Effect of maleated natural rubber on tensile strength and compatibility of natural rubber/coconut coir composite

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Abstract. Natural rubber (NR)/coconut coir (CF) composites were fabricated using co-rotating twin screw extruder with maleated NR (MNR) used as compatibilizer. The MNR was produced at three level of maleic anhydride (MA), and analyzed qualitative and quantitatively using FTIR and titration technique. Analysis on MNR using FTIR and titration methods showed that MA was grafted on NR chain at different percentage (0.76, 2.23, 4.79%) depended on MA concentration. Tensile strength data showed the best tensile strength was produced at 7 phr of MNR with 1 phr of MA level in MNR resulting 16.4 MPa. The improvement of compatibilized samples were more than 300% compare to uncompatibilized composite attributed to better interfacial bonding. The improvement on tensile strength was significantly influenced by MNR level and amount of MA added to produce MNR, as well as their interaction. The optimum conditions for producing NR-CF composite were predicted at 6.5 phr of MNR level with 1 phr of MA concentration added in MNR production, regardless screw rotation settings. Results from verification experiments confirm that developed model was capable of describing phenomena during composite preparation. Morphology analysis using scanning electron microscopy shows smooth covered fiber in compatibilized samples than that of without MNR. The morphology also showed less voids on compatibilized samples attributed to better interfacial bonding leading to tensile strength improvement.

1. Introduction

Natural fibers (NF) have been studied as reinforcement in composites due to its availability, environmental benign, and renewable. One of NF that widely applied in many applications is coconut coir [1-5]. It could be applied in range of application such as building, automotive, and packing materials [3] using wide range matrix variation ranged from thermoplastics [1, 2, 6, 7], thermosets [8-10], or rubbers [11-13]. It is also low density with high strength and elongation at break [14, 15]. This is beneficial to produce lightweight product with high performance. However, the coconut coir should be treated properly to improve mechanical [1, 8, 16, 17], thermal [17], and flammability [1] properties of composite.

In composite preparation, natural rubber (NR) is a material commonly used as matrix [11, 13, 18-20]. The combination between NR and natural fiber as coconut coir was good combination to produce strong but elastic material. The NR composites could be fabricated using solid processing techniques as roll mill or mixer [21, 22]. Despite its popularity, NR composite fabrication using roll
mill had low dispersion of fiber, while batch processing was time consuming. On the other hand, extruder might produce better filler dispersion and improve mechanical properties [23, 24]. It also had higher production rate than mixer due to continuous process. However, there was limited study on the use of extruder for preparing NR composites. Therefore, it is of interest to better understand the use of extruder on NR composite preparation.

To improve interfacial bonding and mechanical properties, compatibilizer was commonly added. One of compatibilizer popularly produced was maleic anhydride (MA) grafted on polymer backbone. It was evidenced that the addition of MA based compatibilizer would increase mechanical properties. Maleated natural rubber produced in internal mixing improved tensile strength about more than 10% for natural rubber composite [25-28]. Higher improvement was obtained by grafting polymerization in torque rheometer [29], combining liquid natural rubber (LNR) and Polyethylene grafting MA to improve HDPE/NR/aramid composite [22], and modifying maleated natural rubber (MNR) with zinc acetate using solution technique [30]. The disadvantages of available techniques are time consuming and not environmental friendly due to solvent consumption. Therefore, our previous work studied the application of extruder to produce MNR [31]. However, there is limited information about amounts of compatibilizer and MA content, as well as their interactions in NR composite preparation using extruder. Moreover, as higher MA content produces higher gel content on compatibilizer thus decreases composite mechanical properties [32], it is beneficial to study the amount of MA in compatibilizer to produce the highest mechanical properties of NR composites.

This research aims to explore the composite of coconut coir and natural rubber with maleated NR (MNR) as the compatibilizer. The MNR was fabricated using twin screw extruder and characterized qualitative and quantitatively using FTIR and titration method. The composite samples were prepared according to three levels and three factors Box-Behnken experimental design. The effect of various level of MNR, amount of MA added in MNR preparation, and screw rotation on tensile strength were analyzed and optimized. The effects of MNR on sample morphology were observed using Scanning Electron Microscopy.

2. Materials and Methods
2.1. Materials
Natural rubber (NR), Standard Indonesia Rubber (SIR) 20, produced by Indonesian local company, Aneka Bumi Pratama, Palembang was used as matrix. Compatibilizer used in this research are maleated natural rubber (MNR) produced in our laboratory. Coconut fiber (CF) was obtained from local producer in Indonesia. Commercial grade additives were purchased from local supplier in South Tangerang, Indonesia. Butylated hydroxyl toluene (BHT) as antioxidant, zinc oxide (ZnO) as
activator, N-cyclohexyl-2-benzothiazole sulphonamide (CBS) as accelerator, and sulphur (S) were used as vulcanization agent.

2.2. MNR Preparations

MNR was produced by grafting MA molecules on NR using shearing action in a twin screw extruder Collins ZK 25. Various MA concentrations namely 1, 8 and 15 phr were used to produce three different percentage of grafted MA. Chemical initiators was not used to minimize gel content and difficulties in characterization and processing [33]. Process parameters used in extruder are summarized in Table 1.

Table 1. Processing Conditions Applied in Twin Screw Extruder

|   | T1 | T2 | T3 | T4 | T5 | T6 | T7 | T8 |
|---|----|----|----|----|----|----|----|----|
| Screw Rotation | 40 | 160 | 165 | 170 | 175 | 180 | 185 | 190 | 40 |

2.3. Qualitative and Quantitative Analysis of MNR

Grafted MA in MNR was analyzed qualitative and quantitatively according to methods reported in our previous study [31]. The conversion of carboxylic acid concentration to grafted MA content was done as follows [34]:

\[
MA (wt\%) = \frac{(V_0-V_1) \times N \times Mr}{2W} \times 100\%
\]  

(1)

where N is the concentration of NaOH (mol/L) in methanol. \(V_0\) and \(V_1\) are the volumes of NaOH used in blank test and the test with sample, respectively. Mr is the MA molecular weight (98 g/mol). W (g) is the weight of MNR sample.

Qualitative analysis of functional groups of MNR was conducted using FTIR Bruker Tensor 27 spectroscopy. The MNR samples were pressed and melted at 180 °C, 10 ton pressure, for 10 min. The FTIR spectra were recorded using ATR in the range of 4000 – 500 cm\(^{-1}\).

2.4. Composite Preparations

The coconut fiber was immersed using NaOH at 5% concentration for 1 h before composite preparations. It was then washed using distillated water and dried at 100 °C for 1 h. The treated fiber was then cut and sieved with maximum 1 cm in length.

Mixing of NR and CF was done using a co-rotating twin screw extruder Collins ZK 25. The samples were prepared according to Box-Behnken experimental design (DoE) 15 combinations. Dependent variables used in this work were MNR level, MA concentration in MNR preparation, and
screw rotation. 2 phr of BHT was added as antioxidant to avoid rubber degradation during processing. Variables used in this research are shown in Table 2.

### Table 2. Experimental Conditions

| No | Sample             | MNR level (phr) | MA in MNR Preparation (phr) | Screw Rotation (rpm) | Fiber Content (phr) | BHT level (phr) |
|----|--------------------|-----------------|-----------------------------|----------------------|----------------------|-----------------|
| 1  | NR                 | -               | -                           | 70                   | 0                    | 2               |
| 2  | NR-CF w/o MNR      | 4               | 8                           | 70                   | 30                   | 2               |
| 3  | NR-CF1             | 4               | 8                           | 100                  | 30                   | 2               |
| 4  | NR-CF2             | 7               | 8                           | 100                  | 30                   | 2               |
| 5  | NR-CF3             | 1               | 1                           | 70                   | 30                   | 2               |
| 6  | NR-CF4             | 7               | 8                           | 40                   | 30                   | 2               |
| 7  | NR-CF5             | 1               | 8                           | 40                   | 30                   | 2               |
| 8  | NR-CF6             | 7               | 1                           | 70                   | 30                   | 2               |
| 9  | NR-CF7             | 4               | 8                           | 70                   | 30                   | 2               |
| 10 | NR-CF8             | 4               | 4                           | 40                   | 30                   | 2               |
| 11 | NR-CF9             | 12              | 15                          | 70                   | 30                   | 2               |
| 13 | NR-CF11            | 4               | 15                          | 40                   | 30                   | 2               |
| 14 | NR-CF12            | 4               | 15                          | 100                  | 30                   | 2               |
| 15 | NR-CF13            | 1               | 15                          | 70                   | 30                   | 2               |
| 16 | NR-CF14            | 4               | 8                           | 70                   | 30                   | 2               |
| 17 | NR-CF15            | 4               | 1                           | 100                  | 30                   | 2               |

The extruded material was mixed with another additives using Huicai roll mill. The material was first rolled at 40 °C and 60 rpm for 10 min. After rolling, 5 phr of ZnO was added and rolled for 10 min. It was followed by mixing 2 phr of CBS to the material for 10 min. Vulcanization was done by mixing the rubber compound to 5 phr of sulphur for 30 min.

Composite samples were prepared from the rolled material using hot press Collins P300 P. The rolled compound was preheated at 150 °C without pressure for 5 min for softening the rubber. It was then pressed at 150 °C, 15 Bar for 10 min, and cooled at 25 °C for 25 min. All samples were conditioned for minimum 24 h before testing.

#### 2.5. Composite Characterizations

Tensile tests were carried out to all samples and referred to ASTM D 412 type C. Tensile testing was carried out using universal testing machine Shimadzu AGS10 kNG at 500 mm/min of crosshead rate. Sample morphology was observed for untested selected samples. Analysis was performed using scanning electron microscope (SEM) model JEOL JSM-6510LA with 20 kV of accelerating voltage. Sample surfaces were platinum coated before analysis to minimize charging.
2.6. Modelling on Tensile Strength
Analysis on the effect of each variable on tensile strength was done according to statistical model using Minitab software. The model was developed from collected tensile strength data and regressed using polynomial equation as follows:

\[ y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j \]  

(2)

Where \( y \) is the model response, \( x_i \) and \( x_j \) are independent variables, and \( \beta_0, \beta_i, \beta_{ii}, \) and \( \beta_{ij} \) are the coefficients for the constant, linear, quadratic terms, and interactions, respectively. The model was developed by only considering significance variables (p-value < 0.05) (Table 3). The less p-value suggests that the effect of term is more significant to influence tensile strength.

3. Results and Discussions
3.1. Characteristics of MNR

Figure 1. FTIR Spectra for MNR sample

Figure 1 shows FTIR spectra for MNR with 8 phr of MA content. The MNR was selected because it was at middle position between the highest and lowest level of MA content. The spectra was focused in the range of 600 to 2000 cm\(^{-1}\) as reported in previous studies that the typical peak of MNR were observed in these ranges [28, 29, 34-36]. The absence of peak at 693 cm\(^{-1}\) suggested that MNR was
successfully purified. The present of specific peak at 1785 cm$^{-1}$ and 1850 cm$^{-1}$ reflects symmetric (strong) and asymmetric (weak) C=O stretching vibration of succinic anhydride [28, 34] that suggests the presence of grafted MA onto NR.

The percentage of grafted MA on NR for each compatibilizer was shown in Figure 2. In general, grafted MA increased linearly as higher MA amount. The trend was similar to that of reported by another researchers [28]. This might be attributed to the absent of initiator during the MNR preparation that avoid to produce crosslink reaction among NR molecules. As a result, the interaction possibility of MA and NR chain through free radical reaction was higher. The lower percentage of grafted MA in this research than others [28, 37] might be attributed to different equipment used to produce MNR. The extruder used in this study was not able to facilitate longer mixing time, as it is influenced by screw rotation. On the other hand, mixing time can be controlled in mixer, so it facilitates longer reaction time.

3.2. Modelling on Tensile Strength

![Figure 3. Tensile Strength for All Samples](image-url)
Table 3. P-value of Developed Model for Tensile Strength

| Terms                          | P-Value | Note   |
|-------------------------------|---------|--------|
| Regression                    | 0.006   | Significant |
| Linear                        | 0.003   | Significant |
| MNR level                     | 0.001   | Significant |
| MA in MNR Preparation         | 0.021   | Significant |
| Square                        | 0.013   | Significant |
| MNR level * MNR level         | 0.013   | Significant |
| Interaction                   | 0.003   | Significant |
| MNR level * MA in MNR Preparation | 0.003 | Significant |

The developed model to predict tensile strength was presented as follows:

\[
\text{Tensile strength} = 9.67 + 1.88 \times \text{MNR level} - 0.24 \times \text{MA in MNR} - 0.14 \times \text{MNR level} \times \\
\text{MNR level} - 0.07 \times \text{MNR level} \times \text{MA in MNR}
\]  \hspace{1cm} (3)

The present of quadratic term for MNR level in the model suggested that the optimum value may be predicted in boundary ranges. On the other hand, the absence of quadratic term for MA concentration in MNR suggested that the effect of this factor was linear.

The absence of screw rotation in the model suggested that this factor was not significant to influence tensile strength. The insignificant effect of screw rotation might be due to uncontrollable mixing time in extruder. Low rpm produced longer residence time and facilitated longer reaction time. However, the low rpm would not produce shear as high as the high rpm. As a result, in low rpm, the reactive chain may be less. On the other hand, the high rpm would generate higher shear and produce more reactive chain, but it was not able to provide optimum reaction time.

![Figure 4. Surface Plot Effect of MNR Level and MA in MNR](image-url)
Figure 4 describes effect of MNR level and MA in MNR interaction. At low MNR level (1 phr), the strength increased as higher MA concentration in MNR attributed to higher percentage of grafted MA (0.76 to 4.79%). On the other hand, the property decreased as higher MA in MNR (0.76 to 4.79%) at high MNR level (7 phr). This might be attributed to the migration of MNR to fiber, causing self-entanglement and resulting slippage [22]. These suggested that optimum percentage of grafted MA in final composite formulation should be considered as a crucial factor rather than single factor (MNR level or MA in MNR only).

![Figure 4.](image)

**Figure 5.** Response Optimizer Plot for Tensile Strength

The optimum conditions to produce tensile strength were predicted using response optimizer plot, shown in Figure 5. Screw rotation was not shown and optimized due to insignificant effect on strength as explained above. The plot suggests that the best tensile strength in applied boundaries are 6.5 phr of MNR level and 1 phr of MA concentration in MNR, at screw rotation 40 to 100 rpm, giving value of 15.6 MPa.

In order to verify the developed model, two additional experiments were performed. One experiment was carried out at optimum condition, while the other was done at random settings. 40 rpm was applied to produce sample at optimum condition (verification 1), because it needs less energy than at higher rpm. Random experiment (verification 2) was chosen in any condition within the boundary as proof of reproducibility.

| Sample       | MNR level (phr) | MA in MNR (phr) | Screw Rotation (rpm) | Prediction (MPa) | Actual (MPa) | Error (%) |
|--------------|-----------------|-----------------|----------------------|------------------|--------------|-----------|
| Verification 1 | 6.5             | 1               | 40                   | 15.6             | 15.2         | 3%        |
| Verification 2 | 7               | 1               | 100                  | 15.5             | 15.8         | 2%        |
Table 4 shows settings applied to confirmation experiments. The results show that errors for both selected and randomly chosen experiments were less than 5% for all verification samples. These suggest that the model is capable of describing effects of processes and formula phenomena. Marginal difference in prediction of tensile strength (0.1 MPa) for optimized and verification 2 sample suggested that the effect of 0.5 MNR level was not significant to change tensile strength. This was also shown in Figure 5 that present flat region in the range of 6 to 7 phr MNR level. Moreover, the actual difference on tensile strength of verification samples shows 0.6 MPa. The value was lower than the standard deviation of mid-setting (NR-CF1, NR-CF8, NR-CF14) resulted 1.4 MPa. By considering insignificant effect of screw rotation (Section 3.2), this confirms result on modeling that shows insignificant difference between 6 and 7 of MNR level.

3.3. Compatibility of Natural Rubber / Coconut Coir

![Sample Morphologies at 300x Magnification](image)

(a) Rubber without filler, (b) NR-CF Composite without MNR, (c) Verification 1, (d) Verification 2

Figure 6. Sample Morphologies at 300x Magnification: (a) Rubber without filler, (b) NR-CF Composite without MNR, (c) Verification 1, (d) Verification 2

Morphology observations were done for selected samples, namely rubber, NR-CF composite without MNR, and verifications. The sample morphologies were shown in Figure 6. In general, the
fiber morphologies of both verification samples (Figure 6 (c) and (d)) were covered smoothly than that of composite without MNR (Figure 6 (b)) suggested improvement in interfacial bonding. The reason behind this is the compatibility between MNR and NR which has similar backbone. Meanwhile, the grafted MA might effectively react to hydroxyl functional group of bio fiber, as reported elsewhere [38, 39]. Moreover, by this chemical bonding, less voids was produced due to strong matrix fiber interaction for compatibilizer samples. As a result, stress could be transferred effectively from matrix to fiber leading to improvement in strength.

4. Conclusions
Natural rubber/coconut fiber composites were fabricated using twin screw extruder with MNR as compatibilizer. Qualitative and quantitative analysis on MNR samples show that maleic anhydride molecule was grafted on NR chain suggested that MNR was successfully produced. Analysis on collected tensile strength data showed that effect of MNR level and amount of MA in MNR were significant to improve tensile strength. On the other hand, there is no effect of screw rotation on tensile strength due to uncontrollable mixing time. Developed equation shows interaction between MNR level and amount of MA in MNR to improve tensile strength, with optimum conditions predicted at 6.5 phr of MNR level and 1 phr of MA concentration in MNR, regardless screw rotation settings. Analysis on the sample morphology showed that the improvement on tensile strength was influenced by the matrix fiber compatibility leading to better interfacial bonding.

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