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Natural Rubber and its Derivatives

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Abstract

This chapter summarizes various types of chemical modification of natural rubber (NR). These chemically modified NRs are known as NR derivatives. Chemical modification reviewed includes chemical modification without introducing new atom such as cyclized natural rubber and deproteinized natural rubber (DPNR), modification by introducing a chemical group such as hydrogenated natural rubber (HNR), **chlorinated natural rubber (CNR)** and epoxidized natural rubber (ENR) and lastly modification by grafting on NR. Grafting can be carried out using DPNR latex to yield styrene-grafted-NR, methyl methacrylate-grafted-NR and styrene and methyl methacrylate-grafted-NR. The NR derivatives are reviewed in terms of their preparation, mechanism, properties and applications.

Keywords: natural rubber, chemical modification, graft copolymerization

1. Introduction

In this chapter, various types of chemically modified natural rubbers (modified NRs) are reviewed in terms of their preparation, physical, chemical and mechanical properties and their potential applications. These NR derivatives include liquid natural rubber (LNR), cyclized natural rubber, deproteinized natural rubber (DPNR), chlorinated natural rubber (CNR), epoxidized natural rubber (ENR), styrene-grafted NR (SNR) and methyl methacrylate-grafted NR.

Commercial natural rubber (NR) or *cis*-1,4-polyisoprene is obtained from *Hevea brasiliensis* [1]. The NR latex, which is exuded from *H. brasiliensis* bark, is processed in either wet or dry form. Rubber bale is obtained from either field latex or coagulum. The field latex will be coagulated, formed into crepe, dried and packed. Commercial NRs are graded based on dirt content, ash content, nitrogen content, volatile matter content, etc. as specified by International Standards Organisation (ISO). The technically specified rubbers were first introduced into the market

by Malaysia in 1965 as the Standard Malaysian Rubbers (SMRs). Currently, commercial NRs are also specified according to Standard Thailand Rubber (STR), Standard Indonesian Rubber (SIR) and Standard Vietnam Rubber (SVR). Due to the high molecular weight of NR as well as its low glass transition temperature (T_g), NR vulcanizates are elastic with high tensile strength and low heat build-up. However, due to the presence of allylic carbons, the vulcanizates have poor abrasion, ageing and weathering resistance. These drawbacks can be overcome by chemical modifications of NR. In chemical modifications, changes in molecular structure occurred. Some examples of chemical modifications are hydrogenation and grafting.

Chemical modifications on NR can be carried out in either solid, solution or latex state. The modifications can be categorized into three categories:

- Modification by bond rearrangement without introducing new atoms. This type of modification will lead to changes in the chemical structure and/or reduction in molecular weight of NR. Cyclization is an example of bond rearrangement.
- Modification by introducing a chemical group such as hydrogen, chloride or epoxy via addition or substitution reactions at the olefinic double bonds. The resultant modified NR will possess the properties of the new chemical groups. For example, epoxidation of NR results in higher T_g and mechanical properties as well as higher hydrophilicity.
- Modification by grafting with one or two molecules, usually vinyl monomers at the allylic carbon. The new grafted polymer can either have low or high molecular weight. The degree of grafting and degree of polymerization measure the efficiency of the modification. Grafting of methyl methacrylate (MMA) onto NR; commercially known as Heveaplus MG results in harder and stiffer copolymer.

2. Modification by bond rearrangement

2.1. Cyclized NR

Cyclization is the simplest and earliest chemical modification of NR [2, 3]. Cyclization can be carried out by treating NR with a proton donor. Examples of the proton donors are sulphuric acid [2, 4–6], sulphonic acid [7], stannic chloride [8] and acid hydrochloric [9]. Modification can be carried out either in solution or in solid or emulsion form [2, 4–9]. For modification in emulsion state, destabilization of the NR latex is crucial and Lewis acid is not suitable. **Figure 1** shows the cyclization mechanism of NR.

Recently, cyclization on deproteinized natural rubber (DPNR) latex was reported by Riyajan et al. [6, 10, 11]. Cyclization on DPNR was reported to be more effective as the presence of the protein can retard and disturb the chemical modification [12]. Cyclized NR in general was reported to be tough, hard and brittle but some elastic behaviour is still maintained. The T_g of cyclized NR increases with higher cyclization where the degree of cyclization is measured from unsaturation of the cyclized NR. For example, the elastomeric behaviour is retained at 30% cyclization but at 60% cyclization, it has a leather-like characteristic. Cyclization up to

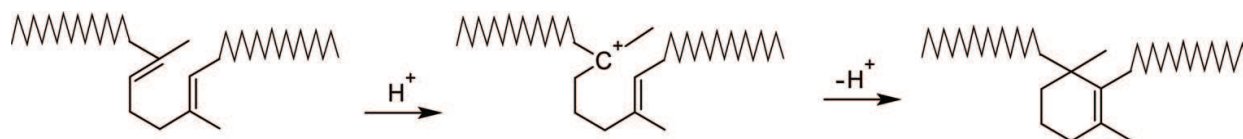


Figure 1. Mechanism of NR cyclization [6].

90% resulted in a powdery form material indicating high brittleness [11]. Cyclized NR is used as adhesives, printing ink as well as paints [10, 13].

2.2. Liquid natural rubber

Liquid natural rubber (LNR) can be derived from depolymerization of NR. The initial objective to prepare LNR was to reduce the internal viscosity of NR. NR with lower viscosity facilitates the addition of additives [14]. This can be achieved via mechanical shearing using either two roll mill or internal mixer. Depending on the milling time and temperature, the average molecular weight in the range of 400,000–1,000,000 Da was achieved [15].

LNR with reactive terminal groups received high attention by researchers as the terminal groups can undergo further chemical reaction or take part during vulcanization. LNR with reactive terminal groups can be prepared via redox couples, photochemical or oxidation. Different preparation methods yield different molecular weights. The oxidation approach yields lowest number average molecular weight, M_n ; that is, 2500–3000 Da while the redox couples approach reported M_n in the range of 3000–35,000 Da [16]. The photochemical approach received high attention from researchers. Its range of M_n is of 3000–8400 Da [16].

The only LNR obtained from oxidation is the hydroxyl-terminated LNR. It was prepared by depolymerizing masticated NR in toluene solution under pressure of 200–300 psi and temperature of 150°C with the presence of hydrogen peroxide [17]. LNR prepared via redox couples used both oxidizing and reducing agents either in solution or in emulsion state [16, 18]. LNR with hydroxyl or carbonyl or phenylhydrazone terminal groups was prepared using either hydrogen peroxide or organic peroxide/sulphanilic acid or phenylhydrazine, or phenylhydrazine/ferric chloride/oxygen, or phenylhydrazine/oxygen.

Photochemistry of NR was achieved by ultraviolet (UV) light or sunlight in the presence of compounds such as nitrobenzene and hydrogen peroxide [19, 20]. The former compound will produce carboxyl-terminated LNR, while the latter compound hydroxyl-terminated LNR. **Figure 2** shows an example of light-induced photochemical approach in producing hydroxyl-terminated LNR [20]. Free radicals formed from the bond cleavage under either sunlight or UV light will lead to depolymerization of NR.

Metathesis of NR is a reaction which can induce the cleavage and reforming of the double bonds as well as exchange of substituents in depolymerization of NR. A study by Alimuniar et al. [21] shows that cyclic oligomer of isoprene was produced from intra- and inter-molecular reaction by using tungsten hexachloride and tetramethyl tin in chlorobenzene with purified NR. Depending on the reaction temperature and duration, the molecular weight was in the range of 5800–110,000 Da.

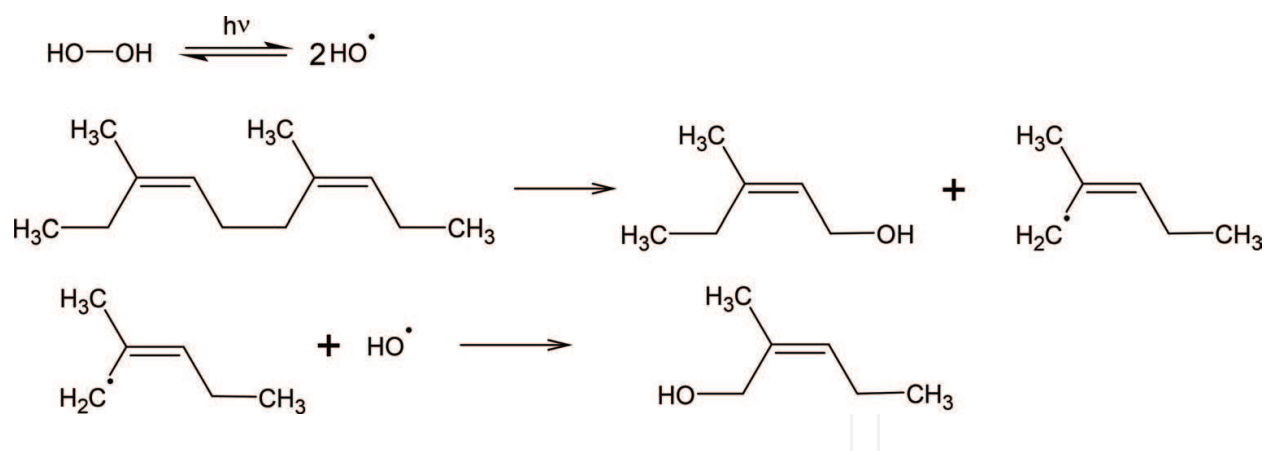


Figure 2. Mechanism of photochemical reaction of NR induced by light [20].

LNR can be used as viscosity modifier, adhesive, tackifier, sealing agent, plasticizer as well as compatibilizer [14, 22]. LNR was reported to be a good compatibilizer in linear low-density polyethylene/natural rubber (LLDPE/NR) blends, polypropylene/natural rubber (PP/NR) blends, high-density polyethylene/natural rubber (HDPE/NR) blends and low-density polyethylene/natural rubber (LDPE/NR) blends. The presence of LNR in HDPE/NR blend changed the morphology from co-continuous to dispersed phase suggesting better degree of compatibility. The tensile strength and elongation at break results were reported to be consistent with the morphological analysis [14].

2.3. Deproteinized natural rubber

Studies on deproteinized natural rubber (DPNR) were initiated due to protein allergy issue on dipped rubber products. DPNR latex is prepared by removing the protein layer covering the rubber particles [23]. The protein layer can be removed by centrifugation, enzymatic degradation or irradiation [24, 25]. Since the protein layer actually acts as stabilizer, surfactant is added during deproteinization. **Figure 3** shows the schematic diagram on removing of protein layer from high ammonia natural rubber (HANR) particle [26].

There are two typical methods used to prepare DPNR latex from field latex or commercial HANR latex. Deproteinization via centrifugation and hydrolysis of protein are the common methods [24]. In centrifugation, the latex is diluted in deionized water containing surfactant. The cream fraction is re-dispersed into deionized water containing sodium dodecyl sulphate (SDS) surfactant. After five times of centrifugation, the total solid content (TSC) of the DPNR obtained is adjusted to 60%. In enzymatic method, the latex is diluted with deionized water and stabilized with surfactant such as SDS. The pH is adjusted to the pH which is suitable for hydrolysis of the enzyme. The range of the pH studied was 5.4–9.2 [27–29]. **Table 1** shows the nitrogen content of the untreated latex and DPNR latex from field latex and HANR latex.

Irradiation of latex was also reported by Makuuchi [25]. In this method, the proteins decomposed during irradiation at 20 kGy. **Table 2** shows the nitrogen content before and after irradiation.

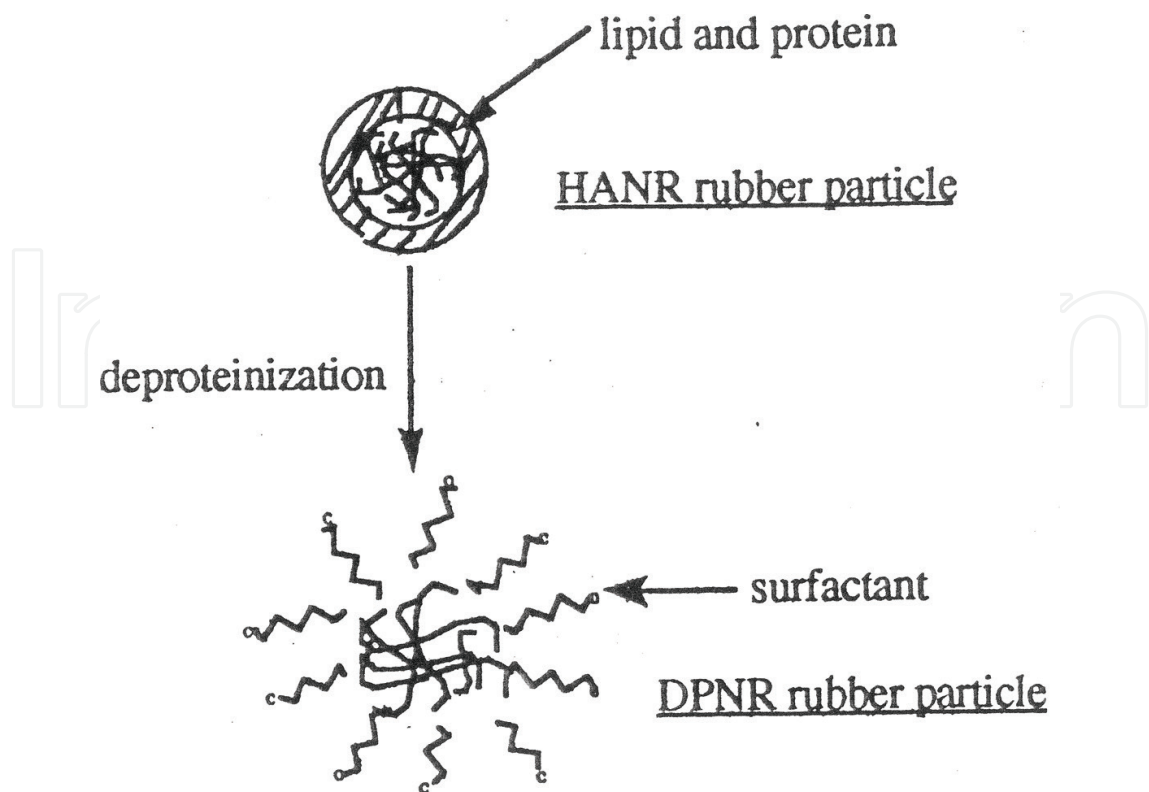


Figure 3. Schematic diagram of deproteinization of rubber particles in HANR latex [26].

Source of latex	Treatment on the latex	Nitrogen content (%)
Field latex	Untreated	0.87
	Five times of centrifugation	0.03
	Enzymatic method	0.008
HANR latex	Untreated	0.56
	Five times of centrifugation	0.03
	Enzymatic method	0.008

Table 1. Nitrogen content of untreated latex and DPNR latex [24].

Treatment type	Nitrogen content (%)
Non-irradiated latex: non-leached	0.26
Non-irradiated latex: leached	0.19
20-kGy-irradiated latex: non-leached	0.53
20-kGy-irradiated latex: leached	0.06

Table 2. Nitrogen content of non-irradiated and irradiated latex [25].

DPNR latex is mainly used to manufacture dipped product such as gloves as lower protein gloves are preferred. A significant amount of protein may cause allergies issue [23, 30]. Chemical modification on DPNR latex with vinyl monomers was also studied as the absence of protein layer was reported to enhance the degree of polymerization, degree of grafting and stability of the grafted NR latex [23, 26].

3. Modification by introducing a chemical group

3.1. Hydrogenated natural rubber

Hydrogenation is a process where hydrogen molecule was added onto NR which results in saturation of NR. **Figure 4** shows the hydrogenation of NR [13].

The purpose of preparing hydrogenated natural rubber (HNR) is to improve NR retention properties while maintaining its T_g . HNR can be prepared in either solution or emulsion forms where the latter has greater interest due to environment and economic reasons [31–33]. There are three methods of hydrogenation: catalytic homogeneous hydrogenation, catalytic heterogeneous hydrogenation and non-catalytic hydrogenation. These methods differ in terms of yield, selectivity, side reactions and/or catalyst poisoning and removal.

Catalytic homogeneous hydrogenation usually uses organotransition metals as the catalyst together with reducing agent such as hydrocarbon activator. Thus, this method of hydrogenation has high selectivity with the absence of microscopic diffusion problems. The catalyst used such as nickel is sensitive to impurities where the catalyst will react with the impurities [31, 34–44]. Catalytic homogeneous hydrogenation results in high yield of hydrogenation but degradation of NR occurs. The degradation can be overcome by using nickel catalyst [13].

Catalytic heterogeneous hydrogenation yields high purity HNR with 100% hydrogenation without any foreign groups or large-scale structural changes [36, 37, 41, 45–47]. Recent study by Kongparakul et al. [48] on metathesis hydrogenation of DPNR using second-generation Grubbs catalyst reported more than 97% hydrogenation.

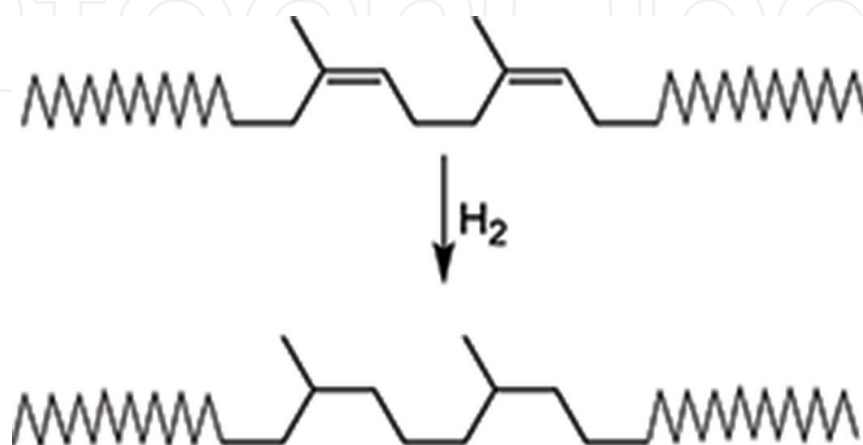


Figure 4. Hydrogenation of NR [13].

Non-catalytic hydrogenation normally is via diimide reduction [37]. Diimide can be obtained from hydrazine [37, 49–56]. Interest in non-catalytic hydrogenation is because of its mild reaction conditions [55, 56]. However, this hydrogenation usually results in chain scission [37]. In recent study by Mahittikul et al. [32], it was observed that hydrogenation of NR latex with diimide generated *in situ* by thermolysis of *p*-toluenesulphonyl hydrazide (TSH) results in >90% hydrogenation without affecting the T_g of the NR.

3.2. Chlorinated natural rubber

Chlorination of NR can be carried out in solution or emulsion forms in the presence of gaseous chlorine [33, 57, 58]. Four reactions of chlorination of NR are addition, substitution, cyclization and crosslinking, and are shown in **Figure 5** [6].

In an early study, chlorinated NR (CNR) was prepared by dissolving NR in a solvent followed by chlorination [59]. Zhong et al. [60] later prepared CNR by passing chlorine gas into pH-adjusted water, followed by the addition of stabilized NR latex. The water pH was adjusted with chloric acid. Chlorination of 60% was reported at where the CNR showed flame resistance, corrosion resistance, better thermal stability, acid-proof, alkaline-proof and wear resistance [60–63]. Due to these properties, CNR found its applications as a raw material for paints (for ships, containers, airport roads, etc.), adhesives, inks and coatings [3, 33]. Surface chlorination, supported by Fourier transform infrared spectroscopy (FTIR) analysis, on vulcanized NR sheets was investigated by Radabutra et al. [64] where the chlorination results in variation of surface roughness and stiffness. The surface roughness enhanced the bonding between CNR sheet and nitrile rubber (NBR) sheet.

3.3. Epoxidized natural rubber

Epoxidation of NR is carried out by converting the carbon-carbon double bond into oxiranes. Epoxidized NR (ENR) was reported since 1920s by Pummere and Burkard [65]; however, its commercial value was only realized in 1980s. Epoxidation of NR latex usually used peracid where the peracid can either be prepared separately or formed *in situ* from a precursor using acid and hydrogen peroxide. **Figures 6** and **7** show the epoxidation of NR with peracid prepared separately and *in situ*, respectively. The latter approach is preferable commercially because of the peracid instability at room temperature and higher temperatures [66].

ENRs with 25 and 50% mol of epoxidation are available commercially under the trade name of Epoxyprene 25 and Epoxyprene 50, respectively. ENR has a higher T_g compared to NR, thus giving higher damping, better air permeability, higher hysteresis, better wet grip as well as higher polarity [3, 66–68]. Therefore, blends of ENR were studied extensively. Blends of ENR with poly(vinyl chloride) (PVC), NR, styrene butadiene rubber (SBR), poly(acrylic acid), poly(ϵ -caprolactone) (PCL), nitrile rubber (NBR), and polychloroprene (CR) were reported [69–75]. Studies on ENR as pressure-sensitive adhesive were also reported extensively by Hashim and Ong [76]. Epoxidation of NR not only maintains the elasticity of the original NR even at modification higher than 20 mol% but also opens the opportunities to utilize the oxirane groups in various chemical reactions. These reactions included novel crosslinking systems and reinforcement systems.

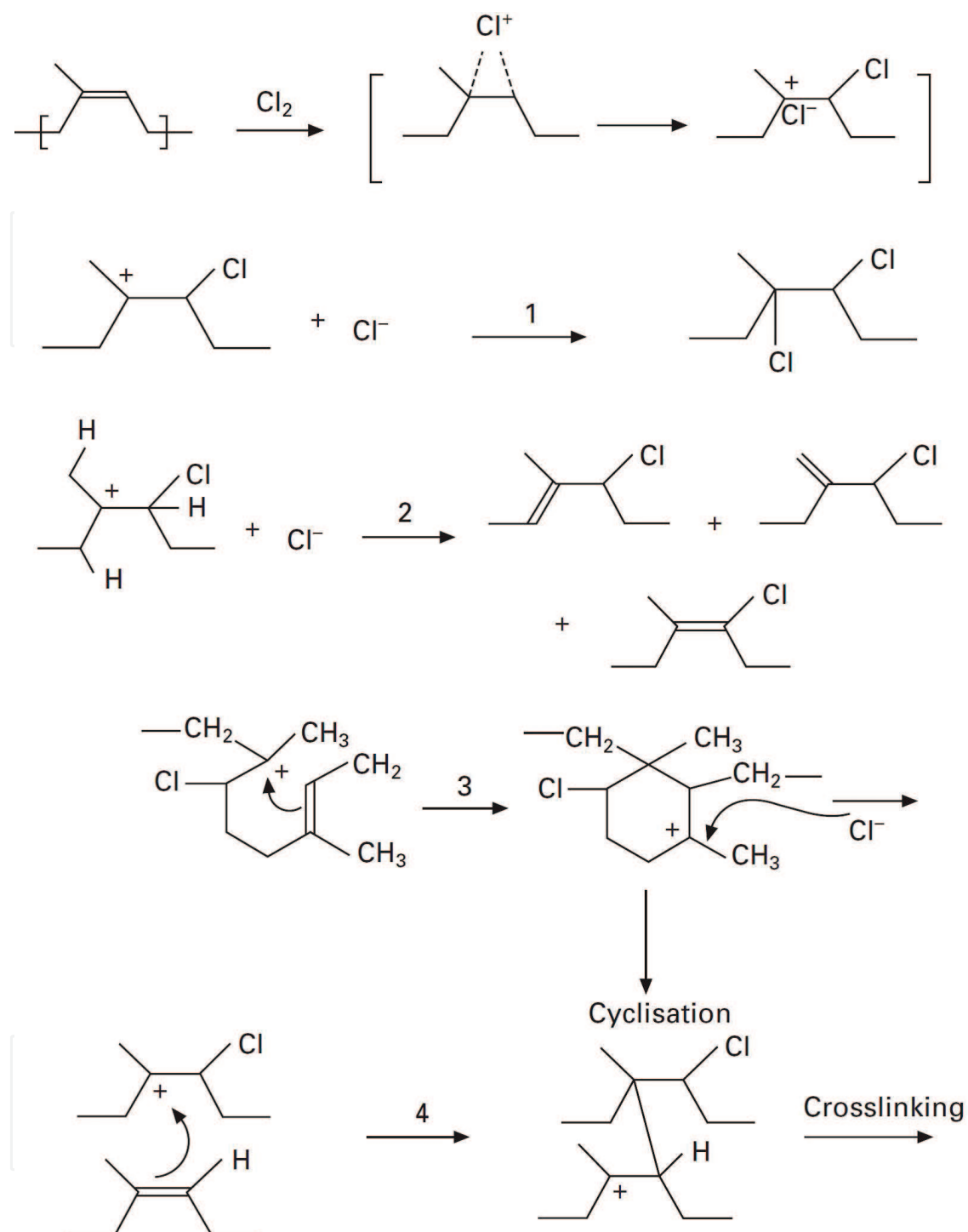


Figure 5. Chlorination of NR: (1) addition of chlorine, (2) substitution chlorination, (3) cyclization, (4) crosslinking [6].

ENR can be vulcanized with typical sulphur-vulcanizing systems, peroxide, amine compounds, aminosilanes and moisture [66, 77–80]. It was reported that in sulphur-vulcanized ENR, the residual acidity of ENR is neutralized with sodium carbonate, magnesium oxide, calcium oxide or calcium stearate [80]. The ENR-amine network formed via ring-opening reaction of *p*-phenylenediamine (catalysed by bisphenol A) was reported to be more rigid, less stretchable and with higher T_g compared to the conventional sulphur-vulcanized ENR

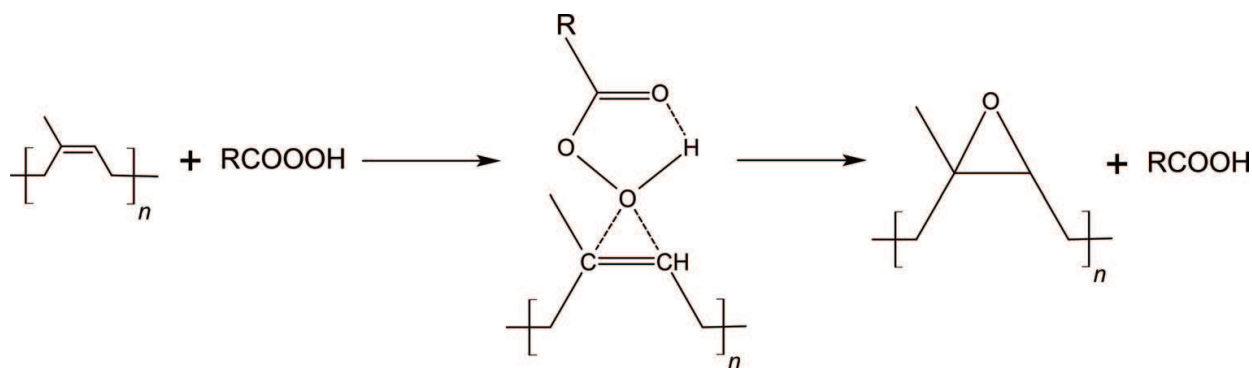


Figure 6. Epoxidation of NR with peracid [66].

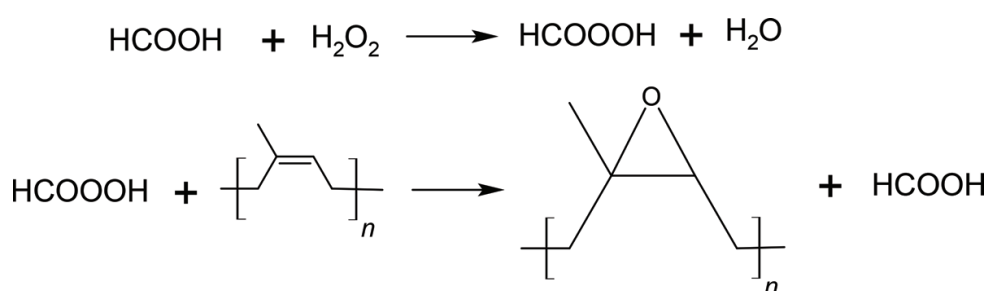


Figure 7. *In situ* epoxidation of NR [66].

at similar physical crosslink density [77, 78]. The curing of ENR with *p*-phenylenediamine is shown in **Figure 8** [77, 78].

Moisture-cured ENR was carried out by first procuring ENR with 3-aminopropyltriethoxysilane (APS) followed by hydrolysis and condensation. The ENR-APS moisture-cured vulcanizate reported lower tensile strength than the sulphur-cured vulcanizate but higher than the peroxide-cured vulcanizate. Partial strain-induced crystallization was demonstrated by moisture-cured vulcanizate [79]. The moisture-cured ENR-APS reaction is shown in **Figure 9** [79].

The precured ENR-APS was also reported to be suitable in preparing sol-gel silica-reinforced ENR vulcanizate via *in situ* sol-gel process using tetraethyl orthosilicate (TEOS) as the silica precursor [79, 81]. The *in situ* sol-gel process to produce sol-gel silica-filled ENR-APS vulcanizate is visualized in **Figure 10** [81].

Tensile properties of sol-gel silica-filled ENR-APS network and silica-filled ENR-sulphur are shown in **Figure 11** [81]. It is obvious that both the sol-gel silica-filled ENR-APS network is stiffer and stronger as compared to the ENR-sulphur system. By assuming that both particle size and dispersion of silica are not the dominant factors, sol-gel silica is a better reinforcing agent [81].

3.4. Epoxidized liquid natural rubber

Epoxidized liquid natural rubber (ELNR) can be produced by the degradation of ENR. This low-molecular-weight ENR can be produced via mechanical breakdown with two roll mill, photo-oxidation with UV radiation, or chemical degradation [82–87].

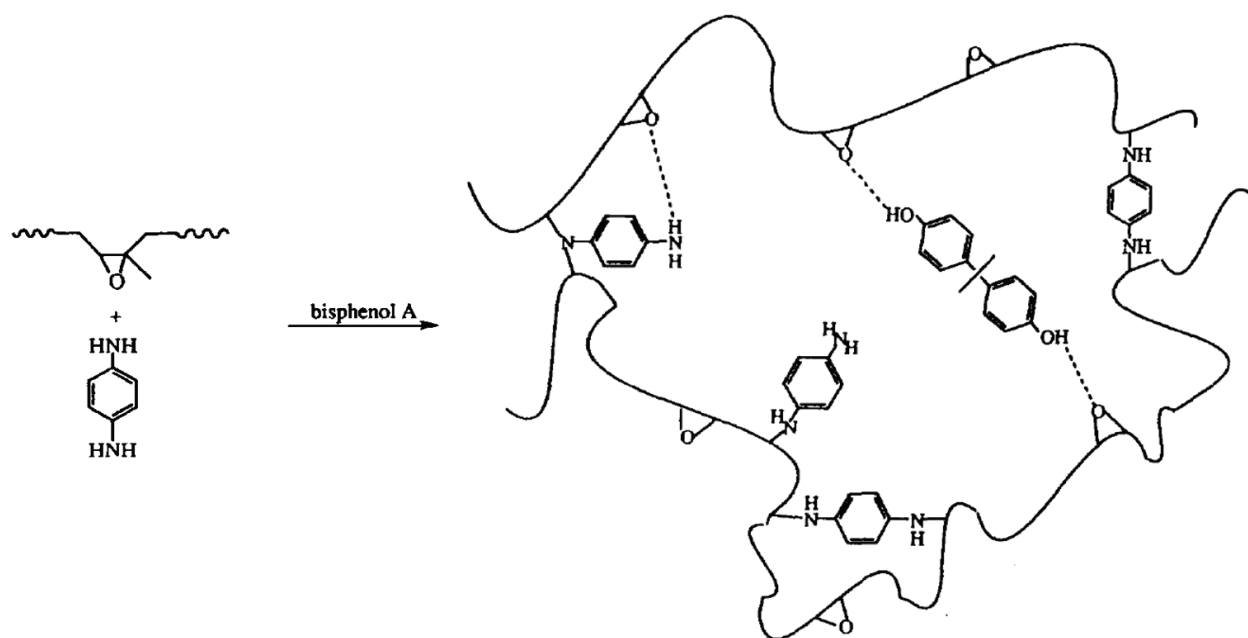


Figure 8. Proposed crosslinking reaction of ENR with *p*-phenylenediamine catalysed with bisphenol A [77, 78].

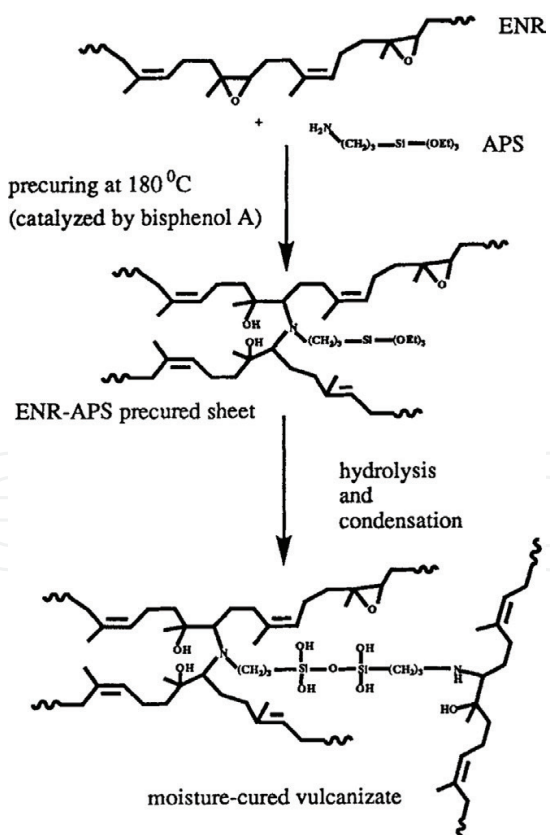


Figure 9. Reaction in obtaining ENR-APS moisture-cure vulcanizate [79].

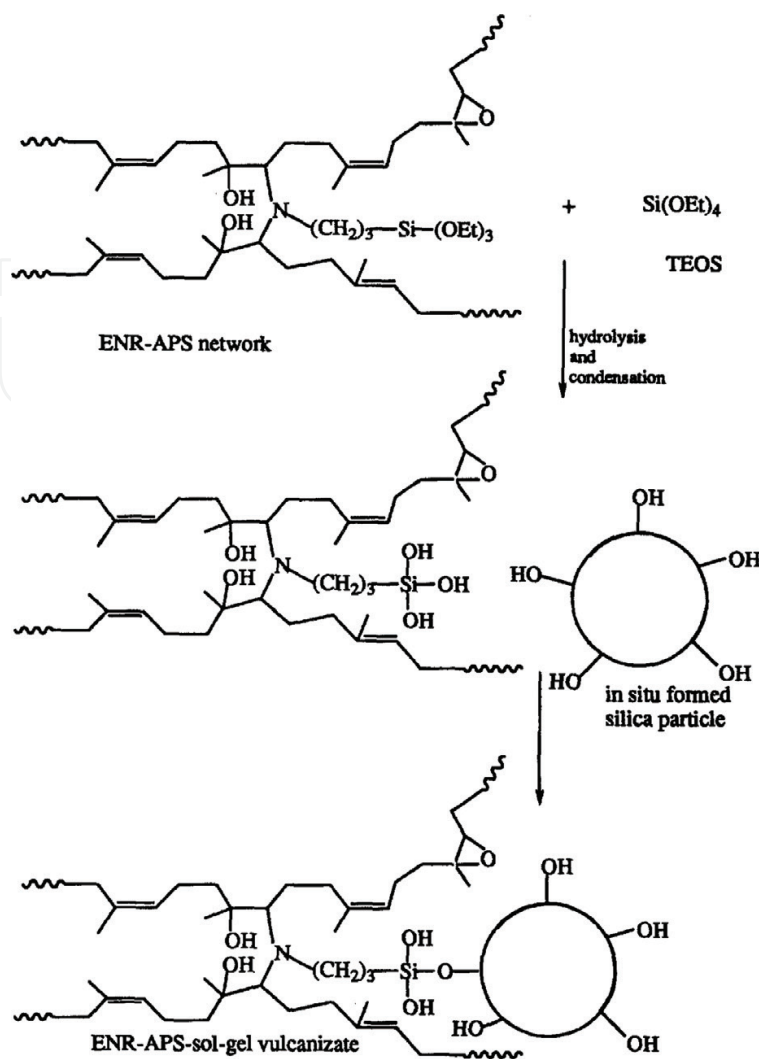


Figure 10. Sol-gel process of ENR-APS network with TEOS to produce silica-filled ENR-APS vulcanizate [81].

A study by Rooshenass et al. [87] observed the degradation of ENR 25 using UV radiation and chemical degradation initiated by potassium peroxodisulphate occurred predominately at the carbon-carbon double bonds. Degradation via mechanical breakdown occurred due to chain scission of the saturated carbon-carbon bonds. The photo-oxidation resulted in more carbonyl and hydroxyl groups on the backbone of the ELNR and fewer double bonds compared with mechanical breakdown and chemical degradation.

Phinyocheep et al. [83] obtained ELNR by reacting ENR in emulsion state using periodic acid. Derouet et al. [82] prepared ELNR by epoxidized LNR where LNR was obtained in the presence of phenyl hydrazine and oxygen and followed by epoxidation via performic acid formed in situ. Apart from the applications mentioned earlier, ELNR is also used as polymeric herbicide [84], compatibilizer in polystyrene/natural rubber blend [86], glass coating [88] and toughening agent [89–91].

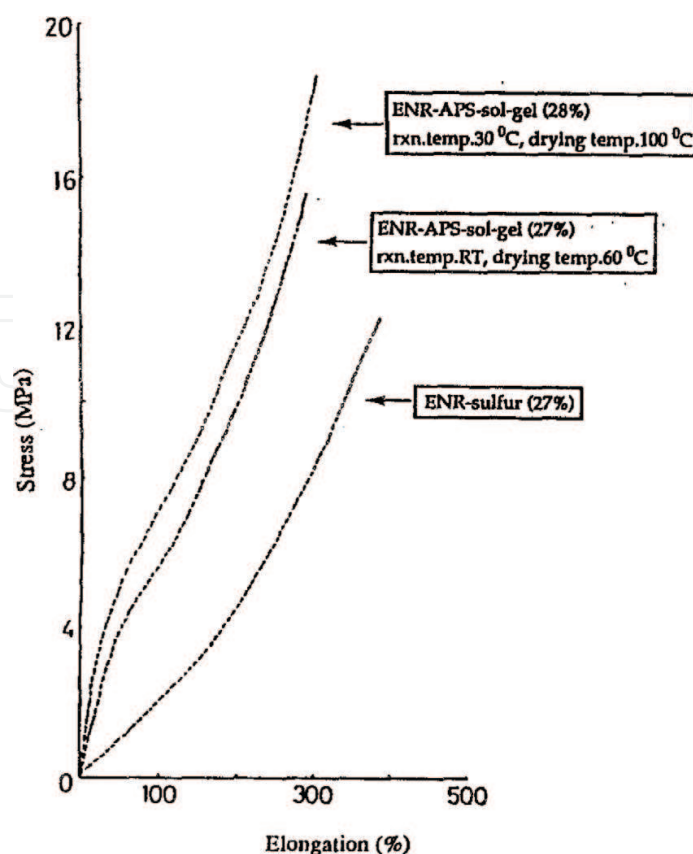


Figure 11. Tensile properties of ENR-APS network and ENR-sulphur network filled with different amounts of silica [81].

ELNR can undergo further reaction to yield hydroxylated LNR (LNR-OH) or hydroxyl-terminated ELNR (ELNR-OH). LNR-OH was obtained when ELNR produced via $\text{Na}_2\text{WO}_4/\text{CH}_3\text{COOH}/\text{H}_2\text{O}_2$ catalytic system in toluene underwent higher reaction time, reaction temperature and higher amount of catalyst [86]. Figure 12 shows the schematic diagram on the reaction of ELNR to LNR-OH. The LNR-OH is used as compatibilizer in polystyrene/natural rubber blend.

ELNR-OH was prepared from oxidative degradation of ELNR with cobalt (II) acetylacetonate in toluene, and the molecular weight depends on the reaction time and cobalt amount [85]. The lowest M_n , approximately 34,000 Da, was reported at 20-h reaction time when the cobalt amount was fixed at 1 wt%. Increasing the cobalt amount leads to greater reduction in M_n where the M_n reported was approximately 20,000 Da at 5-h reaction time and 3 wt% of cobalt. The ELNR-OH produced was used as binder for solid rocket propellant.

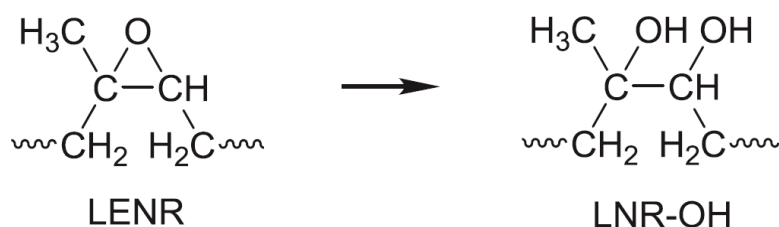


Figure 12. Schematic diagram representing reaction of ELNR to LNR-OH [86].

4. Modification by grafting

4.1. Maleated NR

Maleated NR can be prepared via NR solid phase by adding maleic anhydride using kneader, two roll mill or internal mixer [92–94]. Maleated NR can also be prepared in toluene solution [95]. NR was first masticated to reduce the NR molecular weight prior to dissolving in toluene (100 g NR in 1000 cm³ toluene). Then, maleic anhydride and benzoyl peroxide were added. The degree of conversion is in between 95 and 97% at 1–10 phr maleic anhydride at 80°C for 2 h and benzoyl peroxide at 3.0 phr. The degree of grafting is reported to be same as the degree of conversion as homopolymerization does not exist.

The proposed mechanism of preparing maleated NR initiated with benzoyl peroxide is shown in **Figure 13** [96]. Maleated NR can be used as compatibilizer in polyamide/NR blends [92, 93] and maleated NR/cassava starch blends [94].

4.2. Methyl methacrylate-grafted NR

Methyl methacrylate (MMA) and styrene are the two monomers which are most suitable for grafting with NR [13, 97]. Vinyl monomer-grafted NR can be carried out in solid phase, solution

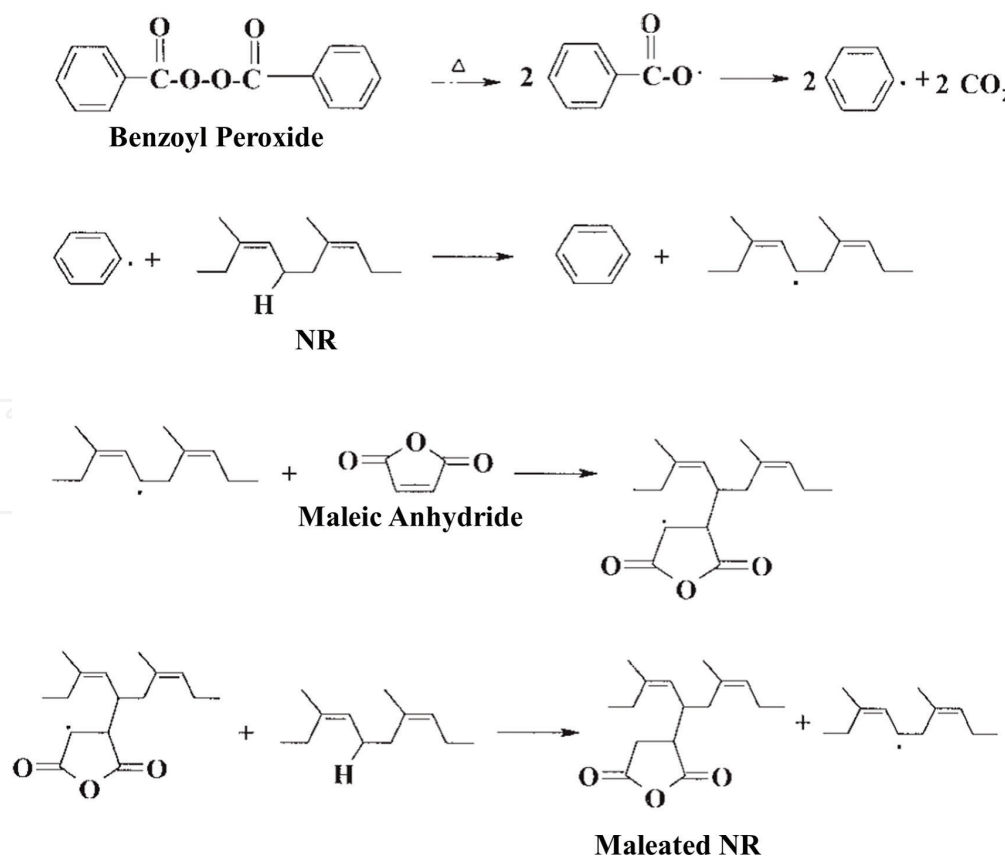


Figure 13. Proposed mechanism of benzoyl peroxide-initiated-maleated NR [96].

phase and emulsion phase. Emulsion phase graft copolymerization is preferable due to economical reason, and it is also more practical than the other phases. The radical-initiated grafting of vinyl monomers onto NR is shown in **Figure 14** [3].

MMA-grafted NR (MMA-NR) is available commercially under the trade name of Heveaplus MG 30 and Heveaplus MG 49 with 30 and 49% of MMA concentration, respectively. Heveaplus MG has the degree of grafting ranging in 60–80%. Heveaplus MG is harder, stiffer, and has higher abrasion resistance and electrical resistance as compared to the unmodified NR. Heveaplus MG is used as an impact modifier as well as a reinforcing agent. The solution or emulsion form of Heveaplus MG is used as an adhesive or a bonding agent between rubber and PVC, leather, textiles and metal [13, 98].

Several literatures have reported on the grafting of MMA onto NR using different initiator systems [99–111]. These studies show that at NR/MMA ratio (w/w), the range is between 50/50 and 80/20 with grafting efficiency between 70 and 95% and degree of conversion of the monomer up to about 96% depending on the polymerization-processing parameters.

A comparative study of *in situ* polymerization of MMA in HANR latex and DPNR latex observed that the latter is more stable and efficient in terms of grafting efficiency. It was

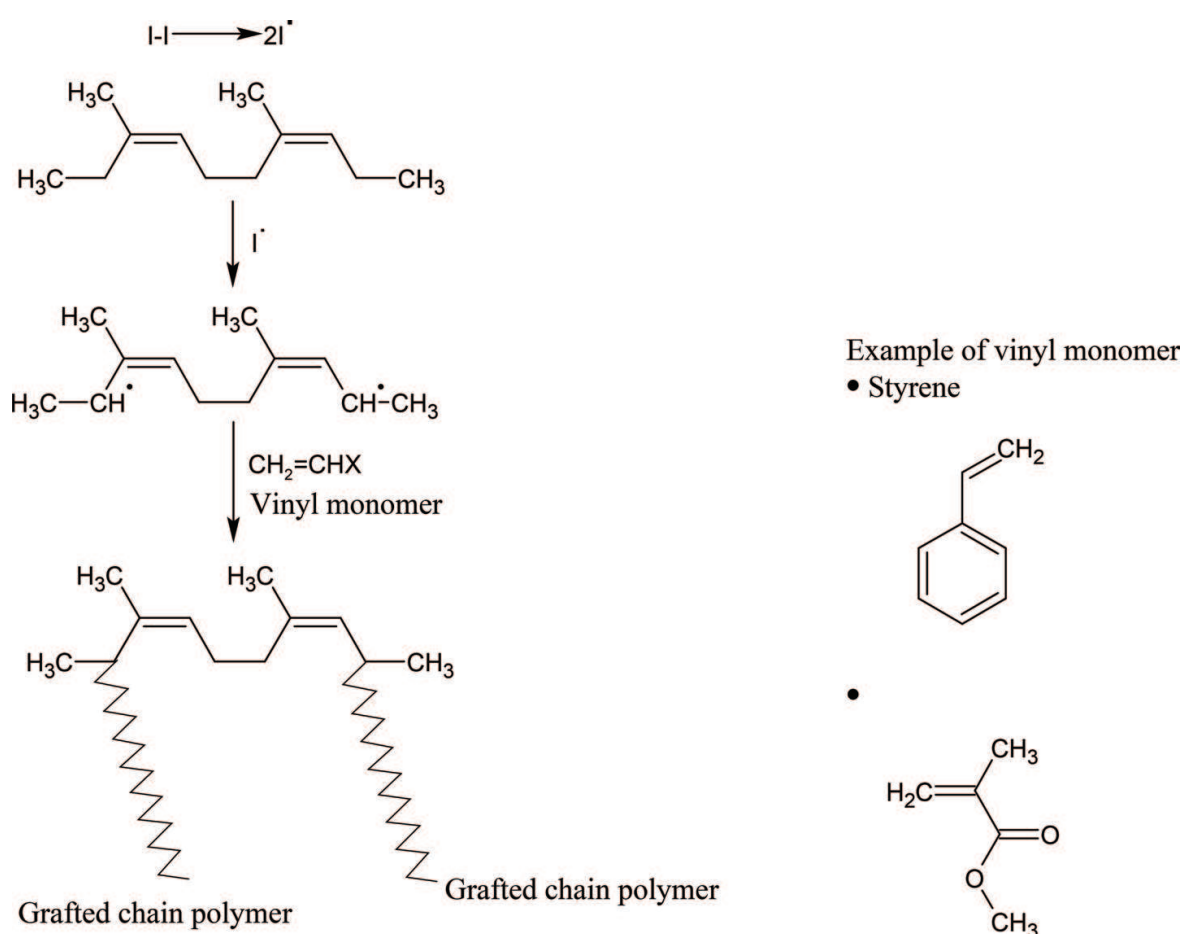


Figure 14. Schematic diagram on grafting of NR with vinyl monomer via radical polymerization [3].

hypothesized that both the radical initiator and MMA diffused better and faster into the rubber particles in using DPNR latex [26]. Further investigation was carried out by Jessy and Hashim [112] on *in situ* polymerization of MMA in DPNR latex via seeded emulsion polymerization. The rubber:water ratio and initiator:monomer ratio were fixed at 0.2109 and 0.05, respectively, with monomer:rubber of 5:95 weight ratio with the reaction temperature of 65°C and the stirring speed of 340 rpm. The grafted DPNR, that is, MNR, had degree of conversion and degree of grafting of 99 and 96%, respectively.

MNR can be used as an impact modifier for poly(methyl methacrylate) (PMMA) [113]. In this study, MNRs (at 2.5, 5.0, 7.5 and 10.0% by weight) were blended with PMMA and compared with PMMA/poly(butyl acrylate) (PMMA/PBA):80/20 blend. The performance of PMMA/PBA:80/20 blend was investigated by Neliappan et al. [114]. **Figure 15** summarizes the fracture toughness, K_{IC} of PMMA, PMMA/MNR blend [113] and PMMA/PBA blend [114]. It is obvious that the presence of both MNR and PBA results in higher K_{IC} . The energy required to fracture the glassy and rubber phases is due to either chain stretching or chain scission or chain pull-out or any of these combinations [115]. It is obvious that that presence of either MNR or PBA results in higher K_{IC} indicating that higher energy is required to fracture both glassy and rubber phases. It is worth noting that with only 10 wt% of MNR content, the K_{IC} is comparable with PMMA toughened with 20 wt% PBA.

4.3. Styrene-grafted NR

Styrene-grafted NR (SNR) has been reported by a comparative study on *in situ* polymerization of styrene in HANR latex and DPNR latex [23]. **Table 3** shows the formulations, reaction

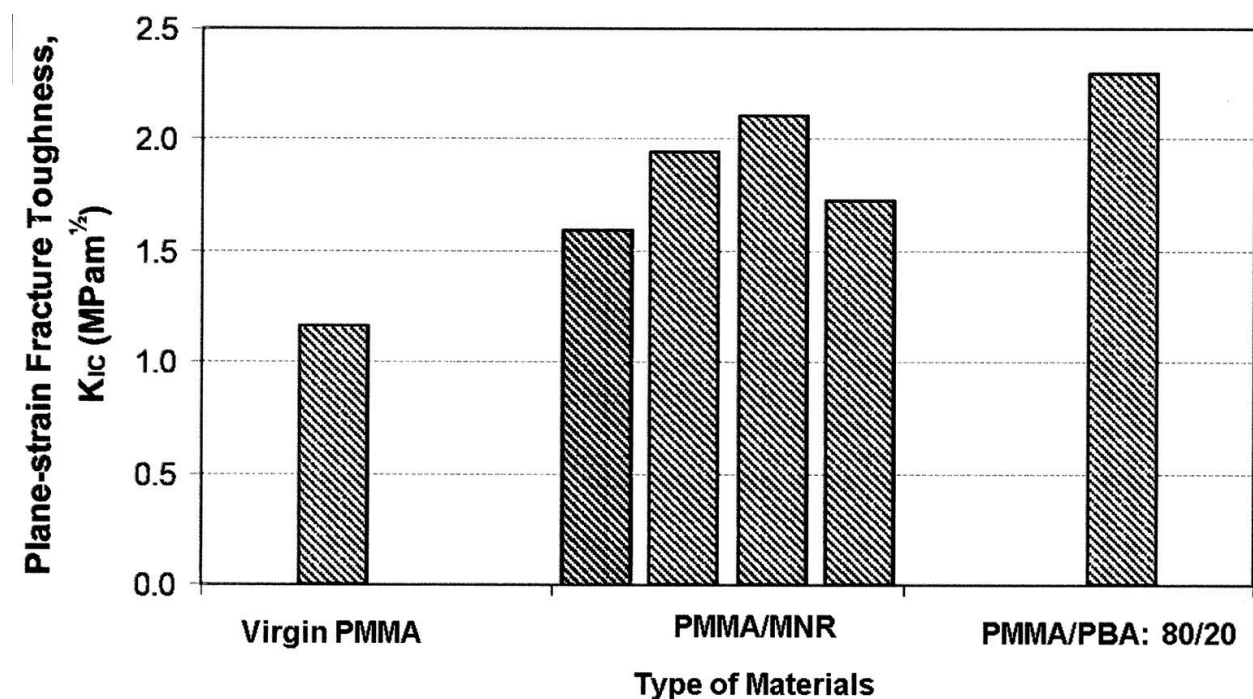


Figure 15. Fracture toughness of virgin PMMA, PMMA/MNR blends and PMMA/PBA: 80/20 blend [113].

	HANR latex			DPNR latex		
Formulation	1	2	3	4	5	6
HANR latex (g)	100.0	100.0	100.0	–	–	–
DPNR latex (g)	–	–	–	100.0	100.0	100.0
Styrene (g)	20.0	20.0	20.0	19.7	19.7	19.7
Initiator (g)	0.40	0.40	0.40	0.39	0.39	0.39
Surfactant (g)	0.00	0.24	0.36	0.00	0.23	0.35
Water (g)	80.0	80.0	80.0	77.0	77.0	77.0
Styrene:rubber ratio	25:75	25:75	25:75	25:75	25:75	25:75
Surfactant concentration (g/water)	0.0	2.0	3.0	0.0	2.0	3.0
Degree of conversion (%)	*	66.7	65.8	97.1	89.8	86.7
Degree of grafting (%)	–	24.4	–	79.1	–	–

*Sample coagulated after 2.5 h.

Table 3. Formulations, reaction conditions and the degree of conversion of polymerization of styrene in HANR latex and DPNR latex [23].

conditions and the respective formulation of the study at 60°C for 10 h. Both the initiator, that is, ammonium peroxy disulphate concentration and TSC were fixed at 2.0% of styrene weight and 40%, respectively. The TSC is the total weight of both styrene and dry rubber.

From the results, it is obvious that the presence of protein/lipid layer in HANR latex rubber particles results in lower conversion. This is because of poorer diffusion of monomer and initiator into the rubber particles. Non-rubber substances such as protein and lipid were found to inhibit free radical polymerization [116]. Consistently, the degree of grafting (via sol-gel method) in DPNR is higher than in HANR as shown by Formulations 4 and 2, respectively.

SNR has a potential application as an impact modifier for PS [117]. As impact modifier for PS, 5–20 wt% of SNR results in 141–1050% increment in impact strength in relation to the pure PS. The presence of 15 wt% of SNR in PS was reported to give a 25% higher impact strength compared to a commercial high-impact polystyrene (HIPS).

SNR can also be used as compatibilizer in polypropylene/natural rubber (PP/NR) blends and PP/PS blend [118–120] as well as a modifier in PP-based binary blend [121]. As a high-molecular-weight compatibilizer in PP/NR blend, 10 wt% of SNR was reported to increase

the tensile strength and Young's modulus by 28 and 24%, respectively. Some improvement in elongation at break and flexural properties was also observed.

The effectiveness of SNR as compatibilizer, in comparison with commercial compatibilizers, in PP/PS blend is summarized in **Table 4**. It is obvious that SNR is a better choice compared to the others [120].

To highlight the effect of SNR as a high-molecular-weight modifier, PP/SNR 70/30 blend and PP/NR 70/30 blend were investigated where both blends were dynamically vulcanized [121]. The PP/SNR blend was observed to be stiffer and stronger with higher tensile strength, higher modulus and higher impact strength but with comparable elongation at break as shown in **Table 5** [121]. The tensile properties of the PP/SNR blend are better than those of polyolefin/NR blends [121]. Compared to Santoprene®, a commercial product, the properties are with the range although the modulus is significantly higher indicating a stiffer material.

Compatibilizers	Tensile strength (MPa)		Elongation at break (%)		Impact strength (kJ/m ²)	
	0 wt%	7.5 wt%	0 wt%	7.5 wt%	0 wt%	7.5 wt%
SNR	20.3	21.9	7.9	177.5	198.4	437
^a SEBS		16.0		7.88		304
^b Surlyn		20.3		4.24		240
^c EVA		13.17		4.95		250
^d 4 ssa,ssh		17.61		3.06		198

^aSEBS: styrene-ethylene-butylene-styrene block copolymer.

^bSurlyn: ionomer from ethylene acid copolymers.

^cEVA: ethylene-vinyl acetate copolymer.

^d4 ssa,ssh: 4-Styrenesulfonic acid sodium salt hydrate.

Table 4. Mechanical properties of PP/PS blends using various compatibilizers [120].

Properties	PP/SNR: 70/30 blend	PP/NR: 70/30 blend	*Polyolefin/NR blend	**Santoprene®
Tensile strength (MPa)	25.3	21.7	6–20	4.4–27.6
Elongation at break (%)	341.9	362.4	200	330–600
Modulus at 100% elongation (MPa)	17.0	12.7	–	2.1–10
Impact strength (J/ m ²)	150.3	140.8	–	–

*[122].

**[123].

Table 5. Some properties of PP/SNR: 70/30 blend, PP/NR: 70/30 blend, polyolefin/NR blends and Santoprene® [121–123].

4.4. Styrene/methyl methacrylate-grafted NR

Grafting of two monomers could also be carried out in DPNR latex. It should be noted that, from chemical structure point of view, both HANR and DPNR are still NR, except that the latter contains much less protein content and the rubber particles are stabilized by adding surfactant as mentioned earlier. Styrene/methyl methacrylate-grafted NR (SMNR) can be prepared using DPNR latex via seeded emulsion polymerization using ammonium peroxydisulphate ($\text{N}_2\text{H}_8\text{O}_8\text{S}_2$) as an initiator resulting in 97.4% degree of conversion [124]. The styrene:MMA:rubber ratio studied was 10:10:80 by weight. The amount of styrene in SMNR was reported to be higher due to higher styrene reactivity [124]. Man et al. [125] later varied the concentration of both styrene and MMA concentration between 10 and 30 wt% fixing the styrene:MMA ratio at 1:1 by weight. It was observed that the highest degree of grafting is at 20 wt% total monomer concentration as shown in **Figure 16**. At 10 wt% total monomer concentration, no grafting was observed indicating that only copolymerization took place. At 20 wt% total monomer concentration, the degree of grafting observed was at approximately 50%. At 30 wt% total monomer concentration, the degree of grafting reduced to 30% due to copolymerization between the two monomers is more pronounced. This was evidenced from the ^1H NMR results where similar styrene and MMA content was detected in the grafted rubber.

Based on the thermogravimetric analysis (TGA), the decomposition temperature of SMANR at different monomer concentrations was consistently higher than the DPNR. Both the SMNR gum and N330-filled SMNR vulcanizates are stiffer and less elastic compared to the DPNR gum and filled vulcanizates, respectively [125].

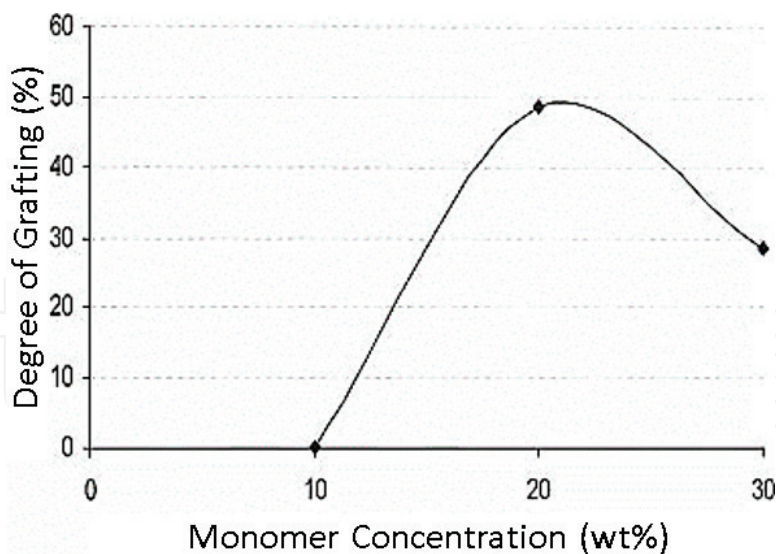


Figure 16. Degree of grafting of SMNR at different total monomer concentration where the styrene-MMA ratio is fixed at 1:1 [125].

5. Conclusions

Compared to NR, NR derivatives exhibit different physical, mechanical and chemical properties; for example, the oxirane groups in ENR enable novel crosslinking system such as

ENR-APS-crosslinking system. The *in situ* sol-gel silica-filled ENR-APS network system was reported to have better reinforcing efficiency giving higher mechanical properties. The degree of grafting of vinyl monomers onto NR backbones, carried out via emulsion polymerization in DPNR latex, was found to be more efficient than in HANR latex; the degree of grafting for styrene-grafted NR, when carried out in DPNR latex, was observed to be four times higher than in HANR latex. The vinyl monomer-grafted DPNR such as SNR was found to be stiffer and stronger and can be used as impact modifier for PS and as compatibilizer for PP/PS and PP/NR blends.

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