due to strong interactions between their particles. Up-to-date, this technology can successfully be applied only for solid rubbers because mixing active fillers with solid rubbers generates sufficient high shearing force in the system. This shearing action arose during compounding are essential for breaking the agglomerates of the filler, leading to improved filler dispersion in the compounds. Regarding high interest in super thin film-based rubber products, in particular condoms and surgical gloves, the addition of active fillers might be an effective approach to produce them with the desired wall thickness and acceptable mechanical properties. However, incorporation of reinforcing fillers in latex compounds is inconvenient due to a rather low shear force involved during compounding. The latex compounding is commonly done in a slowly stirring system, i.e. about 20-30 rpm stirring speed. Therefore, the internal shear forces are insufficient to break the agglomerates of fillers, leading to poor filler dispersion and so decreased overall vulcanizate properties.

Active fillers added into rubber compounds typically provide higher modulus or stiffness, while flexibility and softness of vulcanizates are reduced. In case of the products with thin walls, it is important to compromise between their flexibility and stiffness because the two properties significantly affect texture and mechanical properties of the products. Nanoclay is one of the most attractive fillers due to its highly active specific surface area. When comparing with conventional reinforcing fillers, nanofillers can provide remarkably enhanced properties with only a small dosage.

Owing to a hassle in dispersibility of active fillers encountered during latex processing, a technique to modify fillers prior to adding them into latex compounds is taken into account. In the present study, organo-nanoclay will be modified in isoprene rubber (IR) or polyisoprene (PIP) particles through in-situ emulsion polymerization. The synthesized PIP latexes were blended with natural rubber latexes. Under the assumption that PIP is the synthesized form of natural rubber and so exhibits good compatible with a regular natural rubber latex. In addition, the encapsulated nanoclay in PIP particles will possibly result in good dispersibility of nanoclay in NR matrix without high shearing energy input. Based on the literature, there were prior researches related to the topic of clay-insertion in polymer particles during its polymerization. However, many aspects in polymerizations still remain unclear and need to be developed in particular for the application of reinforcing NR thin films. Nowadays, there are some special types of condoms commercially produced with a thickness as the thinnest as 0.03 mm or 30 microns. However, the technological information on fabricating this thin wall-based article are limited.

This research project aims to improve the properties of natural rubber thin film by using nanoclay-modified rubber particle of polyisoprene latexes as a reinforcing agent. The in-situ modification process was conducted through batch, mini and starve-fed emulsion polymerization techniques. Polymerization conditions such as monomer content, surfactant content and feeding sequence of reagents on synthesizing efficiency were investigated. After optimizing polymerization conditions, the intrinsic properties of resulting colloidal nanoclay-modified polyisoprene (Clay-PIP) latexes including morphology and stereochemistry along with thermal properties were determined. At the final stage, the synthesized Clay-PIP latexes were blended with natural rubber latex to prepare NR thin film nanocomposites through a casting process. The obtainable thin films were further investigated for their properties. Reinforcement efficiency of the Clay-PIPs towards NR thin films was evaluated.

1.2. Project objectives

1. To study three different methods of emulsion polymerization: conventional batch; mini-emulsion and starved-fed emulsion techniques, for polyisoprene synthesis; an appropriate polymerization technique is required. Key parameters influencing polymerization properties were identified.
2. To prepare nanoclay-modified polyisoprene latexes through an appropriate emulsion polymerization method.
3. To characterize chemical and technical properties of the obtained polyisoprene latexes with and without nanoclay modification.
4. To prepare latex compounds by blending natural rubber and synthesized polyisoprene latexes to be used for preparing NR thin film nanocomposites using a casting process.
5. Investigation of technical properties of the obtained NR thin films in order to evaluate reinforcement efficiency of the nanoclay-modified polyisoprene latexes in natural rubber thin films.

1.3 Scope of the project

1. The polymerization parameters for synthesizing polyisoprene latexes without nanoclay modification were investigated so that an optimum condition can be applied for preparing nanoclay-modified polyisoprene latexes.
2. Basic and technical properties of the polyisoprene latexes synthesized from section 1 were investigated, including molecular weight and molecular weight distribution, chemical structure, morphology, stereochemistry, particle size and particle size distribution, thermal properties as well as d-spacing of the nanoclay structure.
3. Polyisoprene latexes were modified with organo-nanoclay through an in-situ emulsion polymerization. An appropriate emulsion technique suggested from sections 1 and 2 was applied in this section. Further adjustment of the emulsion technique for in-situ modification of nanoclay was carried out.
4. Natural rubber thin films blended with Clay-PIPs were studied. Reinforcement efficiency of the Clay-PIPs in isoprene rubber particles towards improvement of properties of rubber thin films.
5. Physical, mechanical and thermal properties of the resulting NR film nanocomposites were determined.
6. The correlations of overall aspects with reinforcing efficiency will be focused.

1.4 Deliverables of the project

1. Knowledge based on comparative study of emulsion polymerization of polyisoprene latexes with different emulsion techniques.
2. An optimum condition for synthesizing isoprene latexes with and without nanoclay modification.
3. Principles of reinforcing natural rubber thin film-based products using nanofillers and nanoclay-modified polymer latexes.
4. A core technology to improve product performance based on natural rubber which is one of the key agricultural products of Thailand.

CHAPTER 2

LITERATURE REVIEW

2.1 Natural rubber

Natural rubber (NR) is a natural polymer which has chemical structure of repeating units of cis-1,4 isoprene or polyisoprene as shown in Figure 2.1. This natural polymer has high molecular weight that is in the range of 10^5-10^7 g/mol with a broad molecular weight distribution, depending on clone, weather, tapping frequency and other factors [1]. Natural rubber can be derived from nearly five hundred different species of plants. The most important and effective production source of natural rubber is the trees in a genus of *Heavea brasilliensis* or the so-called Para´ rubber tree. The Para´ tree is tapped and then its milky liquid which is termed as latexes is exuded along the cut-bark. Farmers use a small bowl set below the cut-bark to collect this NR latexes from the trees.

Fresh NR latexes is in a form of colloidal liquid with aqueous medium and composes of several components that typically contain 34 wt% of dry rubber , 2 - 3 wt% of proteins, 1.5 - 3.5 wt% of resins, 0.5 – 1 wt% of ashes, 1.0 - 2.0 wt% sugar, 0.1 - 0.5 wt% of sterol glycosides and 55 - 60 wt% of water [1]. *Hevea latexe*s have a pH in the range of 6.5 - 7.0, a density of 0.98 g/cm^3 and a surface energy 4.0-4.5 µJ/cm^2. Rubber particle sizes are variable from 0.15 to 3 µm [2].

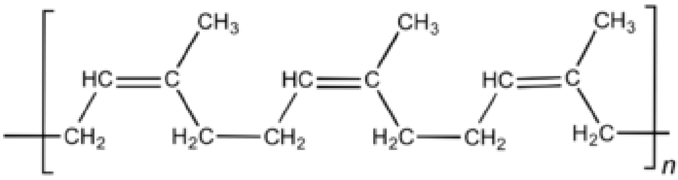

Figure 2.1 Chemical structure of cis-1,4 polyisoprene natural rubber.

2.1.1 Compositions in natural rubber latex

The NR latex is a colloidal dispersion of rubber particles in an aqueous medium. Dry rubber content is in the range of 20 to 40 wt% (typically about 30 wt%) and about 5 wt% of non-rubber components, such as carbohydrates, proteins, phospholipids and metal salts. The remaining fraction of approximately 50 – 60 wt% is water medium mixed with serum. Figure 2.2 shows the separated compositions of field natural rubber latexes after vigorous centrifugation [3]. The quantity of these compositions in latexes depends on various factors, such as type of Para tree, location of plantation, season, age of trees and so on. The rubber particles are surrounded by phospholipids and proteins which are effectively negatively charged [4] as shown in Figure 2.3. When exposed to environment, latexes coagulation occurs as proteins are decomposed rapidly by bacteria and enzymes. Fresh natural rubber latex coagulates within a few hours after its collection from the trees. This means that the colloidal stability of fresh NR latexes spontaneously drops upon handling in further processes because of the main problem of a microbial infection. In order to overcome against coagulation and putrefaction of NR latexes, addition of small amount of ammonium hydroxide is the most widely used to stabilize NR latexes to prolong its handling life [5].

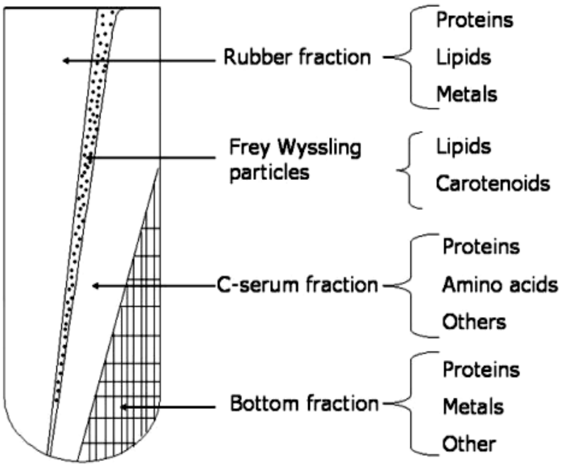

Figure 2.2 Fraction of components in natural rubber latexes after centrifugation [3]

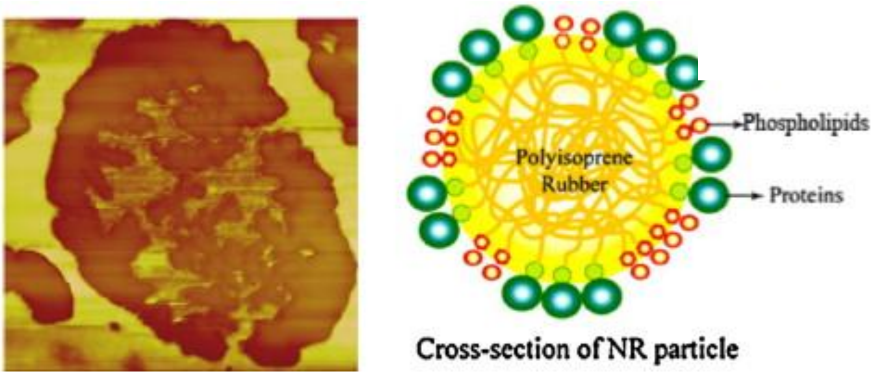

Figure 2.2 The profile of natural rubber particle consisting of a mixed layer of proteins and lipids [4]

2.1.2 Chemical structure in correlation with basic properties of natural rubber

The molecular chain of this natural polymer is a regular succession of isoprene units, with every fourth carbon atom in the chain carrying methyl ($-CH_3$) side-group. The double bond in its molecule significantly determines the chemical reactivity, in particular the ability to react with the vulcanizing agents, i.e. sulfur, peroxide, and other reagents in various modification processes. In addition to the strong reactivity of the double bond in NR molecules, this site has an important impact on elastic properties of rubber. Three intermolecular aspects affecting the natural rubber to exhibit excellent elasticity are as followings [6]:

1. The molecule with a presence of freely rotating methyl side-group conjugated at the double bond; the present of long chain molecule, with free rotating link;
2. Non-polar hydrocarbon chain, leading to weak intermolecular interaction (Van der Waals forces) among the molecules as a consequence of easy chain mobility; weak secondary forces between the molecules;
3. Physical chain entanglement of long molecules creating a three-dimensional network of which acts as a chemical crosslink: an interlocking of molecule at a few places along their length to form a three-dimensional network.

2.2 Polymer nanocomposites

Nanocomposite is the material that comprises of nanometer-size particulates dispersed in the matrix. The matrix can be one or multi-components with specific functionalities, for instance, reinforcement, conductivity, toughness, etc. In addition, it may be metallic, ceramic or polymeric materials. Polymeric nanocomposites have been an attractive material for industrials and academic research in the past decades. The large interfacial interaction between nanoparticles and matrix significantly improve composite properties when compared to unfilled or micro-particulate filled polymer composites, in particular modulus, strength and heat resistance [7], [8]. The nanoparticles can generally be in lamellar, fibrillar, tubular, spherical or other shapes. Different particle dimensions provide variable properties to the composites, for instance, lamellar shape gives an improvement in mechanical and barrier properties; the stiffness and strength can be increased with the use of fibrillar-structure nanoparticles; spherical functionalized nanocarbon blacks improve optical, electrical and conductivity properties [9].

2.3 Reinforcement in rubber

Reinforcement of elastomers by mineral fillers is essential in rubber products, since it can practically improve processing and end-use properties of rubber compounds and vulcanizates, especially for mechanical strength and modulus. Structure, surface chemistry, particle size and surface modification of fillers are the crucial parameters which determine reinforcing efficiency and technical performance in rubber applications. The interfacial interactions between an organic (rubber) and an inorganic (filler) phase play a significant role on the reinforcing mechanism[10], [11].

Carbon black and silica have been widely used as reinforcing fillers in elastomeric compounds. These conventional fillers must be used at an optimum loading level in order to obtain desired properties of compounds and vulcanizates [12]. Some active fillers, like silica, need to be modified on its surface so that such a filler has better compatibility with general purpose hydrocarbon rubbers or non-polar rubbers, i.e. NR, SBR, BR, leading to a remarkably improvement in reinforcement. Preferred aspects of active filler-added rubber compounds include good dispersion degree of filler, a sufficient extent of rubber-filler interactions and good compound stability. Recently, the reinforcing nanofillers have extensively been used for rubber reinforcement since they have a greater active surface area compared to the conventional ones. The overall properties of nanofiller-based rubber compounds can prominently be improved by applying only a small amount of nanofillers (less than 10 wt% relative to rubber content). These nanometer-scale particulates, such as silica, titanium dioxide, layer silicates or clay, carbon black and fibers as well as carbon nanotubes have shown to reinforce rubbers with a significant enhancement of physical and mechanical properties of rubber vulcanizates

Compared to the conventional reinforcing filler, nanofillers are important for reinforcement in rubbers. Due to very small particle size with high specific surface area, they can increases the interaction between rubber and filler phases resulting in high reinforcement efficiency. The reinforcement performance of nanofillers in rubbers is influenced by many factors, including particle size, particle shape, particle structure and surface reactivity of the fillers. In addition, type of rubbers also has an important effect on compatibility with each type of fillers. These factors result in variable reinforcement efficiencies, due to rubber-filler interactions, filler dispersion and three-dimensional networks in the compounds are altered [13]. The evaluation of reinforcement performance in rubbers can be carried out by monitoring the change of storage moduli under a dynamic deformation, a so-called Payne effect phenomenon. Figure 2.4 shows the shear modulus of a reinforcing filler-based rubber compound, decaying under a dynamic mechanical deformation from small to large shear strains [14].

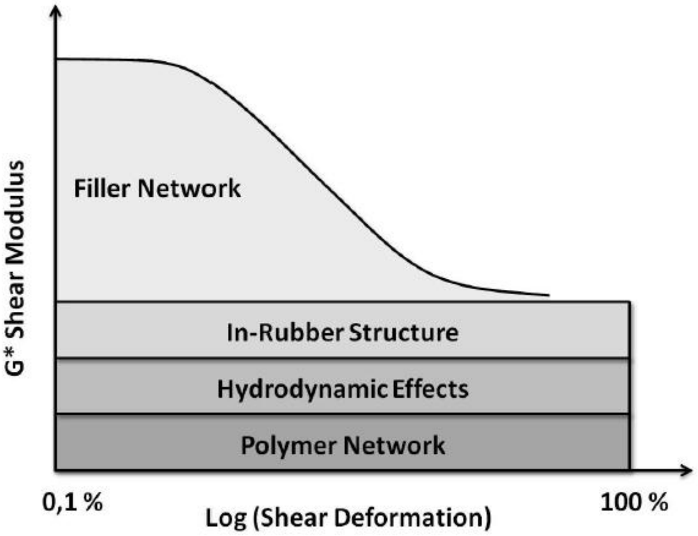

Figure 2.4 Payne effect on filler-reinforced rubber [14]

The Payne effect concept: see Figure 2.4, is able to elucidate the reinforcement mechanism of active fillers in rubbers. The shear modulus of filled compound changes over shear strain, attributed to filler clusters or agglomerates in the compound are destroyed leading to deteriorated shear modulus. Therefore, the difference between the shear moduli at small and large deformations can be used as a measure of ‘filler-filler interaction’ or filler network. As explained earlier, the reinforcement mechanism comes from strong interactions between rubber molecules and filler particles. This filler-rubber interaction is independent with shear deformation because it has strong bonds with filler particles. High extent of this interaction is required in the compounds, however, it is variable depending on various parameters, e.g. type and amount of fillers and rubbers, mixing process, coupling agents, and so on. When we add a filler at a certain amount, it results in a proportional increment of the material modulus. This phenomenon is called ‘hydrodynamic effect’, of which it is not dependent on material deformation; the higher the filler content, the higher the hydrodynamic effect. Another factor which is also independent on material deformation is ‘polymer network’ plays a certain influence in the increase of modulus. A higher polymer network density gives a higher material modulus.

2.4 Rubber products based on thin films

Elastomeric thin films can be processed using rubber latexes as raw materials. The latexes will be compounded with chemical dispersions and maturated for 48-72 hours to obtain the so-call prevulcanized latex compounds. The latex compounds will be further processed to form a thin film through dipping or casting processes. Dipping is a commonly used technique for glove and condom products. There are three methods of dipping technique including direct, coagulation and heat sensitive dipping processes. The direct dipping process is used in condom production. While the coagulation dipping is commonly used in the production of gloves. The heat sensitive dipping is applied to obtain special thick rubber films such as elastic pacifier for kids and some medical devices like rubber tubes and hoses, wound supporters, etc. The thickness of these film products, therefore, depends on various influencing factors, e.g. concentration of latex compound, condition of dipping process, concentration of coagulant, and so forth.

2.5 Reinforcement in rubber thin films

For the products based on dry rubber raw materials, fillers are added into rubber compounds for two main purposes. The first is to improve mechanical properties of the product, and the second is to reduce production costs. The latter can be done by adding low price fillers as much as possible, however, the overall product properties must remain acceptable. It is still challenging that there is limited approach to reinforce rubber thin films from latexes. While some type of commodity gloves which are fabricated from latexes can be filled with inexpensive fillers to minimize their production cost. But the thin films based on latexes can hardly be reinforced by fillers as discussed earlier in Chapter 1. Very thin rubber films have low mechanical properties, in particular modulus. To improve the mechanical properties, the latex compounds can be modified using stiffness modifying agents. Recently, there is a commercial silica dispersion available in the markets to be used for reinforcing latex-based thin films [19]. However, this silica type has rather high cost. Therefore, an alternative to the silica dispersion with a lower price would be much attractive by the users. The reinforcing agents for latexes must have special characteristics, e.g. very small particle size (preferable in nanoscale), good compatibility with the latex, no adverse effect towards coagulation of the latex.

2.6 Nanofillers

Nowadays, there are various types of nanofillers to be used for reinforcing polymeric nanocomposites, including graphene, carbon nanotubes, nanoclay and nanofibers, and so on. General information of these nanofillers is discussed in the following paragraphs which will be emphasis on nanoclays.

2.6.1 Graphene

Nanoparticulate graphene consists of pure carbon like graphite, diamond, charcoal and carbon nanotubes, but they have a different carbon configuration. Graphene can be synthesized using graphite as a starting material. The graphite is reacted with a strong acid in order to separate its structure into single carbon layers. This layer composes of carbon atoms configured in hexagonal lattice which exhibits a honeycomb-like formation as shown in Figure 2.5. The graphene thickness is equal to one layer of carbon atomic-scale. The outstanding properties of graphene are strength, heat-conducting and electrical-conducting. Graphene is widely used for the production of small electronic circuits [15].

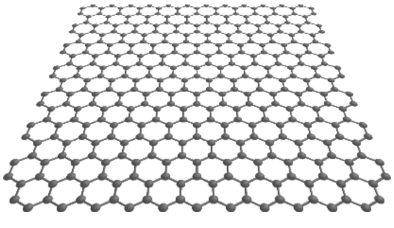

Figure 2.5 Graphene layer consisting of carbon atoms configured in hexagonal lattice [15].

2.6.2 Carbon nanotubes

Carbon nanotubes consist of pure carbon as same as graphene, but their particle shapes are different. Graphene has a plate shape structure, while carbon nanotube has a rolled form of a graphene layer, exhibiting a tube shape of the particles as depicted in Figure 2.6. They provide outstanding properties to composites, in particular toughness. The ratio between length and diameter is remarkably high, e.g. 132,000,000: 1. In addition, the use of carbon nanotubes as a filler in composites give the products with prominent properties such as thermal conductivity, mechanical properties and electrical properties [16].

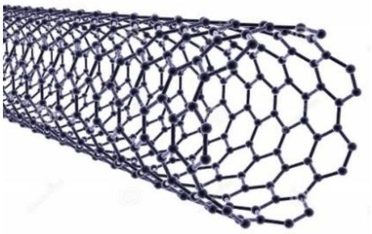

Figure 2.6 Carbon nanotube having a hollow cylindrical structure of a single layer of carbon atoms configured in hexagonal lattice [16].

2.6.3 Nanosilicas

Nanosilicas are reinforcing fillers widely used in polymeric composites. Because of their highly reactive surface characteristics, silica particles tend to form agglomerate structure. This structure needs to be broken down during mixing to obtain adequate dispersion in a polymer matrix [17]. Silica has high polarity due to hydrophilic surfaces composing of silanol groups. Consequently, silica is incompatible with general purpose rubbers which are mostly non-polar ones, e.g. natural rubber (NR), styrene–butadiene rubber (SBR) and butadiene rubber (BR). However, it has better compatibility with polar rubbers such as polychloroprene rubber [18]. So, the use of silica in non-polar rubbers without a compatibilizer results in poor dispersibility of silica. Successful use of silica for rubber reinforcement, therefore, requires a silane coupling agent to develop the bonds between silica and rubber or silica–rubber interaction and hydrophobize silica surface giving good dispersion to a composite.

2.6.4 Nanoclays

Clay originates from alkaline volcanic ashes and rocks for about 85-120 million years ago. The airborne ash deposits at high volume in the sea and alkaline lakes. Many hypotheses have been proposed regarding the transformation mechanism of ash to clay which is probably because the concentration of Mg^{2+} and Na^{+} in marine is sufficient to react with ash deposited and so becoming as clay structures [9]. Clay particles are generally in a bundle from of layer silicates, i.e. plate shape or sheet, which possess at least one dimension in nanosize scale as determined by aspect ratio. High aspect ratios indicate large specific surface area of clay. They are several types of crystalline clay, for instance kaoline, serpentine, micas, chlorites, smectites, etc., the latter is the most widely used in polymeric nanocomposites, in particular montmorillonites. It has a triple-layer sandwich structure as depicted in Figure 2.7 [19]. The octahedral plate bearing aluminum atom is in between two plates of tetrahedral layer.

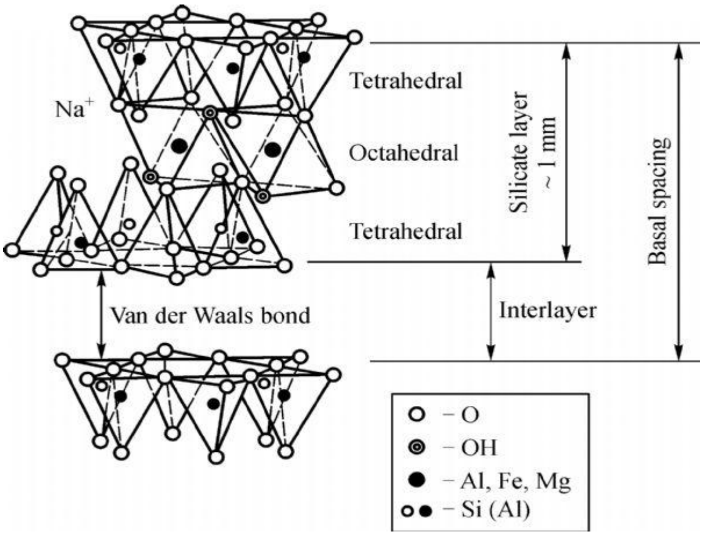

Figure 2.7 Proposed structure of smectites [19].

It is noted that the layer silicates exhibit charge imbalance due to a presence of cationic charges which come from Na^{+}, Ca^{2+}, K^{+} adsorbed on the silicate plates. These cationic charges are readily to be exchanged with other cations. Several triple-silicate layers tend to form stacks with the interlamellar divided in between them. Ones of smectites become commercially used include montmorillonites and hectorites, but the latter has some limitation in polymer field applications.

Montmorillonite or MMT is the name of one city in France. It is the most commonly used in the production of polymeric nanocomposites. MMT has been called in several names: smectites, sodium monrillonite, sodium bentonite, swelling bentonite, etc. Its color can be in brick red, yellow, blue grey. A single layer of the triple-silicate plates has 0.22 nm thick with the interlayer spacing of 0.92 nm (characterized with XRD technique). The CEC value is in the range of 0.8 – 1.2 meq/g and specific surface area is approximately 750-800 m^2/g. In addition, the density of silicate-sandwich plates is 4.03 g/ml when its interlamellar spacing is 0.79 nm [9].

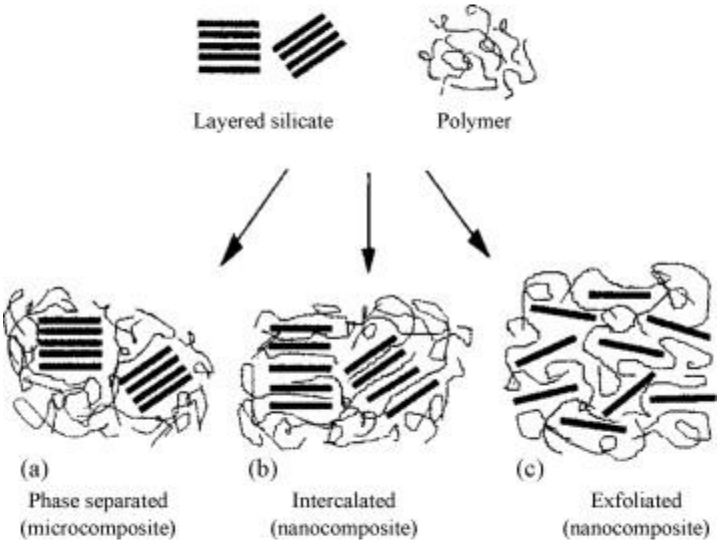

Figure 2.8 The possible structures of clay dispersed in a polymer/clay nanocomposite [20]

In the previous works, MMT can be treated with acids to prepare organoclay. The metallic ions, such as Ca^{2+}, Fe^{3+}, Al^{3+}, Mg^{2+} are replaced by H^+. The use of clay in polymer nanocomposites gives significant improvement in physical and mechanical properties when good dispersion and great interfacial interactions between clay and polymer phases are accomplished. There are three key patterns of dispersion aspect of layered silicates in clay-filled polymer composites as displayed in Figure 2.8 [20].

From Figure 2.8, it illustrated three possible structures of clay being dispersed in a composite, detailed as follows:

(a) The clay particles dispersed in the polymer matrix are not separated into a single silicate layers. Polymer molecules cannot insert into the clay structure. So, the clay added is basically still in a basic form.

(b) The polymer molecules are inserted in the gallery of layered silicates. Such a molecule is flanked by two clay layers and is immobilized and shielded. Width of the gallery is not much affected during intercalation.

(c) The gallery expanded from its normal size for 1 nm to about 20 nm or higher, which is called “delaminating process”. It is a full disruption of the layers resulting in a spatial separation of sheets and thus dispersing in nanoscale of clay particles in polymer matrix. In other words, the macromolecules of polymer can fully be inserted in the expanded gallery and interlamellar of clay as a consequence of excellent improvement of nanocomposite properties.

2.6.5 Preparation of clay-nanocomposites

The most widely used nanoclay for polymeric nanocomposites is montmorillonite (MMT). This nanoclay can effectively improve mechanical properties of the nanocomposites because it has high aspect ratio which is the value between length to diameter of the clay. Therefore, it possesses very high specific surface area giving high extent of filler-rubber interactions. Moreover, it is claimed to be an environmentally friendly substance. Generally, the nanoclay which is a silicate filler with a layered structure has a relatively high polarity, while the general purpose polymers are non-polar. Therefore, polar fillers face some difficulties in dispersibility. The modification of these fillers is necessary to improve compatibility with the polymer phase [21]. Clay-nanocomposite can be prepared using various techniques, each method has its advantages and drawbacks. Fine-tuning the optimum processing conditions and composite properties is highly important.

2.6.5.1 In-situ intercalation of clay during polymerization

The modified silicate nanofiller is homogenized in a monomer before polymerization. The efficiency of this method depends on the ability of polymer chains to insert into silicate layer of nanoclay as shown in Figure 2.9 [22].

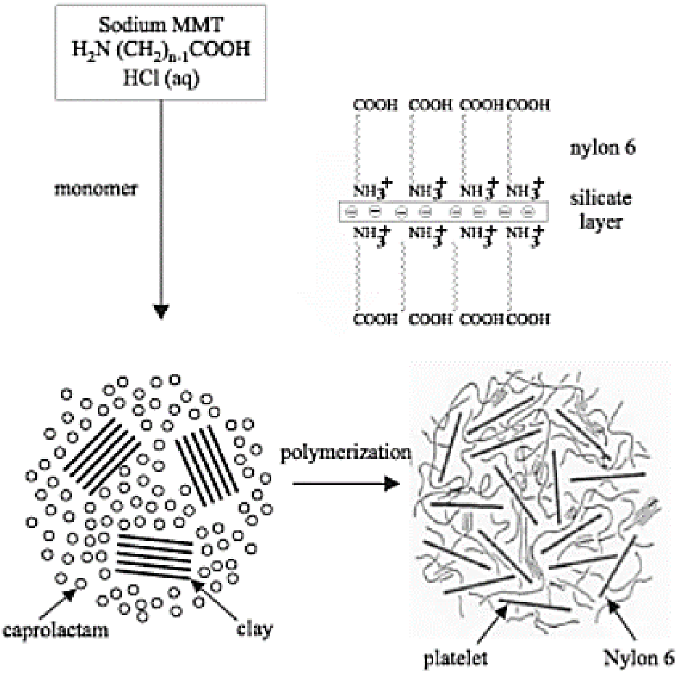

Figure 2.9 Synthesis of Nylon-6/MMT *via* in-situ intercalation during polymerization[22].

2.6.5.2 Intercalation of clay in polymer solution

Clay-nanocomposite can be prepared using solution techniques by blending a pre-dispersed nanoclay and a pre-dissolved polymer in a suitable solvent, e.g. water, acetone, chloroform, etc. Then the polymer molecules interpenetrate into the delaminated silicate plates. The nanocomposite can be achieved by evaporating the solvent out as illustrated in Figure 2.10 [23].

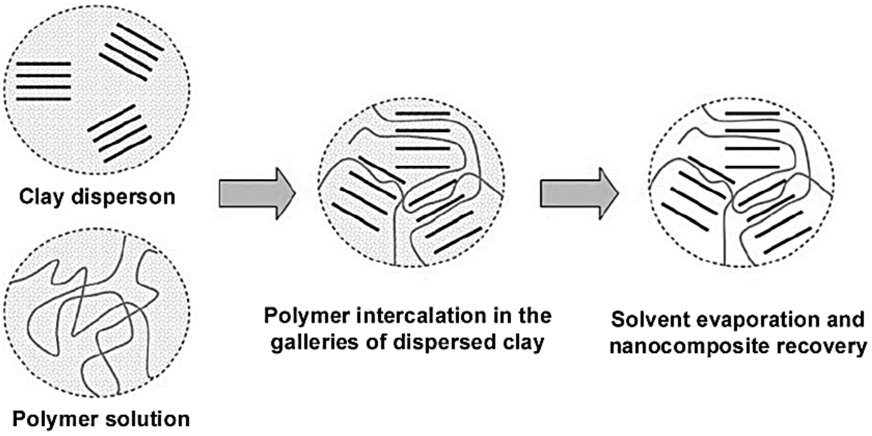

Figure 2.10 Preparation of clay nanocomposite through a solution technique [23].

2.6.5.3 Melt blending

For the melt mixing process, nanoclay is mixed with a polymer in an internal mixer that generates high sufficient shear forces and a high temperature to melt the polymer. The nanoclay will be delaminated giving intercalation or exfoliation structure, while the polymer molecules exhibit good mobility penetrating into the clay structure: see Figure 2.11. This method is widely used for preparing thermoplastics and thermoplastic elastomers. Melt blending is more effective when a polymer and nanoclay have a polar similarity. Thus, either the polymer or the nanoclay needs to be modified having a segment compatible with each other.

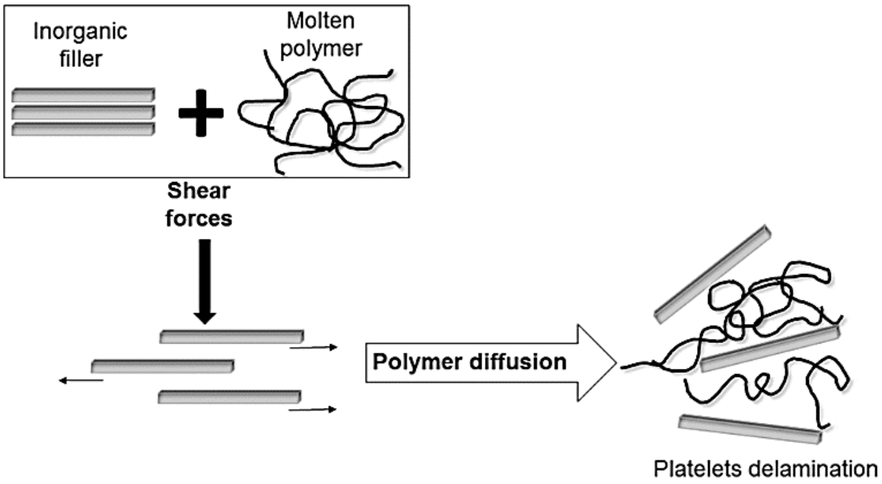

Figure 2.11 Preparation of nanocomposite *via* Melt blending [24].

2.7 Polymer modification by nanoclays during polymerization

2.7.1 Conventional emulsion polymerization

Emulsion polymerization is very useful technique for synthesizing polymer latexes and their solid counterparts. There are three main ingredients involved in the reaction, i.e. non-water soluble monomer, water soluble initiators, surfactant/emulsifier and water as a medium. A variety of emulsion-synthesized polymers can be produced, including synthetic rubbers (in solid and latex state), plastics, paints, adhesives, etc. The diameter of monomer droplets significantly depends on shear rate and can typically be altered from 50 to 5,000 nm [25] [26].

During emulsion polymerization, three types of emulsified particles are present in the system, i.e. monomer droplets, non-active micelles and active micelles [3]. When the surfactant is excessively added over the critical micelle concentration (CMC), the monomer is stabilized and formed as so-called monomer swollen micelles. The micelles with radicals diffused inside are active species. Due to the continuous diffusion of monomer radicals into active micelles, the size of this micelle is significantly increased. Thus, it requires higher amounts of the surfactant which can be adsorbed by the non-active micelles or some portion of the surfactant dispersed in the aqueous phase. This results in a decrease of a surfactant concentration in the system, leading to destabilization of the non-active micelles, and that they subsequently deconstruct into independent monomer molecules [26].

There were some research works dealing with clay-nanocomposites prepared through conventional or batch emulsion polymerization[27], [28], [29], [30], [31]. The TEM images confirmed that the clay particles were mostly located on the surface of polymer particles.

2.7.2 Miniemulsion polymerization

Miniemulsion polymerization (ME) is a heterogeneous synthesizing system as the mechanism is similar to suspension polymerization. However, there are some differences: the mini-emulsion requires a hydrophobe (co-surfactant). Besides, fatty alcohol or acetyl alcohol [32], e.g. hexadecanol [33], hexadecane [33], is used to surround monomer droplets, preventing against monomer aggregation.

The preparation of miniemulsion starts from dispersing monomer droplets in an aqueous solution using a homogenizer, e.g. microfluidizer and sonificator, that can break the droplets into nanosize scale and provide good homogeneity of the monomer particles in the system. The initiation reaction occurs in the monomer micelles to obtain the colloidal polymer particles dispersed in the water medium or the so-called polymer latexes [32]. The miniemulsion polymerization is effective method to prepare latexes with polymer particle size in the nanoscale. The particle size distribution of rubber particle is comparable with monomer droplets prepared from the sonification process. In addition, this method provides latexes with relatively high solid content. However, micro- or nano-scale in size of monomer droplets is hardly to be achieved. Appropriate homogenizer and stabilizing aids for monomer droplets/micelles are crucial parameters in obtaining desired polymer latexes. The miniemulsion polymerization process is illustrated in Figure 2.12.

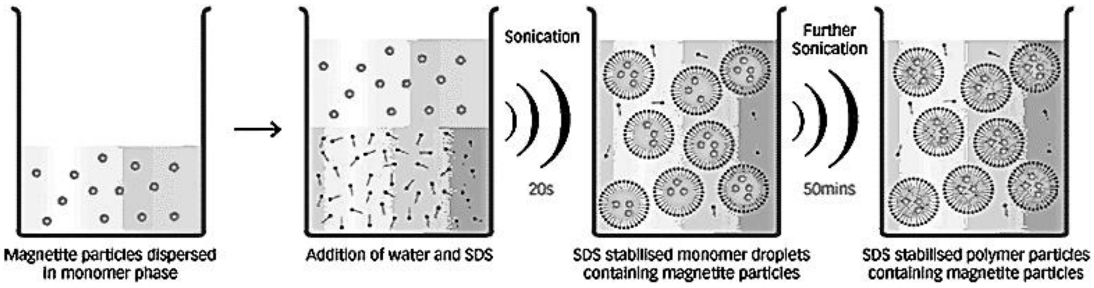

Figure 2.12 Preparation of a nanocomposite *via* a miniemulsion polymerization [34]

The polymerization of clay-encapsulated polymers through ME system is different from CE system. The monomer in ME system is pre-inserted into the monomer milles, while the monomer in CE system is split out from monomer droplets, that causes flocculation and undesired nucleation process occurred. Moreover, the clay particles can hardly be inserted into the monomer micelles in this case. For ME system, the efficiency of encapsulation is also dependent on the medium that nanoclay prefers to disperse. If the clay is dispersed better in the medium, it will situate/attach on the surface of polymer particles. Whilst if nanoclay disperses well in the monomer phase, it will result in the consequent encapsulation morphology [35].

A mixture of monomer and nanoclay is first prepared by applying a high frequency sonication to the system, that can delaminate the silicate plates of the nanocaly dispersing in the monomer. After that, it is sonicated again to make the clay-monomer mixture dispersed in the form of micelle particles in an aqueous medium. The monomer droplets are stabilized in the medium using surfactants, e.g. sodium dodecyl sulfate (SDS) [33], [36], [37], [38], [39] and sodium lauryl sulfate (SLS) [40]. For the initiator system, there are water-soluble and insoluble types available, such as benzoyl peroxide (BPO) [9] [36], hydrogen peroxide [7], potassium sulfate (potassium persulfate: KPS) [32], [33], [38], [39] and azobis-isobutyronitrile (AIBN) [33], [38], [39]. The synthesizing conditions and recipes need to be optimized in order to find tune the most appropriate ones for a particular polymer.

2.7.3 Starve-fed emulsion polymerization

Starve-fed emulsion polymerization (SFE) is similar to batch emulsion polymerization, of which is sometimes called a semi-batch polymerization. A monomer is continuously fed into a reactor. The concentration of the monomer in the reactor should be very low. Molecular weight of the obtained polymer is effectively influenced by feeding rate of the monomer. The solid fraction in SFE system is rather high with less gel fraction because of a lower molecular weight of the product [41]. This strategy was originally developed by Hawkett and co-workers and was successfully applied to encapsulate Gibbsite platelets using monomer mixture, consisting of MMA and BA in emulsion system, resulted in efficiently encapsulation where every latex particle contained the Gibbsite platelets [42]. Bourgeat-Lami *et al.* (2011) [43] synthesized PMMA–Clay nanocomposite particles and soap-free latexes which were stabilized by clay platelets, the TEM images shows that the MMT platelets can be encapsulated inside polymer particles.

2.8 Previous works related to this project

2.8.1 Synthesis of polyisoprene *via* emulsion polymerization

Natural rubber (NR) has excellent elasticity since it consists almost entirely (98%) of cis-1,4-isoprene units giving rise to helical chain; however, this gives it a lower modulus than polyisoprene with a greater proportion of trans-1,4 isomerism. NR latex based products such as rubber gloves and condoms require both high elasticity and a high modulus, and there is a continual need to improve modulus without sacrificing elasticity [44]. Addition to NRL of synthetic polyisoprene (PIP) latex with a higher proportion of *trans* isomerism may be a good candidate for this purpose, as it is in the latex form and has a high compatibility with NR [45]. One problem with the use of IP latex is the relatively high gel content typically seen in products of emulsion polymerization [46]. This gel can adversely affect the reactivity of the rubber, giving poorer vulcanization [47] [48].

The kinetics of emulsion polymerization differ greatly from bulk or suspension polymerizations, because it depends on a complex interplay of chemical and physical processes. The initiation process of emulsion polymerization reaction occurs when a water-soluble initiator has been added into the aqueous phase, generating the reactive radicals on the monomer molecules. At the initial stage, only a small amount of monomer molecules can disperse in the water medium due to its hydrophobic character. The major part of the monomer forms droplets and micelles. The monomer molecules dispersed in the medium start to propagate, creating the growth chains of polymer as a consequence in an increased hydrophobicity. In this state, the growing chains with larger molecules will diffuse into the monomer droplets before propagated [49]. Based on a previous study, it was reported that the size of monomer micelles is much smaller than that of the droplets. Thus, the polymerization mostly takes place in the micelles due to a greater surface area [25].

Miniemulsion polymerization is one of a number of heterogeneous polymerizations similar to emulsion polymerization. Rather than the relatively large monomer droplets being reservoirs of monomer for a polymerization process occurring at other loci, in miniemulsion polymerization monomer droplets are homogenised to a smaller size range of 50 nm to 500 nm. These droplets are the loci of polymerization. Ostwald ripening: see Figure 2.13 [50], the thermodynamically-driven growth in droplet size seen in an emulsion on standing is avoided by incorporation of insoluble, nonpolar species of low molecular weight such as hexadecanol [51] or hexadecane [52] (a "hydrophobe").

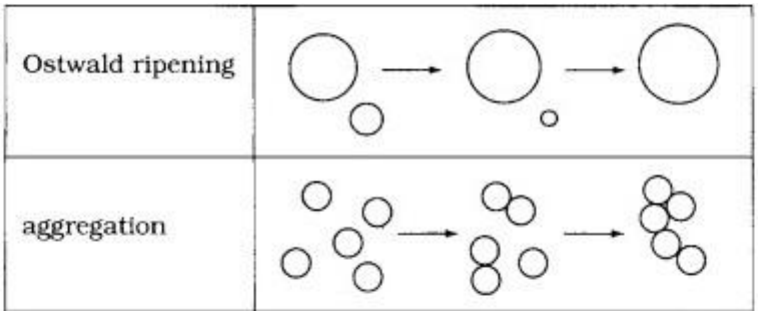

Figure 2.13 Possible occurrence of the physical instabilities of monomer particles in an emulsion polymerization system [50]

Recently much research has been carried out on the synthesis of isoprene rubber (IP) latexes and their use for thin-film based rubber applications such as gloves and condoms. Apolinar *et al.* [53] synthesised polyisoprene using microemulsion polymerization [54], a method which uses extremely high concentrations of surfactant to achieve stabilised small droplets initiated using a redox couple of tert-butyl hydroperoxide/ tetraethylenepentamine with SDS as stabiliser. The final conversion was low and low molecular weights were obtained, which was attributed to chain scission. Cheong *et al.* [55] performed emulsion polymerization of polyisoprene with the use of both thermal and redox initiators. They found that polymerizations of isoprene using redox initiator at 25°C and t-dodecyl mercaptan as chain transfer agent gave a high yield and negligible gel fraction. Boonchoo *et al.* [56] synthesised polyisoprene montmorillonite (Mt) nanocomposites *via* differential microemulsion polymerization using AIBN as initiator, and studied the effect of monomer and surfactant concentration on particle size, yield and solid-content. Results showed that the conversion was influenced by the ratio of isoprene monomer to water and the Mt loading. The mechanical properties of Mtmodified isoprene rubber were improved when compared to unmodified NR.

The radical polymerization of polyisoprene results in branched molecules typically containing more than 65 mol% of the 1,4-trans configuration [46], followed by 1,4-cis units and low percentages of 1,2 and 3,4 units [53], [55]. A high fraction of 1,4-cis units can be achieved using coordination polymerization [46], [57] or anionic polymerization [46], [58] but such polymerizations are not suitable for application in dispersed aqueous systems.

A gel content of 10 – 80% is normally obtained, increasing with conversion and with temperature. With excessive branching, polyisoprene prepared by radical polymerization becomes an insoluble gel [55]. On the other hand, the radical polymerization is an approach to synthesize polyisoprene as well as is low–cost in terms of both chemicals and processing compared to anionic or coordination polymerization.

The effect of monomer and surfactant concentration on the colloidal properties, thermal behaviour and stereochemistry in radical emulsion polymerization have not been extensively studied. Thus in this work, we seek to overcome the restrictions of radical polymerization using polymerization conditions which should lead to a high content of 1,4-trans structure of polyisoprene and acceptable colloidal properties of the obtained latex. The effect of the emulsion system, monomer and surfactant concentration on the thermal behaviour, colloidal properties, kinetics and the stereochemistry of the product are assessed.

2.8.2 Modification of polyisoprene latexes by nanoclay for reinforcing NR thin films

Thin film-based natural rubber (NR) products are typically fabricated from NR latex and other compounds. Condoms and gloves are good examples of products in this category [59], [60]. One of the crucial end-use properties of these products, which is highly required by the users and a selling point of these products, is the film thickness [61]. In general, users prefer these rubber film products as thin as possible since touch sensitivity is better while wearing a thinner film [62]. However, reducing a thickness of the rubber films is usually accompanied by a decrease in the mechanical properties [63]. Thus, a proper trade-off between these aspects of the thin film products needs to be fine-tuned.

To reinforce rubber thin films based on rubber latexes, the conventional reinforcing fillers that are commonly employed for solid rubbers, e.g. tires, high mechanical goods, etc., are not feasible. These fillers require a high mechanical shear rate during mixing them with a rubber.

With films applied under low-shear conditions, the particles of reinforcing fillers are mostly in the structure of agglomerates or clusters [64], [65].

Basically, the reinforcing power of filler is significantly enhanced by breaking these clusters to increase the surface area of filler particles dispersed in the rubber matrix, giving an increased filler-rubber interaction [7]. Hence, a sufficient high shearing action during mixing is necessary to develop this interfacial interaction, contributing to the preferable reinforcement level [10], [66]. For solid rubbers, the mixing is commonly carried out in a high-shear mixer that has an adequate power to break and disperse the filler particles [24], [67]. However, compounding a rubber with additives in the latex state needs to be done under a rather low stirring speed or shearing action which is insufficient to break the filler particles. Too high a speed of stirring during latex compounding causes undesired coagulation of the latex due to the inherent instability of colloidal systems. Therefore, conventional reinforcing fillers are not applicable in this case [68], [69].

Nanofillers in a colloidal or dispersion form may fulfill the requirements to effectively reinforce rubber thin films based on latexes. Fumed silica has been used to prepare a nanosilica dispersion for reinforcing NR using water as a medium [70], [71]. This nanosilica dispersion did not require high shear rate to break the particles during compounding since it was composed already of dispersed nanoscale particles (50 – 200 nm). Hence, it could easily be mixed with the compounds in latex state and gives high reinforcement to rubber thin films [72]. However, this colloidal nanosilica is rather expensive which in turn increases the production costs. Therefore, the alternatives to colloidal nanosilicas, which provide comparable or superior reinforcing property while offering much lower price, could be highly beneficial to the latex-based manufacturing industry. Even though commercially acceptable prices of thinner condoms or gloves can be two to three times higher than the normal film products [73], any attempt to reduce the production costs is attractive to the manufacturers.

In order to make nanofillers well-dispersed in a rubber matrix, the researchers in this field have paid closely attention to many aspects of the particular composites. These include: studies concerning intrinsic properties of raw materials in the composites, e.g. the modifications of polymers [74], [75], fillers [76], [77] and processing aids [78], [79]; novel syntheses of key materials for the composites [80], [81], [82]; and the optimizations of different processing techniques and conditions, e.g. melt [83], [84] and solution [85], [86] mixing, mixing time and temperature, mixing procedure, pre-dispersion methods, etc. [87]. This technology remains challenging since the properties of a composite depend strongly on processing conditions as well as composition.

In-situ modifications of polymers by nanofillers during polymerizations were recently introduced [88]. The obtained polymers containing nanofillers can be used either as a raw material or as an additive to reinforce other polymers [89], [90]. Several techniques have been applied to synthesize these modified polymers, for instance, emulsion [47] and solution [91] polymerizations. Polyisoprene (PIP) has been used as a base polymer for this objective. Boonchoo *et al.* (2014) [56] conducted the in-situ modification of PIP by nanoclay *via* micro-emulsion polymerization. The latexes were then employed to reinforce NR thin films. The results showed that the nanoclay-modified PIP latexes can improve the mechanical strength of the NR thin films. However, some crucial aspects of this topic have not yet been reported, e.g. the effect of different emulsion polymerization techniques, the impact of variation of nanoclay content on the modified PIP latexes, and investigation of the reinforcing mechanism of this system.

The aim of the present work was to synthesize PIP latexes modified with the nanoclay Cloisite 15A or Clay-PIP and utilize them as reinforcing agents for NR thin films. Two different emulsion polymerizations, i.e. batch and starve-fed techniques, were used to prepare the Clay-PIP latexes. The efficacy of the two techniques was evaluated and the influence of nanoclay content on polymerization efficiency, latex properties and reinforcement capability in the NR thin films was studied. Basic properties of the obtained latexes investigated were gel and coagulation content, product conversion, particle size and morphological properties. Thermal properties of the Clay-PIP solids were further analyzed to assess the immobilized polymer in the film nanocomposites. Finally, the ability of the Clay-PIP latexes to reinforce NR thin films was evaluated.

CHAPTER 3

EXPERIMENTAL

3.1 Materials

1. Isoprene (IP) monomer (analytical reagent or AR grade) from Sigma-Aldrich, USA.
2. Sodium hydroxide (NaOH) as a neutralizer to remove the inhibitor 4-tert-butylcatechol in the isoprene monomer (RCL Labscan) from Thailand.
3. Sodium sulfate anhydrous (Na_2SO_4) as a moisture absorber (AR grade) from Ajax Finechem, Australia.
4. Potassium persulfate (KPS) as initiator (Laboratory reagent or LR grade) from Ajax Finechem, Australia.
5. Hexadecanol (HD) as a hydrophobe (AR grade) from Sigma-Aldrich, Germany.
6. Sodium dodecyl sulfate (SDS) as a primary surfactant (LR grade) from Ajax Finechem, Australia.
7. Sodium bicarbonate ($NaHCO_3$) as a buffer to control the pH of the emulsion (AR grade) from Ajax Finechem, Australia.
8. n-dodecyl mercaptan (n-DM) as a chain transfer agent to control the molecular weight distribution (LR grade) from Sigma-Aldrich, USA.
9. Organo-nanoclay (Cloisite 15A) used as a reinforcing nanofiller from BYK Additives & Instruments, Germany, supplied by Colossal International, Thailand
10. High ammonia natural rubber latex (HA) from Had Sin Rubber, Thailand.
11. Sulfur used as a vulcanizing agent from Siam chemicals, Thailand.
12. Zinc oxide (ZnO) used as an activator from Univentures, Thailand.
13. Zinc diethyl dithiocarbamate (ZDEC) as a primary accelerator from Performance additives, Malaysia.
14. Zinc 2-mercaptobenzothiazole (ZMBT) used as a secondary accelerator from Polymer innovation, Thailand

15. 2, 2’-methylene bis-(6-t-butyl-p-cresol) used as an antioxidant from SI group, USA.
16. Potassium hydroxide (KOH) from Unid, South Korea.
17. Potassium laurate (K-Laurate) used as a surfactant from Hangzhou dayangchem, China.
18. Ethyl methyl ketone (MEK) as a coagulating agent (LR grade) from Ajax Finechem, Australia.
19. Methanol used for washing the coagulated polymer (commercial grade) from Liquor Distiller Organization Excise Department, Ministry of Finance, Thailand.
20. Toluene as a gel extraction reagent. (AR grade) from Fisher Scientific, UK.
21. Deionized water (DI), locally produced from PSU laboratory.

3.2 Instruments and characterizations

3.2.1 Percentages of conversion, coagulation and gelation

Conversion, coagulation and gel content – The latexes were filtered using a 300 mesh steel wire cloth (see Figure 3.1). The residual retained on the steel wire cloth is considered as the coagulum; it was dried and weighed (W_1). The coagulation percentage can be calculated following Eq. (3.1).

$$\text{Coagulation (wt\%)} = W_1/W_M \times 100 \qquad (3.1)$$

Where W_1 and W_M are the weights of dried residual coagulum and initial weight of monomer, respectively

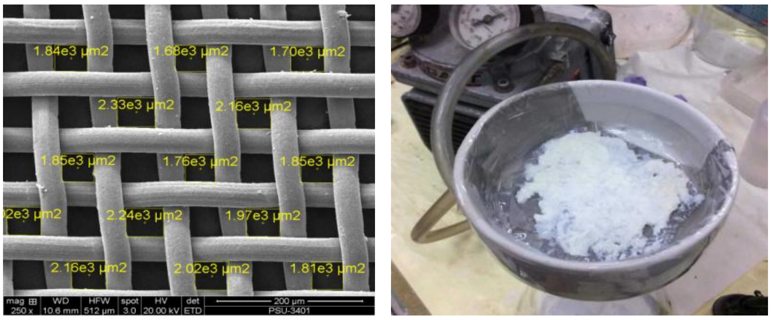

Figure 3.1 A magnified image of the 300 mesh steel cloth (left) and a rubber coagulum on the cloth (right)

The percentage of conversion was assessed by precipitation of the obtained latexes. 10 grams of the latex was precipitated with methyl ethyl ketone (MEK), then washed with methanol and dried to a constant weight (W_2). The conversion can be calculated using Eq. (3.2).

$$\text{Conversion (wt\%)} = W_2/W_M \text{ x } W_L/10 \tag{3.2}$$

Where W_2 and W_L are the weight of dried polymer and the final weight of the latex obtained, respectively.

Gel content of the synthesized polymer latexes can be measured by a Soxhlet extraction of the precipitated polymer using toluene as a solvent. The extraction process was performed at the boiling temperature of toluene for 24 hrs. The residual in a filtering paper was dried until a constant weight (W3). The gel content was calculated following Eq. (3.3).

$$\text{Gel content (wt\%)} = W_3/W_2 \times 100 \tag{3.3}$$

Where W_3 is the dried residual after a Soxhlet extraction.

3.2.2 Chemical structure

The structure of polyisoprenes in deuterated chloroform or ($CDCl_3$ AR grade, ReAgent, UK) was measured by proton nuclear magnetic resonance (^{1}H-NMR) at a frequency of 500 MHz, 25°C, pH = 7 (Unity Innova 500, Varian, USA). 5 mg of dried rubber was dissolved in 0.5 ml of chloroform-d ($CDCl_3$). Then, the solution was characterized.

3.2.3 Molecular weight and molecular weight distribution

The dried rubber samples were dissolved in tetrahydrofuran (THF) (AR grade, RCI Labscan, Thailand) at a concentration of 1 mg/mL and then the molecular weight (MW) was determined using gel permeation chromatography (GPC, Shodex KF-806, Showa Denko, Japan) equipped with a column plus reflective index detector. THF was used as an eluent at a flow rate of 4.0 mL/min at 40 °C. The number- and weight-average molar masses (M_n and M_w, respectively) were calibrated with six polystyrene standards possessing M_w of 2.90×10^3, 6.87×10^3, 1.98×10^4, 4.60×10^4,

1.11×10^5 and 2.55×10^5 g/mol. The MW of synthesized polyisoprene was calculated by means of universal calibration applying a Benoit factor of 0.67 [92].

3.2.4 Morphology

Transmission electron microscopy (TEM) (Model JEM-2010, JEOL, USA) was utilized to image polymer particles and nanoclay dispersed in the synthesized latexes. The JEM-2010 has a standard LaB_6 (Lanthanum hexaboride) filament generating the electron beam which transmits through an ultrathin specimen onto a fluorescent screen as an imaging device operated using a voltage of 160 kV. A latex sample was diluted with DI water at 400 wt% relative to the sample quantity. After that, 10 ml of the diluted latex was undergone in a staining process using 10 µl of 0.1 M osmium tetraoxide (OsO_4) as a dye. The sample was kept in a dark container for 24 h prior to performing the TEM analysis.

3.2.5 Clay nanostructure analysis

X-ray diffraction (XRD) (Model PW1050, Philips, USA) analysis with a Rigaku D/Max II X-ray diffractometer and Cu K-alpha radiation (1.54 Å) generated at 25 mA and 45 kV was used to determine basal d-spacing. A dried rubber sample was cut into a dimension of 10 x 10 x 1 mm and then placed on a glass plate. The analysis was operated at 2θ of 1.5–12° with a thermally scanning rate of 0.5°/min.

3.2.6 Particle size, particle size distribution and particle number concentration

Laser particle size analyzer (LPSA) (COULTER LS230, Jinan Winner Particle Instrument Stock, China) was used to determine the particle size and particle size distribution of polymer particles in latexes. A tungsten-halogen lamp was used as a laser light source with a polarization intensity differential scattering detector, scanned from 40 to 2000 µm at scattering angle of 90°.

The particle number concentration (N_c) can be calculated following Equation 3.4 [55]. M_p is the initial mass of polymer solid (as dried weight of seed latex) per unit volume of the aqueous phase, d_p is the density of polymer, and r is the average radius of (unswollen) polymer particles dispersed in the latex, which can be derived from a particle size analysis.

$$N_c = M_p / (4\pi r^3/3)\, d_p \qquad (3.4)$$

3.2.7 Mechanical properties

Tensile tester (Model Z005, ZwickRoell, USA) was used to measure the mechanical properties of the NR thin films filled with nanoclay-modified PIPs. The test protocol was in accordance with ASTM D412, operating with a 100 N load cell and a crosshead speed of 500 mm/min. The samples were prepared using a dumbbell die cut type C. Five samples from each compound were tested and the median stress-strain curves are reported.

3.2.8 Thermal analyses

Thermal behaviors of the nanoclay-modified polyisoprene were analyzed using differential scanning calorimetery (DSC 2920, TA Instruments, USA) and thermogravimetic analysis (HI-Res TGA 2950, TA Instruments, USA). For DSC analysis, a sample (ca. 5 mg) was cooled down to -100^{o}C with a cooling rate of 10 °C/min. The sample was then heated from –100 to 50 °C with a heating rate of 5 °C/min under a nitrogen atmosphere. Glass transition temperatures (T_g) and heat capacity (ΔC_p) at the transition region from glassy to rubbery state were determined.

Thermogravimetric analysis was carried out over the temperature range 30 to 1000 °C. Approximately 5 mg of sample was heated at a rate of 10 °C/min under nitrogen to evaluate the effect of nanoclay contents on thermal stability of the Clay-PIP.

3.3 Synthesis of polyisoprene (PIP) latexes) *via* conventional emulsion (CE) and miniemulsion (SFE) polymerization

3.3.1 Synthesis procedure

The reactor employed in this work is the autoclave high-pressure reactor (Well & J Technology, China) as shown in Figure 3.2, was employed for this synthesis. It consists of a steel jacket inserted with a Teflon inner chamber possessing a capacity of 300 ml, rated to withstand a maximum pressure of 6.0 MPa and a maximum temperature of 250°C; it is coupled with a pressure gauge as well as inlet and outlet valves.

Figure 3.2 The high pressure reactor used in this study.

Table 3.1 Synthesizing recipes of PIP Latexes.

Latexes	System	IP monomer (wt%)	SDS (wt%)
ME 10 IP	ME	10	7.5
ME 20 IP	ME	20	7.5
ME 30 IP	ME	30	7.5
ME 40 IP	ME	40	7.5
ME 2.5 S	ME	40	2.5
ME 5.0 S	ME	40	5.0
ME 7.5 S	ME	40	7.5
CE 40 IP*	CE	40	7.5

*without of hydrophobe

The recipes employed in this work are shown in Table 3.1. The mixture combines DI water, 0.05 wt% of hydrophobe (HD), 0.15 wt% of buffer ($NaHCO_3$) and 0.05 wt% of chain transfer agent (n-DM) and 0.15 wt% of initiator (KPS), all quantities are relative to the total weight of an obtainable latex (i.e. 100 wt% = 200 g). The IP monomer contents were varied at 10, 20, 30, 40 wt%, while the surfactant contents were 2.5, 5.0, 7.5 wt%. Different procedures were adopted for preparing latexes by conventional (CE) and miniemulsion (ME) techniques as depicted with a flowchart shown in Figure 3.3. For CE polymerization (see Figure 3.4), all ingredients with 40 wt% IP (CE 40 IP) were emulsified under stirring with a magnetic bar at 150 rpm for 1 h at 0 - 3 °C to prevent evaporation of IP monomer. For ME polymerization (see Figure 3.5), the same mixture of chemicals (ME 40 IP) was sonicated using an ultrasonic sonicator as shown in Figure 3.6 (Model 275TAE, Crest Ultrasonic, Malaysia) at a frequency of 60 Hz for 30 min to generate the small monomer droplets. The sonication was performed at low temperature (ca. 1 – 3 °C) using a water/ice bath. 22.56 mL of 0.10 M KPS solution was then added as a single shot. The resulting emulsions were placed in oil bath at temperature of 70 °C under N_2 atmosphere and continuously stirred with a magnetic bar at 150 rpm. The polymerization proceeded for 24 h prior to isolation of the products. The internal pressures inside the reactor during polymerization were recorded in order to elucidate the reaction progress.

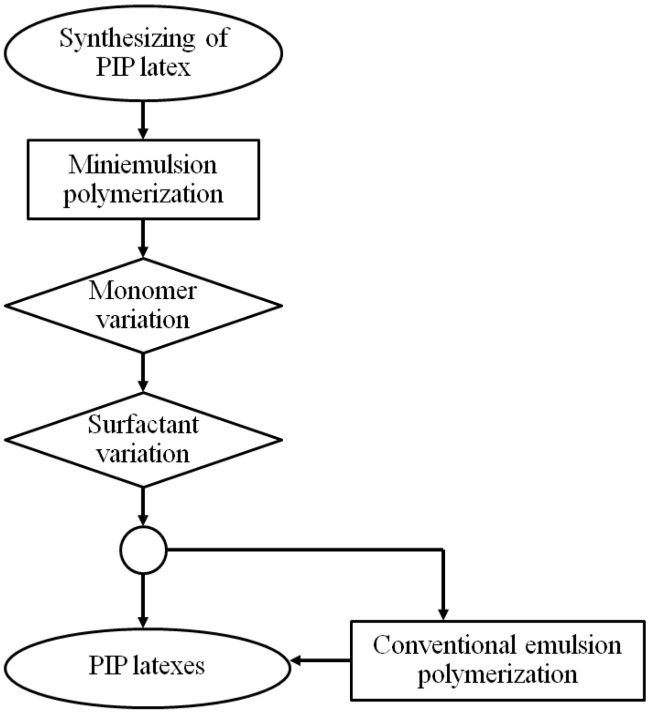

Figure 3.3 The strategy used for investigating the polymerization techniques as well as optimizing the polymerization formulation.

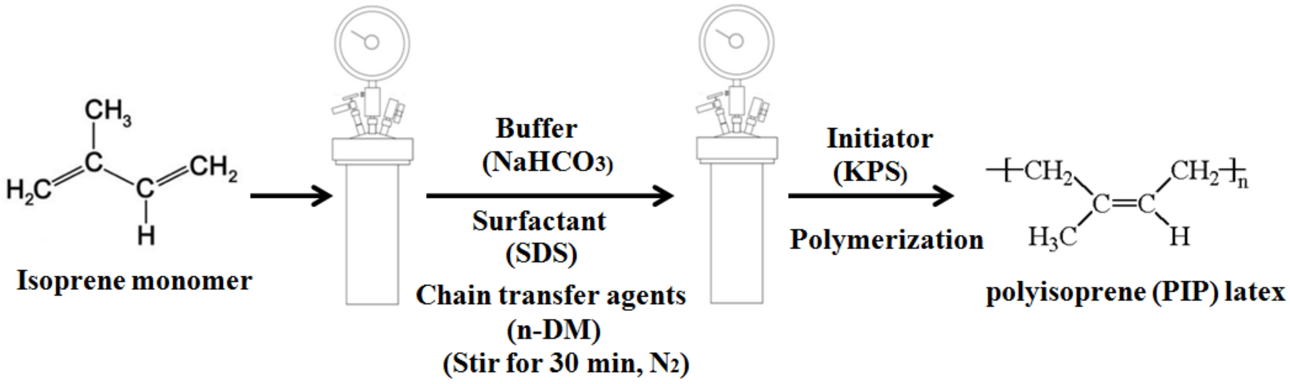

Figure 3.4 The synthesizing procedure for conventional emulsion (CE) polymerization.

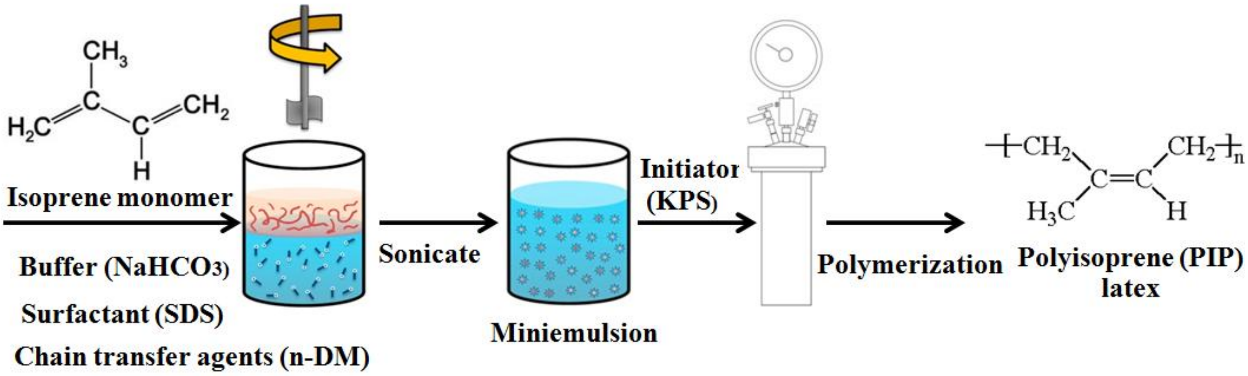

Figure 3.5 The synthesizing procedure for mini-emulsion (ME) polymerization.

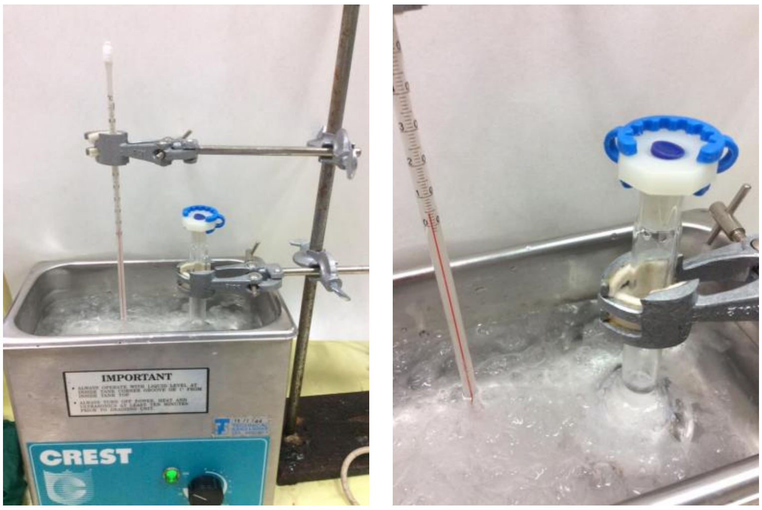

Figure 3.6 The homogenizing process using an ultrasonic sonicator
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3.4 Synthesis of nanoclay-modified polyisoprene (Clay-PIP) latexes *via* batch or conventional emulsion (BE) and starve-fed emulsion (SFE) polymerization

3.4.1 Synthesis procedure

Table 3.2 Synthesizing recipes of PIP and Clay-PIP Latexes containing various nanoclay contents. Two techniques were employed: batch (BE) and starve-fed (SFE) emulsion polymerizations.

Latexes	System	Nanoclay (wt%)
Clay-PIP (BE) with 5 wt% clay	BE	0.5
PIP without clay	SFE	-
Clay-PIP with 1 wt% clay	SFE	0.1
Clay-PIP with 3 wt% clay	SFE	0.3
Clay-PIP with 5 wt% clay	SFE	0.5
Clay-PIP with 7 wt% clay	SFE	0.7
Clay-PIP with 10 wt% clay	SFE	1.0

3.4.1.1 Starve-fed emulsion polymerization (SFE)

The isoprene monomer was fixed at 10 wt% relative to the total amount of the obtainable polymer latex (i.e. 200 g); it was divided into two parts, ¼ and ¾ by weight. The ¼ portion of the monomer was designed to be a part generating initial micelles for the polymerization reaction [93], [94]. It was first mixed with varied amounts of the nanoclay according to the formulations illustrated in Table 3.2 and then homogenized *via* a sonicator (Model 275TA, Crest Ultrasonic, Malaysia) with a frequency of 60 Hz for 30 min at low temperatures of ca. 1-3 °C to prevent evaporation of the isoprene monomer. The obtained suspension was introduced into a flask containing a mixed solution of SDS at 0.25 wt%, n-DM at 0.05 wt%, $NaHCO_3$ at 0.15 wt% and KPS at 0.15 wt% relative to the total weight of an obtainable were used. The mixture was stirred for 30 min and sonicated again at a frequency of 60 Hz for 30 min. The obtained mixture became emulsified and was then introduced into a high-pressure reactor. Then, KPS solution was added at once (see Figure 3.7). The reactor was purged with nitrogen gas through the inlet for 5 min and then tightly sealed. The mixture was heated up to 70 °C while stirring with a magnetic bar at 150 rpm. After that, the other ¾ portion of the isoprene monomer was fed into the reactor *via* a peristaltic pump (BT 100M, Baoding Shenchen Precision Pump, China): see Figure 3.8, with a feeding rate of 1 ml/min. Then, the polymerization proceeded for 12 h prior to isolation of a product.

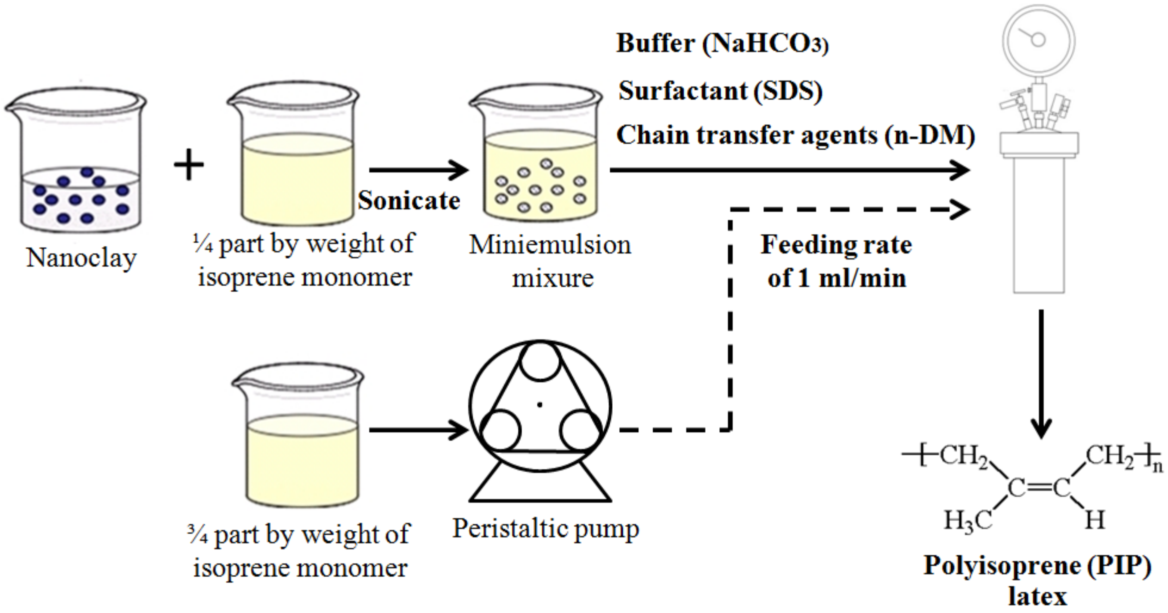


Figure 3.7 The synthesizing procedure for starve-fed emulsion (SFE) polymerization.

Figure 3.8 The peristaltic pump used in this study.

3.4.1.2 Batch emulsion polymerization

5 wt% relative to monomer content of nanoclay was mixed with the entire amount of the monomer and homogenized using a sonicator at a frequency of 60 Hz for 30 min at low temperatures of about 1-3 °C. The nanoclay-suspended isoprene monomer was mixed with the same aqueous solution of the SFE system. Homogenization of the mixture was again done by sonication following the same procedure of the SFE method. Then, KPS solution was added. Polymerization was performed at 70 °C under a nirtogen atmosphere for 12 hours. The obtainable polymer latexes were kept in sealed brown containers to exclude air and light before analysis of their properties.

3.5 Preparation of natural rubber thin films reinforced with nanoclay-modified polyisoprene (NR/Clay-PIP)

3.5.1 Latex compounding

The unmodified and nanoclay-modified PIP latexes obtained from this synthesis were blended with natural rubber concentrated latex (HA or high ammonia grade, Had Sin Rubber, Thailand) at 10/90 by dry weight of the Clay-PIP/NR in order to fabricate rubber thin films containing variable amounts of the organo-nanoclay. The compound formulation is shown in Table 3.3. The blended latex was stirred in a container at 25 rpm for 2 hrs. Then, the surfactants KOH and K-Laurate were added and stirred for 10 min. After that, the other ingredients were charged into the container, and continually stirred for 48 hrs. This step is commonly known as prevulcanization and is carried out to improve processing properties which in turn lead to optimized final properties of the films [63]. The resulting material is called prevulcanized latex.

Table 3.3 Latex compound formulations used for preparing the NR/Clay-PIP films.

Ingredients	**Dry weight (phr)**[b]
60% Rubber latex[a]	100
3.3% KOH	0.5
20% K-Laurate	0.5
50% Sulfur	1.4
50% ZDEC	0.9
50% ZMBT	0.5
50% Antioxidant	0.9
50% ZnO	2.7

[a] Rubber latex was based on the blend of NR and Clay-PIPs.

[b] The total solid content (TSC) of each compound was kept constant at 40%

3.5.2 Preparation of the NR/Clay-PIP thin films.

Rubber thin films were prepared by casting. 30 g of a latex compound was poured onto a glass plate with a dimension of 200 x 300 mm, followed by casting process using a metal thickness-controlling bar as shown in Figure 3.9. The glass plate with a layer of the rubber film deposited was then placed in a hot-air oven at 120 °C for 15 min to vulcanize the film. After that, it was removed from the glass plate with applying talcum powder as an anti-tacking agent on the film surface. The final films had a thickness in the range of 0.03 – 0.05 mm; they were kept in a dry container prior to measuring their physical and mechanical properties. The properties of the casted films were determined in order to evaluate the reinforcement efficiency of the Clay-PIP latexes. When normalizing the tensile modulus at 500 % strain with the modulus at 100 % strain (M100), the resulting value can indicate the reinforcing efficiency, i.e. M500/M100, of a reinforcing component.

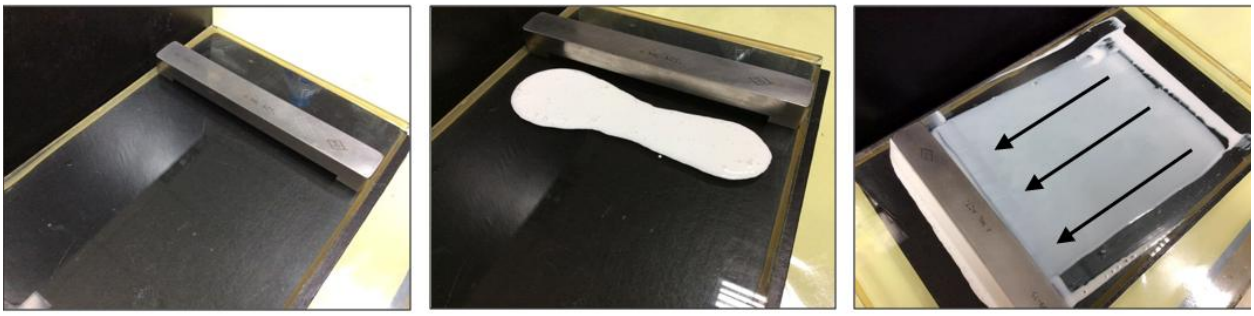


Figure 3.9 Casting procedure and equipment used to prepare the films in this study.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Synthesis of polyisoprene (PIP) latexes

4.1.1 Effects of polymerization technique on properties of PIP latexes

As isoprene has a low boiling point at 34 ºC, it is necessary to use a high-pressure reactor for reactions at 70 ºC to prevent loss of volatile monomer. Pressure rises within the chamber due to evaporation of isoprene monomer at 70 °C giving elevated pressure within the closed system. As the reaction proceeds, pressure decreases as polymerization of isoprene gives a reduced pressure of vapor in equilibrium with the liquid isoprene (Figure 4.1). The obtained latex was turbid white in color (see Figure 4.2(a)), and it was coagulated in MEK solvent before drying at 60 ºC for 24 to acquire the solid form of PIP rubber (see Figure 4.2(b)).

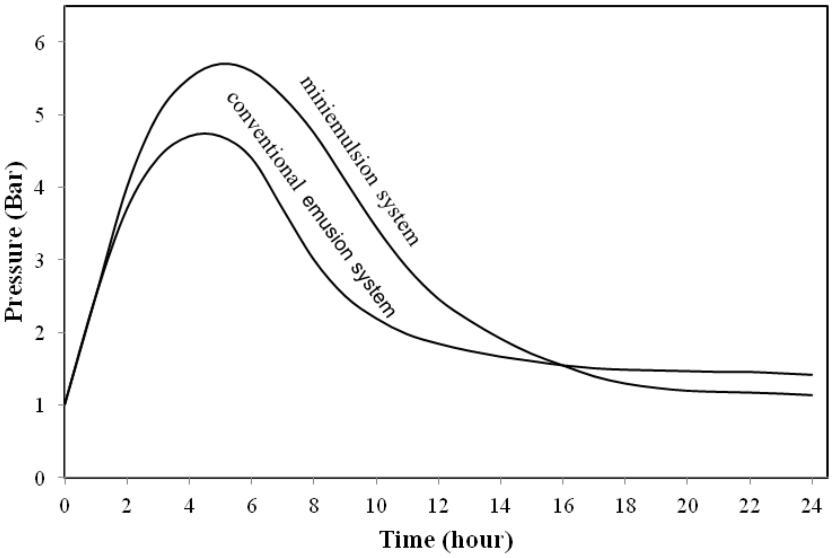


Figure 4.1 Effect of emulsion polymerization systems on the internal pressure of reactor as a function of time at a constant temperature of 70 ºC. The monomer concentration for both system was 40 wt%.

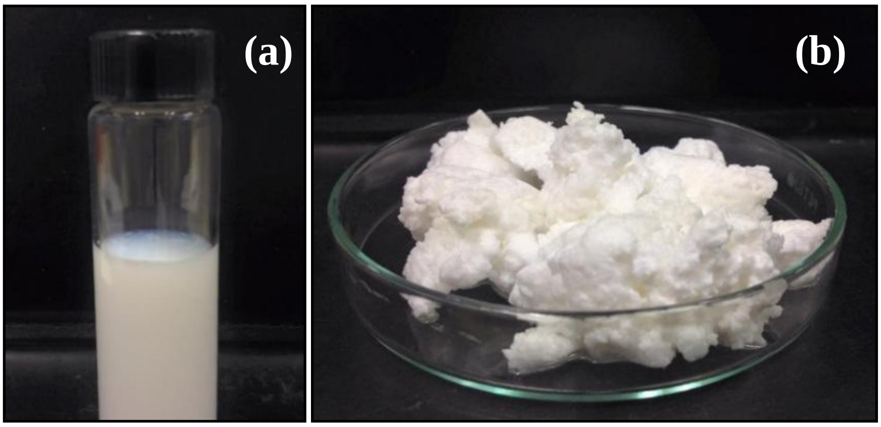


Figure 4.2 the obtained PIP latex (a) and coagulated rubber (b)

The rate of increase in the internal pressure of the ME reaction shown is higher than for CE, but the ultimate pressure obtained is lower. This is attributed to the greater number concentration of particles (N_C) for ME = 1.4×10^{18} L^{-1} as compared to CE with $N_C = 6.4 \times 10^{17}$ L^{-1}. The ME system has more loci of polymerization compared to CE system, leading to a faster rate of polymerization (R_p), which is directly related to the particle number (N_p) according to Eq.4.1 [55].

$$R_p = k_p [M] n(N_p / N_A) \tag{4.1}$$

Where k_p is the rate coefficient of the propagation process, [M] is monomer concentration, n is the average number of the radicals per particle and N_A is Avogadro's constant. As the propagation reaction is exothermic, this leads to a higher rate of temperature increase and hence pressure increase.

Since the half-life of KPS at 70 ºC in water is about 5 hours, beyond 5 hours both systems have a slow reaction rate because of the exhaustion of the initiator. The conventional reaction is slower overall because of the smaller number of polymerization loci, so does not get as close to completion as the miniemulsion reaction which retains unreacted isoprene monomer. This outcome is consistent with what is normally expected at high conversions (Table 4.1).

Table 4.1 Technical properties of PIP obtained in this study.

Recipes	Conversion (%)	Gelation (%)	Coagulation (%)	TSC (%)	Particle diameter (nm)	Polydisperse index (%)
CE 40 IP	62.8	19.2	1.8	23.8	94	26.6
ME 10 IP	94.9	29.6	0.1	9.2	74	16.2
ME 20 IP	91.1	25.8	0.6	17.7	79	20.1
ME 30 IP	92.2	25.5	0.9	26.4	79	21.5
ME 40 IP	78.5	23.4	3.3	30.7	78	26.9
ME 2.5 S	61.5	22.3	4.2	24.2	100	23.0
ME 5.0 S	65.2	22.3	3.8	25.6	91	14.2
ME 7.5 S	78.5	23.4	3.3	30.7	78	26.9

Apart from the higher conversion of products obtained by ME technique, the size of the particles dispersed in latex is smaller (Table 4.1). This is the expected result for mini-emulsion polymerization, due to the action of the hydrophobe in controlling particle size distributions by preventing Ostwald ripening [50]. This phenomena result in an increase in overall average particle size with time [95] and the effect of the hydrophobe can be seen both in terms of influence of monomer content (Figure 4.3 (a)) and surfactant content (Figure 4.3 (b)). However, greater coagulation was observed for the ME experiments due to the higher *Nc*. The ME latexes also had higher gel content compared to the CE latex. This is also a consequence of the larger number of loci of polymerization: as the reaction is faster, particles will experience more time with a high polymer:monomer ratio at a relatively high radical flux, which will encourage branching and crosslinking reactions.

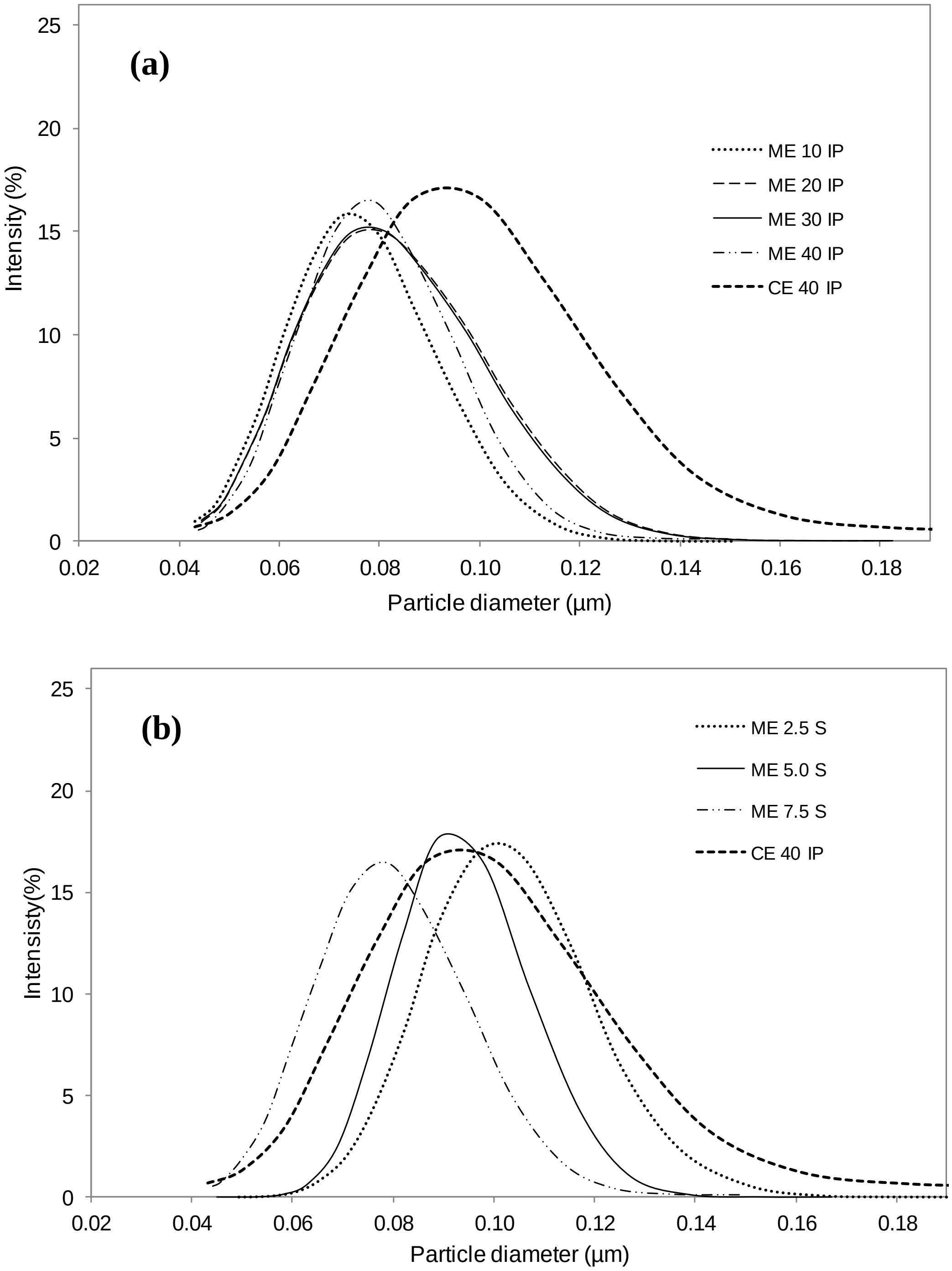


Figure 4.3 Particle size distribution of the synthesized polyisoprene prepared with varied monomer concentrations (a) and surfactant concentrations (b).

Considering the molar mass distributions obtained from the two polymerization methods (Figure 4.4), the polymer synthesized from CE has a lower MW and Đ and less of a shoulder at high MW region. The lack of a shoulder can be attributed to the reduction in crosslinking reactions. Crosslinking is expected to be less at lower conversions and hence lower polymer:monomer ratios [55], while the larger cross-sectional area of the particles formed in CE in comparison to ME should lead to a greater entry rate of radicals into the CE particles, other things being equal, and hence more rapid termination of growing polymer radicals on average.

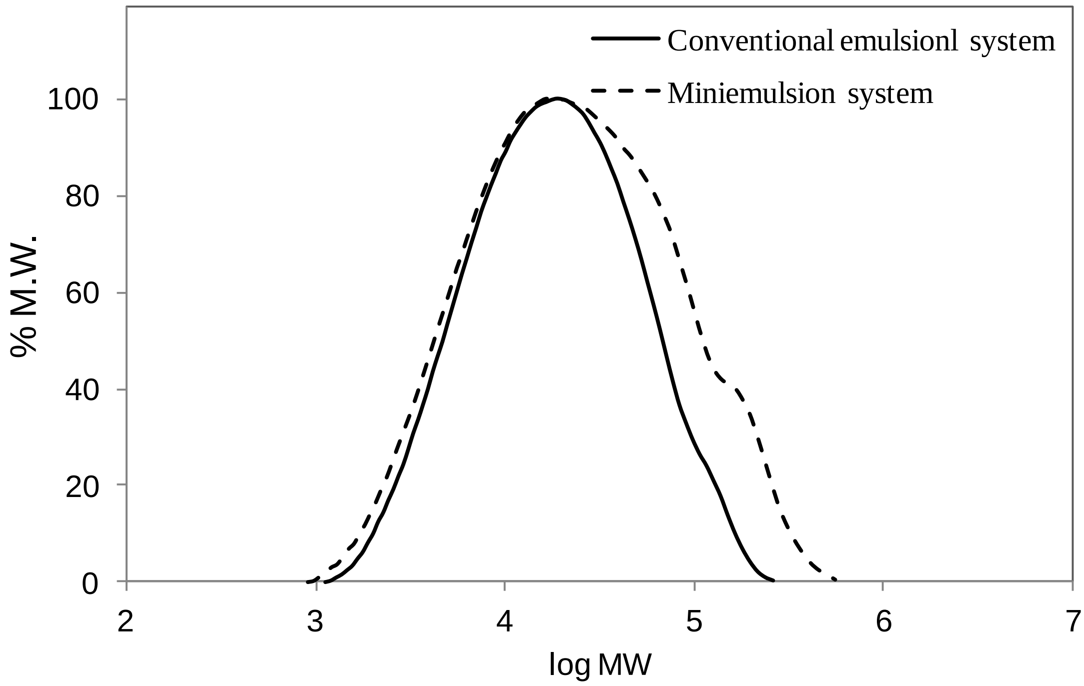


Figure 4.4 Molecular weight distribution of PIP synthesized with conventional emulsion and miniemulsion techniques using a fixed monomer concentration at 40 wt%.

The chemical structure of the synthesized latexes was confirmed using proton NMR [96] (see Figure 4.5). This spectrum is consistent with previous spectra obtained for polyisoprene. The percentage of each isomer was calculated by taking the integral area of the corresponding proton-resonance peak of an isomer into percent comparison with the total integral area of all considered isomers. The proportion of *trans*-1,4 isomer is about double higher than *cis*-1,4 isomerism. While, the intensities of 1,2 and 3,4 units are less than the previously reported data which gave values of 5-7 % for each of these units [44] (Table 4.2). The only difference which may be significant between the structure of the CE and ME latexes was a reduction in the apparent amount of 3,4 addition in CE relative to ME, which is counter-intuitive as this is the functionality that is most likely to react at high conversions (as it gives a pendant double bond with a stabilizing methyl substituent at one end).

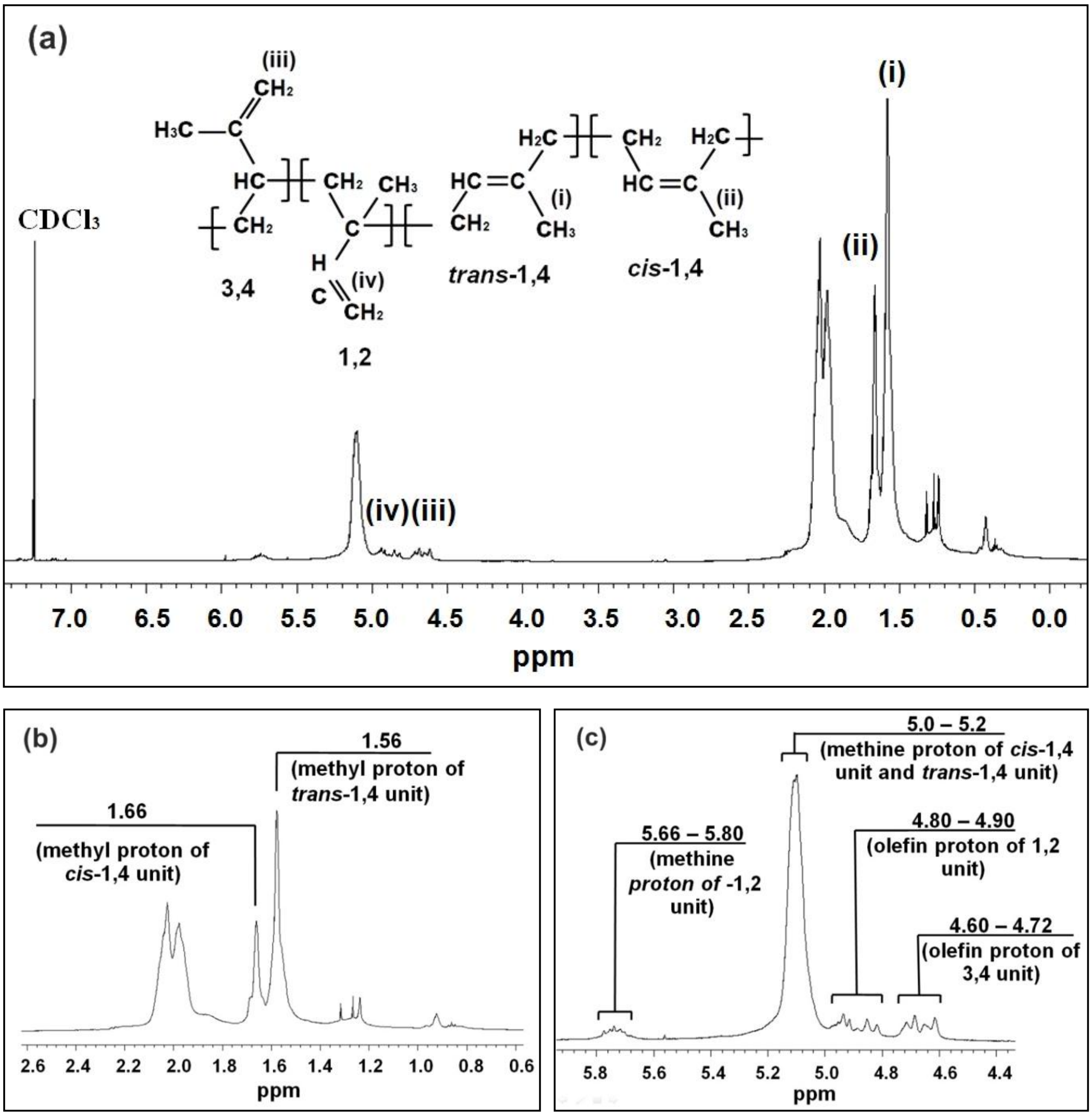


Figure 4.5 ^{1}HNMR spectrum of PIP prepared with miniemulsion technique using 40 wt% monomer: the entire spectrum (a); the peaks assigned for *cis*-1,4 and *trans*-1,4 unit (b); and the peaks assigned for 1,2 and 3,4-unit (c).

Table 4.2 Effect of emulsion polymerization system, monomer concentration and surfactant content on stereochemistry of the synthesized PIP.

Latexes	*Trans*-1,4 (%)	*Cis*-1,4 (%)	3,4-addition (%)	1,2-addition (%)
Commercial PIP	3.6	93.5	3.0	n/a
CE 40 IP	63.7	29.3	3.2	3.8
ME 10 IP	63.6	28.4	4.1	3.9
ME 20 IP	63.6	28.4	4.2	3.9
ME 30 IP	63.4	28.4	4.3	3.9
ME 40 IP	63.2	28.6	4.3	4.0
ME 2.5 S	63.3	27.6	4.4	4.7
ME 5.0 S	63.1	28.0	4.8	4.1
ME 7.5 S	63.2	28.6	4.3	4.0

4.1.2 Effects of varying monomer concentration

The results of experiments carried out with different monomer concentrations are shown in Figure 4.6, Table 4.1 – 4.4. The conversion remained similar in ME experiments when monomer content is increased from 10 – 30 wt%, i.e. 95 to 92 wt%. However, a substantial drop is seen at a monomer content of 40 wt%, giving a yield as low as 79 wt%. This is likely to be due to the competition between miniemulsion and bulk polymerization in droplets as the potential instability at the higher concentration of monomer will give fewer loci of polymerization, resulting in a slower reaction rate and thus reduced percent yield. This is consistent with the increased amount of coagulum obtained at 40 wt% monomer.

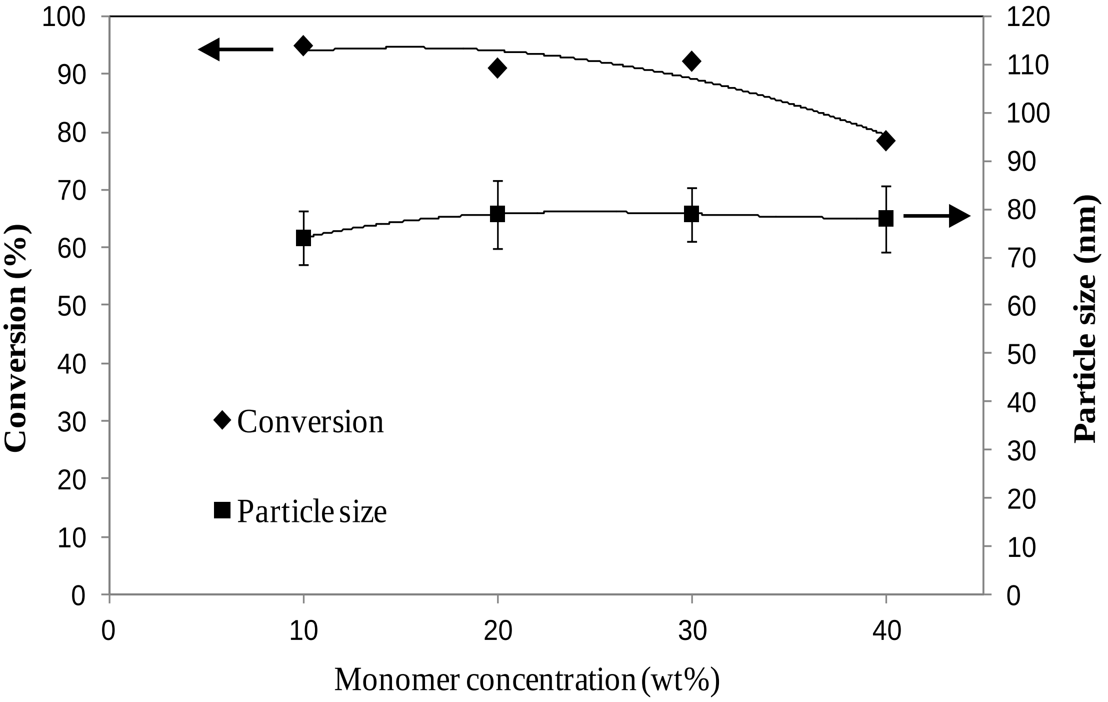


Figure 4.6 Effect of monomer concentration on the conversion and particle size of the obtainable PIP.

An average particle size in the range of 74 – 79 nm was found for all ME experiments carried out with 7.5 wt% SDS. It is not surprising that the particle size and dispersity are independent of monomer concentration (Figure 4.3(a)), as the monomer:hydrophobe ratio and monomer:surfactant ratios remain constant and these will be the main determinants of particle size in a well-stabilized miniemulsion.

The particle number concentration N_C can be determined by calculation of the solid mass per volume, which results in variable values subject to the monomer concentrations as follows: 10 wt% = 4.9×10^{18} L^{-1}, 20 wt% = 7.8×10^{17} L^{-1}, 30 wt% = 1.2×10^{18} L^{-1}, and 40 wt% = 1.4×10^{18} L^{-1}. It can be seen that the particle number concentration decreases with increasing monomer concentration up to 20 wt%, and then slightly increases with further increasing monomer content, in good agreement with the decreasing conversion obtained.

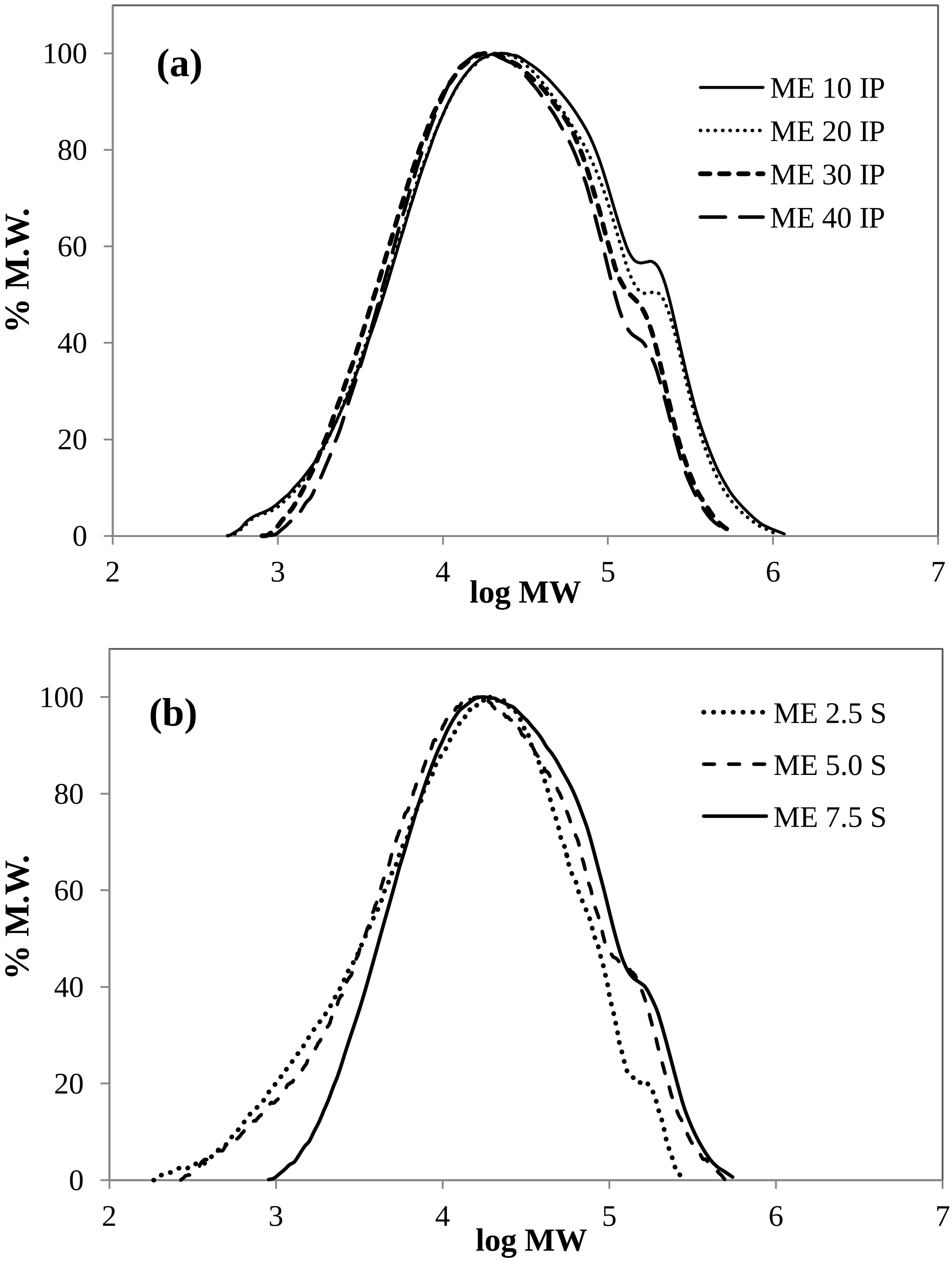


Figure 4.7 Molecular weight distribution of the synthesized polyisoprene prepared with different monomer concentrations (a) and surfactant concentrations (b).

A difference in the MW distributions with monomer concentration is the increasing shoulder seen at high molar mass (Figure 4.7 (a)). Figure 4.8 shows the mechanism of chain transfer in polyisoprene. The effect of this chain transfer on MW will be most significant at the end of a radical polymerization when almost all monomer has been consumed.

In the present study, chain transfer is likely to influence the dispersity of the product by creating more branched polymer into the system, as monomer adds to the new radical site which is located along the polymer backbone (Figure 4.9). It can clearly be seen that 10 wt% IP latex gives the most complete polymerization (~95 %); it has the most significant shoulder in the molar mass distribution and a broad MW distribution, in agreement with the mechanisms of gel formation.

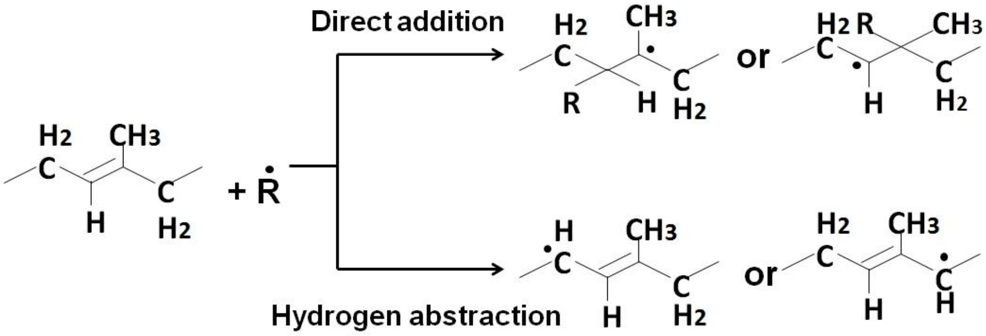


Figure 4.8 Chain transfer mechanism during polymerization of PIP.

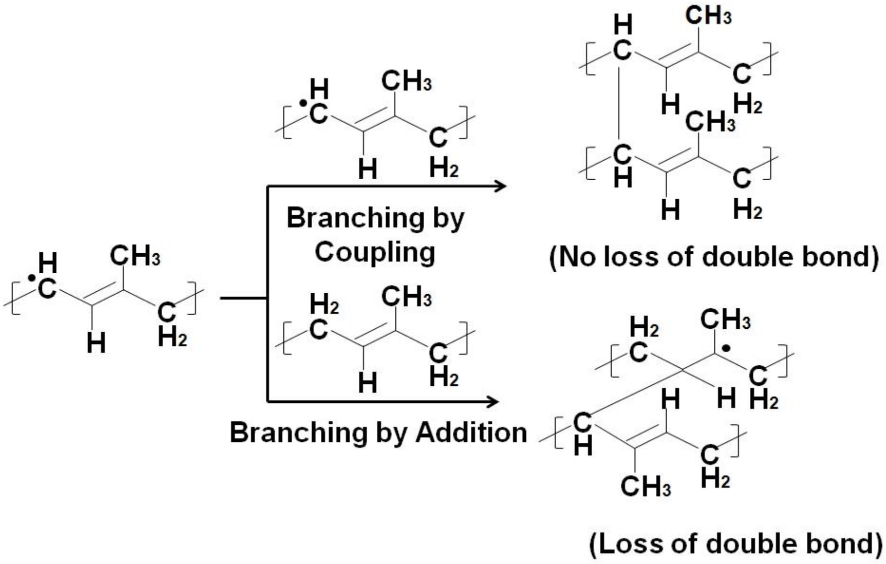
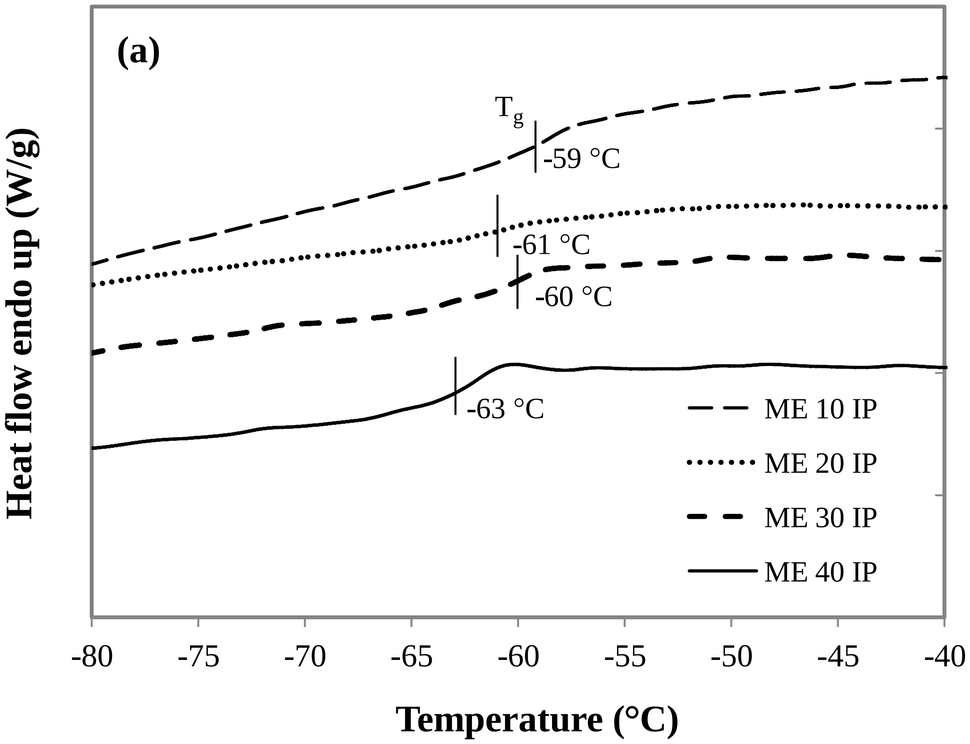


Figure 4.9 Branching and crosslinking mechanisms during polymerization of PIP.

Glass transition temperature (T_g) slightly increases with decreasing monomer content (Figure 4.10(a)) and Table 4.3 consistent with the higher molar mass observed at lower monomer contents. However, extrapolating these results to infinite molar mass according to the Flory-Fox Equation [97] (Eq.4.2):

$$T_g \;=\; T_{g,\infty} - K\,/\,(M_nM_w)^{1/2} \qquad (4.2)$$

The $T_{g,\infty}$ of the obtained PIP rubber is -54 °C, which is higher than that reported in the literature, i.e. -60 °C [98], suggesting that crosslinking plays an important role in raising the T_g of these particles. This value is also significantly higher than the typical T_g of natural rubber, which is approximately -70 ^{o}C [6]. This is because the obtained PIP have a relatively high percentage of *trans*-1,4-polyisoprene in their structure (Table 4.2). The trans structures is normally associated with close packing of adjacent molecules and therefore gives a more glassy material compared to one which has predominantly *cis*-structure. The results show that the T_g values tend to increase with decreasing the monomer contents. It might be attributed to a higher density of crosslink, showing the similar trend observed on the effect of surfactant contents (Table 4.3).



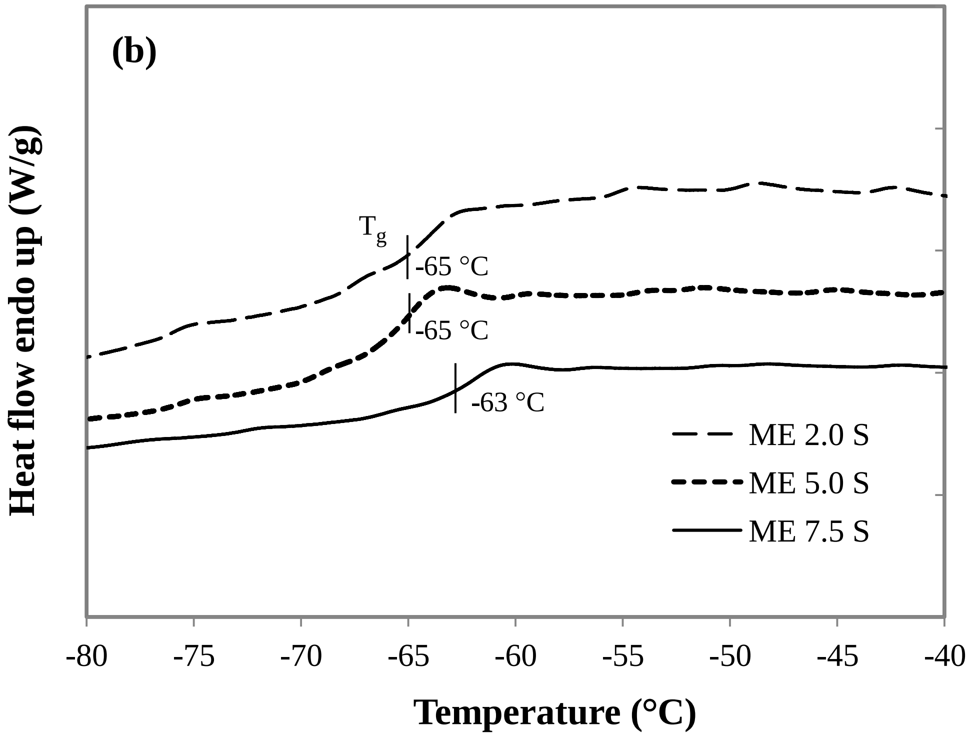


Figure 4.10 DSC thermograms of the synthesized PIP prepared with different monomer concentrations (a) and surfactant concentrations (b).

Table 4.3 Thermal properties of PIP obtained in this study.

Latexes	**T_g (°C)**	**T_d (°C)**	**Weight loss (%)**	**Residual (%)**
CE 40 IP	N/A	N/A	N/A	N/A
ME 10 IP	-59	364	95.8	0.2
ME 20 IP	-61	359	94.7	0.2
ME 30 IP	-60	355	94.5	0.3
ME 40 IP	-63	356	93.6	0.4
ME 2.5 S	-65	352	92.7	0.3
ME 5.0 S	-65	353	93.2	0.3
ME 7.5 S	-63	356	93.6	0.4

Table 4.4 Molecular weight of PIP obtained in this study.

Latexes	**Molecular weight (g/mol)**		
	M_n	**M_w**	**Đ**
CE 40 IP	1.07×10^4	2.85×10^4	2.68
ME 10 IP	1.49×10^4	4.93×10^4	3.31
ME 20 IP	1.10×10^4	4.39×10^4	3.99
ME 30 IP	8.67×10^3	3.94×10^4	4.54
ME 40 IP	9.29×10^3	3.68×10^4	3.96
ME 2.5 S	1.16×10^4	3.51×10^4	3.03
ME 5.0 S	7.79×10^3	3.54×10^4	4.54
ME 7.5 S	9.29×10^4	3.68×10^4	3.96

The samples with the higher molar masses and higher degrees of crosslinking are correlated with higher decomposition temperatures in thermal analysis (Figure 4.12 (a)), which is reasonable.

4.1.3 Effects of varying surfactant concentration

In order to understand the role of surfactant in this system, its amount was varied as described in Table 3.1. Figure 4.11 clearly shows that with increasing surfactant levels, the product conversion increases from 62 – 79 wt%, and the average size of rubber particles decreases from 100 to 78 nm (Figure 4.3(b)). Variation of surfactant content thus has a more significant impact on latex properties than variation of monomer content. Particle numbers are 2.5% surfactant, 5.2 × 10^{17} L^{-1}; 5.0% surfactant, 7.3 × 10^{17} L^{-1}; 7.5% surfactant, 1.4 × 10^{18} L^{-1}.

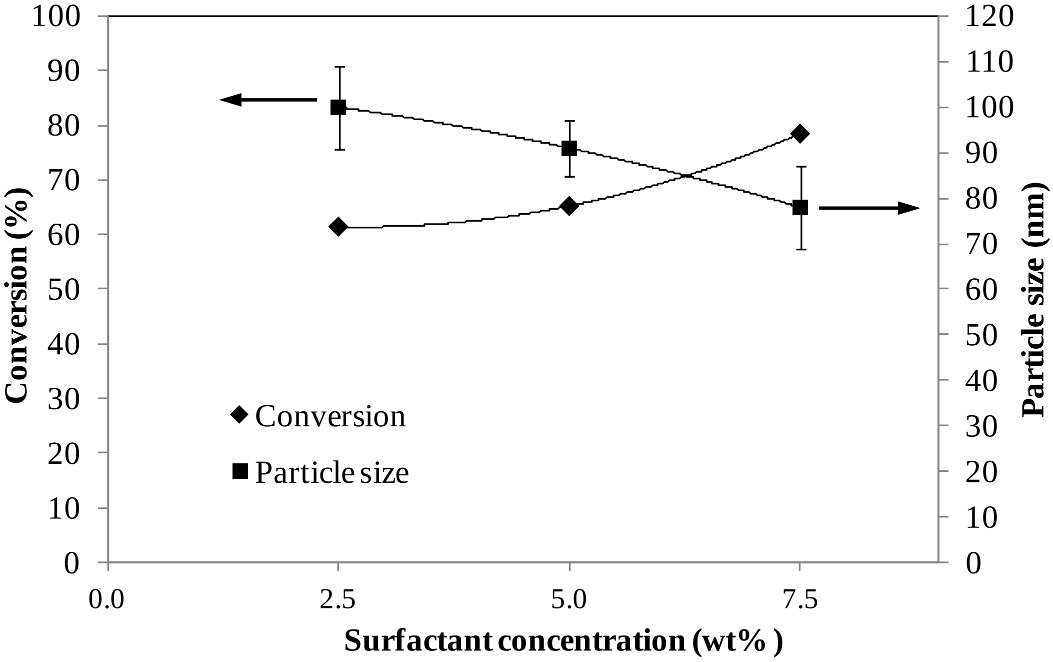


Figure 4.11 Influence of surfactant contents on conversion and particle size of the resulting PIP.

Increasing the amount of surfactant leads to higher particle number concentration as a consequence of a reduced amount of coagulation. The smaller particles lead to more complete conversion due to the large number of polymerization loci, again giving rise to a more extended period of time at a high polymer:monomer ratio where crosslinking and branching reactions can take place.

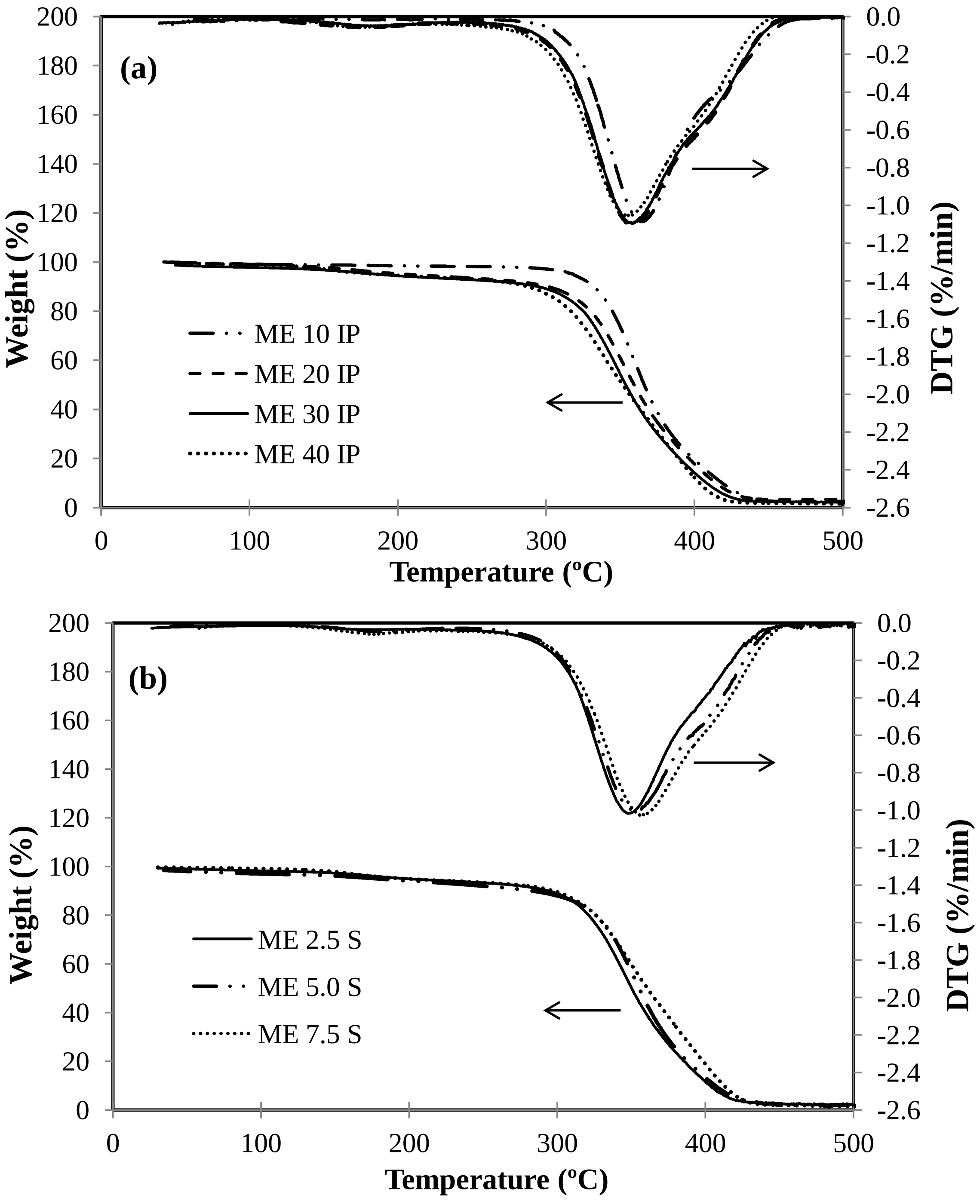


Figure 4.12 TGA and DTG thermograms of PIP synthesized with varied monomer concentrations (a) and surfactant concentrations (b).

All three curves show small shoulders due to branching in the high MW region, with larger extents of branching again corresponding to higher conversions (Figure 4.7(b)). The batches containing lower surfactant contents (2.5 and 5.0 wt% relative to monomer content) show broader curves deviating particularly in the region of low MW: it appears that adding a smaller amount of emulsifier leads to a greater proportion of short chains of PIP.

A slight increase in T_g was found with increasing surfactant loading (Figure 4.10 (b)). This is again consistent with the higher molar mass found at higher surfactant loadings, and the higher molar masses are again correlated with higher decomposition temperatures in thermal analysis (Figure 4.12 (b)).

4.2 Preparation of clay modified polyisoprene (Clay-PIP) latexes

The outcomes derived from section 4.1 gave useful hints for the development of nanoclay-modified polyisoprene latexes. Mini-emulsion polymerization technique is an essential batch process, especially, to control the particle size of polymer particles as they can be tailored to have as small as 80 – 100 nm. However, the Clay-PIP latexes need to have an average polymer particle size of 1 micron in order for nanoclay particles to be encapsulated as well as suitable to blend with natural rubber latex. Similar average size of polymer particles of the two latexes would lead to a better compatibility and homogeneity of the blended latexes.

This section started from the development of Clay-PIP latexes with an appropriate polymer particle size using knowledge based on the earlier section. The attempt to enlarge the polymer particle size was made by varying the key factors which influence the particle size of polymer, i.e. amount and type of surfactant, ratio of nanocaly/media and synthesizing method. Based on the results illustrated in **Appendix A**, they show that the starve-fed emulsion (SFE) technique gives a slight increase in conversion, gel and coagulation content, and larger particle size compared to the batch process. In addition, the ratio between clay/medium and the utilization of hydrophobe have an influence on polymer particle size as well. Therefore, this work was designed to proceed with the SFE technique mainly due to the desired polymer particle size obtained.

The synthesized nanoclay-modified polyisoprene (Clay-PIP) latexes require appropriate colloidal stability with nanoclay particles being well-dispersed and inserted in or attached on polymer particles. The following parts demonstrates how the Clay-PIP latexes were developed *via* the starve-fed emulsion process. After that, the reinforcing efficiency of the modified latexes in natural rubber (NR) thin films was investigated.

4.2.1 Effect of different emulsion polymerization techniques.

Two emulsion polymerization techniques: batch (BE) and starve-fed (SFE) emulsion polymerization, were utilized to synthesize the nanoclay-modified PIP latexes. The results shown in Table 4.6 illustrates that these two techniques give similar final properties of the latexes when modified with the same amount of nanoclay, i.e. 5 wt% relative to the monomer content. The BE gives a slightly lower conversion compared to that obtained from the SFE technique, i.e. 65.4±5.9 and 69.9±5.1 wt%, respectively. The internal pressure inside the reactor of SFE shows significantly lower than that of the BE for the whole period of the synthesis. The difference between them becomes smaller over the synthesizing time since the monomer vapors were circulated into the medium and then participated in the polymerization reaction, finally converting into the polymer chains.

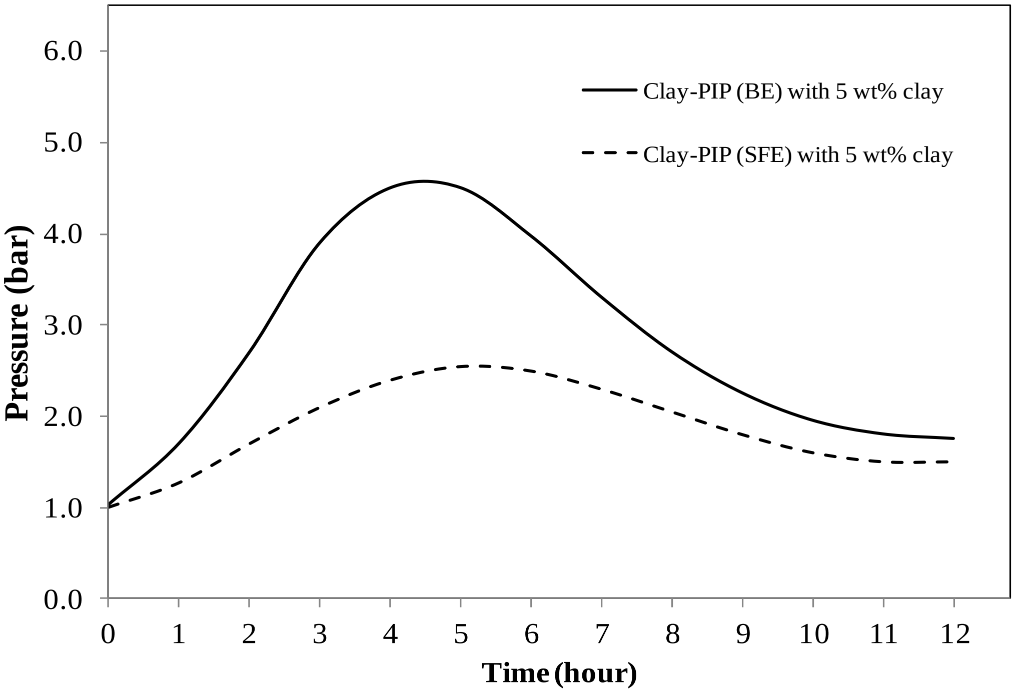


Figure 4.13 Internal reactor pressures built up in BE and SFE systems as a function of reaction time.

Real-time internal reactor pressures as a function of reaction time during synthesizing Clay-PIP latexes through batch (BE) and starve-fed (SFE) emulsion polymerization techniques were recorded. The organo-nanoclay at 5 wt% relative to the monomer content was employed. Results demonstrate that the SFE system generates a lower internal pressure inside the reactor because the amount of monomer concentration at the initial stage of polymerization was lower than that of the BE. The monomer of SFE system was continually fed into a reactor slowly with a precisely controlled amount of monomer. Hence, that is why this technique is called ‘starve-fed emulsion polymerization’. The fed monomer will participate rapidly in the on-going polymerization reaction due to the monomer being the limiting reagent, which in turn minimizes the monomer vapors inside the reactor and makes the polymerization more efficient when compared to the BE system. The internal pressure of reactor and the conversion of obtainable polymers show a good agreement with the results from particle size analysis as displayed in Figure 4.14.

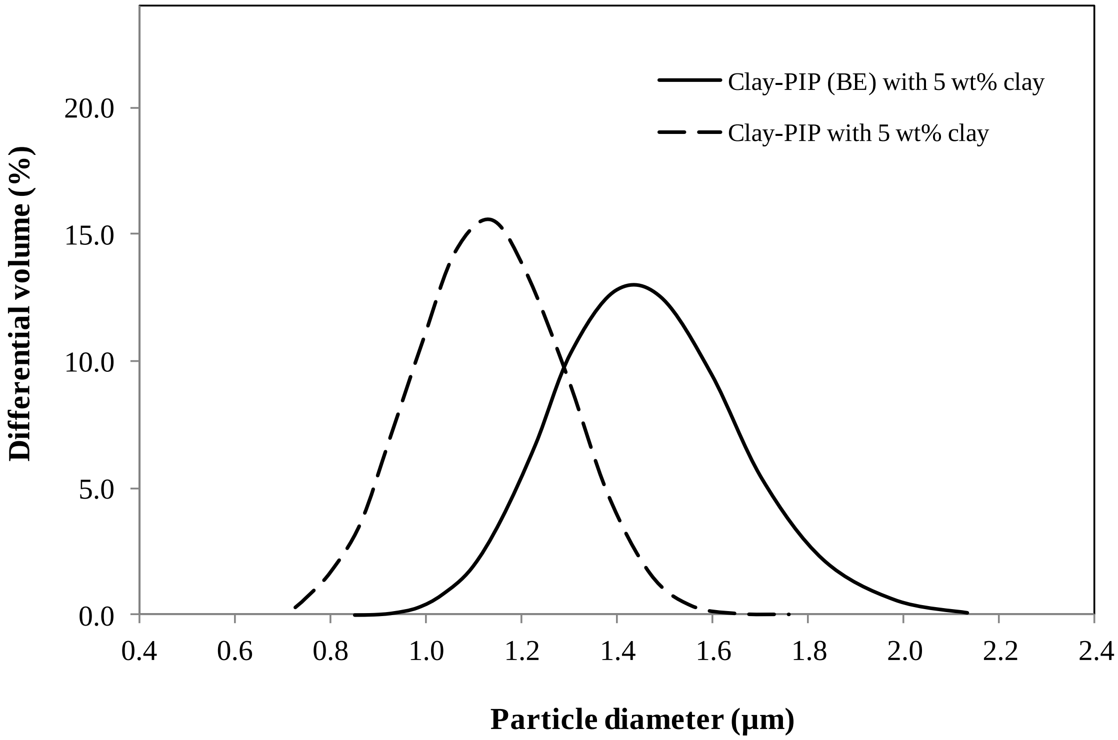


Figure 4.14 The effect of different emulsion polymerization methods batch (BE) and starve-fed (SFE) techniques, on the particle size of the PIP latexes modified with 5 wt% nanoclay relative to the monomer content.

In general, the polymer particle size from a typical emulsion polymerization is commonly in the range of 50-500 nm. However, the synthesizing recipes in this study contain a rather small amount of surfactant, i.e. 0.25 wt%, moreover they have organo-nanoclay involved during polymerization which induces more flocculation of polymer particles, leading to enlarged polymer particle sizes as evidenced in Figures 4.14 and 4.15. Based on the particle size analysis: see Figure 4.14, the SFE system gives an average size of the polymer particles smaller than that of the latex derived from BE polymerization. This is because the feeding sequences of the monomer into a reactor of the two systems are different as mentioned earlier (Figure 4.13). SFE technique feeds the monomer slowly during the polymerization, while the BE starts its polymerization with an entire amount of the monomer from the initial stage, leading to more coagulation at a given stirring speed when compared to the SFE system and a smaller number of stable particles at the end of the nucleation stage.

The smaller the particle size, the higher particle number concentration (N_c) for the same mass, meaning that these two systems have different number of loci of the polymerization reaction. The SFE technique appears to have more polymerization loci since it shows a greater N_P compared to the BE system, According to the calculation [99] based on the data from this particle size analysis, the N_P of the latexes have been shown in Table 4.5. The result indicates that the SFE has a faster rate of polymerization due to more reaction loci resulting in a higher percentage of polymer conversion: see Table 4.6. The results are in line with the influence of nanoclay contents as will be discussed in section 4.2.2.

Table 4.5 Polymer particle size and polymer particle number of Clay-PIP latexes with varied nanoclay contents prepared using batch (BE) and starve-fed (SFE) emulsion polymerization techniques.

Latexes	Particle size (µm)	Particle dispersity	Particle number (L-1)
Clay-PIP (BE) with 5 wt% clay	1.40	0.43	5.2×10^{13}
Clay-PIP without clay	1.01	0.10	15.5×10^{13}
Clay-PIP with 1 wt% clay	1.05	0.19	14.0×10^{13}
Clay-PIP with 3 wt% clay	1.11	0.36	11.7×10^{13}
Clay-PIP with 5 wt% clay	1.14	0.35	9.8×10^{13}
Clay-PIP with 7 wt% clay	1.24	0.40	7.3×10^{13}
Clay-PIP with 10 wt% clay	1.46	0.62	4.2×10^{13}

4.2.2 Variation of nanoclay contents in the Clay-PIP latexes

Table 4.6 Basic properties of the Clay-PIP latexes with different amounts of nanoclay prepared using batch (BE) and starve-fed (SFE) emulsion polymerization techniques.

Latexes	Conversion (wt%)	Gelation (wt%)	Coagulation (wt%)
Clay-PIP (BE) with 5 wt% clay	65.4 ± 5.9	21.7 ± 4.3	0.8 ± 0.2
PIP without clay	91.7 ± 8.2	22.5 ± 5.2	0.3 ± 0.0
Clay-PIP with 1 wt% clay	78.3 ± 7.1	21.8 ± 4.8	0.3 ± 0.1
Clay-PIP with 3 wt% clay	77.8 ± 6.3	21.1 ± 4.0	0.4 ± 0.1
Clay-PIP with 5 wt% clay	69.9 ± 5.1	18.9 ± 3.5	0.5 ± 0.2
Clay-PIP with 7 wt% clay	67.3 ± 5.8	18.1 ± 3.1	0.7 ± 0.2
Clay-PIP with 10 wt% clay	63.4 ± 6.3	19.2 ± 3.9	1.5 ± 0.4

Based on the results shown in Table 4.6, adding nanoclay results in a significant decrease in the product conversion. The control sample which was prepared without nanoclay added has the highest product conversion of 91.7 wt%. Adding nanoclay at 1.0 wt% relative to the monomer amount leads to a considerable drop in the conversion to 78.3 wt%, with further addition of nanoclay from 3.0 to 10.0 wt%, the conversions gradually decrease from 77.8 to 63.4 wt%. This implied that the nanoclay incorporated during the emulsion polymerization of isoprene latexes has an enormous impact on the polymerization efficiency. An addition of organo-nanoclay appears to intervene stabilizing ability of SDS surfactant towards isoprene micelles. The hydrophobic side of nanoclay can adsorb the SDS as a consequence in less surfactant available to stabilize polymer particles. Thus, the latexes tend to have more aggregations and larger particles. It is commonly known that the concentration of surfactant or stabilizer strongly influences polymer particle size and particle size distribution. Hence, when the SDS surfactant exhibits low affinity towards isoprene micelles, it could result in an increased interfacial tension between them that causes larger average sizes of polymer particles as illustrated in Figure 4.15. Consequently, the polymerization loci are reduced, and so a decreased conversion. Regarding an inferior shielding efficiency of the surfactant, the rubber particles appear to aggregate, which leads to an increase in polymer particle sizes as well as broadened particle size distributions. This corresponds to the morphology of polymer particles in the resulting latexes as will be discussed in the following section. Furthermore, it could attributed to the nanoclay causes a physical barrier towards the diffusion ability of intermediate monomer species from a droplet to micelles as a consequence in decreased polymer conversion [43].

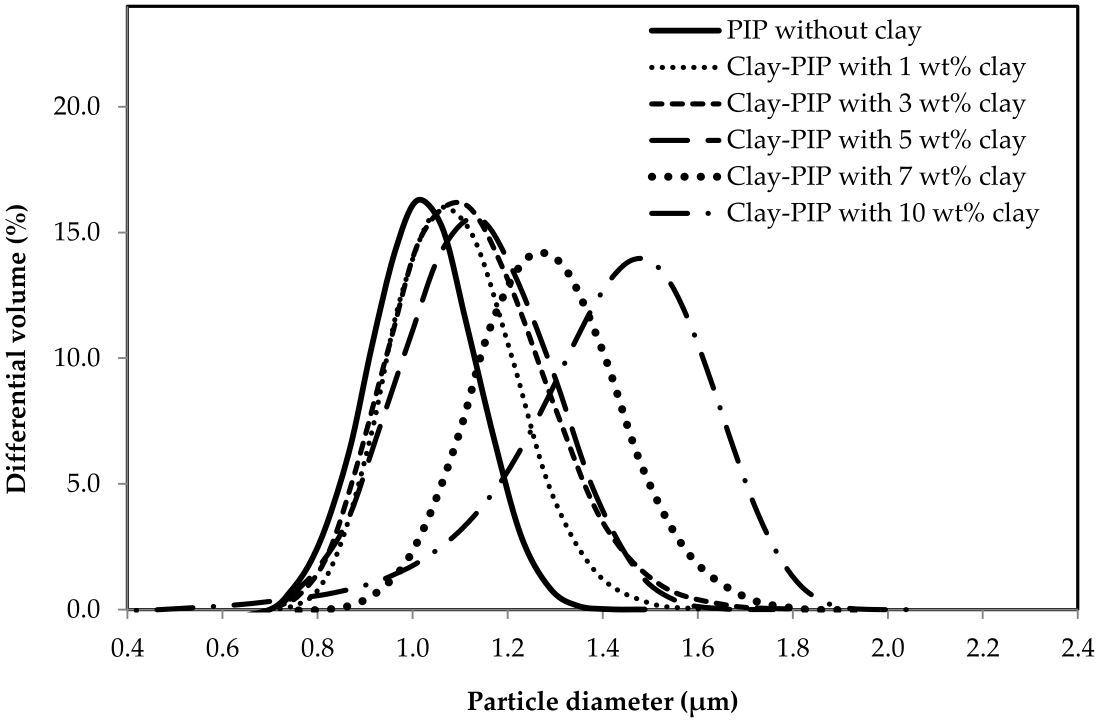


Figure 4.15 The effect of nanoclay content on the particle size of the nanoclay-modified polyisoprene latexes prepared using SFE polymerization.

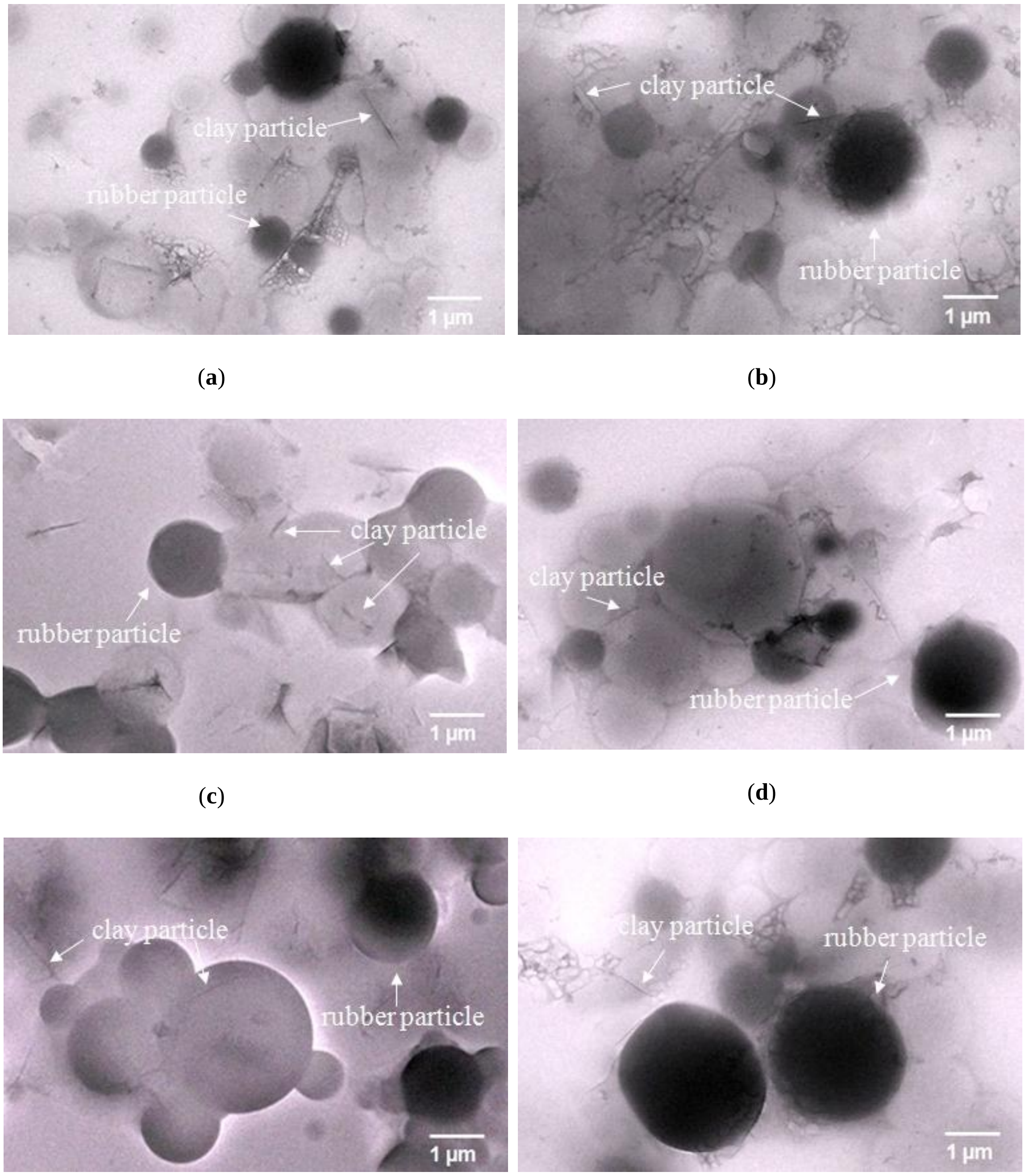
Considering the outcome from the calculation of polymer particle concentration, the latexes prepared with SFE technique without nanoclay, as well as with nanoclay as shown Table 4.5. This clearly confirms that an increase of nanoclay content significantly decreases the polymer particle concentration of the resulting latexes. With this circumstance, the system which has a higher polymer particle concentration, i.e. the one with a higher nanoclay content, exhibits lower polymerization loci leading to the reduced product conversion: see Table 4.6.

The latexes with higher nanoclay contents also tended to have a gradual increase in the coagulum content: see Table 4.6. The inclusion of 1 – 5 wt% of nanoclay relative to the monomer content gives a smaller particle size with a narrower particle size distribution compared to the ones with 7 and 10 wt% nanoclay of which they show a significant increase in the particle size with a broader particle size distribution. A broader particle size distribution is mainly caused by the presence of organo-nanoclay that can reduce stability and induce flocculation of polymer particles. Excessive amounts of the organo-nanoclay cause less shielding capability of the SDS
]

surfactant towards monomer micelles as mentioned earlier, contributing to a tendency of the aggregation.

4.2.3 Morphology of the obtained Clay-PIP latexes

It is obvious from the different product conversions that the particle concentration during emulsion polymerization significantly influences the final properties of the latexes. To confirm this elucidation, a TEM technique was employed to visualize the actual polymer particles and the nanoclay particles distributed in the colloidal latexes. Figure 4.16 clearly shows that the synthesis technique and the nanoclay content play a role on the morphology of polymer particles. The TEM images of the latexes synthesized with the SFE technique (Figures 4.16a – 4.16e), show that there are nanoclay particles inserted into and/or attached onto the PIP particles, while the BE system (Figure 4.16f) gives polymer particles with the nanoclay attached onto them, often known as 'nanoclay-armored particles' [100].



(**a**) (**b**)

(**c**) (**d**)

(**e**) (**f**)

Figure 4.16 TEM images of nanoclay-modified isoprene latexes prepared through starve-fed emulsion (SFE) polymerization with the variation of nanoclay content: (a) 1 wt%; (b) 3 wt%; (c) 5 wt%; (d) 7 wt%; and (e) 10 wt% of nanoclay relative to the amount of monomer. The image (f) belongs to the latex prepared with batch emulsion (BE) system with 5 wt% of nanoclay relative to the monomer content.

As aforementioned, the initial polymer particle sizes of a typical emulsion polymerization should be too small compared to the dimensions of clay particles. However, the present system contains only a small amount of SDS surfactant, therefore the polymer particles could exhibit reduced colloidal stability. In addition, less amount of the hydrophobe was used, the clay particles and polymer particles tend to aggregate after the polymer particles have grown to a certain size, leading to insertion of the nonoclay particles in the clusters of polymer particles. Furthermore, it could be ascribed to that the SFE system has a faster reaction rate as discussed in Figure 4.14. Additionally, the monomer plus nanoclay was fed into a reactor by continually dispensing a small amount of monomer droplets, thus the nanoclay particles could be trapped in the cluster of polymer droplets during the aggregation in which the polymerization reaction occurs more rapidly than that of the BE system as a consequence in a better holding of the nanoclay. On the other hand, the BE system possesses a slower polymerization rate and the entire amount of monomer plus nanoclay was charged into the reactor from the initial stage. The nanoclay particles might be more likely to lose their holding around the rubber particles cloud due to gravity and agitation effects. Hence, more amounts of nanoclay from the monomer phase are liberated into the water medium. And, some parts of them migrate to the surface of polymer particles due to high interphase tension between the monomer and nanoclay.

The variation of nanoclay amount also influences the morphology of polymer particles significantly. In general, the plate shape of nanoclay particles has d-spacing of about 3.63 nm and lateral dimensions in the range 0.2-1.0 μm [43]. All synthesized latexes show their average polymer particle sizes sufficient to encapsulate the nanoclay particles. The TEM images confirm that, when increasing the amounts of nanoclay, the polymer particles tend to have higher aggregation and thus broader particle size distribution. This is due to less shielding efficacy of the surfactant as discussed earlier.

To investigate the degree of dispersion of nanoclay within PIP latex, an XRD technique was utilized. Figure 4.17 shows the XRD patterns of pristine organo-nanoclay and the composites based on Clay-PIP with varied amounts of such nanoclay. The XRD patterns of the pristine nanoclay and the Clay-PIP solids show two important intensity peaks at the 2θ in the range of 2.3 - 3.1 (larger peak height) and 4.2-5.4 (smaller peak height). These peaks are assigned to the basal spacing of d_{001} and d_{002}, respectively. The basal spacing of d_{001} is considered as an indication of the interlayer distance between the silicate crystal plates of nanoclay structure that can be calculated following the Bragg's equation [101].

According to the results based on calculation, the d-spacing values of pure nanoclay and polyisoprene solids modified with 1, 5 and 10 wt% of nanoclay relative to the monomer content are 3.63, 3.77, 3.81 and 3.54 nm, respectively. It is clear that the incorporation of nanoclay into the polyisoprene as low as 1 wt% the d-spacing is increased when compared to that of the pristine organo-nanoclay. Adding 5 wt% of nanoclay has shown to be an optimum amount since it gives the maximum d-spacing of the silicate plates. After adding the nanoclay beyond the optimum level, in this case at 10 wt%, the d-spacing of nanoclay tends to reduce, attributed to the overloading of nanoclay and thus a closer distance between the silicate plates. This phenomenon is often ascribed to the effect of reagglomeration of nanoclays [80], [102], [103] As expected, the organo-nanoclay is, to some extent, compatible with isoprene monomer. Utilizing a sonication process results in an enlarged d-spacing of the silicate layers, giving the desired structure of nanoclay in the polymer matrix, often known as ‘intercalation and exfoliation’ dispersion [20]. These dispersion structures are required since the nanoclay exhibits high power in reinforcing polymeric composites [104].

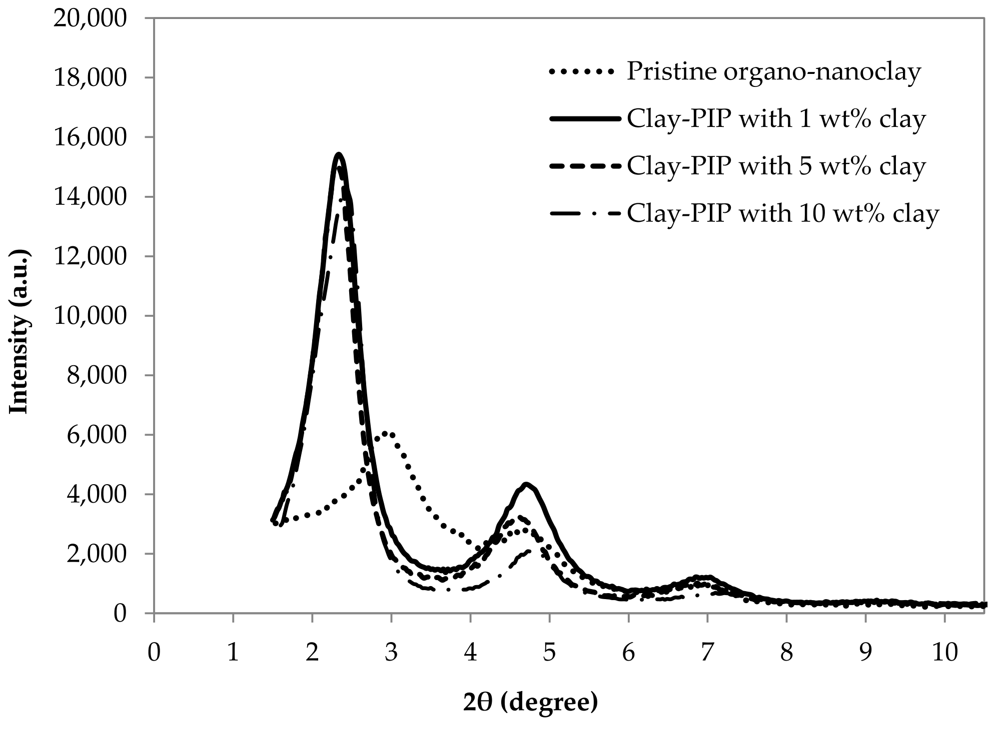


Figure 4.17 XRD patterns of pristine organo-nanoclay and solid composites based on the Clay-PIP latexes with varied amounts of nanoclay

4.3 Reinforcement efficiency of nanoclay-modified polyisoprene latexes in NR thin films

4.3.1 Effect of clay content in Clay-PIPs on properties of NR thin films

4.3.1.1 Mechanical properties

Variable amounts of nanoclay in the modified PIP latexes differently influence the dispersion and distribution degree of nanofiller added as well as the interaction between nanofiller and polymer, often known as ‘in-rubber structure’ or ‘bound rubber constituent’ [105]. Figure 4.18 illustrates that the addition of Clay-PIP latexes into NR latex compounds has a significant positive impact on the mechanical properties of NR thin films. The NR films filled with modified PIP latexes containing organo-nanoclay from 1 to 5 wt% relative to the monomer content show an increase in tensile strength and modulus with a slightly reduced elongation at break. However, adding the modified isoprene latexes containing nanoclay at 7 and 10 wt% leads to reduced strength and modulus of NR thin films, while maintaining elongation at break. The Clay-PIP latexes containing 1 to 5 wt% nanoclay have shown to be able to reinforce NR thin films since they contain the organo-nanoclay predispersed in the PIP latexes, giving a larger d-spacing of the silicate plates (Figure 4.17). Thus, the interaction between polymer and nanoclay could be enhanced, leading to a better reinforcement of the natural rubber thin films. Further addition of the nanoclay to the Clay-PIP, i.e. 7 and 10 wt%, gives an adverse effect on film strength, attributed to the excessive amount of nanoclay causing reagglomeration of the nanoclay as evidenced by the XRD analysis that shows a reduced d-spacing of nanoclay structure (Figure 4.17).

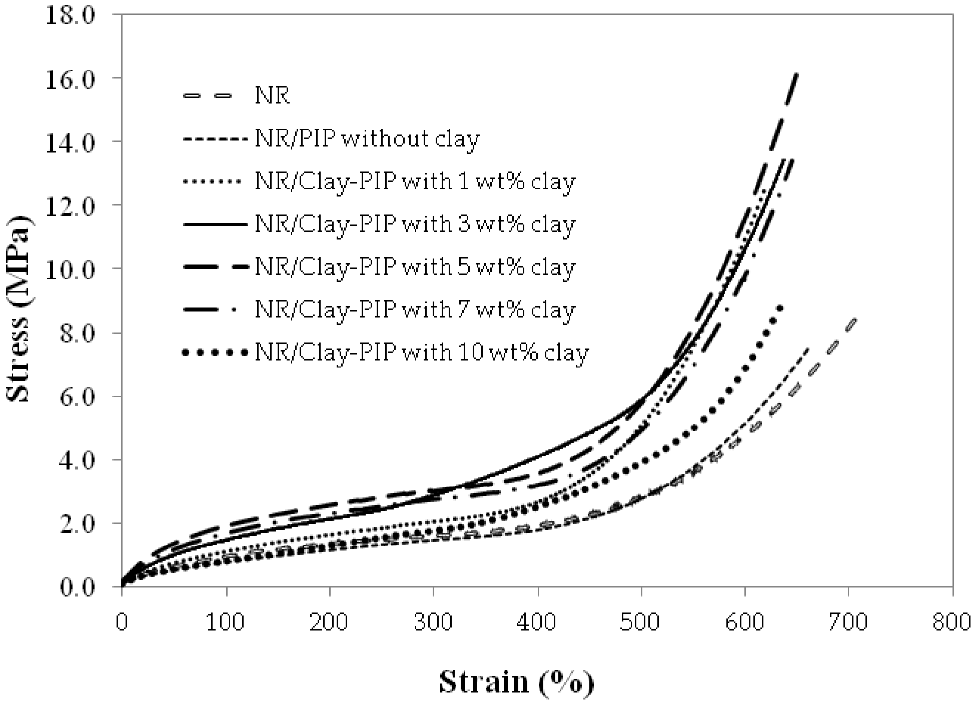


Figure 4.18 The effect of nanoclay content in Clay-PIPs on stress-strain behavior of NR thin films blended with the Clay-PIPs. Each curve was taken based on the median value among five test specimens. The clay contents are relative to the monomer amount.

4.3.1.2 Indication of immobilized polymer in the composites

The immobilized polymer constituent which is the ‘bound layer’ of polymer molecules on the surface of nanofiller particles is one of the key factors altering the glass transition temperature T_g of polymer composites [106]. This filler-polymer interaction causes the bound polymer molecules to be restricted and immobilizable. An increase of the immobilized fraction of the polymer layer surrounding filler particles leads to a shift of the T_g to a higher temperature since the polymer molecules are more constrained or in the other words less flexibility. Reinforcement of polymers by a particulate filler requires this immobilized polymer structure to be present because the filler and polymer phases become more compatible due to better intermolecular interfacial interactions. When the reinforced composites undergo a high loading condition, they can withstand the forces better due to low energy dissipation throughout the material [56] – the increase in mechanical strength and modulus (Figure 4.18) As the immobilized polymer or in-rubber structure is an essential constituent which determines the reinforcing efficiency of polymeric composites, DSC and TGA techniques were used to analyze this structure in order to elucidate the reinforcing mechanism of the rubber films in this study.

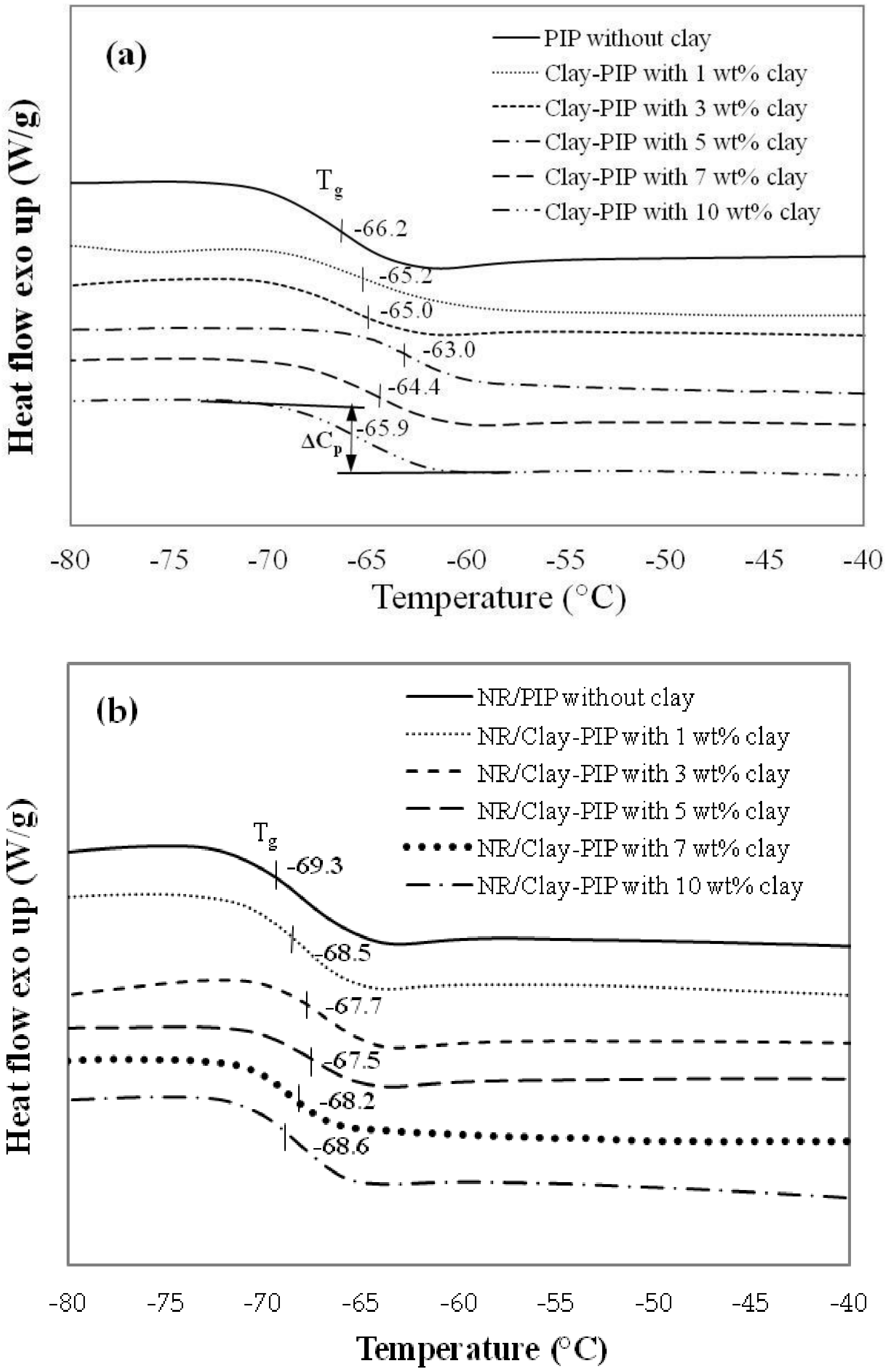


Figure 4.19 DSC thermograms of the (a) Clay-PIP and (b) NR/Clay-PIP composites containing various nanoclay contents. The Clay-PIP latexes were prepared using SFE technique. The clay contents are relative to the monomer amount.

Figure 4.19 shows DSC thermograms of the Clay-PIP solids with variable clay content. The variation of nanoclay amount in the modified isoprene latexes causes the T_g

to shift to the highest values at the same wt% that give the optimal mechanical properties (Figure 4.18). Adding the nanoclay at an optimum amount, i.e. 5 wt% rel. to the monomer content, increases the T_g of the composite to the maximum value, i.e. –63.0 °C, while the modified latexes without and with nanoclay at 1 and 3 wt% give T_g values of –66.2, –65.2 and –65.0 °C, respectively. Based on the concept of immobilized polymer as mentioned earlier, this result suggests the generation of a greater extent of immobilized polymer structure in the rubber composites. As a consequence, the better reinforcement could be achieved when using the Clay-PIP modified with an optimum quantity of the nanoclay, i.e. 5 wt% relative to the monomer content. The modified isoprene latexes with a higher amount of nanoclay than the optimum level (>5 wt%), i.e. 7 and 10 wt% relative to the monomer content, give a drop in the glass transition temperatures. This is attributed to these amounts of nanoclay used are excessive, resulting in aggregation and poor dispersion of nanoclay in the polymer matrix, which leads to more inhomogeneity of the composites as well as lessened immobilized polymer constituent, consistent with the XRD results (Figure 4.17).

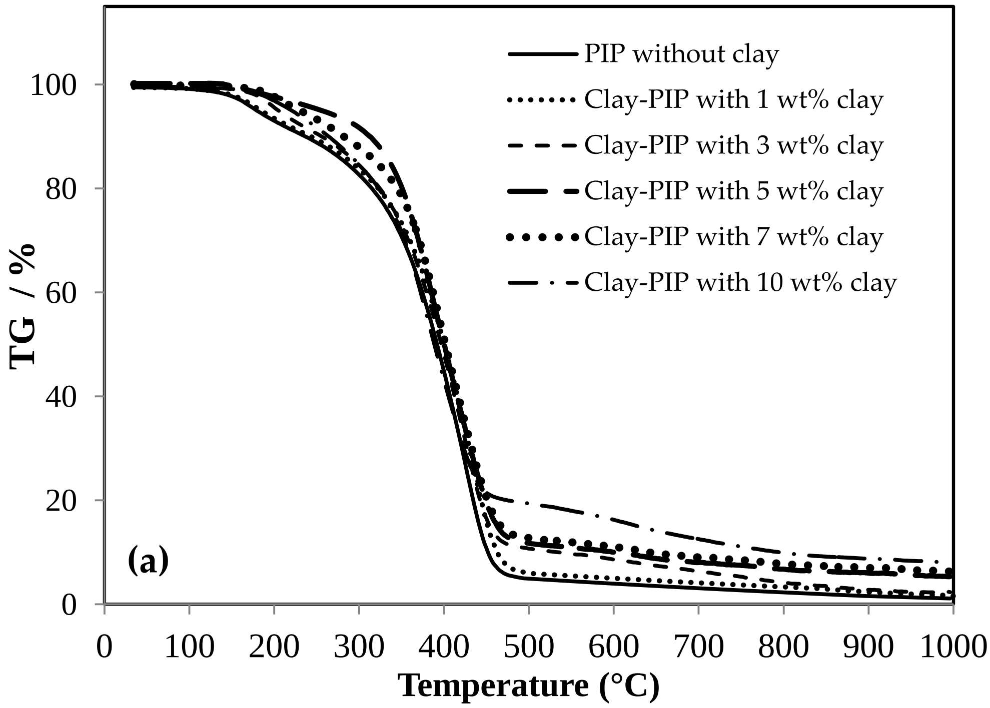
Another indicator used to determine the extent of the bound polymer layer at the interface between nanoclay and polymer matrix is the heat capacity (ΔC_p) caused by molecular relaxation at the T_g transition region. The polymer molecules which interact with filler particles have less heat capacity throughout the molecular relaxation process, i.e. from on-set to end-set of the transition, since they are more restricted in mobility. The ΔC_p values of Clay-PIP with nanoclay of 1, 3, and 5 wt% are 0.25, 0.27 and 0.20 W/g, respectively, less than the value without nanoclay, i.e. 0.36 W/g. The composites with 7 and 10 wt% nanoclay relative to the monomer content have a higher ΔC_p value, i.e. 0.22 and 0.31 W/g, respectively, compared to the composite with 5 wt% nanoclay. The result of the ΔC_p measurement thus show a good agreement with the T_g of the Clay-PIP composites.

Table 4.7 Thermal properties of Clay-PIP and NR/Clay-PIP composites with different amounts of nanoclay. The Clay-PIPs were prepared using starve-fed (SFE) emulsion polymerization technique.

Composites	**T_g (°C)**	**ΔC_p (W/g)**	**T_d (°C)**	**Actual nanoclay content (wt%)[a]**
PIP without clay	-66.2	0.31	374	0.00
Clay-PIP with 1 wt% clay	-65.2	0.25	377	0.60
Clay-PIP with 3 wt% clay	-65.0	0.27	378	1.70
Clay-PIP with 5 wt% clay	-63.0	0.20	382	4.20
Clay-PIP with 7 wt% clay	-64.4	0.22	380	5.90
Clay-PIP with 10 wt% clay	-65.9	0.31	375	7.60
NR/PIP without clay	-69.3	0.38	378	0.00
NR/Clay-PIP with 1 wt% clay	-68.5	0.36	371	0.01
NR/Clay-PIP with 3 wt% clay	-67.7	0.31	376	0.04
NR/Clay-PIP with 5 wt% clay	-67.5	0.31	383	0.08
NR/Clay-PIP with 7 wt% clay	-68.2	0.34	369	0.12
NR/Clay-PIP with 10 wt% clay	-68.6	0.36	371	0.15

[a] The amount of nanoclay in the composites was calculated based on the TGA results. A residual at 1000 °C was considered as the total weight of non-decomposed carbon (ash) and filler. The ash contents were corrected for the ones containing Clay-PIPs by taking into account the residual weight of unfilled PIP and NR/PIP in order to obtain only the amount of nanoclay.

Another method to verify the extent of immobilized polymer structure of polymeric composites is to analyze their decomposition temperature (T_d) since this bound polymer layer behaves as a rigid segment like filler particles [107], increasing stability towards decomposition at high temperatures. In other words, adding an appropriate amount of nanoclay results in a good heat resistance of NR/Clay-PIP composites. It can clearly be seen on the TGA curves that, in the temperature range of 200-350 °C, the curves are more stable when the composites contain a higher nanoclay content. The results shown in Figure 4.20 and Table 4.7 correspond well with the results of glass transition temperature (Figure 4.19). It reveals that the Clay-PIP composites containing nanoclay from 1-5 wt% relative to monomer content have an increase in the T_d. The Clay-PIP solids with 7-10 wt% nanoclay have a gradual reduction in the T_d compared to the optimum one containing 5 wt% relative to the monomer content of nanoclay. This trend in Td is the same as seen in the tensile properties, morphology, XRD and DSC results and can be ascribed to the same cause.



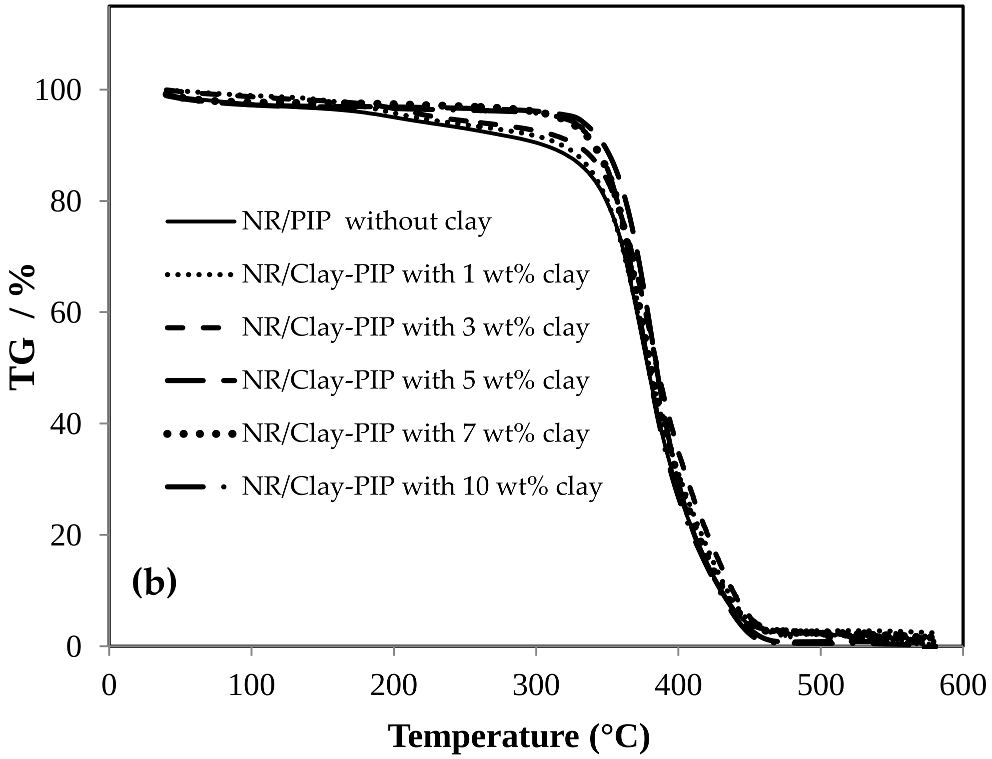


Figure 4.20 TGA thermograms of the (a) Clay-PIP and (b) NR/Clay-PIP composites containing various nanoclay contents. The Clay-PIP latexes were prepared using SFE technique. The clay contents are relative to the monomer amount.

The 5 wt% relative to the monomer content of nanoclay used to modify the polyisoprene latex gives the optimum mechanical properties of the NR thin films because this amount provides the maximized reinforcing power due to an optimum level of in-rubber structure or immobilized polymer as well as an appropriate degree of filler distribution in the elastomeric matrix.

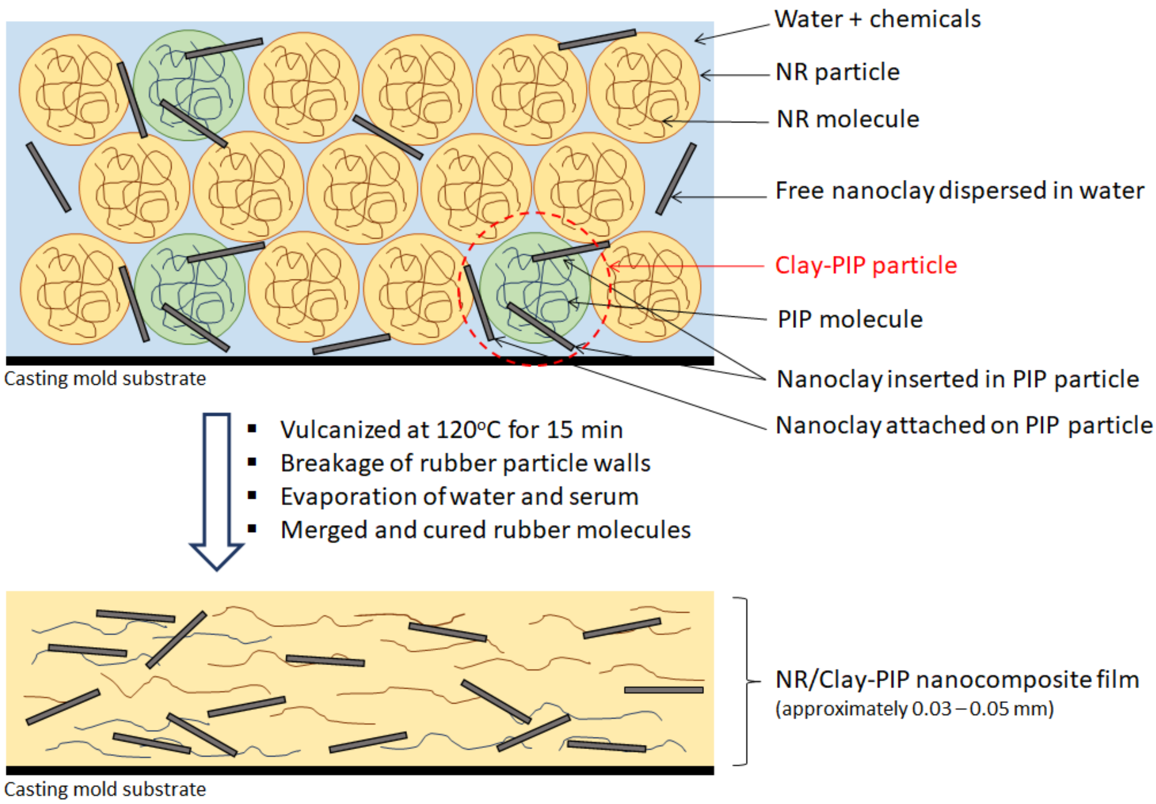


Figure 4.21 Possible model of film formation of the NR/Clay-PIP nanocomposite.

Figure 4.21 demonstrates how the NR/Clay-PIP latex can form a nanocomposite film. According to the actual values of nanoclay content in the dried form of Clay-PIP and NR/Clay-PIP film nanocomposites (Table 4.7), nanoclay contents in the composites increases with increasing the nanoclay used to modify the PIP latexes. Based on the information of this organo-nanoclay from the supplier, it contains the modifier ‘dimethyl, dehydrogenated tallow, quaternary ammonium’ at about 40 wt% [108]. Therefore, the actual value of the nanoclay in the Clay-PIP with 1 wt% nanoclay relative to the monomer content (Table 4.7) is approximately 0.6 wt%, consistent with the TGA results. Applying the Clay-PIPs in the NR thin films, the actual amounts of nanoclay in the film composites appear to be very low. However, the reinforcing power is considerable, especially in the case of the Clay-PIP containing 5 wt% nanoclay relative to the monomer content. It could be not only due to the greatest extent of immobilized polymer in this composite, but also to an intrinsic character of the Clay-PIPs as reported in our previous work [99]. Polyisoprene synthesized in the present work consists of about 63 mol% trans molecular configuration which exhibits rather rigid compared to the cis-structure of natural rubber: see Figure 4.18. Therefore, this nanoclay-modified polyisoprene can increase the modulus of the NR film composites, as clearly observed from the stress-strain curves in Figure 4.18, contributing to improved reinforcement efficiency.

4.3.2 Influence of Clay-PIP contents in NR thin films

According to the outcome from the previous investigation in 4.3.1, the Clay-PIP latex with 5 wt% of nanoclay related to monomer content (i.e. 10 wt% of total weight of the Clay-PIP latex) provides the best overall properties to the NR thin film. While the ratio between NR and Clay-PIP latexes was fixed at 90/10 phr in dry weight for all latex compounds of this series. Therefore, this investigation was carried out in order to check the actual proportion of the Clay-PIP required to obtain optimum properties, in particular reinforcing level, of natural rubber thin films. The ration between NR and Clay-PIP latexes for this series was varied at 100/0, 95/5, 90/10, 85/15 and 80/20 phr in dry weight. The results from this investigation are shown in Figures 4.22 and 4.23 as well as in Table 4.8.

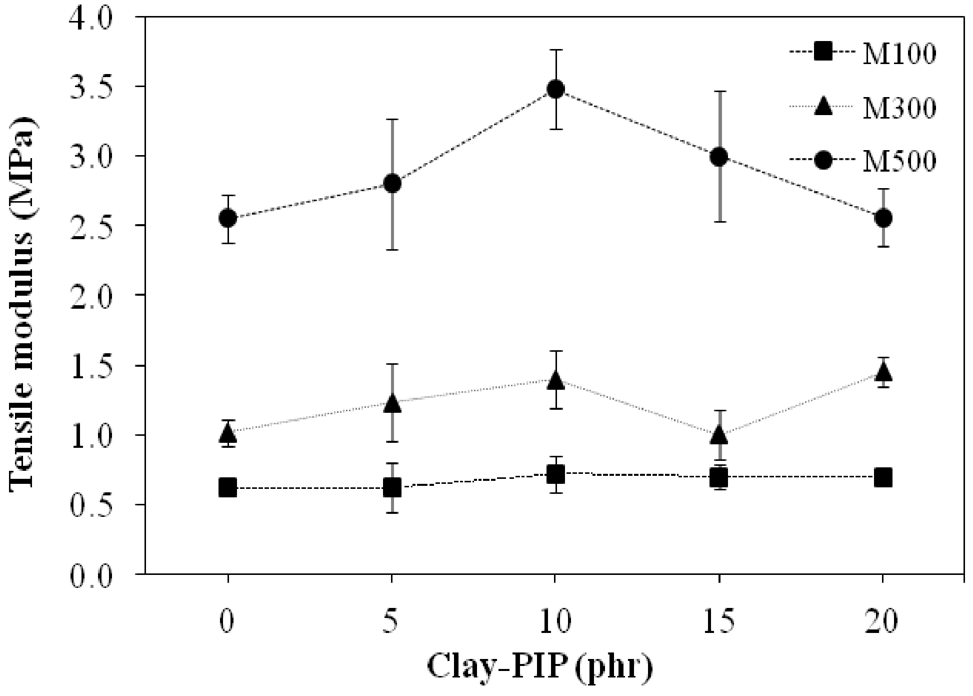


Figure 4.22 Influence of Clay-PIP content in NR/Clay-PIP thin films on tensile modulus

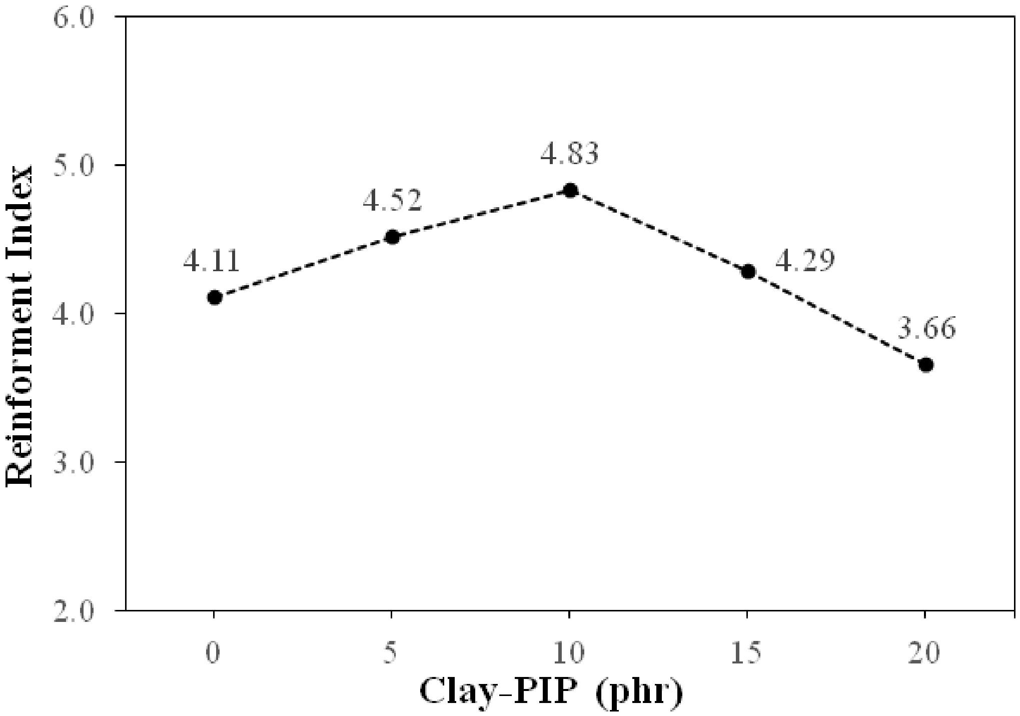


Figure 4.23 Reinforcement index of NR thin films filled with different amounts of Clay-PIPs.

Considering the tensile moduli of film vulcanizates shown in Figure 4.22, the addition of Clay-PIP to NR films from 5 to 10 phr increases tensile modulus of the film nanocomposites, in particular the modulus at 500 % strain (M500). However, further increasing the Clay-PIP from 15 to 20 phr appears to decrease the modulus of the films. Figure 4.23 reveals that reinforcement indices of the films show the same trend with tensile moduli as the NR film with the Clay-PIP at 10 phr shows an optimum reinforcement index. It is obvious that the Clay-PIP latex has an ability to reinforce NR thin films when compared to the one without the Clay-PIP, due to the presence of nanoclay which is pre-dispersed in the modified latex. In addition, as discussed earlier, PIP synthesized in this work consist rather high trans-conformation in polyisoprene molecules, as a result in a more rigid or a stiffer material. However, the inclusion of the Clay-PIP beyond 10 phr leads to a deterioration in modulus and reinforcement index of the films.

When considering the actual amount of nanoclay inside the NR films with the Clay-PIP at 10 phr: see Table 4.7, the film contains only 0.08 wt% which is very small compared to an optimum amount needed for a composite. In general, a typical nanoclay gives a maximum reinforcement level to polymer composites at 3 – 5 wt% of total weight of a composite [35], [56], [109]. It is most likely that, besides the effects of nanoclay and rigid molecular structure of Clay-PIP, the homogeneity and heterogeneity can also have a strong impact on the ultimate mechanical properties of a composite. Adding excessive amount of the Clay-PIP results in increased heterogeneity of the composite. This factor overshadows the reinforcement power of the nanoclay. In other words, these parameters inside NR/Clay-PIP film composites competitively influence final properties of the films.

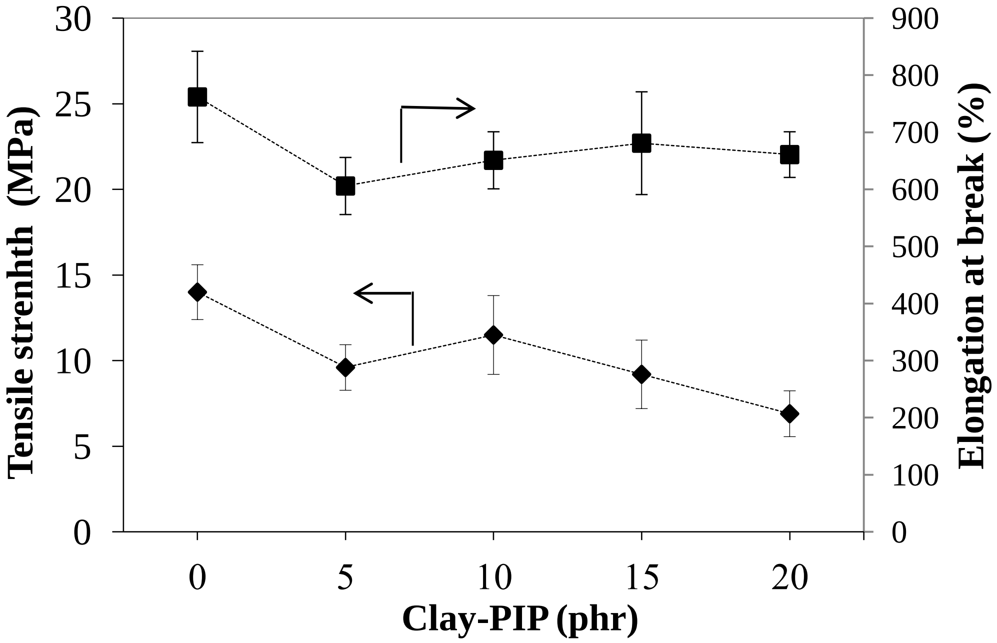


Figure 4.24 Influence of Clay-PIP content in NR/Clay-PIP thin films on mechanical properties

The ultimate tensile properties clearly show the effect of competitive factors inside the composites: see Figure 4.24. An incorporation of Clay-PIP into a NR thin film results in a reduced tensile strength when compared between the films without and with Clay-PIP at 5 phr. This is due to the material gains a higher modulus (Figure 4.22) but a less extensibility or elongation at break, resulting in the lower ultimate strength property. However, with 10 phr Clay-PIP, the composite shows a maximum strength, attributed to better reinforcement power of nanoclay and rigid molecules of the Clay-PIP. After that, the tensile strengths significantly reduce, due to a dominant effect of the more heterogeneity of the system.

Table 4.8 Glass transition temperatures from DSC analysis of NR thin films containing different quantities of Clay-PIP.

NR/Clay-PIP	**T_g (°C)**
100/0	-67.6
95/5	-66.6
90/10	-66.4
85/15	-68.7
80/20	-67.1

Based on the results from thermal analysis shown in Table 4.8, the film composites with 5 and 10 phr Clay-PIP exhibit higher glass transition temperatures (T_g) compared to the one without the Clay-PIP, indicating that the films constitute higher extent of immobilized polymer which contributes to the stronger reinforcement. This result is in a good agreement with the mechanical properties of the film nanocomposites (Figures 4.22-4.24). Once the amount of Clay-PIP is overdosed, the T_g tends to decrease, that could be due to the more heterogeneity of the composites as discussed in the results of mechanical properties. Therefore, it is obvious that the results from mechanical measurement and thermal analysis could mutually explain each other, which essentially supports the elucidation for reinforcement mechanism of the Clay-PIP in NR thin film system.

CHAPTER 5

CONCLUSIONS

5.1 Synthesis and characterizations of polyisoprene (PIP)

Miniemulsion technique gives a smaller size of rubber particles, hence a larger number of loci for polymerization, leading to high conversion and concomitant higher amounts of gel and coagulum. This extent of gelation is not significantly greater than conventional polymerization, and the coagulation can be minimized by control of the monomer and surfactant concentration. The proportion of *cis*-polyisoprene was greater than commonly reported for isoprene polymerization, which may be attributable to the relatively high temperature at which the polymerization was carried out, as the *cis*-isoprene fraction has been reported to increase with temperature. Intriguingly an increased amount of 3,4-addition was seen in the miniemulsion polymerization compared to the conventional polymerization. With increasing monomer concentration from 10 – 30 wt%, the conversion slightly decreases, but dramatically drops at 40 wt% of monomer. This was consistent with the number of stable droplets maintained in the miniemulsion, with the fall in conversion being accompanied by a drop in particle number and increase in coagulum consistent with some loss of stabilization and polymerization in large droplets. Surfactant had a significant effect on polymer particle size, with a higher surfactant:monomer ratio giving smaller particles. All results were consistent with an increase in branching and crosslinking reactions at high conversions, giving an increasing gel fraction and shoulders in the molar mass distributions at high molar masses. The better understanding derived from this work will be useful in further improvements in synthesis of polyisoprene latice with the aim of reducing the gel content.

5.2 Preparation of nanoclay-modified polyisoprene (Clay-PIP) latexes

This section was developed further from the earlier part as mini-emulsion technique gave rather small polymer particle size of the obtained latexes. An attempt to enlarge the polymer particles was made in this part. The polyisoprene latexes were modified with organo-nanoclay during emulsion polymerization. Starve-fed (SFE) and Batch (BE) emulsion techniques have similar gel and coagulation contents. However, the SFE provides a better product conversion compared to the BE technique, i.e. approximately 5 wt% higher, since the SFE generates a smaller average polymer particle size or a higher particle concentration, leading to more loci of the reaction and thus the better polymerization efficiency. Increasing organo-nanoclay contents results in a larger average polymer particle size as well as a broader particle size distribution. The TEM images correspond with the particle size analysis, revealing that the nanoclay particles are inserted in and/or attached on the polyisoprene particles suspended in latexes. XRD results show that the addition of nanoclay from 1 to 5 wt% relative to the isoprene monomer content increases the d-spacing of nanoclay structure. At 10 wt% of nanoclay, the d-spacing is reduced due to reagglomeration effect. The obtained nanoclay-modified polyisopre latexes with varied nanoclay contents were taken to be used as a reinforcing agent for natural rubber thin films.

5.3 Reinforcement of NR thin films by Clay-PIP latexes

NR film nanocomposites filled with Clay-PIP latexes containing organo-nanoclay from 1 to 5 wt% relative to the monomer content show an increase in tensile strength and modulus with a slightly reduced elongation at break, attributed to the reinforcing effect. However, adding the modified isoprene latexes containing nanoclay at 7 and 10 wt% leads to a reduced strength and modulus of NR thin films, while maintaining elongation at break. DSC and TGA analyses confirm that the reinforcement mechanism of this nanoclay-modified polyisoprene to the natural rubber thin films occurs mainly through the contribution of immobilized polymer due to the inclusion of nanoclay. The optimized amount of nanoclay is 5 wt% relative to the monomer content because it gives the highest mechanical strength and modulus corresponding well with the maximum extent of immobilized polymer which can be implied by thermal properties of the composites. Investigation of the influence of Clay-PIP contents on properties of NR thin films indicates that there are three crucial parameters affecting reinforcement mechanism of the composites: 1) nanoclay, 2) molecular characteristics of polyisoprene and 3) material homogeneity/heterogeneity. These influencing factors play a competitive role on reinforcement efficacy in the nanocomposites. The best possible formulation for a NR thin film based on Clay-PIP as a reinforcing component is NR/Clay-PIP at 90/10 phr using the Clay-PIP containing 5 wt% of nanoclay relative to the monomer content.

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List of Publication and Communications

Publications:

Chouytan, J., Beraheng, S., Kalkornsurapranee, E., Fellows, C. M. and Kaewsakul, W., Synthesis of polyisoprene via miniemulsion polymerization: Effect on thermal behaviour, colloidal properties and stereochemistry. *Journal of Rubber Research*, 21(4), 236-255, 2018.

Chouytan, J., Kalkornsurapranee, E., Fellows, C. M. and Kaewsakul, W., In-situ modification of polyisoprene by organo-nanoclay during emulsion polymerization for reinforcing natural rubber thin films, *Polymers*, 11(8), 1338, 2019.

Communications:

Chouytan, J., Fellows, C. M. and Kaewsakul, W., Controlling the particle size of polyisoprene modified with nanoclay during emulsion polymerization. The International Conference on Advanced and Applied Petroleum, Petrochemicals, and Polymers 2018. Bangkok, Thailand, December 18 –20, 2018. (Presentation)