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Molecular Structure of Natural Rubber and Its Characteristics Based on Recent Evidence

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1. Introduction

Natural rubber (NR) latex collected from the *Hevea* trees exists as a colloidal suspension (Verhaar, 1959). The amount of latex obtained on each tapping is about 300 mL. The tapping is usually done once every 2–3 days for 9 months each year. Usually, the collected latex is treated with formic acid to coagulate the suspended rubber particles within the latex (Gazeley et al., 1988). After having been pressed between rollers to consolidate the rubber into 0.6-micrometre in thickness slabs or thin crepe sheets, the rubber is air-dried or smoke-dried for shipment. These rubbers are known as air-dried sheet (ADS) and ribbed smoked sheet (RSS), respectively. The treatment of latex with $NaHSO_3$ is used to produce rubber of pale color, termed pale crepe. The other forms of rubber as block rubber are known as Standard Malaysian Rubber (SMR) or Standard Thai Rubber (STR), which are mainly graded by dirt content.

Fresh latex from the *Hevea* tree contains 30–35% rubber. After collection, the latex is stabilized with NH_3 and transported from the plantation to a factory where it undergoes continuous centrifugation to produce a concentrated NR latex containing ~60% rubber. For long-term preservation of concentrated latex, the NH_3 content is usually raised to 0.6–0.7%; this is referred to as high-ammonia preserved concentrated latex. Low-ammonia preserved concentrated latex contains only 0.2–0.3% NH_3 plus tetramethyl thiuram disulfide (TMTD), as a bactericide.

Rubber particles in latex show a wide range of diameter, from 0.01 to 5 µm, with the majority being 0.1–2 µm diameter (Pendle & Swinyard, 1991). The latex is composed of the rubber phase, Frey–Wyssling particles, serum, and the bottom fraction (Archer et al., 1969; Jacob et al., 1993). Protein has been considered to be an essential component of NR for its characteristic properties. Recently, several proteins in NR were found to cause type I allergic responses that led to life-threatening anaphylactic reactions. In 1991, the FDA stipulated that rubber products made from NR latex (e.g., gloves and condoms) should be treated to remove extractable proteins. Deproteinization of latex was carried out by using a proteolytic enzyme in the presence of surfactants to reduce the extractable proteins to less than their detection limit (Sakaki, et al., 1996; Nakade, et al., 1997). It is remarkable that the physical properties of deproteinized NR (DPNR) are almost equivalent to those of ordinary natural rubber; moreover, the dynamic properties such as resilience and rebound are improved as a

result of increasing the content of rubber hydrocarbon after deproteinization. These findings support the idea that the protein component of NR is not essential to produce its outstanding and characteristic properties.

Commercially available solid NR contains neutral lipids (2.4%), glycolipids and phospholipids (1.0%), proteins (2.2%), carbohydrates (0.4%), ash (0.2%), and other compounds (0.1%) (Sentheshanmuganathan, 1975; Nair, 1987). Free fatty acids in solid rubber are composed of mainly long-chain saturated and unsaturated fatty acids such as stearic, oleic, and linoleic acids (Crafts et al., 1990; Arnold & Evans, 1991). Recently, it was presumed that rubber chains also contain long-chain fatty acids, presumably occurring as phospholipids covalently linked to the chain-end (Eng et al., 1994a). While saturated fatty acids induce the crystallization of rubber chain, unsaturated fatty acids – which are present in NR as a mixture – act as a plasticizer of rubber and accelerate synergistically with saturated fatty acids on the crystallization of rubber chains (Kawahara et al., 1996; Nishiyama et al., 1996). These linked and mixed fatty acids were presumed to bring about outstanding mechanical properties through rapid crystallization of natural rubber. Highly purified NR can be obtained by removing proteins, blended fatty acids, and linked fatty acids (lipids). This can be achieved by the deproteinization of the latex, acetone extraction of the resultant deproteinized solid rubber, and transesterification of acetone-extracted rubber with sodium methoxide in toluene solution (Eng et al., 1994a; Tangpakdee & Tanaka, 1997a). It is remarkable that transesterified NR showed stress-strain properties of unvulcanized rubber (termed 'green strength') similar to synthetic *cis*-1,4-polyisoprene (Figure 1).
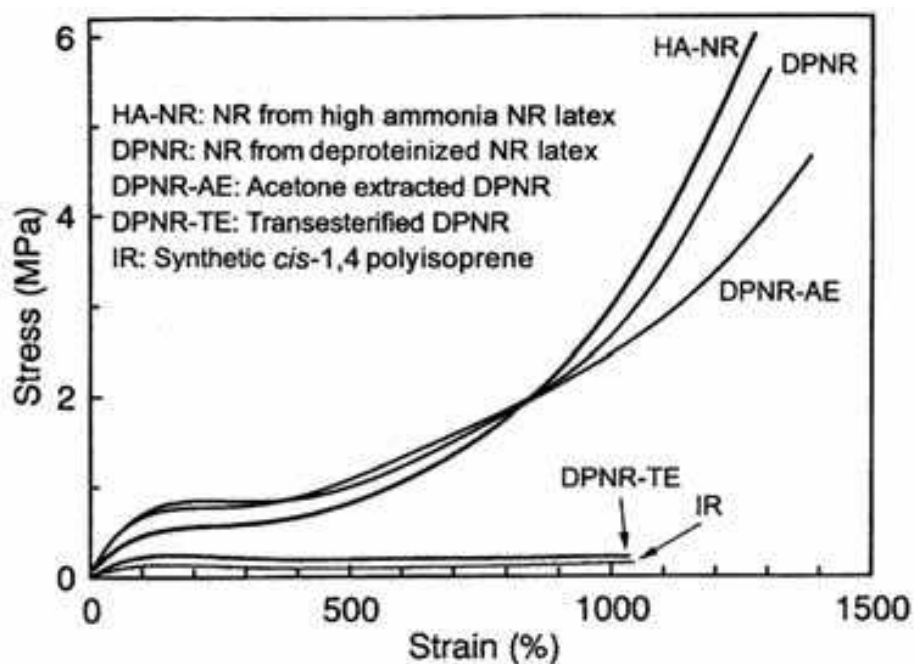

Fig. 1. Green strength of purified natural rubbers and synthetic *cis*-polyisoprene

The effect of linked and blended fatty acids in NR was confirmed by the preparation of a model *cis*-1,4-polyisoprene grafted with small amounts of stearic acid at the 3,4 unit after introducing hydroxyl group selectively at 3,4 units by a hydroboration reaction. The C_{18} grafted *cis*-1,4-polyisoprene mixed with linoleic acid showed a crystallizability similar to that of NR (Kawahara et al., 2000). These findings suggest that the structure of chain-end groups in NR confers major characteristic properties of natural rubber.

2. Molecular structure of both chain-ends of natural rubber

2.1 Initiating terminal of the rubber molecule

^{13}C-NMR spectroscopy of low-molecular weight natural rubber, obtained by fractionation, shows the signals corresponding to the *trans* methyl and methylene carbons, suggesting the presence of *trans*-isoprene units in the structure of NR (Figure 2) as similar to those of rubber from goldenrod leaves (Tanaka et al., 1983). However, the signals due to a dimethylallyl group are not detected in the case of *Hevea* rubber. The absence of *trans*-isoprene units in the *cis-trans* sequence suggests that the *trans*-isoprene units are in the *trans-trans* linkage, but not derived from isomerization of *cis*-isoprene units (Eng et al., 1994a).
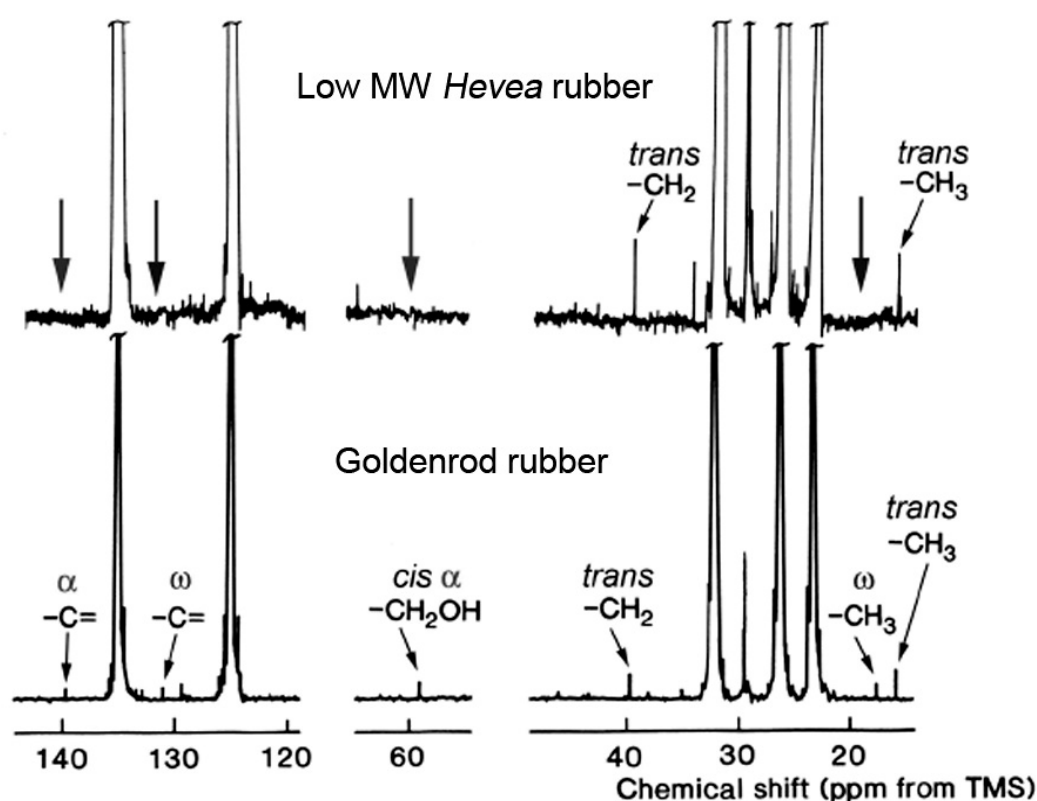

Fig. 2. ^{13}C-NMR spectra of low-molecular weight fraction of *Hevea* rubber and rubber from Goldenrod.

As shown in ^{1}H-NMR spectra (Figure 3), the *trans*-isoprene units in NR show the methyl proton signals corresponding to two-*trans*-polyprenol (Eng et al., 1994b). The absence of a dimethylallyl group in NR suggests that the initiating species for rubber formation in *Hevea* is a derivative of *trans-trans*-farnesyl diphosphate (FDP) modified at the dimethylallyl group or ordinary *trans-trans*-FDP, which is selectively modified after polymerization (Tanaka et al., 1996; Tanaka et al., 1997; Tanaka & Tangpakdee, 1997). The former assumption is consistent with the finding that the methyl proton of the *trans*-isoprene unit in the ω'-*trans-trans* group shows a similar chemical shift as that of the dimethylallyl-*trans-trans* arrangement (Eng et al., 1994b; Tanaka et al., 1996). This suggests that the ω'-group has a structure similar to that of the dimethylallyl group, and shows a similar magnetic shielding effect on the subsequent *trans*-isoprene unit.
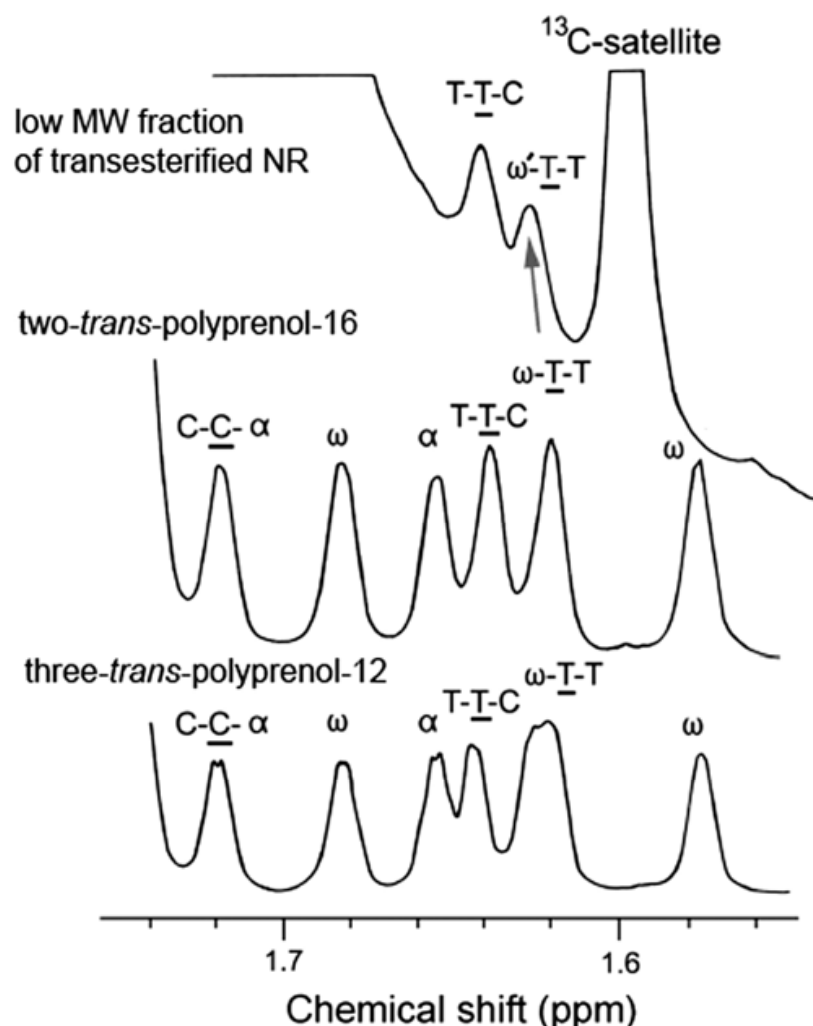
Fig. 3. ¹H-NMR spectra of low-molecular weight fractions of transesterified natural rubber, two-*trans*-polyprenol-16 and three-*trans*-polyprenol-12

The dimethylallyl group is not detected even in the low-molecular weight rubber isolated from seedlings (Tangpakdee et al., 1996), or even long-chain polyprenols in *Hevea* (Tangpakdee & Tanaka, 1998a). However, it is difficult to ignore the possibility that FDP directly initiates polymerization, because it was reported that FDP stimulates *in vitro* rubber formation upon incubation with isopentenyl diphosphate (IDP) and washed rubber particles (Archer & Audley, 1987; Audley & Archer, 1988; Madhavan et al., 1989; Cornish & Backhaus, 1990). Under the same conditions, [1-³H]neryl diphosphate was incorporated into rubber molecules (Audley & Archer, 1988). Recently, a high yield of rubber formation was reported for *in vitro* rubber synthesis by incubation of the bottom fraction of freshly tapped latex with IDP (Tangpakdee & Tanaka, 1997a). The resulting rubber showed no dimethylallyl group, whereas the rubber obtained in the presence of IDP and FDP clearly showed the dimethylallyl group and *trans*-isoprene units as shown in Figure 4 (Tangpakdee et al., 1997). This suggests that FDP will be the initiating species of rubber formation in *Hevea* tree. The fact that newly formed rubber contains no dimethylallyl group is additional evidence supporting the presence of ω'-*trans-trans* group at the initiating terminal arising from unidentified initiating species.
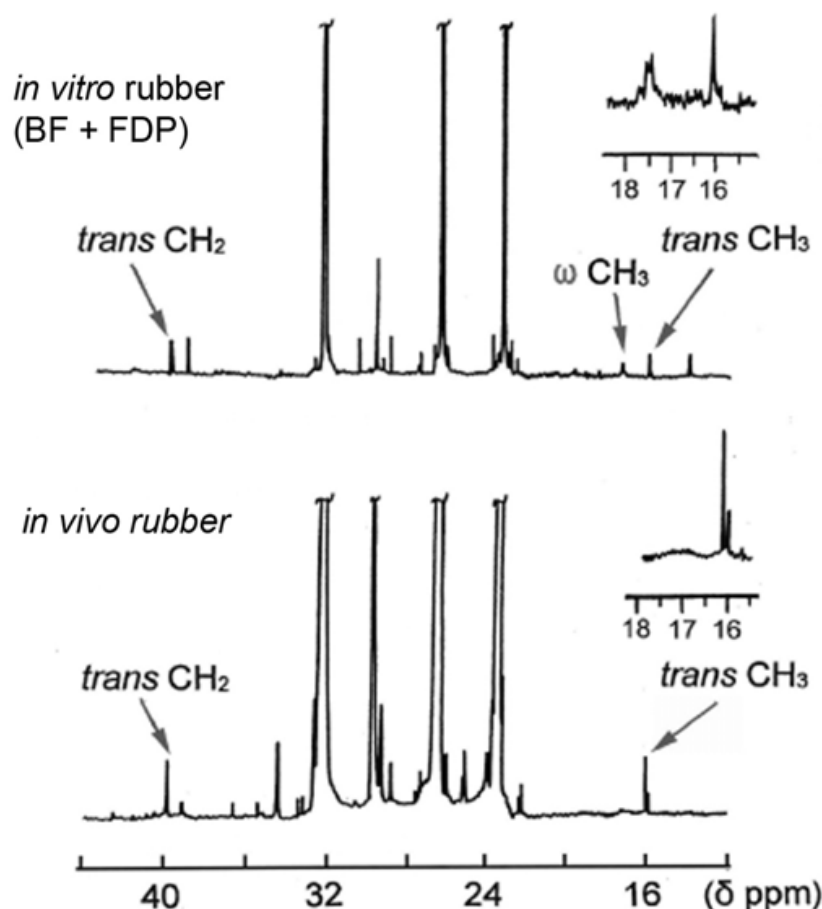
Fig. 4. ^{13}C-NMR spectra of *in vitro* NR formed on incubation of fresh bottom fraction (BF) and FDP (above) and *in vivo* rubber (below).

At the present, the ω–terminal group of low molecular weight and polyprenol fractions from NR was analyzed using high-resolution ^{13}C- and ^{1}H-NMR and 2D-COSY techniques (Mekkriengkrai, 2005). Very recently, the presence of the dimethylallyl group and two *trans*-isoprene units at the ω-terminal was observed in polyprenol from *Hevea* shootings and fresh bottom fraction as well as the lowest molecular weight fraction of washed rubber particles (WRP) obtained by washing the cream fraction from fresh latex with surfactant. This finding suggests that the initiating species of rubber biosynthesis is *trans, trans*-FDP as in the case of two-*trans* polyprenol. This ω–terminal was not detected in the high molecular weight fractions of WRP and low molecular weight fractions of the ordinary NR and DPNR, suggesting the occurrence of a modification at the dimethylallyl residue. Thus, it can be concluded that the structure of dimethylallyl group at the ω–terminal of the ordinary NR is modified by some enzymatic or chemical reactions. Figure 5 shows the presumed mechanism of ruber formation mediated by an enzyme based on hypothesis of Ogural *et al*. (1997). It has been postulated that the methyl group in dimethylallyl diphosphate is connected to a phenylalanine of the FQ (phenylalanine-glutamine) motif which is found not only in all prenyl diphosphate synthases but also in tRNA-dimethylallyl transferase, to hold this molecule in the direction necessary for a condensation reaction with IDP. This suggests that some reactions can proceed to modify the dimethylallyl group according to the removal of the ω–terminal from the pocket of the enzyme, which may result in the formation of various dimethylallyl group derivatives.
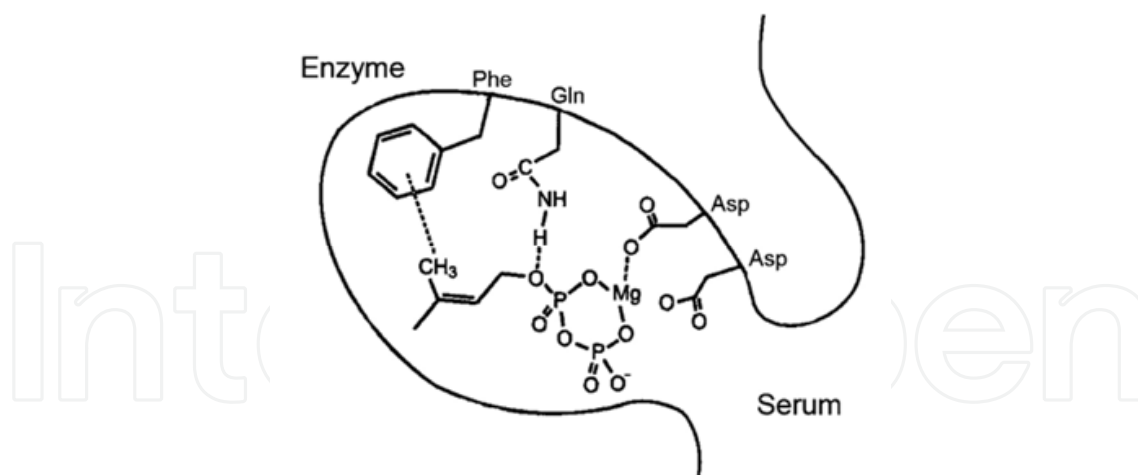
Fig. 5. Presumed role of enzyme on initiation and chain elongation steps

2.2 Terminating chain-end of rubber molecule

The primary alcohol or their fatty acid ester groups is a popular structure of the α-terminal group in many naturally occurring polyisoprenes such as the rubbers from *Lactarius* mushrooms and leaves of goldenrod and sunflower, even though rubber as well as polyprenols were presumed to be synthesized by the addition of IDP. This is owing to the fact that diphosphate group can be hydrolyzed to hydroxyl group or transesterified to fatty acid ester. However, signals corresponding to these structures at the α-terminal are not detected in the ^{13}C- and ^{1}H-NMR spectra of natural rubber. On the other hand, long-chain fatty acid ester groups are clearly observed, even after purification by deproteinization and acetone extraction (Eng et al., 1994a) (Figure **6**).
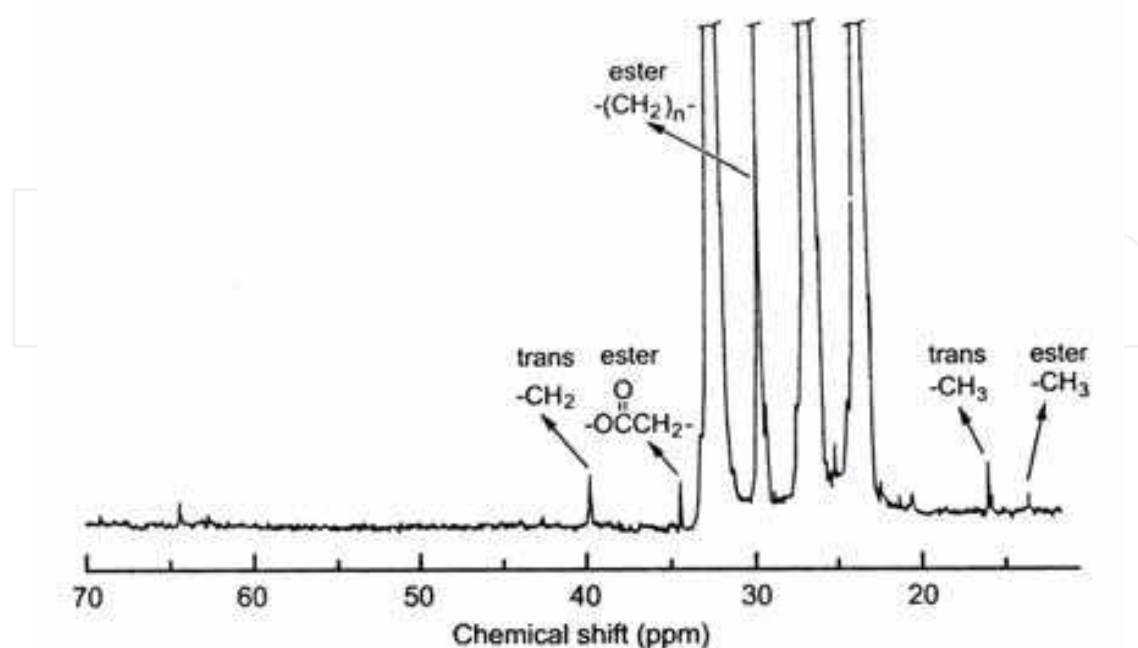

Fig. 6. ^{13}C-NMR spectrum (aliphatic region) of low-molecular weight fractions from deproteinized natural rubber

The long-chain fatty acid ester group was found to be about two moles per one rubber molecule, by ^{13}C-NMR and FTIR analysis (Eng et al., 1994a; Tangpakdee & Tanaka, 1997a; Tanaka, Y. et al., 1997). In addition, the ^{1}H-NMR spectrum of low-molecular weight rubber from 1-month-old *Hevea* seedlings shows the signals corresponding to $-CH_2OP$ and glyceride (Tangpakdee & Tanaka, 1997a). These groups can be removed by transesterification or saponification. These findings suggest that most of the chain-ends of NR consist of a phosphate group belonging long-chain fatty acid ester (Tangpakdee & Tanaka, 1997a; Eng et al., 1994a), which corresponds to phospholipids as follows (Figure 7):
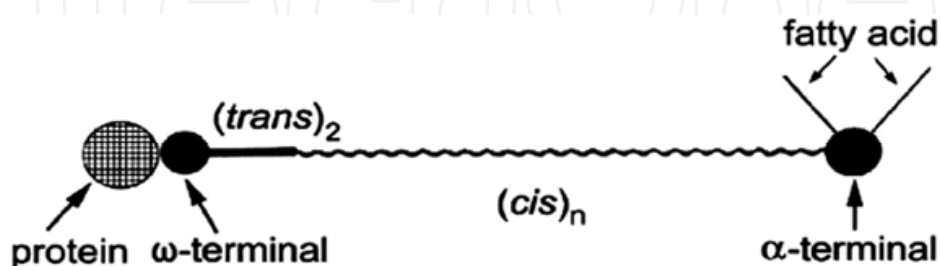

Fig. 7. Presumed structure of NR linear chain (Tangpakdee & Tanaka, 1997a)

The new information of structure of α-terminal group in NR was analyzed recently by selective decomposition of the branch-points followed by structural characterization by using high resolution ^{1}H-, ^{13}C- and ^{31}P-NMR, FTIR, and GPC techniques as well as diluted solution viscometry for highly purified NR (Tarachiwin et al., 2005a, 2005b). The selective decomposition of branch-points was carried out by using lipase, phosphatase, and phospholipases A_2, B, C, and D. The ^{1}H-NMR spectrum of acetone-extracted deproteinized NR (AE-DPNR) at 750 MHz (Figure 8) shows not only the signals derived from phospholipids, but also two small triplet signals due to mono- and diphosphate groups (Tarachiwin et al., 2005a). Figure 9 shows the ^{1}H-NMR spectra of AE-DPNR, lipase-treated AE-DPNR and phosphatase-treated DPNR. It is remarkable that these signals did not disappear even after lipase, phosphatase and phospholipase treatments of AE-DPNR. Lipase can decompose fatty acid ester of acylglycerol including phospholipids at C1 and C3 positions as shown in Scheme 1, while phosphatase decomposes only monophosphate ester linkage. The presence of mono- and diphosphate signals after lipase and phosphatase treatments clearly indicates that these phosphate groups are directly linked to rubber molecule.
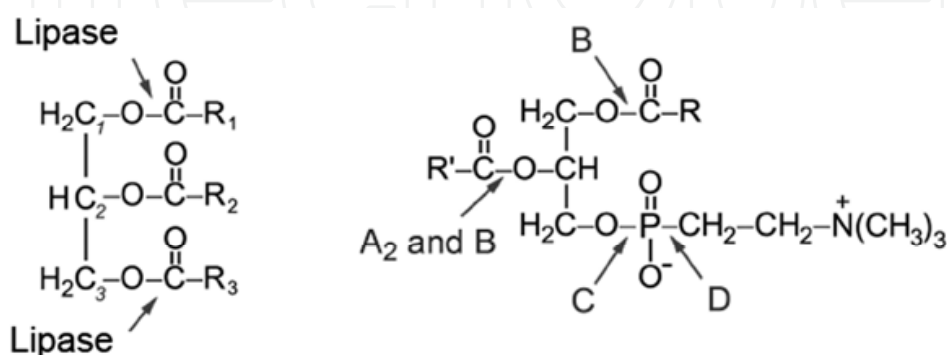
Scheme 1. Decomposition positions of lipase on the acylglycerol (left) and phospholipase on L-α-phosphatidylcholine (right)
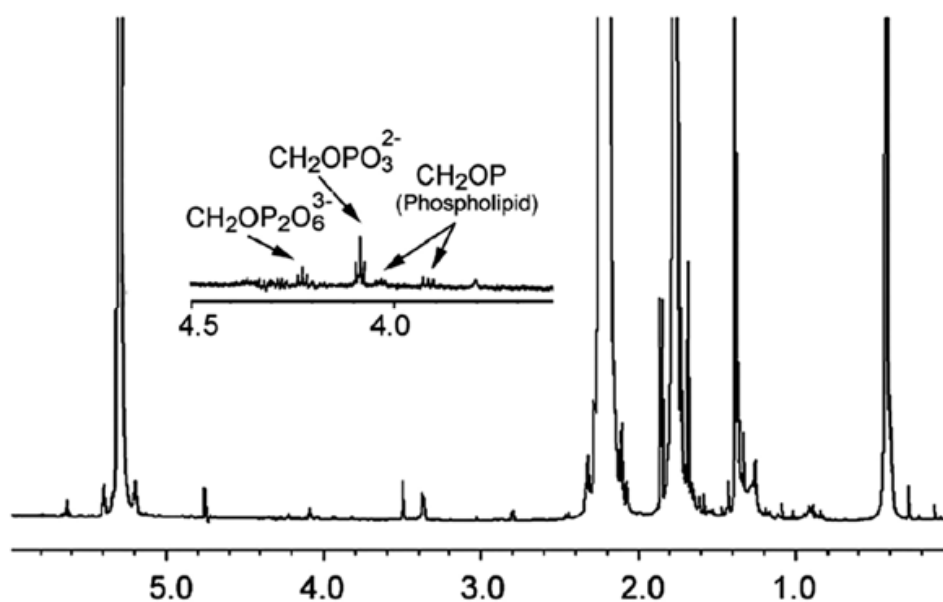
Fig. 8. ^{1}H-NMR spectrum of acetone-extracted DPNR

The phospholipids, which are the origin of long-chain fatty acid esters, are presumed to be linked to phosphate groups mainly by hydrogen bonding with a minor portion by ionic linkage (Tarachiwin et al., 2005a).
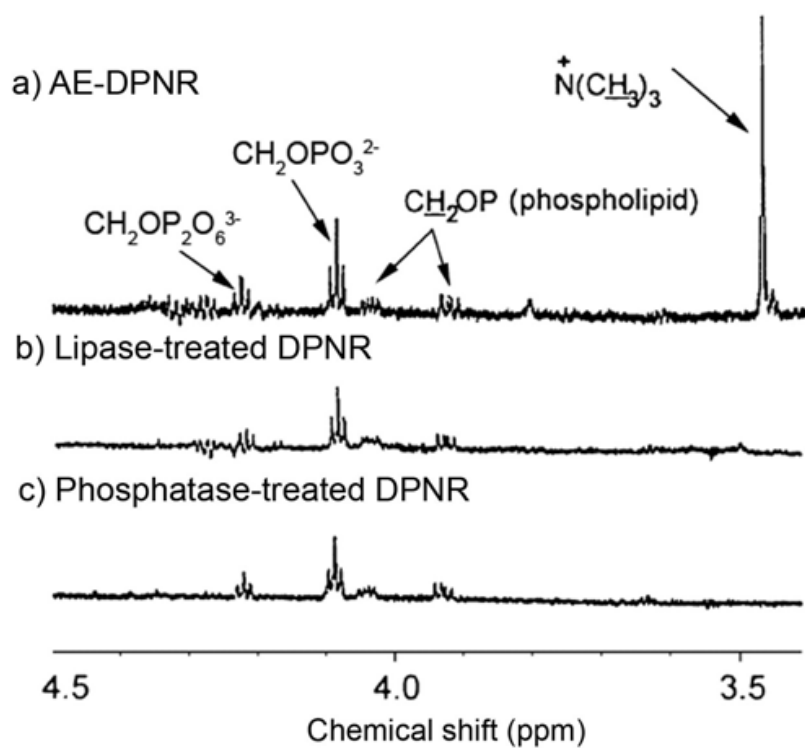

Fig. 9. ^{1}H-NMR spectra of acetone-extracted DPNR, lipase-treated DPNR and phosphatase-treated DPNR.

It is well known that four kinds of phospholipases can decompose selectively the linkages in a phospholipid. For example, the reaction site of L-α-phosphatidylcholine is shown in

Scheme 1. The treatment of DPNR latex with phospholipases A_2, B, and C resulted in the decrease of molecular weight and marked shift of the high-molecular weight peak to the low-molecular weight peak as well as narrowing the molecular weight distribution (MWD), while phospholipase D showed no change. This result demonstrates the presence of phospholipids in rubber molecules, which participate the formation of branch-points (Tarachiwin, 2004). The change of MWD and decrease in the molecular weight of DPNR after the treatment of lipase and phospholipases A_2, B, and C signify that the acylglycerol group and phosphate in phospholipids are directly concerned with the formation of branch-points in NR at the α-terminal.

It was reported that most phospholipids resist solubilization in polar and non-polar solvents by the formation of micelle and inverse micelle structures, respectively (Murari et al., 1982). The polar group in phospholipids has been reported to be participated in inter- and intramolecular hydrogen bonding that restricted the mobility of the phosphate group. (Alenius et al., 2002) These findings suggest that branch-points in NR are predominantly formed by hydrogen bonding between polar groups of phospholipids. However, the formation of branch-points by ionic linkage cannot be neglected. The formation of crosslinking by ionic linkages between negatively charges of phospholipids with divalent cation is plausible, since the process has been implicated in many membranes associated events (Hübner & Blume, 1998).

The presence of Mg^{2+} ions in FL-latex is expected to form ionic linkages between rubber molecules. The addition of ammonium sulfate $((NH_4)_2SO_4)$ in NR-latex for removing Mg^{2+} ions slightly decreased the molecular weight and polydispersity index. This indicates that Mg^{2+} ions have less effect on the branching formation than hydrogen bonding. Therefore, the α-terminal group of NR was postulated to consist of two kinds of functional group, i.e., monophosphate and diphosphate groups, which are linked with phospholipids *via* hydrogen bonding as a predominant linkage and some parts *via* ionic linkage as shown in Figure 10.
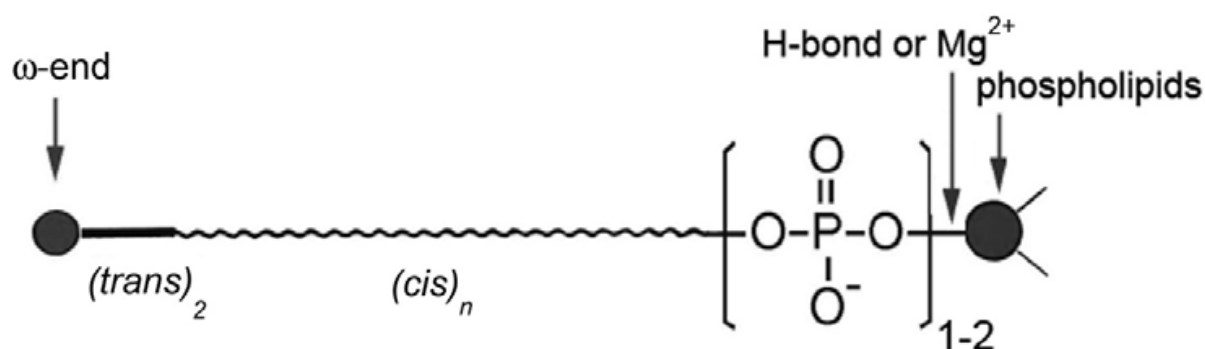

Fig. 10. Presumed structure for the α-terminal group for NR (Tarachiwin et al., 2005a)

2.3 Structural change of rubber molecule in rubber tree

Rubber tapped from the first opening mature tree, also known as virgin tree, contains a solvent-insoluble fraction formed *via* carbon–carbon linkages that are referred to as 'hard-gel', as high as 80–90% of whole solid rubber. This gel fraction showed the structure and cross-linking density corresponding to the rubber cured with peroxide. In contrast, the

residual solvent-soluble fraction (the 'sol fraction') is of low molecular weight and formed by oxidative degradation. Both the ^{1}H- and ^{13}C-NMR spectra of the sol fraction of the rubber from virgin tree show prominent signals due to epoxide and hydroperoxide, as well as aldehyde (Tangpakdee & Tanaka, 1998b; Sakdapipanich et al., 1999a). It is remarkable that the ^{13}C-NMR signals due to methyl protons of *trans*-isoprene units in the initiating terminal were not detected in the sol fraction of virgin tree. The absence of both, the dimethylallyl group and the *trans*-isoprene units in the rubber from virgin tree, indicates that the oxidative degradation of rubber chains occurs by loss of *trans*-isoprene units at the initiating terminal.

2.4 Structure of branch-points, gel and storage hardening

It is well known that commercial high ammonia latex (HA-latex) increases the mechanical stability during storage, but it is always accompanied with the increase in the gel content as high as 60% after storage for a long period. The gel fraction in commercial HA-latex is assumed to be due to the reaction of branched chains to form three-dimensional chains. A slight increase in the gel content was also observed from DPNR-latex, although the rate is very slow compared to that of commercial HA-latex (Kawahara, 2002a). Accordingly, the gel formation in DPNR latex is not due to proteins, but by some reactions of the functional α-terminal group or by radical crosslinking reaction.

NR contains both soft-gel and hard-gel (Tangpakdee & Tanaka, 1997b). The content of soft-gel fraction in NR decreases by deproteinization with a proteolytic enzyme or can be partly decomposed in solution by the addition of small amounts of a polar solvent into a good solvent and almost completely solubilized by transesterification. These suggest that branch-points are originated mainly from functional groups at ω- and α-terminals. The molecular weight between the crosslinks (M_c) of the gel fraction in NR was 2-3 times of the number average molecular weight (M_n) value suggesting the presence of 2-3 rubber chains per crosslink, although the measurement is based on many assumptions.
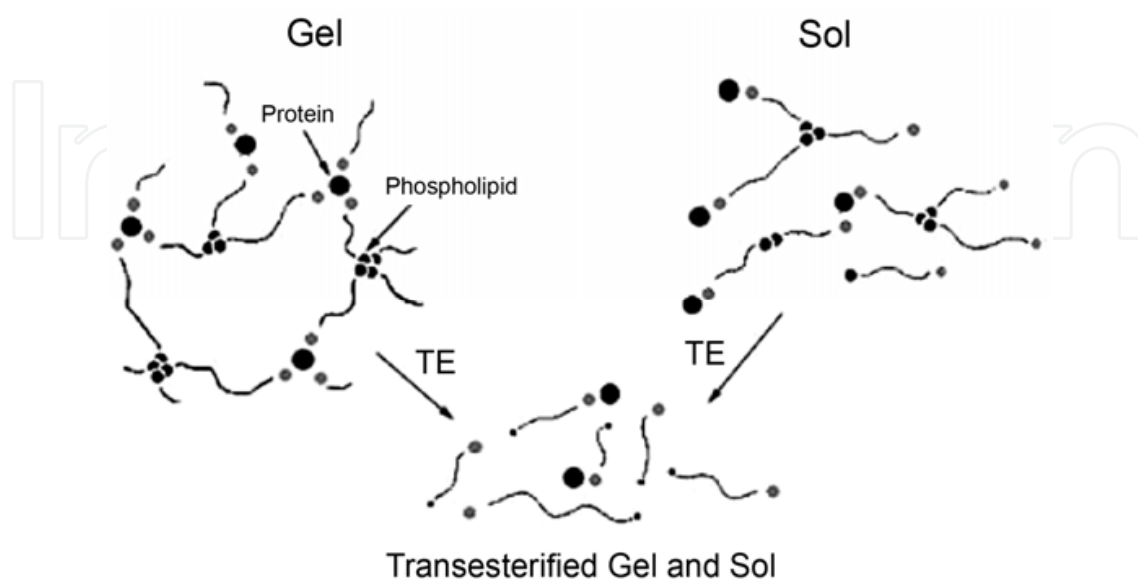

Fig. 11. Presumed structure of gel and sol phases in NR after transesterification

Based on these findings, it is possible to illustrate the structure of gel and sol phase in NR as shown in Figure 11. Two types of branch-points are presumed in rubber chain, the formation of branchings by both types of branch-points results in the formation of crosslinked chains. Here, one to two chains are assumed to be between the crosslink-points. The sol fraction may be a branched polymer having no three-dimensional branching. It is remarkable that all the branch-points containing ester linkages of fatty acid and/or phosphates can be decomposed by transesterification and the resulting rubber chains cannot form three-dimensional branched-chains because of only one type of the residual branch-points in the rubber chains.

It is noteworthy that a part of the gel fraction in commercial HA-latex cannot be solubilized by transesterification or saponification (Tarachiwin et al., 2003). This hard-gel has been presumed to be formed by radical reactions between rubber chains and tetramethylthiuram disulfide (TMTD), which is normally used as bactericide preservatives, in latex together with zinc oxide (ZnO). As shown in Figure 12, the addition of TMTD and ZnO into HA- and DPNR-latices resulted in a rapid increase in the gel content. The resulting gel fraction was hard-gel insoluble in toluene even after chemical or enzymatic treatments mentioned above. This suggests that TMTD and ZnO can be another factor to increase the gel content during storage of latex (Tarachiwin et al., 2003).
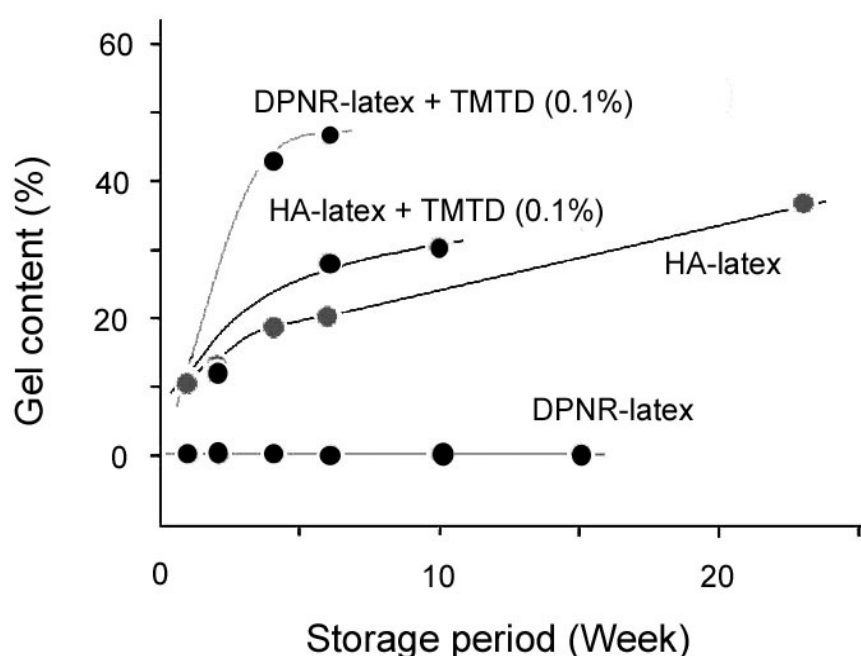

Fig. 12. Gel content in commercial HA-latex and DPNR-latex, prepared from HA-latex, with and without TMTD and ZnO (Tarachiwin et al., 2003)

Another example of hard-gel formation is observed for the rubber obtained from virgin *Hevea* trees, which have not been collected latex by tapping for a long period. It is known that the latex obtained from virgin *Hevea* trees shows very poor properties. This may be concerned with the fact that the rubber from virgin trees contained the gel fraction as high as 80% (Tangpakdee & Tanaka, 1998b). The gel fraction showed almost the same structure as the crosslinked rubber prepared from FL-latex in the presence of peroxide. This gel

fraction cannot be solubilized by enzymatic or chemical reactions (Tangpakdee & Tanaka, 1998b). The M_c value of the gel fraction was about 3×10^3, showing that the gel is highly crosslinked rubber. It is remarkable that the sol fraction in the latex from virgin tress was very low-molecular weight rubber containing aldehyde and epoxide groups derived by oxidative degradation (Tangpakdee & Tanaka, 1998b). This finding indicates clearly the occurrence of radical reactions in rubber trees during storage as latex for a long period before taking out the latex by tapping. This was further confirmed by the analysis of the molecular weight and gel content after the first tapping of virgin *Hevea* trees as shown in Figure 13. The gel content decreased gradually by successive tapping after the first tapping and recovered to the same level as the ordinary FL-latex after 6 days. A similar tendency was observed for the molecular weight. The molecular weight of soluble rubber fraction increased to the ordinary values after tapping for 6 days. These findings indicate the occurrence of radical reactions on rubber chains in rubber tree during storage, to form carbon-carbon crosslinking and partly oxidative degradation products in laticiferous cells. This also suggests a possible role of rubber as a scavenger of hydroxyl radicals in latex (Tangpakdee & Tanaka, 1998b).
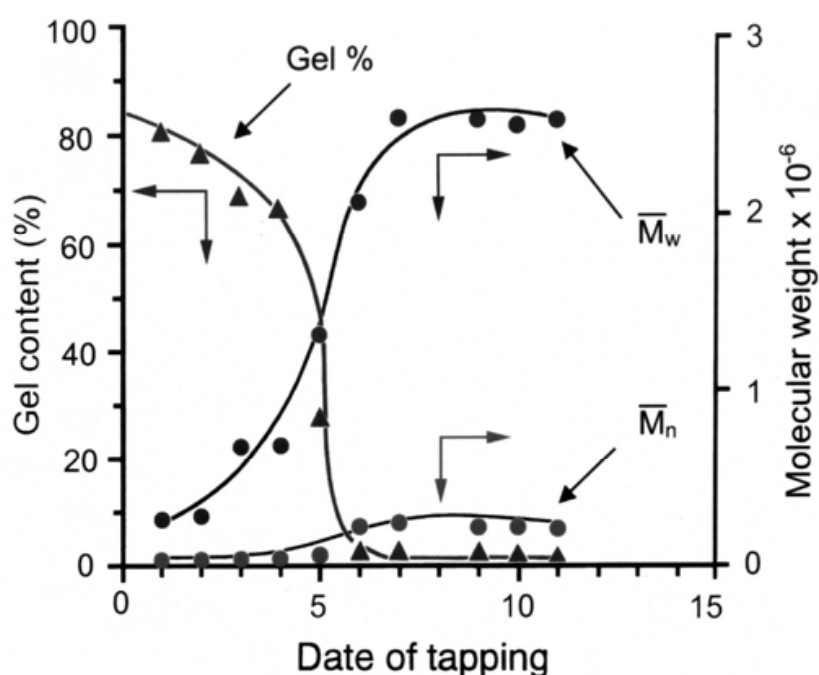

Fig. 13. Change of molecular weight and gel content of NR after the first tapping of virgin tree

Recently, as mentioned above, the structure of α-terminal group of NR was proposed to consist of two kinds of functional group, i.e., monophosphate and diphosphate groups, which are linked with phospholipids *via* hydrogen bonding as a predominant linkage and some parts *via* ionic linkage (Tarachiwin et al., 2005a, 2005b). Here, it is postulated that the branch-points in NR are formed by aggregation of the phospholipids which are linked to phosphate or diphosphate groups at the α-terminal. Phospholipids are presumed to aggregate together to form a micelle structure mainly *via* hydrogen bonding between polar groups in phospholipids molecules, as shown in Figure 14.
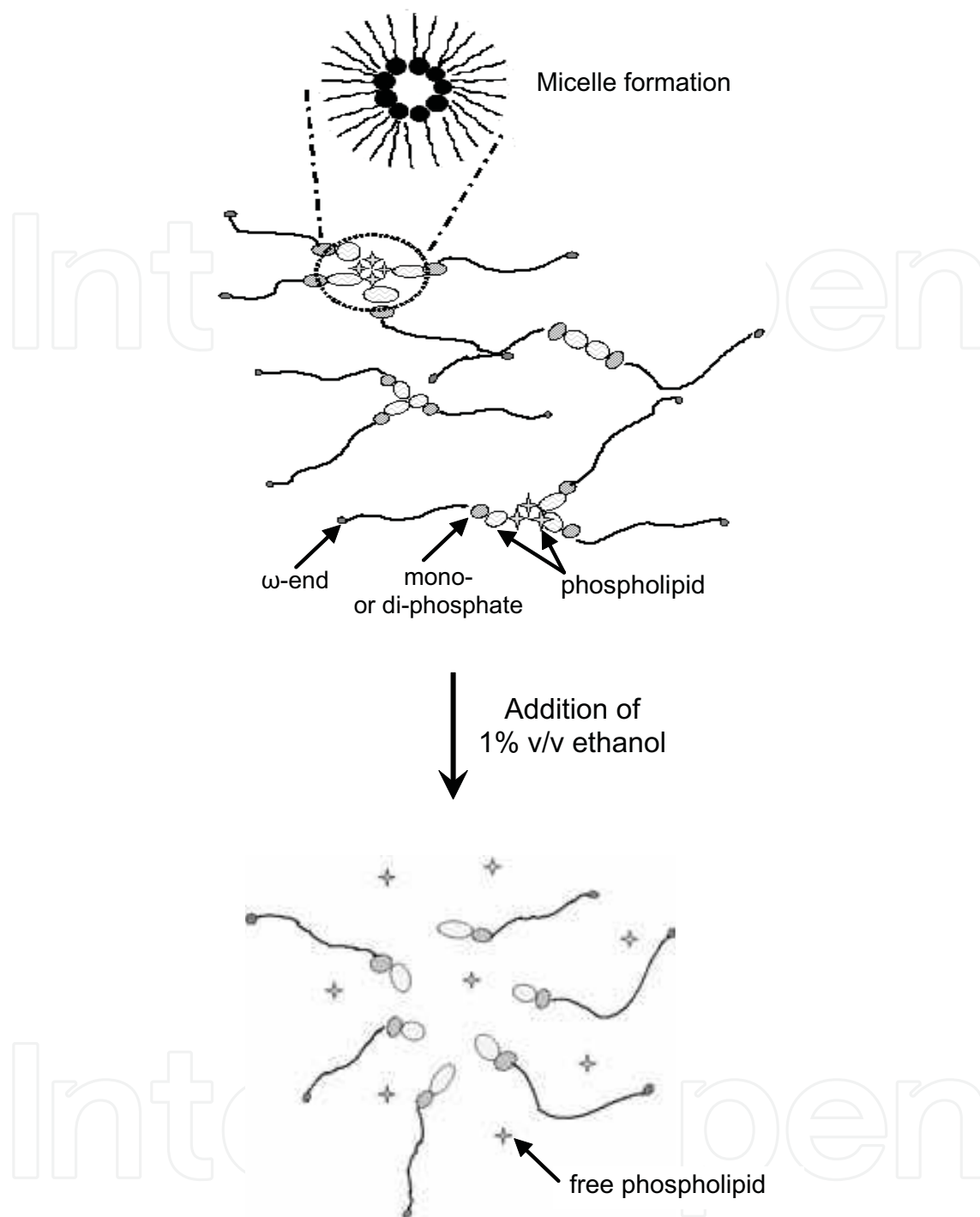
Fig. 14. Proposed structure of branch-points in NR

The storage-hardening (SH) phenomenon in solid NR has long been recognized to be a factor affecting the processing properties such as Mooney viscosity and Wallace plasticity during storage. These phenomena affect directly to the variability of NR in several aspects including processing properties (Sekhar et al., 1958, 1960). The change in the properties of NR during storage was presumed to be due to the cumulative effects of crosslinking and chain-scission, varying with the environmental conditions (Gan, 1997). It has been postulated that the hardening proceeds through the reactions between the rubber chains

and so-called abnormal groups assumed to exist on rubber molecules such as epoxide (Sekhar et al., 1958), carbonyl (Sekhar et al., 1960; Subramaniam, 1976), and lactone (Gregory & Tan, 1976).

The physical properties during long-term storage as real condition for selected commercial Standard Thai Rubber (STR), i.e. STR XL, STR 5L and STR CV60 as high-graded NR, were investigated. Each zone of commercial NR after SH was also subjected to examination. STR 5L showed clearly increase in Mooney viscosity, MR_{30}, gel content and initial plasticity (P_0) which higher than those of STR XL. This result suggested that STR 5L showed the highest inconsistency in physical properties. The increasing in viscosity and gel content of STR 5L and STR XL samples suggest the occurrence of crosslink structure during storage. STR CV60, known as viscosity-stabilized NR sample, also showed increasing in Mooney viscosity, gel content, P_0, and high plasticity retention index (PRI) value during long storage. These findings indicate that SH occurred in the rubber samples even in carefully controlled production procedure. As for the different zones of samples, there is no clear relation about the gel content with respect to storage time, indicating that depth or positions of specimen in a certain rubber bale had not affected to the storage-hardening phenomenon.

In the past several years, branching and crosslinking formations in NR has been postulated to derive from chemical reactions of abnormal groups (Sekhar et al., 1958; Sekhar et al., 1960; Subramaniam, 1976; Gregory & Tan, 1976). However, it has been reported that these abnormal groups in NR are not major factors for branching and gel formations (Yunyongwattanakorn, 2005). The effect of non-rubber components on the gel formation and SH of NR after accelerated storage-hardening test (ASHT) in phosphorous pentoxide (P_2O_5) has been investigated (Yunyongwattanakorn et al., 2003).

SH phenomenon of solid NR is presumed to occur *via* reactions between some non-rubber components and abnormal groups in rubber chains. The main non-rubber constituents in NR are composed of proteins and lipids. The SH behavior under high and low humidity conditions using P_2O_5 and sodium hydroxide (NaOH) was analyzed for the various purified NR samples (Yunyongwattanakorn et al., 2003). The NR obtained from centrifuged fresh NR latex (CFNR) and deproteinized NR latex (DPNR) showed significant increase in the hardening plasticity index (P_H) value during storage under low humidity conditions, while that of the transesterified NR (TENR) and transesterified DPNR (DPTE-NR) was almost constant during storage, as shown in Figure 15. The low P_H value and no gel content in TENR was observed indicating that TENR had not much branch-points enough to form gel phase. The lack of branch-points in both transesterified rubber samples might be the main reason for the constant P_H value, even when using the strong drying agent. The above findings suggest that the fatty acid ester group plays the most importance role in the SH of rubber under low humidity conditions.

After keeping samples under high humidity conditions, the fresh NR (FNR), CFNR and DPNR showed decrease in the P_H value, while that of the TENR and DPTE-NR showed low P_H value and decreased with increasing the storage time, as shown in Figure 16. This implies that the rubber containing no fatty acid groups tended to cause auto-oxidation. It was also observed that the P_H value of all rubber samples decreased as the storage time increased, indicating that the SH was inhibited under high humidity.
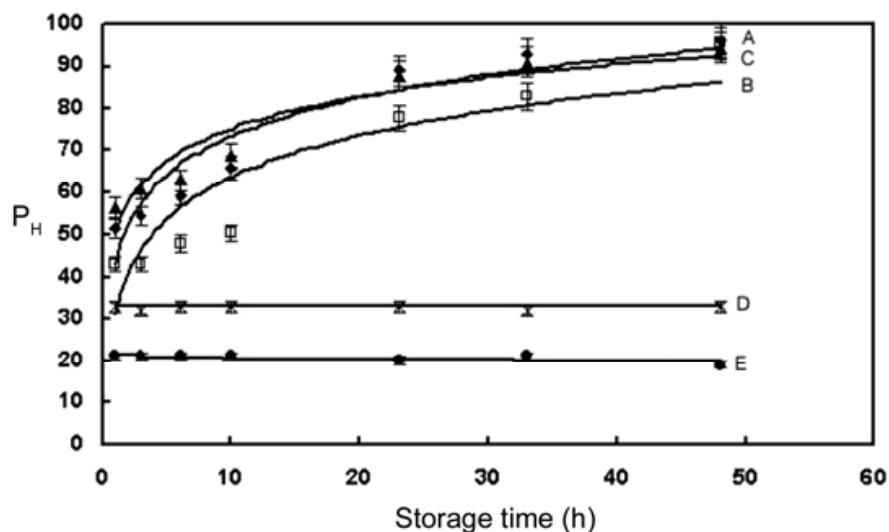
Fig. 15. Change in the hardening plasticity index (P_H) of the rubber samples after storage in P_2O_5 under vacuum; (A) FNR, (B) CFNR, (C) DPNR, (D) TENR and (E) DPTE-NR

The gel phase in rubber samples after SH is soft-gel originated by micelle formation between phospholipids molecules. This finding confirmed by the decrease in gel content of stored FNR after the addition of 2% v/v ethanol into rubber solution and complete decomposition of the gel fraction after transesterification (Yunyongwattanakorn, 2005).
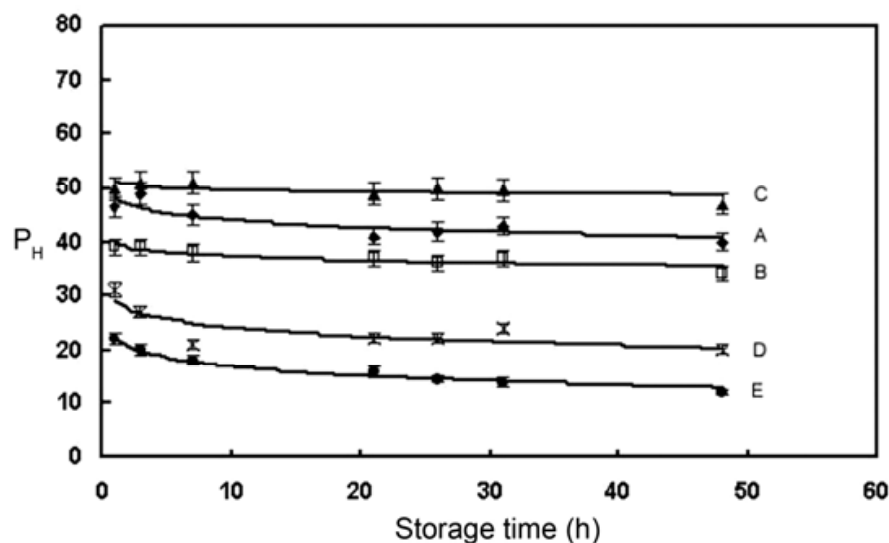

Fig. 16. Change in the hardening plasticity index (P_H) of the rubber samples after storage under high humidity under *vacuum*; (A) FNR, (B) CFNR, (C) DPNR, (D) TENR and (E) DPTE-NR

Significant increase in the plasticity, gel content and molecular weight between the crosslinks (M_c) when the samples were kept under low humidity condition suggested an important role of the humidity on gel formation during SH. The proposed structure of gel formation during ASHT based on all of findings mentioned above was schematically illustrated in Figure 17. The proteins and phospholipids at the chain-ends of rubber molecules may interact with water under ambient condition, thus the water may disturb the formation of branching points by hydrogen bonding.
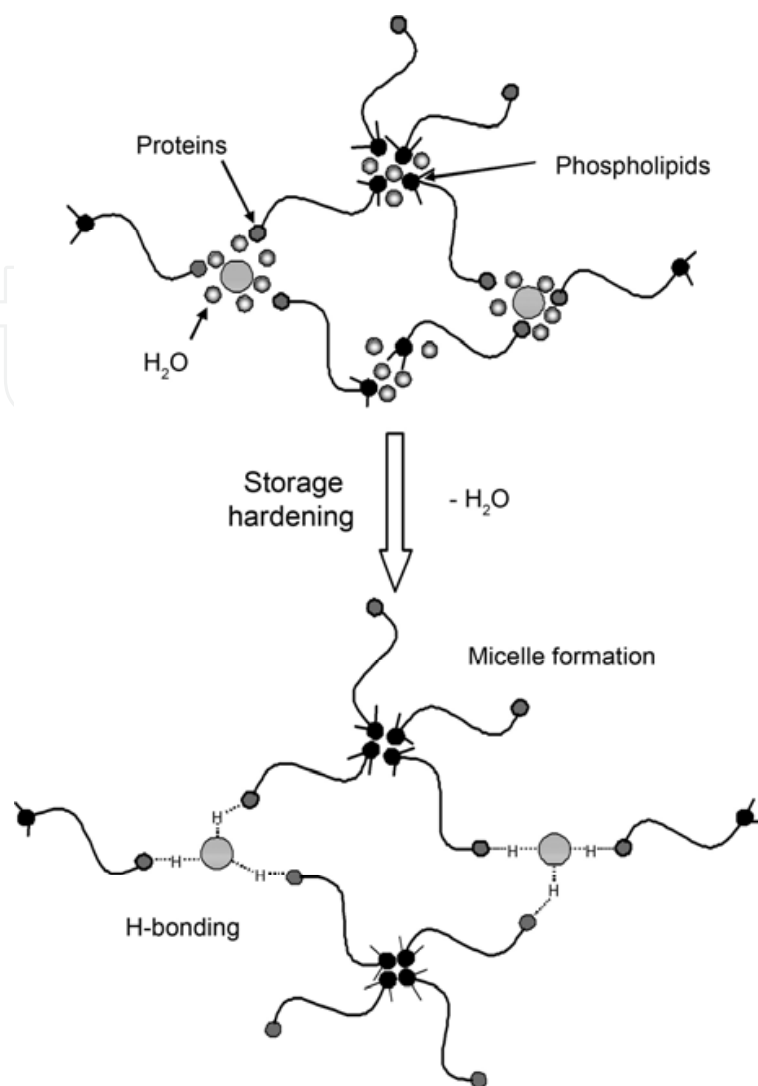
Fig. 17. Proposed structure of gel of NR after storage hardening

When water is removed from the rubber, with a drying agent such as phosphorus pentoxide or sodium hydroxide, proteins and phospholipids at the terminals of rubber chain may have a chance to form branching points by hydrogen bonding. Since both functional groups of NR are active, the gel fraction can be formed during storage due to the reaction between the functional groups of NR chains. Therefore, the formation of gel in NR during SH is presumed to compose of two types of branching points; the first one is expected to originate from phospholipids, which are associated to rubber chains and/or free phospholipid molecules. The phospholipids are associated together by the formation of micelle structure mainly *via* hydrogen bonding between polar groups in phospholipids molecules as reported (Tarachiwin et al., 2005a, 2005b). The other crosslinking point is due to proteins, which can be formed *via* hydrogen bonding.

3. Color substances and obnoxious odor in natural rubber

It is accepted that NR gives naturally occurring color, which restrict many applications such as light-color products. Therefore, characterization of color substances presenting in NR is very useful to develop the certain methodology to eliminate them completely or partly from

NR in the future. Recently, Sakdapipanich and co workers (2006) have tried to purify and characterize the color substances extracted from various fractions of *Hevea* rubber latex by certain methods, using high-resolution structural characterization techniques. It was found that the content of color substances extracted from fresh latex (FL), rubber cream, bottom fraction (BF), Frey Wyssling (FW) particles and STR 20 were different. Based on the high-resolution spectroscopic analyzes, it was found that the color substances extracted from NR were composed of carotenoids, tocotrienol esters, fatty alcohol esters, tocotrienols, unsaturated fatty acids, fatty alcohols, diglyceride and monoglyceride. The results will be useful for rubber-technologist to identify the origin to make obnoxious color in natural rubber, especially in some applications which are restricted by such the color.

3.1 Color substances in natural rubber

3.1.1 Enzymatic browning

Enzymatic browning is the discoloration resulting when monophonic compounds of plants or shellfish in the presence of atmospheric oxygen and polyphenol oxidase (PPO) are hydroxylated to *o*-diphenols and the latter are oxidized to *o*-quinones. PPO is also known and reported under various names (tyrosinase, phenolase, catechol oxidase, catecholase, monophenol oxidase, *o*-diphenol oxidase and *o*-phenolase) based on substrate specificity. Then, quinones may condense and react non-enzymatically with other phenolic compounds, amino acids, proteins or other cellular constituents to produce colored polymer or pigments (Iyidogan & Bayindirh, 2004), as shown in Figure 18 (Lee & Whitaker, 1995).
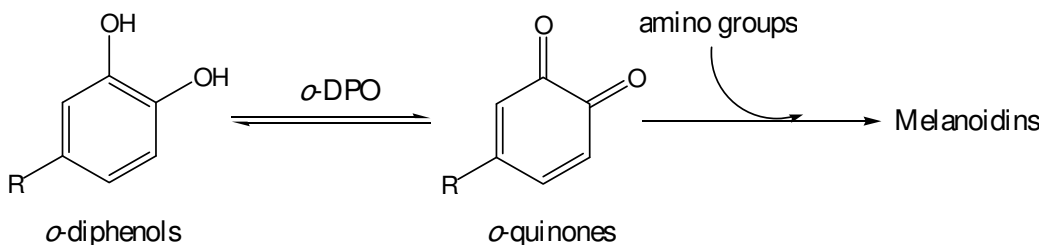

Fig. 18. Enzymatic browning of *o*-diphenols by *o*-diphenol oxidase (*o*-DPO)

PPO was earlier reported to be present in both lutoid and Frey-Wyssling particle (Wititsuwannakul et al., 2002). It was found that the latex PPO activity in lutiods was 5 to 34 folds higher than that of the Frey-Wyssling particles (Table 1).

Rubber clone	PPO activity (nkat/ml latex)[a]	
	Lutiod	Frey-Wyssling
RRIM 600	7.33	0.21
GT 1	9.21	0.65
KRS 21	4.34	0.77

[a] Minimal PPO activity was detected in C-serum and rubber fraction.

Table 1. Distribution of PPO activity in the ultracentrifuged fresh latex

3.1.2 Non-enzymatic browning

Non-enzymatic browning resulted from the following reactions is possibly concerned as the discolorations of NR.

Lipid oxidation

The important lipids involved in oxidation are the unsaturated fatty acid moieties, oleic, linoleic and linolenic. The rate of oxidation of these fatty acids increases with the degree of unsaturation. The mechanism of lipid oxidation is illustrated in Figure 19 (http://www.agsci.ubc.ca).
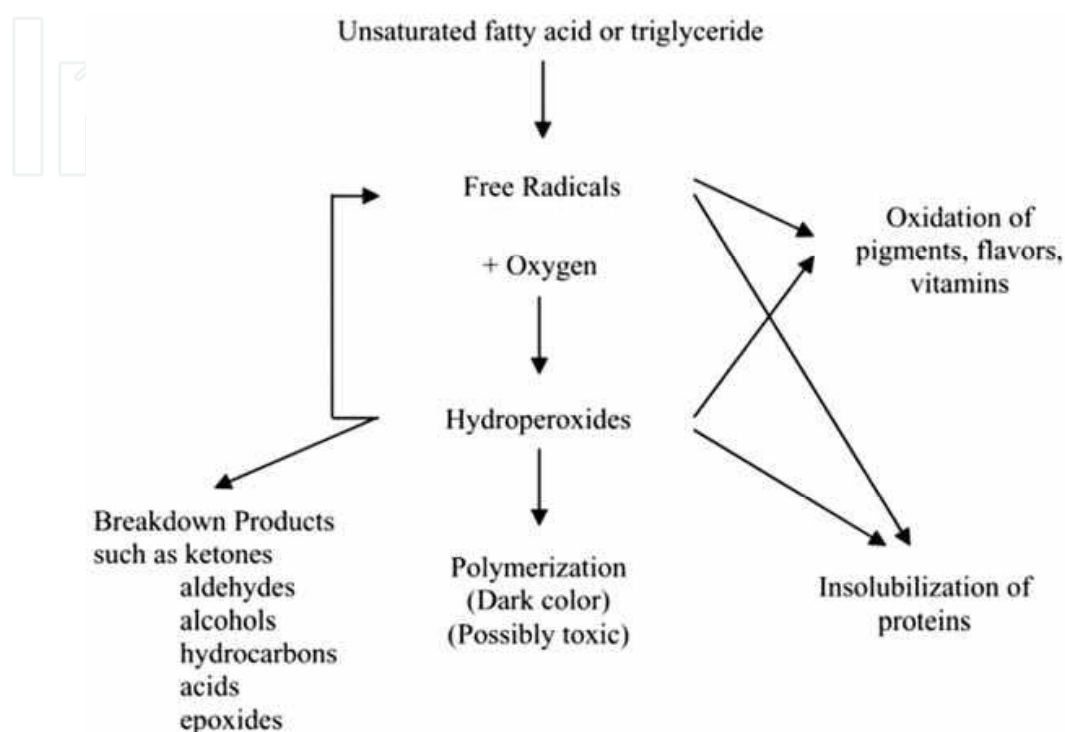
Fig. 19. Lipid oxidation mechanisms

Millard reaction

Millard reaction involves the reaction between carbonyl compounds (reducing sugars, aldehydes, ketones and lipid oxidation products) and amino compounds (lysine, glysine amine and ammonia proteins) to produce glycosyl-amino products, followed by Amadori rearrangement. An intermediate step involves dehydration and fragmentation of sugars, amino acids degradation, etc. A final step involves aldol condensation, polymerization and the formation of colored products.

3.1.3 Enzymatic browning prevention

The principles of browning prevention have not changed with time and are essentially the same as those applying to the inhibition of any tissue enzyme, i.e.:

1. Inhibition or inactivation of the enzyme
2. Elimination or transformation of the substrate(s)
3. Combination of both above

The examples of chemical agent for browning prevention are sulfiting agents, aromatic compounds, such as 4-hexylresorcinol, tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one), kojic acid (5-hydroxy-2-(hydroxymethyl)-γ-pyrone), etc., glucosidated substrates, proteolytic

enzymes, carbohydrates, peptides, carbon monoxide, hypochlorite, and miscellaneous browning inhibitors. The enzymatic browning prevention can be also performed by physical treatments, i.e. blanching, ultrafiltration, sonification, supercritical carbon dioxide.

3.2 Obnoxious odor in natural rubber

Fulton W. S. (1993) has studied the problems of odor during rubber processing. It was found that coagulation and subsequent conversion of coagulum into bale rubber affects the smell of natural rubber. The field grade material tends to have a stronger smell than rubber prepared by the deliberately controlled coagulation of latex. The main constituents of the effluent gases from the rubber industry are low-molecular weight volatile fatty acid, which can be effectively removed by water scrubbers with efficiencies of 92-99%.

Isa Z. (1993) has studied how to control the mal-odor in Standard Malaysia Rubber (SMR) factories. The mal-odor from SMR factories is mainly attributed to the obnoxious volatile components, which are present in the exhaust gases discharged into the air through a chimney during the drying stage of SMR processing. The volatile compounds are originally produced from the microbial breakdown of the non-rubber components during the storage of scraps and cup lumps prior to processing. Before to the characterization by gas chromatography, the exhaust gases were collected by adsorption on charcoal adsorption tube. It was found that the volatile compounds in the exhaust gases were low molecular-weight volatile fatty acids such as acetic acid, propionic acid, butyric acid and valeric acid. The mal-odor can be reduced by a water-scrubber system.

Hoven V. P. and coworkers (2003) have determined the volatile organic components of various grades of solid rubber by gas chromatography (GC) and gas chromatography-mass spectroscopy (GC-MS) using direct sampling collection of head space technique. It was found that about fifty components, with molecular weight in the range of 40-200 amu, were identified. They can be classified into four groups, as follows: (1) compounds having low polarity; aliphatic and aromatic hydrocarbons; (2) compounds having moderate polarity; aldehydes, ketones; (3) compounds having high polarity; volatile fatty acids; (4) derivatives containing nitrogen or sulfur. The components discovered in all samples were ethylamine, benzylhydrazine and low molecular-weight volatile fatty acids, which are acetic acid, propionic acid, isobutyric acid, butyric acid, isovaleric acid and valeric acid. The obnoxious odor of all NR samples is mainly originated from low molecular-weight volatile fatty acids, whose quantity depends upon the odor intensity and the quality of NR latex. In 2004, Hoven V. P. and coworkers have incorporated odor-reducing substances into STR 20 and RSS 5 by physical mixing prior to vulcanization. It was found that according to the GC analysis and olfactometry test, the obnoxious odor from STR 20 and RSS 5 can be significantly reduced by physical mixing of chitosan, zeolite 13X and carbon black. Benzalkonium chloride and sodium dodecyl sulphate (SDS) did not exhibit the desired odor-reducing properties as a consequence of their thermal degradation during vulcanization. The ability to adsorb physically and/or chemically with the volatile fatty acids as well as their reinforcing effect indicates that chitosan and carbon black are strong candidates for odor reduction of NR.

Recently, Sakdapipanich and Insom (2006) have elucidated the mechanisms producing the components of obnoxious odor derived from various solid rubbers using a combination technique between head-space sampling and GC-MS. It was found that volatile components

of STR XL were mainly comprised of hydrocarbons, which were probably derived from lipid oxidation of unsaturated fatty acids or triglycerides. In the case of STR 5L, the small amounts of volatile fatty acids derived from carbohydrate fermentation were detected. They were also liberated from STR 5, STR 20, cup lump and RSS. Finally, in the case of skim crumb rubber, sulfur-containing compounds derived from decomposition of proteins existing in NR were observed.

4. Skim rubber

Skim latex is a material resulting from the production of concentrated latex in the centrifugation process. After centrifuging the fresh field latex, 5-10% of total rubber, together with an enhanced proportion of the non-rubber constituents in the original latex, remains in the serum phase or skim latex (Bristow, 1990). The skim latex is composed of small rubber particles in range of 0.04 µm to 0.4 µm with the mean particle diameter of about 0.1 µm, while those of large rubber particles in concentrated latex is from 0.1 µm to 3 µm with a mean diameter of 1 µm, as shown in Figure 20. The skim rubber obtained from skim latex shows a unimodal distribution with a peak top between the high and low-molecular weight peaks in the MWD of ordinary rubber, centered around 1.0×10^6 g/mol, (Sakdapipanich et al., 2002a) as shown in Figure 21.

Recovery of skim rubber from skim latex

The residual rubber from skim latex is normally recovered by the addition of sulfuric acid. This method can separate skim rubber out from skim latex as coagulum like To-fu. Skim rubber contains 70-85% rubber component. It is known that there are a number of proteins contaminate in skim rubber. Normally, there are hydrocarbon, 5-10% acetone-soluble fatty materials and 10-20% proteins, compared with an average of 95% hydrocarbon, 3% fatty materials and 2% proteins in the case of smoked sheet prepared from fresh field latex. (Nithi-Uthai, 1998)
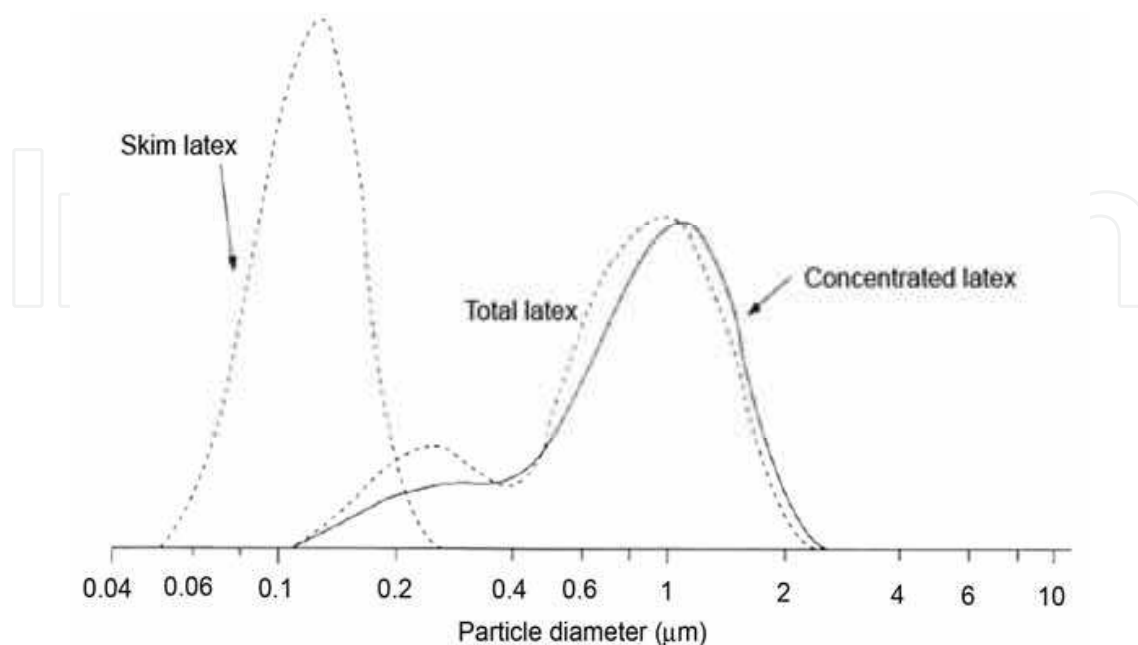

Fig. 20. Particle size distribution of concentrated and skim latices
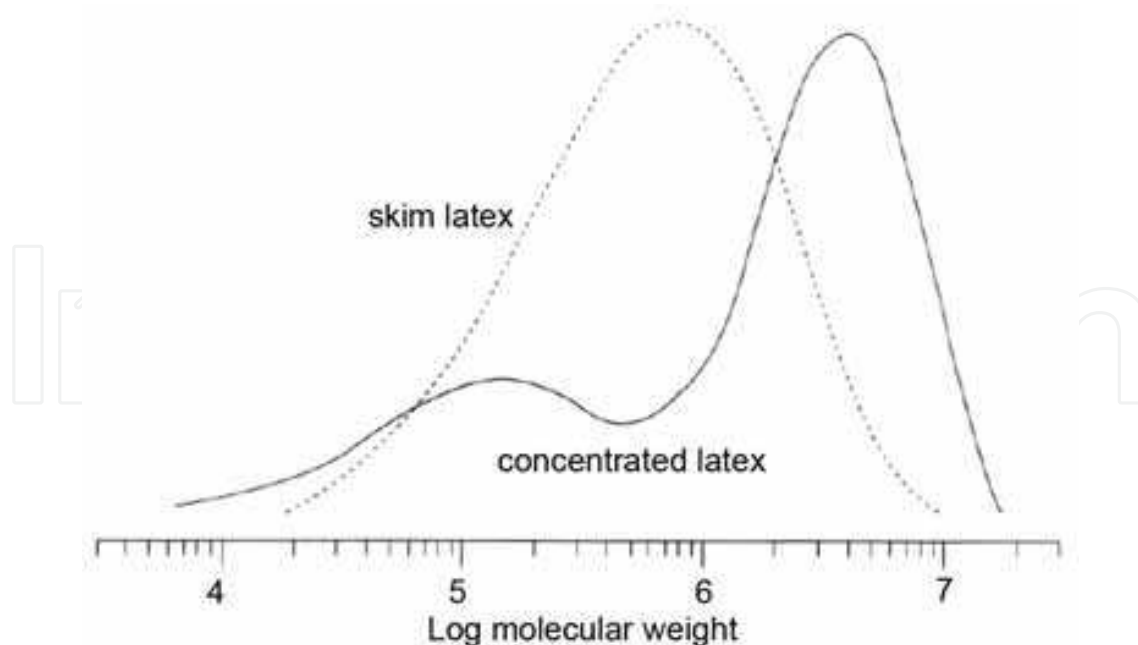
Fig. 21. Molecular weight distribution of the rubber from concentrated and skim latices

In addition to the sulfuric acid coagulation, there are several other methods such as

a. Auto-coagulation of skim latex by de-ammoniating to less than 0.1% and leaving for spontaneous coagulation within 5 days (Smith, 1969). The drawbacks of this method are that it required extensive coagulation-tank capacity to handle large quantities of the resulting coagulum and the obtained dry rubber foul smell.

b. Accelerated auto-coagulation of skim latex by partly de-ammoniation of skim latex and addition of 0.1% di-octyl sodium sulfosuccinate and 1% $CaCl_2$ to skim latex (John & Weng, 1973). This treatment can coagulate the skim latex within 2 days.

c. The addition of enzyme to skim latex before coagulation with acid was also carried out. This process can reduce the nitrogen content in the skim latex to about 0.6-3.5% due to the decomposition of proteins by enzyme. Thus, after enzymolysis, the proteins attached to rubber particles are removed and the possible remaining stabilizer on the particle surface is fatty acid soaps (Nithi-Uthai, 1998; Morris, 1954).

d. Skim NR latex was recovered as concentrated skim latex by using deproteinization and salting-out techniques (DP/S) (Sakdapipanich et al., 2002b). The increase in skim rubber content is owing to the recovery of small rubber particles in the skim latex.

Structure of skim rubber

In the last decade, it was disclosed that skim rubber contains low or no ester content compared to concentrated rubber, i.e., 0.03 per rubber chain. This implies that the rubber molecules from skim rubber are not terminated by phospholipids as could be detected in the concentrated rubber molecules (Sakdapipanich et al., 1999b). Based on the previous results, it was observed that skim rubber showed insignificant increase in gel content during storage while the gel content of fresh and concentrated rubber increased up to 30% and 60%, respectively. Furthermore, in the case of concentrated rubber, the M_w and M_n values decreased after transesterification, the reaction which decomposes gel and branching in natural rubber, by about 20% and 35%, respectively. However, no significant change of

these values was observed in skim rubber. This suggests that skim rubber composed of linear rubber molecules, which differ from concentrated rubber.

^{1}H-NMR spectra of fractionated skim rubber and 1-month old seedlings, as shown in Figure 22, revealed that skim rubber showed three major signals at 1.78, 2.10, and 5.18 ppm, which are assignable to -CH$_3$, -CH$_2$, and =CH of *cis*-1,4 isoprene units, respectively. The rubber from 1-month old seedlings showed additional signals around 4.0-4.3 ppm and 1.2 ppm, which have been assigned to terminal -CH$_2$O and long methylene sequence -(CH$_2$)$_n$- of fatty acids (Tangpakdee, 1998). The absence of both signals in fractionated skim rubber clearly indicates that skim rubber contains no phospholipid linked to rubber chain. Phospholipid groups including long-chain fatty acids were found to play an important role to form branched structure (Tarachiwin et al., 2005c). Thus, the ^{1}H-NMR results provide confirmation that skim rubber is composed of linear rubber molecules.
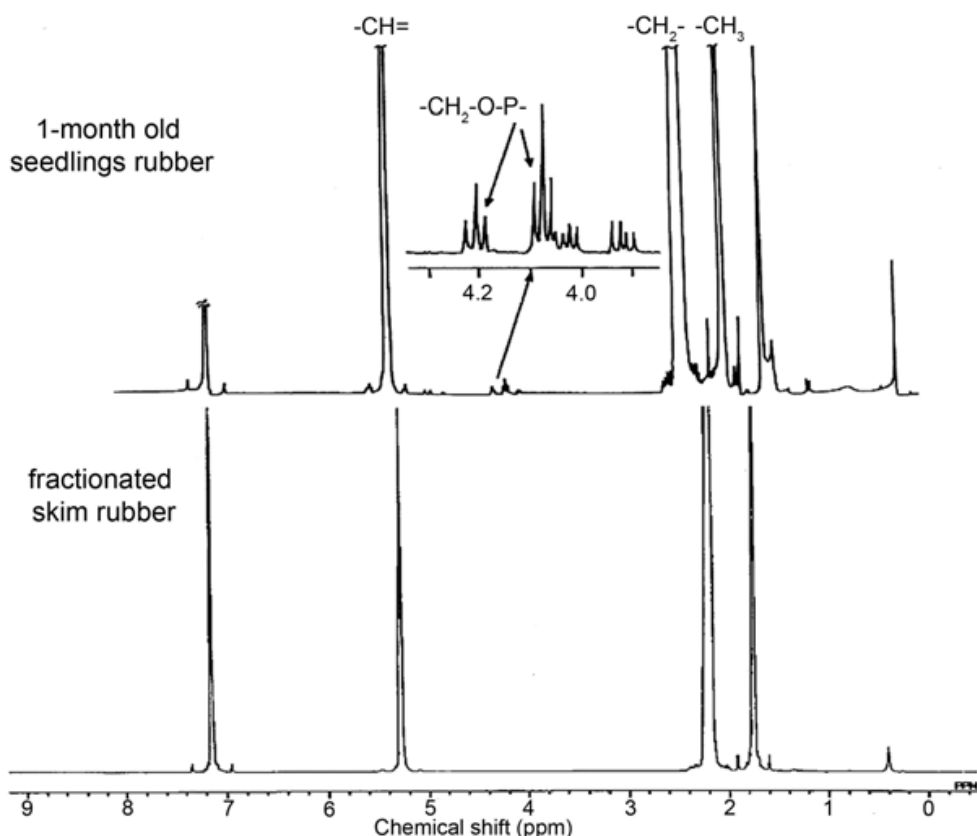

Fig. 22. ^{1}H-NMR spectra of (A) 1-month old seedlings and (B) fractionated skim rubber

Physical properties of skim rubber

The difference in rubber constituent in skim latex is the important parameter related to green strength of natural rubber. Figure 23 shows the green strength of concentarated, skim rubber, synthetic polyisoprene (IR) and transesterified-deproteinized rubber (Nawamawat, 2002). The concentrated rubber is composed of branched molecules, which linked together by hydrogen bonding *via* protein and ionic crosslinks cased by phospholipid groups. The latter branch points have been attributed to the high green strength of NR and induced the crystallization of the rubber on straining (Kawahara et al., 2002b). It was reported that the nitrogen and ester contents were dramatically decreased after deproteinization followed by

transesterification of concentrated rubber, i.e., DPTE (Tangpakdee & Tanaka, 1997). DPTE composed of linear rubber molecules was found to show very low green strength comparable to that of concentrated rubber. Moreover, it was found that skim rubber showed similar green strength to DPTE as well as synthetic IR (Figure 23). Synthetic IR contains no functional terminal group, especially phospholipid group (Gregg & Macey, 1973), which is similar to that in the case of skim rubber. The Mooney viscosity and Mooney relaxation data of skim rubber were also found to be lower than that from concentrated rubber. Thus, this indicates that the skim rubber is softer and lower elasticity than concentrated rubber (Sakdapipanich et al., 2002). The low tensile strength and Mooney viscosity might lead to the benefit of skim rubber on the low energy consumption during processing, which are perfectly different from concentrated rubber.
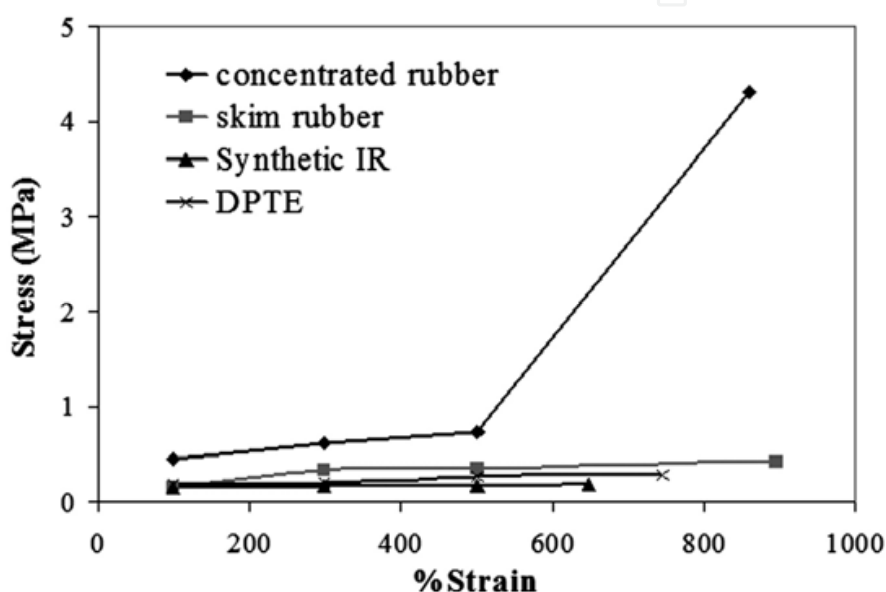

Fig. 23. Green strength of concentrated rubber, skim rubber, synthetic polyisoprene (IR) and DPTE

Application of skim rubber

In the previous work, the application of the skim rubber is used in many fields. For example, the small amounts of skim rubber act as cure-rate boosters, which can replace the secondary accelerators in some applications. In physical processing characteristics, the skim rubber is resembled compounded materials rather than elastomeric gum (Blackey, 1996). This is due to the preponderance of non-elastomeric substances in the material. The increases in hardness and state of curing correlate well with the nitrogen content, due to the physical effect of proteinous substances. The skim rubber can be controlled by a suitable choice of accelerator. About 20-25 parts of skim rubber can be blended with conventional rubber to give a high level of vulcanizate properties retention and reduced variability. The skim rubber was found to give better adhesion between a brassed metal and contiguous skim rubber (Schofeld, 1995). The rubber-metal adhesion and adhesion retention can be obtained by adding copper sulfide to the conventional rubber skim stock composition and followed by vulcanization to yield the end product. In addition, skim rubber was also studied for its use as urea encapsulant in the controlled release application (Tanunchai, 1999).

Recently, it was revealed the effective method using saponification reaction to remove the impurities, especially proteins and lipids, from skim rubber. It was also found that this highly purified skim rubber showed good solubility with no any gel formation, which is a merit on adhesive application (Nawamawat, 2002). The pressure-sensitive adhesive made from high-purified skim rubber also showed good tack and adhesion properties, good transparent and absence of protiens, which might cause allergy (Nawamawat, 2002). Thus, the highly-purified skim rubber can be further developed for more valuable as medical and surgical tape.

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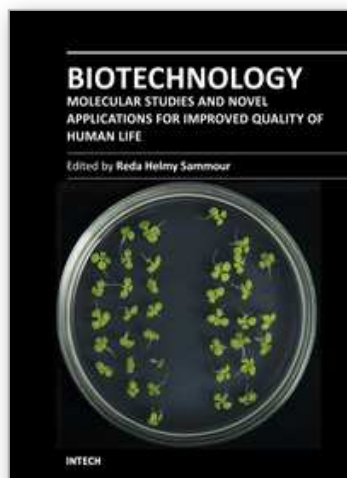
Biotechnology - Molecular Studies and Novel Applications for Improved Quality of Human Life

Edited by Prof. Reda Sammour

This book deals with the importance of application of molecular biology as an approach of biotechnology for improvement of the quality of human life. One of the interesting topics in this field, is the identification of the organisms that produce bioactive secondary metabolites. It also discusses how to structure a plan for use and preservation of those species that represent a potential source for new drug development, especially those obtained from bacteria. The book also introduces some novel applications of biotechnology, such as therapeutic applications of electroporation, improving quality and microbial safety of fresh-cut vegetables, producing synthetic PEG hydro gels to be used as an extra cellular matrix mimics for tissue engineering applications, and other interesting applications.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

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