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Natural rubber modification by vinyl monomers grafting: a review

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Abstract

This review article provides information on chemical modification of natural rubber (NR) by grafting with hydrophilic or hydrophobic vinyl monomers, involving a free radical polymerization on the backbone of the rubber. Graft copolymer can be generated from a latex, solvent, or monomer medium using a variety of initiation systems. Key processing parameters consist of monomer to rubber ratio, type of initiator, initiator concentration, reaction temperature and time. Characterization techniques such as Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS), and transmission electron microscopy (TEM) are presented. The properties of the graft product such as grafting efficiency, conversion, molecular weight, thermal property, mechanical properties, oil resistance, water absorption, and phase morphology are discussed. The review also includes the applications of the presented graft copolymers.

Keywords**:** *natural rubber, vinyl monomers, core-shell, graft copolymerization, free radical polymerization*

บทคัดย่อ

บทความนี้ได้รวบรวมข้อมูลเกี่ยวกับการปรับปรุงโครงสร้างทางเคมีของยางธรรมชาติด้วยวิธีการกราฟต์โคพอลิเมอร์กับไวนิลมอนอเมอร์ชนิดที่ชอบน้ำและไม่ชอบน้ำผ่านกระบวนการสังเคราะห์พอลิเมอร์แบบฟรีแรดิคัลบนสายโซ่ของยางธรรมชาติ กราฟต์โคพอลิเมอร์ของยางธรรมชาติสามารถเตรียมได้ทั้งในภายใต้สภาวะน้ำยาง ตัวทำละลายหรือตัวกลางที่เป็นมอนอเมอร์ด้วยกระบวนการริเริ่มปฏิกิริยาที่แตกต่างกันไป ปัจจัยที่ส่งผลต่อคุณภาพของกราฟต์โคพอลิเมอร์ที่เตรียมได้ประกอบด้วย อัตราส่วนของมอนอเมอร์ต่อยางธรรมชาติ ชนิดและความเข้มข้นของตัวริเริ่มปฏิกิริยา อุณหภูมิและเวลาในการเกิดปฏิกิริยา เทคนิคที่ใช้ในการพิสูจน์เอกลักษณ์ของกราฟต์โคพอลิเมอร์ที่เตรียมได้มีหลายเทคนิค เช่น ฟูเรียทรานสฟอร์มอินฟราเรดสเปกโทรสโกปี นิวเคลียร์แมกเนติคเรโซแนนซ์สเปกโทรสโกปี แมสสเปกโทรเมทรีและการใช้กล้องอิเล็กตรอนชนิดส่องผ่าน สมบัติของกราฟต์โคพอลิเมอร์ที่ได้มีมากมาย เช่น ประสิทธิภาพการกราฟต์ การเปลี่ยนจากมอนอเมอร์เป็นพอลิเมอร์ น้ำหนักโมเลกุลของพอลิเมอร์ที่กราฟต์บนยางธรรมชาติ สมบัติทางความร้อน สมบัติเชิงกล ความต้านทานน้ำมัน การดูดซับน้ำ และ ลักษณะทางสัณฐานวิทยา นอกจากนี้ยังกล่าวถึงการนำกราฟต์โคพอลิเมอร์เหล่านี้ไปประยุกต์ใช้งานต่างๆ อีกด้วย

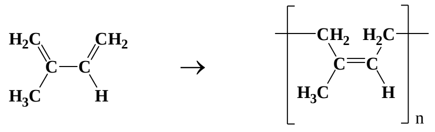
คำสำคัญ: *ยางธรรมชาติ, ไวนิลมอนอเมอร์, แกน-เปลือก, กระบวนการกราฟต์โคพอลิเมอร์, การสังเคราะห์พอลิเมอร์แบบฟรีแรดิคัล*

1. Introduction

From the natural rubber (NR) production statistics, Thailand is the world's biggest producer and exporter of NR (The Thai Rubber Association, 2014). Therefore, many researchers work on improving the properties of products containing NR to increase their values. NR shows excellent tensile strength and elasticity with outstanding resilience (Kohjiya & Ikeda, 2014). However, NR becomes problematic when used in oil and hydrocarbon solvents because of its hydrophobic property in nature. This limits the use of NR in various applications. To overcome such shortcomings, rubber blending can offer combined features of its individual blend partner. Unfortunately, most of NR blended with other polymers that do not have the addition of the third component as a phase combining assistant (compatibilizer) show inferior mechanical properties due to the separation of the rubber phase. To prepare such a compatibilizer to improve the phase separation of the blending system, many kinds of vinyl monomers are applied onto a low polar, polymeric NR backbone by graft copolymerization. This article is to review the methods of how to prepare many kinds of vinyl monomers grafted onto NR. It focuses on the effect of processing parameters on grafting efficiency, conversion, and other properties of the graft copolymer. Characterization techniques and their applications are also discussed.

2. Background

NR is obtained from the milky latex extracted from the *Hevea brasiliensis* tree. It contains 93-95 wt% of *cis-1,4*-polyisoprene (Kohjiya & Ikeda, 2014). Polyisoprene containing a carbon-carbon double bond in the repeating unit is a diene polymer, which is made from a monomer containing two carbon-carbon double bonds. This natural polymer can also be made by the Ziegler-Natta polymerization (Figure 1). The double bonds in polyisoprene are the main reason of high sensitivity to heat and oxidation of the rubber chain unless it is vulcanized.



isoprene polyisoprene

Figure 1 Ziegler-Natta polymerization of isoprene unit

Various types of chemical modifications have been performed to increase the poor characteristics of NR. Graft copolymerization of NR with many kinds of monomers is one modification of interest. Examples of vinyl monomers grafted onto NR are listed in Table 1. The chemical structures of these vinyl monomers are shown in Figure 2.

The graft copolymerization of NR and vinyl monomers has been performed within different kinds of states, such as latex, solution, or monomer medium. Various initiation systems such as redox reaction, thermal decomposition, persulfate dissociation, and photoinitiation will be discussed in next section. Graft copolymers are obtained when free radicals are reacted with NR at the α-methylenic hydrogen atom. All graft reactions involve a free radical polymerization which has the following proposed mechanism (Arayapranee, Prasassarakich, & Rempel, 2002).

2.1 Initiation

Radical formation:

$$\mathrm{RO\text{-}OR} \rightarrow 2\mathrm{RO}^{\bullet} \qquad (1)$$

Attacking monomer:

$$\mathrm{RO}^{\bullet} + \mathrm{M} \rightarrow \mathrm{M}_1^{\bullet} \qquad (2)$$

Attacking rubber and then monomer:

$$\mathrm{RO}^{\bullet} + \mathrm{NR\text{-}H} \rightarrow \mathrm{NR}^{\bullet} + \mathrm{ROH} \qquad (3)$$

$$\mathrm{NR}^{\bullet} + \mathrm{M} \rightarrow \mathrm{NR\text{-}M}_1^{\bullet} \qquad (4)$$

2.2 Propagation

Homopolymerization:

$$\mathrm{M}_1^{\bullet} + \mathrm{M} \rightarrow \mathrm{M}_2^{\bullet} \qquad (5)$$

$$\mathrm{M}_n^{\bullet} + \mathrm{M} \rightarrow \mathrm{M}_{n+1}^{\bullet} \qquad (6)$$

Graft copolymerization:

$$\mathrm{NR\text{-}M}_1^{\bullet} + \mathrm{M} \rightarrow \mathrm{NR\text{-}M}_2^{\bullet} \qquad (7)$$

$$\mathrm{NR\text{-}M}_n^{\bullet} + \mathrm{M} \rightarrow \mathrm{NR\text{-}M}_{n+1}^{\bullet} \qquad (8)$$

2.3 Termination

Homopolymerization:

$$\mathrm{M}_n^{\bullet} + \mathrm{M}_m^{\bullet} \rightarrow \mathrm{M}_{n+m} \qquad (9)$$

Graft copolymerization:

$$\mathrm{NR\text{-}M}_n^{\bullet} + \mathrm{M}_m^{\bullet} \rightarrow \mathrm{NR\text{-}M}_{n+m} \qquad (10)$$

$$\mathrm{NR\text{-}M}_n^{\bullet} + \mathrm{NR\text{-}M}_m^{\bullet} \rightarrow \mathrm{NR\text{-}M}_{n+m}\text{-}\mathrm{NR} \qquad (11)$$

where RO-OR is an initiating molecule; $RO^{\bullet}$ is an alkoxy radical; M is a vinyl monomer; $M_n^{\bullet}$ is a vinyl polymer radical; NR-H is a natural rubber or polyisoprene; H is an α-methylenic hydrogen atom; $NR^{\bullet}$ is a polyisoprene radical; and $NR\text{-}M_n^{\bullet}$ is a growing graft polymer radical.

From the proposed mechanism, there are two types of polymer generated. First is a free polymer or homopolymer as shown in equation (9), and the other one is a graft copolymer. The graft copolymer is not only formed by the combination of polyisoprene and polymer radicals as shown in equations (10)-(11) but is also generated by chain transferring to some species such as initiator, monomer, polymer, and polymer radical as shown in Figure 3.

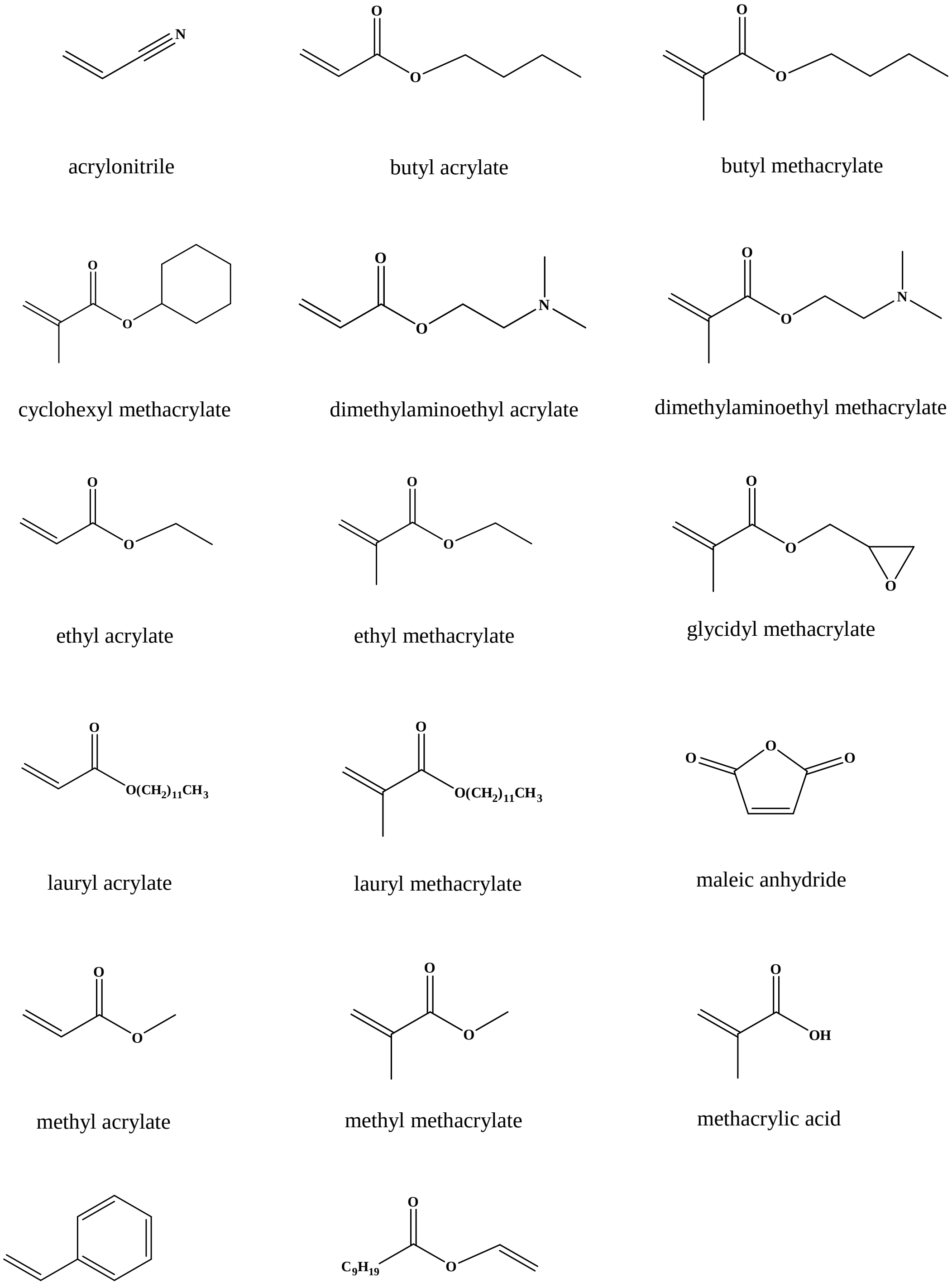
Table 1 List of vinyl monomers grafted onto NR

Vinyl monomers	Monomer symbol	References
Individual monomers:		
acrylonitrile	ACN	Okieimen & Urhoghide, 1996
butyl acrylate	BA	Dafader, Haque, Akhtar, & Ahmad, 2006; Hossain & Chowdhury, 2010
butyl methacrylate	BMA	Dafader et al., 2006
cyclohexyl methacrylate	CHMA	Dafader et al., 2006
dimethylaminoethyl acrylate	DMAEA	Kangwansupamonkon, Gilbert, & Kiatkamjornwong, 2005
dimethylaminoethyl methacrylate	DMAEMA	Lamb, Anstey, Fellows, Monteiro, & Gilbert, 2001; Kangwansupamonkon, Fellows, Lamb, Gilbert, & Kiatkamjornwong, 2004; Kangwansupamonkon et al., 2005; Oliveira et al., 2005a & b
ethyl acrylate	EA	Dafader et al., 2006
ethyl methacrylate	EMA	Thamronganankul, Boonjawat, Sonsuk, & Swasdison, 2007
lauryl acrylate	LA	Subramaniam, Monteiro, Taylor, Simpson-Gomes, & Gilbert, 2000
lauryl methacrylate	LMA	Subramaniam et al., 2000
glycidyl methacrylate	GMA	Juntuek, Ruksakulpiwat, Chumsamrong, & Ruksakulpiwat, 2011
maleic anhydride	MAH	Afifi & El-Wakil, 2008
methylacrylate	MA	Dafader et al., 2006
methyl methacrylate	MMA	Enyiegbulam & Aloka, 1992; Okieimen & Urhoghide, 1996; Oommen, Nair, & Thomas, 1996; Schneider, Pith, & Lambla, 1996; Perera, 1999; Thiraphattaraphun, Kiatkamjornwong, Prasassarakich, & Damronglerd, 2001; George, Bitto, & Sebastain, 2003; Nakason, Kaesaman, & Yimwan, 2003; Nakason, Kaesaman, Rungvichaniwat, Eardord, & Kiatkamjornwong, 2003; Oliveira et al., 2005a & b; Nakason, Pechurai, Sahakaro, & Kaesaman, 2006; Budchar, Ruksakulpiwat, & Khansawai, 2008; Zhang et al., 2008; Derouet, Tran, & Thuc, 2009
methacrylic acid	MAA	Nakason, Kaesaman, & Supasanthitikul, 2004
styrene	ST	Hourston & Romaine, 1989; Schneider et al., 1996; Tho, Kadir, & Hashim, 2002; Kawahara, Kawazura, Sawada, & Isono, 2003; Chuayjuljit, Moolsin, & Potiyaraj, 2005; Nampitch & Buakaew, 2006; Pukkate et al., 2007; Arayapranee & Rempel, 2008a; Pukkate, Yamamoto, & Kawahara, 2008; Suksawad, Yamamoto, & Kawahara, 2011
Mixed monomers:		
glycidyl methacrylate/methyl methacrylate	GMA/MMA	Songprateepkul & Chumsamrong, 2010
glycidyl methacrylate/styrene	GMA/ST	Suriyachai, Kiatkamjornwong, & Prasassarakich, 2004
styrene/methyl methacrylate	ST/MMA	Charmondusit, Kiatkamjornwong, & Prasassarakich, 1998; Arayapranee et al., 2002; Arayapranee & Rempel, 2004; Kreua-ongarjnukool, Pittayavinai, & Tuampoemsab, 2012
acrylonitrile/styrene	ACN/ST	Prasassarakich, Sintoorahat, & Wongwisetsirikul, 2001; Angnanon, Prasassarakich, & Hinchiranan, 2011
acrylonitrile/methyl methacrylate	ACN/MMA	Okieimen & Urhoghide, 2002
vinylneo-decanoate/methyl methacrylate	VND/MMA	Monteiro et al., 2001; Lee, Subramaniam, Fellows, & Gilbert, 2002

styrene

vinyl neo-decanoate

Figure 2 Reported chemical structures of vinyl monomers used to graft onto



acrylonitrile

butyl acrylate

butyl methacrylate

cyclohexyl methacrylate

dimethylaminoethyl acrylate

dimethylaminoethyl methacrylate

ethyl acrylate

ethyl methacrylate

glycidyl methacrylate

lauryl acrylate

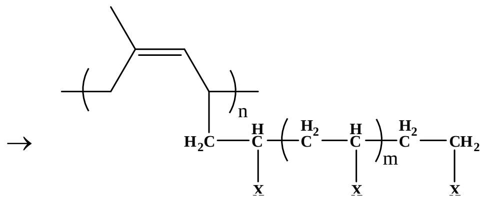
lauryl methacrylate

maleic anhydride

methyl acrylate

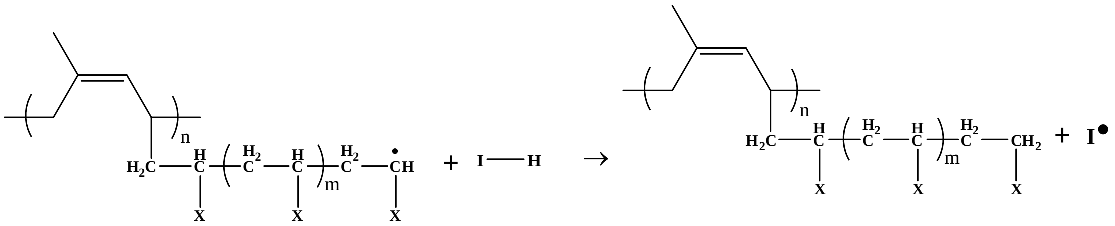
methyl methacrylate

methacrylic acid

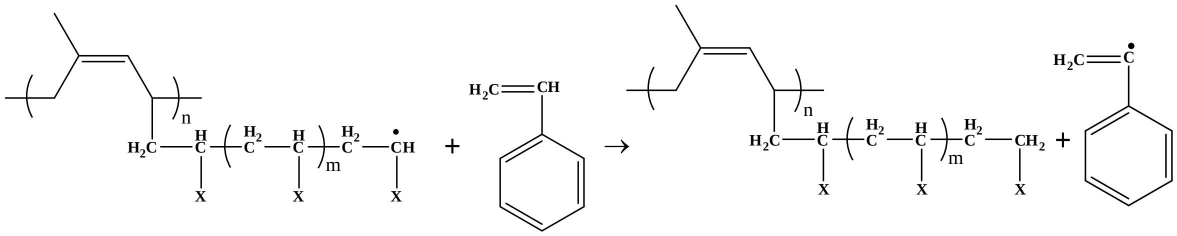


(d)

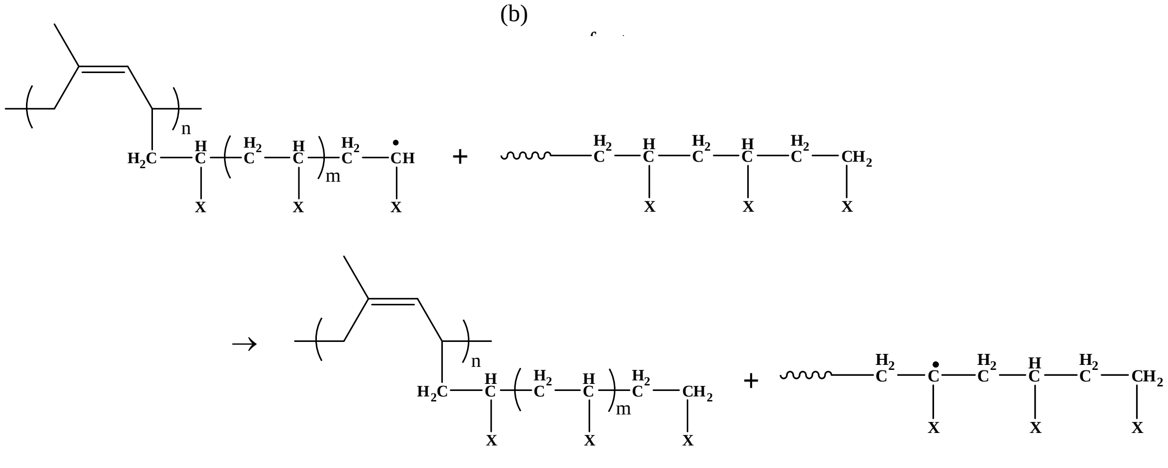
Figure 3 Mechanism of chain-transfer reaction occurring in the graft copo
group; I-H is an initiator (adapted from Pukkate et al., 2008)



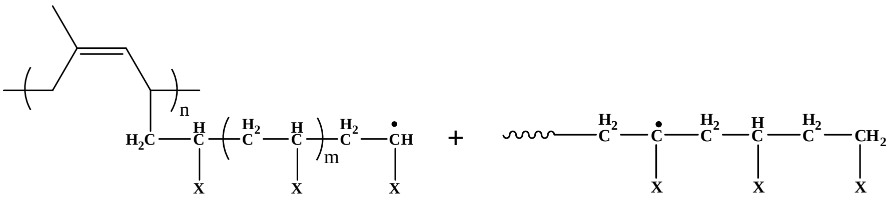
(a) transfer to initiator

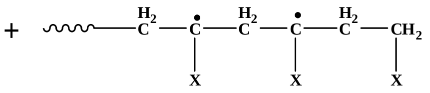


(b)



(c)





$+ \sim\sim C H_2 - \dot{C}(X) - C H_2 - \dot{C}(X) - C H_2 - C H_2(X)$

(adapted from Schneider et al., 1996)

3. Key methods to prepare natural rubber-graft-vinyl polymer

3.1 Emulsion polymerization approach

In an emulsion polymerization technique, composite NR-based latex particles can be prepared into different morphological structures. Many examples in the literature are core-shell, poow, acornlike, sandwichlike, raspberrylike, and inverted structures as shown in Figure 4. In the comparison to other polymerization approaches, most of grafting reactions are carried out in a latex medium to obtain NR-graft-vinyl polymer. There are many systems to initiate the graft copolymerization: redox reaction, thermal decomposition, persulfate dissociation, and photoinitiation.

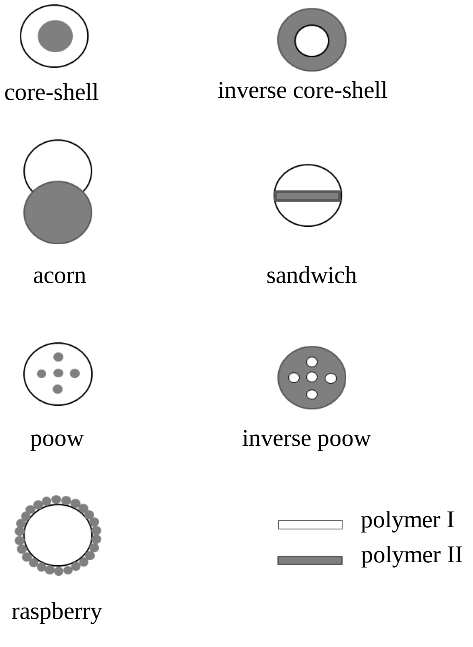
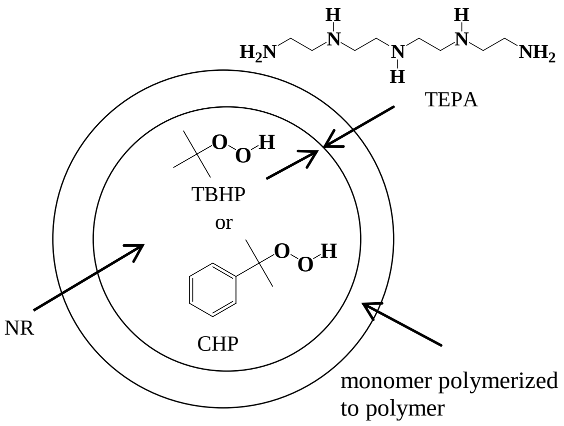


Figure 4 Possible morphological structures of composite latex particles via emulsion polymerization

Redox-initiating systems are proved to be very effective to obtain graft copolymers via the emulsion polymerization. A bipolar redox initiation system consists of cumene hydroperoxide (CHP) (Arayapranee et al., 2002; Kangwansupamonkon et al., 2005; George, 2006; Nakason et al., 2006; Arayapranee & Rempel, 2008a & b; Budchar et al., 2008; Juntuek et al., 2011) or *tert*-butyl hydroperoxide (TBHP) (Schneider et al., 1996; Nakason et al., 2003; Kangwansupamonkon et al., 2005; Pukkate et al., 2008; Suksawad et al., 2011) as an initiator along with tetraethylene pentamine (TEPA) as an activator. The bipolar system produces NR-based core-shell arrangement, which a core NR particle was coated with a shell vinyl polymer. The components of the redox couple CHP/TEPA or TBHP/TEPA are located as shown in Figure 5. In a hydrophobic redox initiation system, azobisisobutyronitrile (AIBN) or a redox couple TBHP and dimethylaniline (DMA) is used as an initiator. This system serves for the introduction of hydrophobic polymer subinclusion within the NR particles producing a poow morphological structure. The initiators are soluble in organic phases and the polymerization takes place entirely within the NR particle as shown in Figure 6. By the comparison in terms of hydrophobicity, it is easier to obtain polar poly(methyl methacrylate) (PMMA) in the shell region of the NR particles than is polystyrene (PS), which forms small subinclusions with in the NR phase (Schneider et al., 1996).



latex particle dispersed in water

Figure 5 Bipolar redox initiation system representing the location of its components: TBHP or CHP soluble in organic phase and TEPA soluble in water (adapted from Schneider et al., 1996)

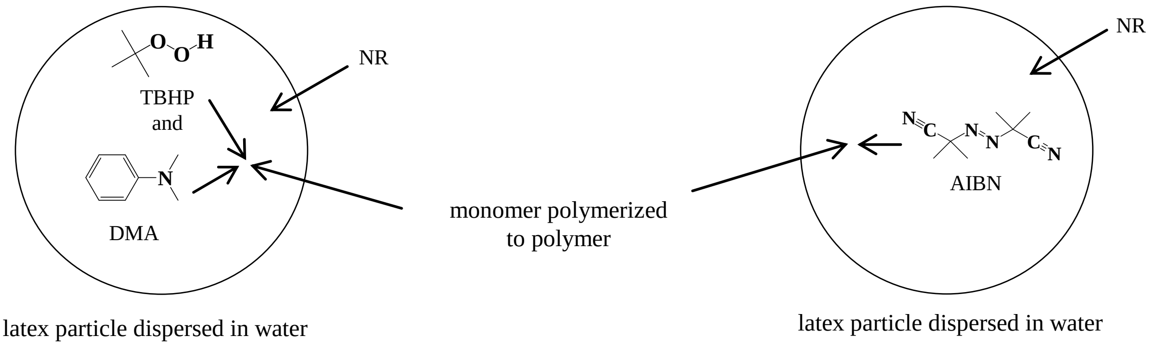


Figure 6 Hydrophobic redox initiation systems representing the location of their components: (a) TBHP/DMA and (b) AIBN soluble in organic phases (adapted from Schneider et al., 1996)

In a thermal initiation system, an organic peroxide, such as benzoyl peroxide (BPO), is usually used as an initiator (Perera, 1999). The initiator is heated until the oxygen-oxygen bond is homolytically cleaved, revolving into free radicals (Figure 7). The radicals might interact either with the monomer, producing vinyl polymer radicals, or with the rubber molecule, producing polyisoprene radicals as mentioned before. The graft NR with methyl methacrylate (MMA) monomer was prepared by adding MMA/BPO mixture dropwise to NR latex. The reaction was heated to 80°C under nitrogen gas overnight. The results showed that the lower the amount of MMA in the feed, the higher was the grafting efficiency. In addition, the chemically polymerized sample via BPO showed a better phase miscibility compared to a gamma radiation polymerized samples. Zhang et al. (2008) synthesized NR-graft-poly(methyl methacrylate) or NR-*g*-PMMA in the presence of supercritical carbon dioxide ($scCO_2$) using BPO as an initiator. The polymerization reaction was performed in the autoclave at 70°C with the stirring speed of 100 rpm. The optimum conditions were found to be 70:30 of NR-to-MMA ratio, 1.2% BPO content, and the reaction pressure of 23 MPA for 6 h. Furthermore, the $scCO_2$ swelling polymerization was compared to the solution polymerization and it was found that using the $scCO_2$ as reaction medium gave better properties of the graft copolymer in terms of grafting efficiency, grafting level, and oil resistance.

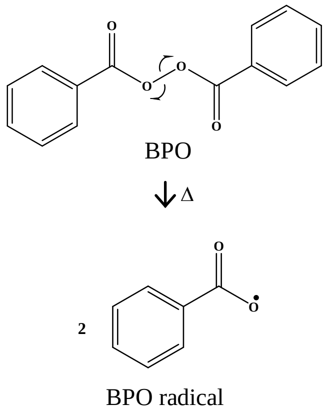


Figure 7 Thermal decomposition of BPO

For a persulfate initiation, it is useful in the emulsion polymerization where a radical diffuses into a hydrophobic monomer-containing droplet (Qudsieh et al., 2004). The dissociation of a persulfate, which requires energy, demonstrates in Figure 8. Potassium persulfate (PPS) was reportly used as a thermal initiator in NR graft copolymerization with MMA (Budchar et al., 2008) and ST (Nampitch & Buakaew, 2006). It was found that the temperature of 70°C is required to dissociate the oxygen-oxygen bond of PPS. The highest level of grafting efficiency (97.2%) was obtained using 0.5 mol% of PPS and 20 mol% of MMA within 24 h. In comparison to the use of a redox initiator (CHP/TEPA) under the same condition, this thermal initiator showed better grafting efficiency and conversion of the graft copolymer.

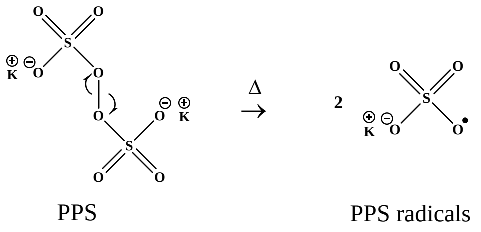


Figure 8 Thermal degradation of PPS

Besides the chemical initiations, high energy radiation was also used to initiate graft copolymerization. A gamma source from Co-60 was used for irradiation of many types of acrylic monomers (Dafader, et al., 2006). In the gamma-aided grafting of MMA and NR latex mixtures without the addition of any initiator (Perera, 1999), the grafting efficiency (94.2%) could be improved by using a low radiation dose rate of 0.3 kGy h to a total dose of 5 kGy. Rather than using gamma ray, UV light was used to synthesize NR-graft-polymer (Derouet et al., 2009). The photopolymerization of vinyl monomers was initiated from *N*,*N*-diethyldithiocarbamate (DEDT) groups previously introduced onto NR chains as shown in Figure 9. The DEDT-NR, which acts as a macroinitiator, was introduced in a Schlenk tube containing the monomer, deoxygenated, and placed under nitrogen atmosphere at room temperature. A 100-W UV lamp (365 nm) was then used to initiate the graft polymerization.

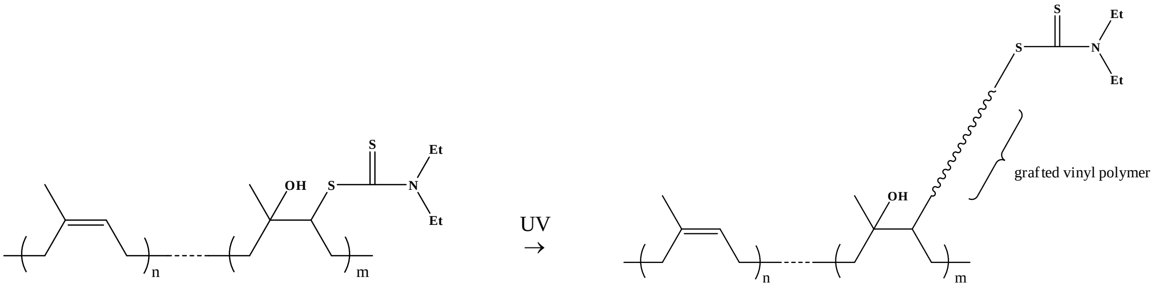
3.2 Solution polymerization approach

The preparation of NR graft copolymer via a solution polymerization technique is rare. This is due to a concern of environmental toxicity.

Toluene is the most popular solvent used to dissolve solid NR bale. It has been reported that NR-*g*-PMMA was prepared in methyl ethyl ketone/toluene mixture using BPO as an initiator (Enyiegbulam & Aloka, 1992). Mixtures of vinyl monomers such as ACN/MMA (Okieimen & Urhoghide, 2002) and ACN/ST (Angnanon et al., 2011) were also incorporated onto the NR backbone. The use of a co-monomer was to promote the higher grafting efficiency of the graft copolymer. Angnanon et al. (2011) discovered that 3/1 (w/w) of ACN/ST initiated with 5 parts per hundred of rubber (phr) BPO at 70°C under 2 bar of N_2 pressure for 6 h was the optimum point to achieve the highest grafting efficiency of 85.1%.

3.3 Bulk polymerization approach

In a bulk polymerization process, the reaction is carried out in the absence of solvent. In other words, a soluble initiator is added into a pure monomer in liquid state. The reaction is initiated by heating or exposing it to radiation. Although the system is simple, NR graft copolymer produced by bulk polymerization is hardly seen. This is because it requires good thermal insulation and the obtained polymer has very low average molecular weights and a broad molecular weight distribution. Derouet et al. (2009) synthesized NR-graft-polymer by photopolymerization of vinyl monomers initiated from DEDT-NR, which is a macroinitiator for vinyl monomers. The solid DEDT-NR was dissolved in monomers (ST, MMA, etc.) for 12 h with the reaction container shaking under room temperature. The polymerization was initiated by irradiation with a UV lamp obtaining NR graft copolymer, which was precipitated in methanol (Figure 9).



vinyl monomer

DEDT-NR

NR-graft-polymer

Figure 9 Photopolymerization of NR-graft-polymer initiated by DEDT-NR

4. Characterization techniques

4.1 Fourier transform infrared (FTIR) spectroscopy

The structure of the graft copolymer is characterized after Soxhlet extraction using FTIR spectroscopy in the range of 400-4000 cm^{-1}. The graft copolymer sample is dissolved in chloroform and then casted onto a NaCl disk. The FTIR spectrum of the graft copolymer is usually compared with that of NR, which exhibits the characteristic absorption bands of C=C stretching vibration at 1664 cm^{-1}, C-H vibration at 2997, 1473 and 1376 cm^{-1} and C=C bending vibration at 853 cm^{-1}. After graft copolymerization, new signals appear depending upon the type of the monomer added. The signals appearing at different positions attribute to different functional groups: 2238 cm^{-1} for C≡N stretching; 1728 cm^{-1} for C=O stretching; 1500 cm^{-1} for C=C stretching of the styrenic benzene ring; 1147 cm^{-1} for C-O-C stretching; 760 and 700 cm^{-1} for monosubstituted benzyl ring.

4.2 Nuclear magnetic resonance (NMR) spectroscopy

The structure of the graft copolymer is qualitatively confirmed by NMR spectroscopy. The graft sample is swollen in $CDCl_3$ and analyzed using ^{1}H-NMR spectroscopy. It indicates the important signals at 1.66 ppm ($-CH_3$), 2.00 ppm ($-CH_2-$) and 5.10 ppm (=CH-). Additional signals appear depending upon H atoms of the grafted groups: 1.25-3.20 ppm for methylene and methane protons overlapping from vinyl polymer chain, 3.61 ppm for methoxy proton of the acrylic group of MMA unit, and 6.40-7.50 ppm for aromatic protons of ST unit. Other vinyl monomers such as DMAEMA grafted onto NR backbone were also reported (Oliveira et al., 2005b). To confirm the structure of the graft copolymer, ^{13}C-NMR spectroscopy is usually used. The ^{13}C peaks of NR are observed at 24 ppm ($-CH_3$), 27 and 33 ppm ($-CH_2-$), and 126 and 135 ppm (C=C). An example of the solid state ^{13}C-NRM spectroscopy of the NR-*g*-PGMA was reported (Juntuek et al., 2011).

4.3 Mass spectrometry (MS)

During the free radical polymerization process, vinyl monomers polymerize into vinyl polymers. One attached to the NR backbone is called grafted polymer. Another one polymerized individually is called free homopolymer. The free homopolymer produced during the graft copolymerization can be confirmed by matrix assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF MS). Derouet et al. (2009) used MALDI-TOF spectrometry to analyze free PMMA produced from the graft copolymerization between NR and MMA. A main series of peaks on the mass spectra showed the mass difference between two successive peaks corresponding to the mass of MMA unit.

4.4 Transmission electron microscopy (TEM)

The particle morphology of the graft NR latex can be examined by TEM. In the sample preparation procedure, the graft NR latex is first diluted with distilled water followed by the addition of a staining solution. The staining solutions that have been reported to use to stain only the rubber domain are osmium tetroxide (OsO_4) and ruthenium tetroxide (RuO_4). The surface layer stained with RuO_4 was reported to appear darker than one stained with OsO_4 (Thiraphattaraphun et al., 2001). The thickness of the grafted polymer on the surface of the NR seed particles increased with increasing reaction time. To obtain a completely closed shell, 8 h of the emulsion polymerization using potassium persulfate as an intiator was required to allow the growing PMMA to reside on the seed particle as a continuous shell (Thiraphattaraphun et al., 2001). Like a persulfate initiation, the bipolar redox-initiating system of hydrophilic vinyl monomers, such as MMA, promoted a core NR-shell PMMA morphology. On the other hand, when the hydrophobic redox-initiating system was used, the hydrophobic vinyl monomers such as ST were introduced into the NR core and the poow arrangement was observed (Schneider et al., 1996).

5. Graft copolymer properties

5.1 Grafting properties

The resulting product obtained from each polymerization technique, which is an emulsion or a solution sample, is precipitated in excess non-solvent such as methanol, ethanol, 3.5% (w/v) formic acid solution, or 10% (w/v) calcium chloride solution or poured into a petridish and dried in an oven. In the single monomer system, the gross product consists of three main components: graft copolymer (NR-*g*-polymer), free homopolymer (ungraft polymer), and free NR (unreacted NR). It is the same as the two-monomer system, which consists of graft copolymer, free copolymer, and free NR. To obtain the graft copolymer, free polymer and free NR are extracted using Soxhlet extraction. The solvent used in a Soxhlet extractor is different depending upon the polymer being removed: for example, free NR removed by petroleum ether, free PMMA or PS by acetone, and free polyacrylonitrile (PAN) or PS-*co*-PAN by dimethylformamide. The residue in each step is then dried to a constant weight in a vacuum oven. Grafting efficiency, %grafting ratio, %grafting level, %conversion, %graft NR, %ungraft NR, and %ungraft homopolymer are defined and calculated as follows (Chuayjuljit, Siridamrong, & Pimpan, 2004; Zeng, Wang, Cai, & Zeng, 2004; Juntuek et al., 2011)

$$\text{Grafting efficiency (\%)} = \frac{\text{weight of polymer grafted}}{\text{weight of polymer grafted} + \text{weight of free homopolymer}} \times 100 \qquad (12)$$

$$\text{Grafting ratio (\%)} = \frac{\text{weight of polymer grafted}}{\text{weight of NR}} \times 100 \qquad (13)$$

$$\text{Grafting level (\%)} = \frac{\text{weight of polymer grafted}}{\text{weight of graft copolymer}} \times 100 \qquad (14)$$

$$\text{Conversion (\%)} = \frac{\text{weight of polymer grafted} + \text{weight of free homopolymer}}{\text{weight of monomer}} \times 100 \qquad (15)$$

$$\text{Graft NR (\%)} = \frac{\text{weight of graft copolymer}}{\text{weight of graft copolymer} + \text{weight of free homopolymer} + \text{weight of free NR}} \times 100 \qquad (16)$$

$$\text{Ungraft NR (\%)} = \frac{\text{weight of free NR}}{\text{weight of graft copolymer} + \text{weight of free homopolymer} + \text{weight of free NR}} \times 100 \qquad (17)$$

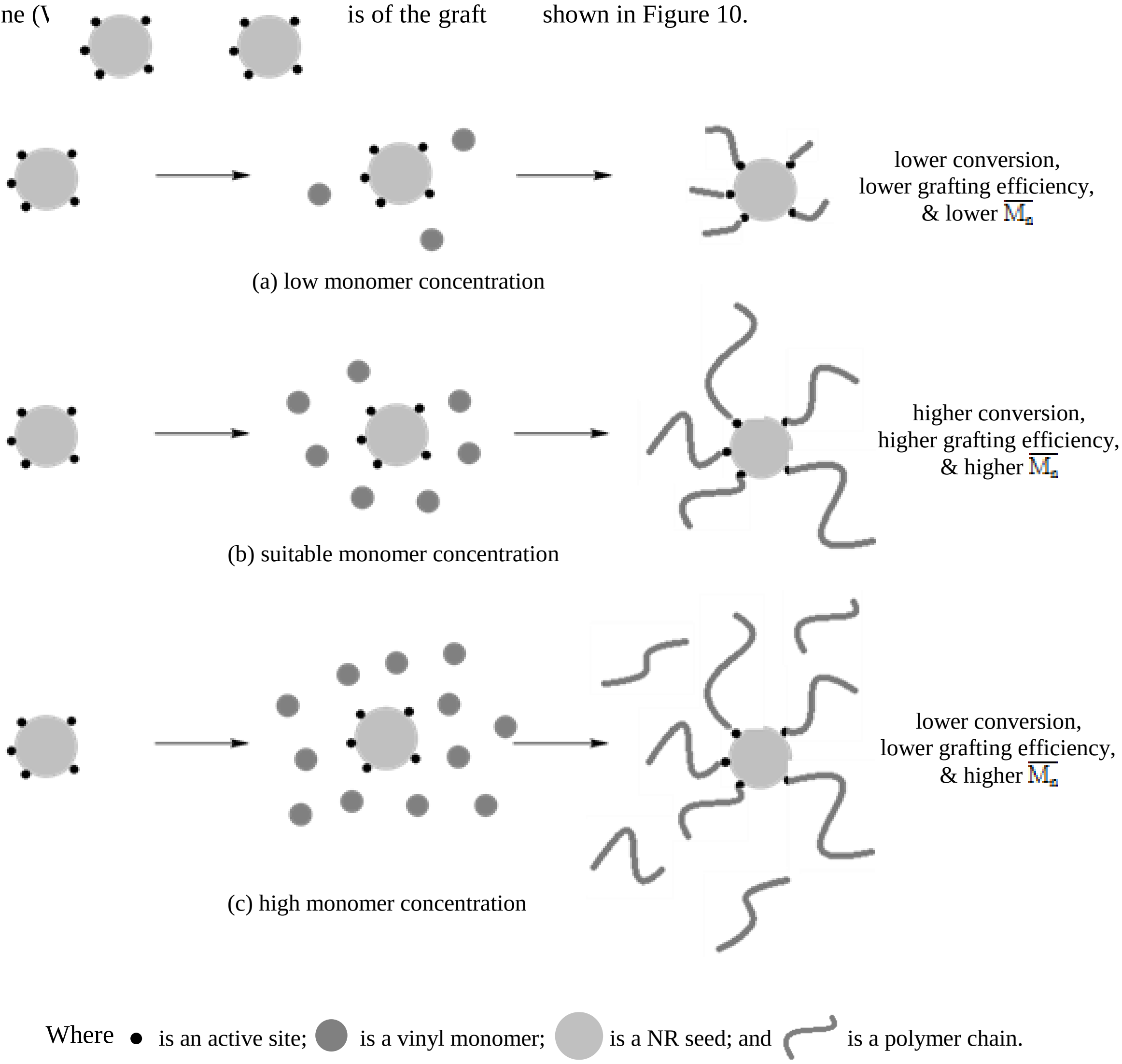
$$\text{Ungraft homopolymer (\%)} = \frac{\text{weight of free homopolymer}}{\text{weight of graft copolymer} + \text{weight of free homopolymer} + \text{weight of free NR}} \times 100$$

where the weight of polymer grafted onto NR is obtained from the difference between weight of extracted NR-graft-polymer and weight of NR; weight of free homopolymer is the weight of dried residue extracted via Soxhlet by acetone or other related solvents; weight of free NR is the weight of dried residue extracted via Soxhlet by petroleum ether; and weight of graft copolymer is the weight of dried extracted NR-graft-polymer.

Kawahara et al. (2003) reported that high grafting efficiency was achieved by using purified natural rubber particles, which was prepared by deproteinization of the rubber particle. This is because the non-rubber components, such as proteins and phospholipids, cause the side reaction with vinyl monomers. Tho et al. (2002) observed that styrene polymerization in deproteinized NR latex is more efficient than in high ammonia NR latex. The system could attain a high conversion of 97% without adding surfactant compared to the high ammonia system which was a surfactant required system and gave relatively low conversion of 66%. Furthermore, a co-monomer with similar polarity to that of the main chain polymer is used to promote the higher grafting efficiency (Shellenberg & Hamann, 1992; Hu & Cartier, 1999). Angnanon et al. (2011) discovered that 3/1 (w/w) of ACN/ST was the optimum point to achieve a high grafting efficiency in the graft copolymerization of ST and ACN onto NR or polyisoprene. Since ST has similar polarity to NR, it is expected to first react with polyisoprene radicals followed by further copolymerizing with ACN monomer, creating an alternating copolymerization.

5.2 Molecular weight determination

The grafted polymer can be isolated from the resulting graft copolymer in order to determine the molecular weight via size exclusion chromatography (SEC) or gel permeation chromatography (GPC). Ozonolysis allows ozone to react with the double bond of polyisoprene to form ozo aldehyde and ketone (is of the graft copolymer, molecular weight of the grafted vinyl polymer is measured. It has been proved by Pukkate et al. (2008) that the number average molecular weight ($\overline{M}_n$) of the homopolystyrene derived from Soxhlet extraction and the grafted polystyrene derived from ozonolysis had no similarity. The $\overline{M}_n$ of the homopolystyrene increased linearly, whereas the $\overline{M}_n$ of the grafted polystyrene increased monotonically. This suggested that at low monomer concentration, almost all vinyl monomers can react completely with the created active site on the rubber particle as shown in Figure 10.



(a) low monomer concentration

(b) suitable monomer concentration

(c) high monomer concentration

Figure 10 Schematic representation of NR graft copolymerization at various monomer concentrations (adapted from Pukkate et al., 2008)

5.3 Thermal properties

Thermal transition phenomena such as glass transition temperature (T_g) of the graft copolymer are investigated by dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). Each specimen is stepwise operated between -110 to +165°C with a heating/cooling rate of 10°C/min or as desired depending upon the vinyl polymer investigated. The T_g (DSC) of NR was reported at -63°C (Moolsin, 2014). Two T_gs were observed for the graft copolymer, consistent with a two-phase morphology, as confirmed by TEM. The low T_g of NR phase (-63°C) and the upper T_g of PMMA (+104°C) or PS (+97°C) phases were reported (Schneider et al., 1996).

The addition of the graft copolymer NR-*g*-PMMA into the blend of NR and PMMA did not make the system single phase. In other words, incorporation of the graft copolymer did not promote the miscibility in molecular level as the results obtained by the DSC and DMA analyses (Oommen, Groeninckx, & Thomas, 2000). This was in an agreement with the work done by Asaletha, Kumaran, & Thomas (1998). In such a completely immiscible system, the main role of the graft copolymer is to act as an interfacial agent.

Graft copolymer, which will be incorporated into thermoplastics to increase their impact resistance, must be stable at processing temperatures of around 250°C. This is necessary to know its degradation temperature or behavior. Thermogravimetric analysis (TGA) is usually used to provide its decomposition temperature (T_d). Schneider et al. (1996) reported that T_d shifted from 365°C of pure NR to 380°C in the case of core-shell particles.

5.4 Mechanical properties

From the tensile stress-strain curve of NR and NR-graft-polymer at various %grafting, NR-*g*-poly(dimethylaminoethyl methacrylate) (NR-*g*-PDMAEMA) showed higher stress level than NR (Oliveira et al., 2005). This was in the agreement with that of NR-*g*-PGMA (Juntuek et al., 2011). They gave the reason that it might be related to the higher crosslinking density of the graft copolymer than that of the NR. Moreover, tensile strength and modulus of the graft copolymer increased with increasing %grafting. However, elongation at break of the graft copolymer decreased with increasing %grafting. The mechanical properties are also evaluated as a function of the graft copolymer in rubber blends or other polymers. Addition of copolymer was reported to improve the interfacial adhesion and the mechanical properties, such as modulus, tensile strength, elongation at break, and so forth. The blends with the graft copolymer exhibited a considerable improvement in the mechanical properties compared to the uncompatibilized blends (Thiraphattaraphun et al., 2001).

5.5 Oil resistance

NR is easily dissolved in oil or non-polar solvents since it is non-polar in nature. Thus, %swelling of the NR vulcanizate is reported with a great value of 152%. Conversely, a rubber with high polarity as NBR shows very low %swelling of 3.5, indicating that it has an excellent oil resistance (Angnanon et al., 2011). After the sample is immersed in oil at room temperature for 70 h, the %swelling can be calculated from equation (19). The oil resistance of NR/NBR vulcanizates with and without NR-*g*-(PAN-*co*-PS) in IRM 903 oil was investigated. It was found that the addition of 10 phr of the graft copolymer into the blends increased the oil resistance. Furthermore, the higher the %graft copolymer, the greater decreased the %swelling.

5.6 Water absorption and contact angle

In case of the modification of NR by grafting with hydrophilic vinyl monomers, water absorption and degree of contact angle are usually reported. To measure %water absorption, the graft copolymer films are immersed into deionized water for 48 h at room temperature. Once the films are removed and blotted dry with filter papers, water absorption is calculated as equation (20). The hydrophilicity of the graft NR latex film is assessed by the contact angle measurement of a drop of distilled deionized water placed on the film surface. Kangwansupanmonkon et al. (2005) discovered that the redox initiator CHP/TEPA was more effective than TBHP/TEPA or $K_2S_2O_8/K_2S_2O_5$, respectively, for grafting of DMAEMA onto NR. Furthermore, the increase in grafted polymers on the NR particles resulted in an increase in water absorption and a decrease in contact angle of the graft copolymer film. For NR-*g*-PDMAEMA films, the water absorption and contact angle were reported of about 20% and 80 degree, respectively.

$$\text{Swelling (\%)} = \frac{\text{weight of specimen after immersion - weight of specimen before immersion}}{\text{weight of specimen before immersion}} \times 100 \qquad (19)$$

$$\text{Water absorption (\%)} = \frac{\text{weight of sample after immersion - weight of sample before immersion}}{\text{weight of sample before immersion}} \times 100 \qquad (20)$$

5.7 Phase morphology

Miscibility property is also evaluated as a function of the graft copolymer in rubber blends. Morphology of the blends is usually observed by scanning electron microscopy (SEM). The blend of unmodified NR and PMMA resulted in highly incompatible mixtures, which undergo a phase separation. Addition of small amount of the graft copolymer decreased the phase separation and reduced the particle size of the dispersed phase (Oommen et al., 2000). The reduction in the phase separation and the dispersed particle size still did not promote molecular level miscibility as mentioned before. This was in an agreement with the conclusions made by Paul and Newman (1978) who suggested that if two polymers are far from being miscible, then, no copolymer is likely to make the system single phase.

6. Applications

According to the polymer particle morphology, there are two main kinds of core-shell copolymers: soft core-hard shell and hard core-soft shell. Polymers with a soft core and a hard shell are used as an impact modifier, for plastics toughening, whereas polymers with a hard core and a soft shell are usually applied to the coating and adhesive fields. Types of polymerization and initiator directly effects to the morphological structure of the final graft product. The resulting graft products are not only used as the impact modifiers but they also act as the compatibilizer for thermoplastic elastomeric materials.

NR-*g*-PMMA has been found useful as shoe adhesives and reinforcing fillers, which has a trade name of *Heaveaplus MG* or *MG rubber* (Perera & Rowen, 2000). Moreover, it could be used as an impact modifier. It was blended with PMMA providing the blend products with higher impact strength. Thiraphattaraphun et al. (2001) reported that the higher the content of the graft NR, the higher was the impact energy of the blend. This made cracking propagation more difficult, leading to a successful use for the fabrication of automobile components. Besides using as an impact modifier, NR-*g*-PMMA prepared by using CHP/TEPA redox initiator was used to compatibilize a heterogeneous NR/PMMA blend. Oommen et al. (1996) reported that morphology of the blends containing the graft copolymer was improved. A sharp decrease in the dispersed domain size was observed by the addition of a few percent of the copolymer. Furthermore, the NR/PMMA blends with the graft copolymer were found to be more thermally stable than the blends without the copolymer (Oommen et al., 2000). This indicated that this kind of graft copolymer can be used as an interfacial agent for the thermoplastic elastomer of NR and PMMA, which is the combination of the excellent processability characteristics of PMMA and the elastic behavior of NR.

Another example of a modified NR used to improve mechanical properties of polymers is NR-*g*-PS. Neoh and Hashim (2004) used NR-*g*-PS as a toughener for PS. Generally, rubber-toughened plastics contain 5-20% rubber, which is dispersed in the polymer matrix. Thus, the rubber loading was limited to 20% by volume. It was found that the mechanical properties of PS/NR-*g*-PS blends were better than that of PS/NR blends. The most pronounced difference between the two blend systems was in their impact strength. The former was about 55-230% higher than the latter.

NR graft copolymer with ethyl methacrylate (NR-*g*-PEMA) was reported to be able to be used as a denture soft lining material, which is a soft elastic material alleviating stresses from the denture base material to the underlying supporting tissues in the patients (Thamrong ananskul et al., 2007). It showed several advantages such as high bonding efficiency to the denture base materials, low water absorption and biocompatible to human tissues.

NR-*g*-(PAN-*co*-PS) via a solution poly merization is used as a compatibilizer for a high polar dissimilarity NR/NBR blend (Angnanon et al., 2011). It can improve the mechanical properties and oil resistance of NR/NBR blends due to the higher compatibility of the rubber phases.

7. Summary

The article reviews the methods to prepare chemically modified NR by graft copolymerization with various vinyl monomers. All graft reactions involve a free radical polymerization on the backbone of NR. Grafting reactions of MMA and ST are the only two extensively studied and reported since they give a high degree of grafting. Many kinds of polymerization techniques such as emulsion, solution, and bulk can be used to prepare NR-graft-vinyl polymer. Among the three, emulsion polymerization is the most popular route with different choices of initiation systems, such as redox, thermal, persulfate, and photoinitiation. To confirm the chemical structure of the graft copolymer, characterization techniques such as FTIR and NMR are necessary. Under TEM, the morphological structure of the graft copolymer is revealed. Graft copolymer properties such as grafting efficiency, polymer conversion, and molecular weight of the grafted polymer are depended upon many processing parameters consisting of monomer to rubber ratio, type of initiator, initiator concentration, reaction temperature and time. Thus, the applications of the NR graft copolymer can be expected to be useful as adhesives, reinforcing fillers, interfacial agents, impact modifiers, and compatibilizers for rubber industry.

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