Grafting the carboxyl groups onto DPNR by seeded emulsion polymerization to enhance the compatibility with silica filler

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Abstract. The modification of deproteinized natural rubber (DPNR) with maleic anhydride (MAH) was synthesized to enhance the better compatibility between silica filler and natural rubber (NR). The presence of carboxylic acid groups (−COOH) of MAH after hydrolysis in the grafted DPNR with MAH (DP-g-MAH) would directly interact with the hydroxyl groups (−OH) of silica filler, resulting from the formation of the ester bonds due to the esterification reaction. It is leading to form the chemical bonding, which is the significantly strong interaction between DPNR and silica filler. The structural characterization of DP-g-MAH was analyzed by Fourier transform infrared spectrometer (FTIR) and proton nuclear magnetic resonance (1H-NMR), respectively. The % grafting level of MAH approximately highs to 99.37 % with the low gel content approximate 14.45 (wt%). In addition, the DP-g-MAH latex was compounded with silica nanofiller 10 phr by latex compounding method. The morphology of silica filled DP-g-MAH (DP-g-MAH/Si 10) was characterized by field-emission scanning electron microscope (FE-SEM) in order to observe the silica dispersion into the DP-g-MAH rubber. The FE-SEM shows that silica filler could disperse in grafted rubber more than the DPNR. In addition, the crosslink density was investigated to confirm the chemical networks, which could occur from esterification between DP-g-MAH and silica filler.

Keywords: modification of DPNR, silica-rubber compatibility, chemical networks

1. Introduction
The chemical modification of NR has been interested in fabricating the satisfactory materials and approaching to various applications in many industrial fields. There are plenty of monomers for grafting NR such as methyl methacrylate (MMA), methyl methacrylate-styrene (MMA-ST), and styrene (ST). Interestingly, maleic anhydride (MA) becomes attractive due to it is one another of chemicals that can improve the polarity into the NR this chemical modification has been known as malenization reaction. However, a grafting efficiency of MA onto NR is inferior comparing with other monomers due to the homo-polymerization of MA difficultly occur onto NR backbone. Thus, there might be one unit of MA grafted on each active site of the polymer chains. Since MA is not reactive due to its chemical structure, which is symmetry and electron density at C=O make it stable.

Sealao et al. used styrene as a co-monomer to enrich the reactivity of MA and found that a small amount of styrene could achieve the higher % grafting MA at the beginning of reaction (~ 2 h) [1]. However, the additional reaction time would not affect the % grafting MA, although there were present
of styrene or without styrene. The address of this result was that styrene and MA could react with each other, one-by-one molecule, to form a charge-transfer complex (CTC), which increased electrical asymmetry of the double bond of MA molecule [1]. Moreover, there are many [2-5] showed that proteins on the rubber particles were one of the interferences of the chemical grafting onto NR backbone.

Thus, to increase the grafting efficiency, the DPNR latex was chosen for the grafting polymerization. Wongthong et al. found the optimal method to synthesize the MA grafting onto DPNR backbone via a differential microemulsion polymerization (DMP) technique with grafting condition DPNR: MA: BPO (85: 9: 6) at 60°C 8 h [2]. In addition, in 2014, they have used styrene as a co-monomer for increasing the reactivity of MA and observed that the percentage of grafting efficiency (G.E) was enhanced from 71.4 to 79.3% [3]. However, there is no further research about applying the Maleinized rubber in the practical fields. That brought to the objective of this research. The introduction of some of the carboxyl groups into DPNR could achieve the esterification between rubber and silica filler, resulting in the increasing of compatibility by the occurrence of chemical networks, which would be studied.

2. Experimental section

2.1. Materials

Synthetic rubber (IR; Bangkok Synthetics Co., Ltd supported cis-1,4 polyisoprene (98%). The 60% of dry rubber content was provided by Thai rubber latex group public Co., Ltd., Rayong, Thailand. Sodium dodecyl sulfate (SDS; 95%) was purchased from Ajax finechem pty. Ltd. Urea (99%) was purchased from ACL Labscan Ltd. (Thailand). Silica (HiSil®233) was purchased from OSC Silica Co., Ltd. Benzyol peroxide (BPO; 75%) was purchased from Merck schuchardt OHG (Germany).

Maleic anhydride (MAH; 99%) was purchased from Acros Organics (Hungary). Sodium carbonate anhydrous (Na2CO3; 99.5%) was purchased from Loba Chemie Pvt. Ltd. (India). Sodium bicarbonate (NaHCO3; 99.5%) was purchased from AnalR® BDH laboratory supplies (England). Potassium hydroxide (KOH) was purchased from Ajax Finechem. Isopropanol (99.9%) was purchased from Beaker analyzed® A. C. S. reagent (USA). Formic acid, acetone and toluene analytical grade were purchased from QR® (New Zealand).

2.2. Preparation of deproteinized natural rubber graft maleic anhydride (DP-g-MAH)

The CNR, which consists of dried rubber content (DRC) 60% was diluted to 30% DRC and incubated with urea 0.1 wt% and SDS 1 wt% at room temperature for 60 min based on the work of Kawahara et al. [6]. The centrifugation 13,000 rpm 30 min (2 times) at 25 °C was required after finishing the reaction to obtain the purified DPNR latex.

First, fill 15% DRC of DPNR latex into glass reactor assembled with a reflux condenser, stirrer-hot plate, and temperature controller. The DPNR latex was stabilized with 1% (w/w) SDS, KOH and buffer solution (NaHCO3/Na2CO3). Then nitrogen gas was purged into the glass reactor for 30 min in order to prevent an oxidative reaction. After that, the reaction was heated at 60 °C to activate the BPO. Next 6 phr of BPO was inserted into the reactor and left for 5 min to generate micro-radicals into the mixture. Then 9 phr of MAH solution was slowly dropped into the reactor, using dropping funnel and left the reaction occurred in 8 h. This suitable condition was obtained from the other published work [2]. The DP-g-MAH latex was purified by high-speed centrifugation at 10,000 rpm for 5 min and redispersed with 1% (w/w) SDS, which would be used in the further mixing with silica filler by latex compounding.

The % grafting level of MAH was defined utilizing the absorbance ratio of FTIR peaks between 1720 cm⁻¹ and 836 cm⁻¹ (A1720/A836). The wavenumber at 1720 cm⁻¹ has corresponded to C=O stretching of grafted MAH and 836 cm⁻¹ was referred to =C–H deformation of main rubber chain. The calculation was based on the following equation (1).

$$\text{% grafting level of MAH} = \frac{\text{amount of MAH in sample (phr)}}{\text{amount of MAH total fed (phr)}} \times 100 \quad (1)$$
2.3. Preparation of silica filled DPNR-g-MAH latex by latex compounding method
To prepare silica solution 10 phr, silica was weight and kept stirring with speed at 800 rpm in DI water at 80 °C for 1 h. Then the hot silica solution was stirred vigorously by homogenizer with speed at 14,000 rpm for one h. The silica solution 10 phr was mixed with DP-g-MAH under mechanical agitation with speed at 1,000 rpm at 80 °C for 1 h. Then the silica filled DP-g-MAH latex was sonicated at room temperature for 1 h. Next, the silica filled DP-g-MAH latex was solidified by formic acid/acetone coagulation and leached with DI water to remove the excess acid. Finally, the sample was dried in a vacuum oven at 40 °C.

2.4. Characterization
Determination of nitrogen content of rubber, referring to the number of proteins was determined utilizing nitrogen analyzer (LECO®, model FP528). The wholly dried rubber sample was weighed approximately 0.3000 g and subjected into the machine. Then the rubber combustion was started and obtained nitrogen gas from the nitrogen compound, which was calculated and converted to numerical values from built-in software.

The chemical function was investigated by FTIR analyzer (JASCO®: model FTIR 4100 spectrometer). The purified sample, which was reprecipitated with light petroleum ether/acetone, was dissolved in chloroform (CHCl₃) to obtain 1% (w/v) solution. Then the solution was cast on KBr disc and transmitted by IR sources with 32 scans at 25 °C.

The chemical structure was investigated by ¹H-NMR (Bruker®: model 400 Ultrashield) The purified sample, which was reprecipitated with light petroleum ether/acetone, was dissolved in chloroform (CDCl₃). The sample was run under the following condition; scan number 500 scans, pulse delay time 10 sec, temperature 25 °C.

The gel content of rubber was determined using the following condition: the exacted dried rubber was weighed 0.1000 g and soaked in toluene AR grade 30 ml at room temperature for 7 days. The insoluble gel was separated by high-speed centrifugation and coagulated by methanol. Then the obtained gel was dried in an air-flow oven for 24 h. The gel content was calculated by the following eq. (2) [7].

\[
\text{Gel content (wt%)} = \frac{\text{weight of obtained gel}}{\text{weight of sample}} \times 100 \tag{2}
\]

The crosslink density of rubber was determined using a swelling test. The exacted dried rubber was weighed 0.1000 g and soaked in toluene AR grade 30 ml at 40 ± 3 °C for 48 h. The solvent would be renewable every 24 h. After that period, the swollen sample was collected and then removed the excess toluene by a cage before weighing in a capped weighing bottle. The crosslink density (υ) of each rubber film was estimated using the Flory-Rehner’s equation (3) [8-9].

\[
\nu = \frac{1}{2M_c} = \left(\ln(1 - V_r^o) + V_r^o + \chi V_r^o \nu^2 \right) / 2\rho_r V_0 \left( V_r^o \frac{1}{2} - \frac{V_r^o}{2} \right) \tag{3}
\]

where \(\nu\) is crosslink density per gram of rubber, \(M_c\) is the molecular weight between crosslinks, \(V_r^o\) is the volume fraction of the vulcanized rubber, \(\chi\) is Huggins interaction constant \(V_0\) is the molar volume of the solvent, \(\rho_r\) is the density of rubber, \(\rho_s\) is the density of solvent.

The \(V_r^o\) was obtained using equation (4) as follow:

\[
V_r^o = \frac{1}{\rho_r/\rho_s} \left( \frac{W_s - W_u}{W_0} \right) + 1 \tag{4}
\]

where \(W_s\) and \(W_u\) are weights of the unswollen rubber sample and weight of swollen rubber sample, respectively. The values of the constants used in above equation (i.e., \(\rho_r = 0.930 \text{ g/cm}^3\), \(\rho_s = 0.886 \text{ g/cm}^3\), \(V_0 = 106.9 \text{ cm}^3/\text{mol}\), and \(\chi = 0.39\)).
The silica dispersion on rubber was investigated by FE-SEM (Hitachi (SU-8010). The silica filled rubber and bare rubber were cut in a cross-section by cryogenic fracture surfaces and coated with Pt-Pd before investigated under FE-SEM [10].

3. Results and discussion

3.1. The confirmation of deproteinized natural rubber

The removal proteins of NR or DPNR was successfully prepared by Kawahara et al. method due to the urea, which is used as a protein denaturant, could change the conformation of proteins on NR particles. This physical attachment between urea and proteins on NR particles could be pulled the proteins out by the centrifugal force, which occur while washing by high-speed centrifugation. The proteins would be soluble in serum fraction, which completely separated from rubber fraction. Moreover, the confirmation of nitrogen content of DPNR is dramatically decreased to 0.044 (%wt), comparing with fresh natural rubber (FNR), which is 0.725 (%wt).

3.2. The elucidation of maleic anhydride grafting on natural rubber

Figure 1 shows the FTIR spectra of DPNR (b), which compares with DP-g-MAH (a) at reaction time 8 h. The characteristic peaks of DPNR main chain present at 1664 and 836 cm⁻¹, which are related to C=𝐶 stretching and =𝐶−𝐻 deformation, respectively. Moreover, there are additional peaks present at 1720 and 3455 cm⁻¹ that represented to C=𝑂 stretching grafted succinic acid groups and −𝑂H groups of hydrolyzed MAH grafting on DPNR, respectively. Conforming to the presence of water in DPNR latex cooperated with temperature at 60 °C, grafted MAH could be hydrolysis by water, and the open-ring of MAH would occur following the chemical equation showing in Figure 2.

![Figure 1. FTIR spectra of (a) DP-g-MAH and (b) DPNR.](image)

![Figure 2. The chemical equation of DP-g-MAH, which was hydrolysis.](image)

The % grafting level of MAH of DP-g-MAH is reported in Table 1, using the linear equation from the calibration curve (𝑦 = 0.0382𝑥) that is obtained by plotting of the absorbance ratio between wavenumber 1720 and 836 cm⁻¹ (𝐴_{1720}/𝐴_{836}) of IR blended MAH (IR/MAH) with the various concentrations of MAH (i.e., 3, 5, and 9 phr). The absorbance peaks at 1720 and 836 cm⁻¹, which
corresponded to C=O stretching of blended MAH in the samples and –C=H deformation of IR main chain, respectively. In addition, the gel content of DP-g-MAH approximates 14.45 (wt%) as shown in Table 1, which is higher than DPNR 5.50 (wt%).

Table 1. The % grafting level of MAH and gel content of DP-g-MAH.

| Grafted rubber | A\textsubscript{1720}/A\textsubscript{836} | grafting level of MAH (%) | Gel content (wt%) |
|----------------|-----------------------------|-------------------------|------------------|
| DP-g-MAH       | 0.34165                     | 99.37                   | 14.54 ± 2        |

The chemical structure of DP-g-MAH is investigated by \(^1\)H-NMR as demonstrated in Figure 3. It was found that the characteristic signals of DPNR presented at 1.68 (a), 2.04 (b, b\(^*\)), and 5.13 (c) ppm, which related to methyl, methylene, and unsaturated methine proton, respectively. Moreover, the additional signals presented the doublet signal at 2.92 and 2.93 (d) ppm of the two methylene protons and the singlet signal at 3.49 (e) ppm of the methine proton of grafted MAH rings. In addition, some chemical shifts were reported about the resonances grafted MAH on DPNR that expected the two methylene protons of grafted MAH rings at the multiple positions along the DPNR chain, such as the triplet signals at 3.64 (f) and 3.71 (g) ppm. The possible reason for this consequence was suggested that the grafted succinic anhydride could subject to the allylic carbon atom. Resulting, the two methylene protons would be deshielded in the position of the C=C bond and presented at the higher chemical shift. At 7.26 (h) ppm, the chemical shift was the chloroform-d that utilized to dissolve the rubber sample.

![Figure 3. The comparison of \(^1\)H-NMR spectra of DPNR and DP-g-MAH.](image)

3.3. The effect of silica dispersion on DPNR and DP-g-MAH
The FE-SEM micrographs of DPNR/Si and DP-g-MAH/Si 10 phr are shown in Figure 3. It could be seen that the silica filler well dispersed on DP-g-MAH than DPNR. Since, the DP-g-MAH presents the higher polarity, which corresponds to be compatible with silica filler than DPNR.
Figure 4. FE-SEM micrographs of plain DPNR (a), DP-g-MAH (b), DP/Si 10 (c), and DP-g-MAH/Si 10 (d).

3.4. The effect of chemical networks by esterification between silica filled DPNR, and DP-g-MAH

The crosslink density, used to affirm the chemical networks between silica filler and rubber, has been investigated. The result is presented in Table 2, which DP-g-MAH/Si 10 is slightly higher than DP/Si 10. Consequently, there would be the part of additional networks between silica filler and rubber, which are ester bonds of carbonyl groups (−COO−) of grafted MAH and hydroxyl groups (−OH) of the silica surface.

Table 2. The crosslink density of silica filled DPNR and DP-g-MAH.

| Silica filled rubber | Crosslink density (mol/g) \(10^{-5}\) |
|----------------------|----------------------------------------|
| DP/Si 10             | 2.85                                   |
| DP-g-MAH/Si 10       | 3.28                                   |

4. Conclusion

The DP-g-MAH is successfully synthesized according to the FTIR and \(^1\)H-NMR results and achieved the % grafting level of MAH approximately to 99.37% accompany with the low gel content around 14.45%. In addition, the silica filled grafted rubber could show the silica dispersion, which is better than the plain rubber. Resulting from the grafted rubber additionally consists of carboxyl groups (−COOH), which could interact with hydroxyl groups (−OH) on silica filler. Moreover, the crosslink density of grafted rubber is marginally increasing from 2.85 to \(3.82 \times 10^{-5}\) (mol/g). It is a consequence of the increment of chemical crosslink networks between rubber and filler. It should be noted that the value of crosslink density is obtained from the unvulcanized rubber or silica filled rubber without curing agents. If commonly used cross-linking agents have also crosslinked the rubber chains, the reinforcing efficiency would be stronger.

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