Effect of epoxidation levels on curing characteristic and mechanical properties of ENR/MFC composites

S Bhakri1,2, K Takenaka2, A Boonmahitthisud1,*, O Boondamnoen1,*

1Department of Materials Science, Faculty of Science, Chulalongkorn University, Bangkok, Thailand
2Department of Materials Science and Technology, Nagaoka University of Technology, Niigata, Japan

*E-mail: anyaporn.b@chula.ac.th* orathai.b@chula.ac.th

Abstract. This study aimed to investigate the effect of epoxidation levels on the curing and tensile properties of epoxidized natural rubber (ENR)/microfibrillated cellulose (MFC) composites. ENRs with different levels of epoxidation were first prepared from natural rubber (NR) latex via 'in situ' performic epoxidation using 0.75 M formic acid and 1 M hydrogen peroxide at 50°C at various reaction times. The results from H-1 NMR revealed that the reaction at 2, 4, and 6 hours could achieve 20, 30, and 40 mol % epoxidation, respectively. The introduction of epoxide groups into NR chains reduced the scorch and cure time along with the increase of the epoxy content. Furthermore, it was observed that the tensile strength rose remarkably at 30 mol% epoxidation (ENR30). Therefore, the ENR30 was subsequently chosen to prepare the composites with various amounts of MFC (1, 3, and 5 parts per hundred rubber, phr). Interestingly, incorporating MFC elevated tensile strength and elongation at break of ENR30. At 5 phr of MFC, the composite possessed the highest tensile strength and elongation at break value, which reached up to 31.07 MPa and 922.92%, respectively.

1. Introduction

Undoubtedly, the profitability of natural rubber (NR) has been contributing in many aspects, including automotive parts, medical devices, sport, and households. It is notable due to its attractive properties (e.g., toughness, high impact, tear strength, exceptional flexibility, high resilience, low hysteresis, and good formation) [1]. Besides, the unsaturated non-polar hydrocarbon along in the repeating unit of NR leads to some drawbacks such as poor ozone, weathering, thermal resistance, oil resistance, and adhesion with polar substances [2]. The introduction of polar groups onto the NR backbone is one of the most successful strategies to tackle these problems. Epoxidation by incorporating the epoxide groups into NR molecular chains is an uncomplicated and effective method to upgrade the polarity of NR [3]. Conceptually, the NR latex is ‘in situ’ epoxidized with peracids generated from hydrogen peroxide and formic acid in order to yield the epoxidized natural rubber (ENR) [4]. The double bonds (C=C) in NR are randomly transformed into epoxide groups along the molecular chains. Consequently, the novel and beneficial properties of NR are obtained while nurturing the elasticity of NR at the specific level of epoxidation. The presence of random epoxy rings in the NR chains imparts a pronounced influence to the oil resistance which even better than synthetic elastomer [5]. Furthermore, due to the strain-induced crystallization (SIC) ability, the tensile strength notably increased at the particular epoxy level as
compared to the original NR [6]. Therefore, it is highly required to study the effects of epoxidation levels of ENR on the curing and mechanical properties aiming to obtain the desired characteristics.

However, the reinforcing fillers are crucially applied to achieve the desired properties and expand the commercial applications in the rubber industries. The non-renewable inorganic minerals such as carbon black, silica, calcium carbonate, and clay have been far-famed as the commercial fillers in NR [7]. Nonetheless, the primary concern of reducing the non-renewable source of raw material has been issued at present. The researchers have attempted to discover alternative renewable materials that able to displace it. The benefits of renewable organic fillers are low cost, less abrasive, fewer hazards, lower specific weight, and biodegradability as compared to non-renewable fillers [8]. Among the renewable organic fillers, microfibrillated cellulose (MFC) is highly possible as a great candidate for reinforcing NR. MFC has some superior properties that benefit for reinforcement reasons, including high strength, stiffness, and low weight [9]. Owing to its long fibril characteristic, entangled cellulose nanofibers, and interconnected web-like structure, the MFC could improve the composite toughness [10]. In addition, the MFC has been declared to denote high interfacial bonding between the resin and fibers since its high aspect ratio coupled with abundant hydroxyl groups on the surface.

Therefore, the current research was aimed to investigate the influence of epoxy level (20, 30, and 40 mol% epoxidation) of ENR and subsequently determine the optimal tensile properties to prepare the composites with MFC at various amounts.

2. Chemicals and Methodology

2.1. Chemicals

NR latex (60 wt% DRC), Terric 16A-6, voltamol, bentonite, and the compounding chemicals including zinc oxide, stearic acid, n-cyclohexyl-2-benzothiazyl sulphenamide (CBS), and sulfur were obtained from the Rubber Research Institute of Thailand (Bangkok, Thailand). 98 wt% formic acid and 35 wt% hydrogen peroxide were purchased from ThermoFisher Scientific and SOLVAY, respectively. Sodium carbonate (Na$_2$CO$_3$) was purchased from KEMAUS. MFC (10 wt%) was donated by Daicel FineChem Ltd. (Japan).

2.2. Synthesis of ENRs

The ENRs were synthesized by reacting the NR with performic acid via ‘in situ’ epoxidation. The NR latex was initially diluted with distilled water to achieve 20 wt% DRC before stabilizing with 3 phr of Terric 16A-16 for one hour at 40°C. The 0.75 M of formic acid was subsequently dropped into the reaction. Prior to add the 1 M of hydrogen peroxide, the reaction temperature was risen to 50°C. The reaction was carried out for 2, 4, and 6 hours to produce the different three levels of ENRs. The obtained ENRs were then coagulated with methanol, thoroughly washed with distilled water, immersed in 5% of Na$_2$CO$_3$ solution to neutralize before drying at 60°C for approximately 48 h.

2.3. Preparation of ENR30/MFC composites

The composites were prepared by latex mixing. The MFC dispersion (3 wt%) at various amounts (1, 3, and 5 phr) was mixed with the ENR with 30 mol% epoxidation (ENR30) using a high-speed mixer at 300 rpm for 30 minutes. Subsequently, the obtained ENR30/MFC latex suspensions were precipitated by methanol. The coagulum was further soaked in Na$_2$CO$_3$ solution, washed with distilled water, and dried in an oven at 60°C for 48 h. The dried ENR30/MFC compounds were used to prepare the composites in the next step.

2.4. Preparation of rubber compound and vulcanizate

The NR, ENRs, and ENR30/MFC compounds were prepared by mixing with ZnO (5 phr), stearic acid (2 phr), sulfur (2 phr), and CBS (1 phr) via an internal mixer (Chareontut, MX500-D75L90) at 60°C and rotor speed at 25 rpm for 9 minutes. It was then followed by a two-roll mill (LabTech Engineering,
LRM-110) for 3 minutes at room temperature for sheeting. The flat sheets were cured by compression molding at 150°C for the obtained optimum curing time ($t_{oo}$) from MDR characterization.

### 2.5. Characterization

The epoxidation degree of ENRs was analyzed by proton nuclear magnetic resonance (1H NMR) using a Bruker Fourier 300 NMR spectrometer operating at 300 MHz. The sample was prepared by dissolving in CDCl$_3$. In order to calculate the mol% epoxidation of the obtained ENRs, two specifics of 1H NMR peaks were considered with the following equation;

$$\text{Mol\% epoxidation} = \left[ \frac{A_{2.7}}{A_{2.7} + A_{5.14}} \right] \times 100 \quad (1)$$

where

- $A_{2.7}$ = Peak integral at 2.7 ppm representing methine proton of the epoxide group
- $A_{5.14}$ = Peak integral at 5.14 ppm representing olefinic proton of unreacted NR

The cure characteristics of the compounded rubber was measured using a moving die rheometer (rheoTECH MD+) according to ASTM D2084-93. Approximately 3.5 g of the sample was placed between a pair of rotating discs at 150°C for 10 minutes. The minimum torque ($M_L$), maximum torque ($M_H$), torque difference ($M_H - M_L$), scorch time ($t_s$), and 90% of cure time ($t_{90}$) were then investigated. Five dumb-bell specimens of each sample were prepared. The tensile properties were determined as tensile strength, modulus at 300% strain ($M_{300}$), and elongation at break using a universal testing machine (Tinius Olsen-5ST) with a 5 kN load cell at a cross-head speed of 500 mm/min in accordance with ASTM 412 (type D).

### 3. Results and discussion

#### 3.1. The epoxidation levels of the obtained ENRs

The formation of epoxide rings was proven by the 1H NMR analysis. The 1H NMR spectra of the obtained ENRs revealed two distinctive peaks at 2.84 and 1.37 ppm, which were assigned to oxirane methine proton and methyl protons of epoxide ring, respectively, while the peak at 5.14 ppm was related to the olefinic hydrogens of the unepoxidized NR (Figure 1) [11]. To be intensely noted, the presence of both characteristic peaks on the 1H NMR spectrum of ENR30, which were not identified in the 1H NMR spectrum of NR, confirmed that the certain amount of C=C bonds of NR molecule were completely switched by epoxide. The epoxide content of ENRs was calculated from the intensity ratio of the signals at approximately 2.7 and 5.1 ppm. Equation 1 estimated to determine ENR20, ENR30, and ENR40 were 19.3, 30.6, and 43.6 mol%, respectively.
Meanwhile, there are some factors affecting the obtained epoxidation degree of ENR including reaction times. Figure 2 revealed that by increasing the reaction times, releasing the generated oxygen atoms from performic acid onto carbon double bond of NR molecular chains was succeeded in increment of epoxy degree. This is mainly caused by the performic acid could react with each repeating unit of the NR chains for a longer time [10].

Figure 2. Effect of reaction times on epoxidation degree

3.2. Curing characterization
The cure characteristics ($t_{90}$, $t_{s2}$, $M_L$, $M_H$, and $M_{H-L}$) of the samples are listed in Table 1. It can be clearly seen that the ENR40, the highest epoxy level in this research, denoted the shortest scorch time ($t_{s2}$) under the same condition, while, NR has the longest $t_{s2}$. This indicated that the amount of epoxide group could upgrade the activation of the nearby double bond to transform into free radical; therefore, it shortened the $t_{s2}$ [12]. The $t_{90}$ of NR is the longest among the samples due to the highest level of double bonds in NR, which requires a longest time to achieve the optimal sulfur vulcanization reaction [13]. Surprisingly, in case of ENRs, the $t_{90}$ of ENR40 slightly increased. This might be because of the very high amount of epoxy induces high polarities of ENR, which impedes the vulcanization [14].

Table 1. The cure characteristic and mechanical properties data of samples

| Samples   | $t_{90}$ | $t_{s2}$ | $M_L$ | $M_H$ | $M_{H-L}$ | Tensile Strength (MPa) | Elongation at Break (%) | M300 (MPa) |
|-----------|---------|---------|-------|-------|-----------|------------------------|------------------------|------------|
| NR        | 7.63    | 5.09    | 0.74  | 6.06  | 5.33      | 20.03±0.8              | 760.89±75.3            | 3.33±0.5   |
| ENR20     | 3.39    | 1.51    | 0.84  | 6.48  | 5.64      | 22.67±0.7              | 744.52±99.7            | 4.13±0.7   |
| ENR30     | 2.86    | 1.47    | 1.03  | 5.15  | 4.12      | 25.17±1.4              | 741.10±77.4            | 4.56±0.4   |
| ENR40     | 4.34    | 1.25    | 1.21  | 5.70  | 3.37      | 22.42±1.4              | 710.12±26.2            | 4.62±0.3   |
| ENR30/1-MFC | 4.96  | 2.26    | 0.53  | 7.03  | 6.50      | 27.32±0.5              | 906.37±11.8            | 4.39±0.1   |
| ENR30/3-MFC | 4.69  | 2.00    | 0.56  | 7.86  | 7.31      | 29.55±0.7              | 908.48±24.2            | 4.76±0.1   |
| ENR30/5-MFC | 4.25  | 1.68    | 0.92  | 9.55  | 8.63      | 31.07±0.9              | 922.92±23.9            | 5.25±0.2   |

Compared with the neat ENR30, the addition of MFC increased $t_{s2}$ and $t_{90}$ of ENR30 because the MFC may participate in the vulcanization reaction. The massive amounts of hydroxyl (-OH) groups on the MFC surfaces absorbed the basic accelerator species resulted the reduction of accelerator efficiency [15]. In addition, -OH groups on the MFC surface limited the free radicals mobility which was generated during vulcanization, a longer $t_{s2}$ and $t_{90}$ were observed [16]. However, at the very high loading of MFC, 5 phr, -OH groups on the MFC surface may create strong interaction with the epoxy ring of ENR.
resulting in the reduction the number of unbounded -OH groups, as a consequence, the amount of absorbed accelerator on the MFC surface was less. Therefore, the low \( t_{12} \) and \( t_{50} \) of composites were attained [15].

In addition, the \( M_L, M_H, \) and \( M_{II}-M_L \) value of composites gradually increased with increasing the content of MFC. At 5 phr MFC, the \( M_L \) slightly lower than neat ENR30 indicating that the MFC reduced the viscosity of uncured ENR. Moreover, at this point, both \( M_H \) and \( M_{II}-M_L \) of composite represented higher than neat ENR30, indicating higher elastic modulus and crosslinking density. The increase of \( M_{II} \) values is related to the increase of the stiffness and hardiness of the cured composite, which may be due to the restriction of chain mobility by MFC [17]. Similarly, the elevation of \( M_{II}-M_L \) may be provided by the strong interaction between ENR30 and MFC, as previously mentioned.

3.3. Mechanical properties of ENRs and composites

The tensile properties of samples are tabulated in Table 1, which depicted the tensile strength increased concurrently with increasing the epoxy degree of ENRs from 0 to 30 mol% epoxidation. This was mainly due to the increase of physical crosslinks from the epoxide groups interaction in ENR, meanwhile, at these levels, the strain-induced crystallization (SIC) is still able to take place during stretching. However, at very high epoxy level (ENR40), the SIC ability declined and thus weakened the mechanical properties [18]. That is why the ENR30 revealed a higher value of tensile strength than that of NR, ENR20, and ENR40. The elongation at break of NR exhibited the highest value since its chains are more flexible compared to ENRs [13]. Conversely, the trend of modulus moderately increased with the increase of epoxidation degree owing to higher crosslinking level in the molecular chain and inflexible structure of epoxy rings [6].

To prove the reinforcement effect of MFC, the mechanical properties of composites were also examined under the same condition with NR and ENRs. The ENR30 was selected as a matrix due to its highest tensile strength. Clearly, the inclusion of MFC in ENR matrix induced the raising values of the tensile strength, elongation at break, and M300 as compared to the neat ENR30. At the highest MFC loading, 5 phr, the considerable improvement in tensile strength was obtained, from 25.17 to 31.07 MPa as compared to the neat ENR30. This result was ascribed to the robust interfacial interactions between ENR and MFC via hydrogen bonding. Therefore, the rubber chains withstand to deformation as the chains are hold more tightly [19]. Meanwhile, the addition of MFC might not change the flexibility of ENR30 due to the insignificant increment in M300 value. In fact, in terms of elongation at break, it can be generally seen that NR exhibited the higher elongation at break compared to ENRs. Nevertheless, the incorporation of MFC at 5 phr exceptionally improved the elongation at break by about 24%. It is fascinating to note that the high aspect ratio and long flexible fibril of MFC might be not only imparted the hydrogen bonding but also filler entanglements. It results in prevention the growth of cracks in nanocomposites and improvement the interfacial adhesion between the ENR matrix and MFC [20, 21]. Hence, it was indicated that MFC have vivid influence in increment the elongation at break of composites.

Conclusions

The ENRs with three levels of epoxidation (ENR20, ENR30, and ENR40) were successfully prepared by varying the reaction times. The reduction of scorch and cure time were found as the epoxy levels were increased. Moreover, the existence of epoxide groups in NR could incline the tensile strength and M300 from 20.03 and 3.33 MPa of NR to 25.17 and 4.56 MPa of ENR30, along with an insignificant decrease in elongation at break. Furthermore, the addition of MFC at 5 phr induced the enhancement in tensile strength and elongation at break of ENR30 due to the formation of hydrogen bonding between ENR and MFC and filler entanglement. Therefore, the MFC could potentially act as an excellent filler for ENR.
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