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## Grafting of Maleic Anhydride onto Cyclized Natural Rubber in the Melt Phase: the Effect of Trimethylol Propane Triacrylate

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**Abstract.** The grafting product of maleic anhydride onto cyclized natural rubber have been produced in the presence of trimethylol propane triacrylate comonomer which is processed in an internal mixer 150°C 80 rpm. In this research, the ratio of Tris / maleic anhydride used is 1: 2; 1: 1 and 2: 1. All grafted product was purified to determine the degree of grafting for each graft product by the titration method. The degree of grafting increases with increasing trimethylol propane triacrylate mole ratio. The highest degree of grafting is obtained in moles ratio of 2: 1 which is to 5.88%.

### 1. Introduction

These Cyclized natural rubber (CNR) can be produced through cyclization reaction by treatment natural rubber with hard acids<sup>1</sup> (such as sulfuric acid, p-toluene sulphonic acid) or Friedel-Crafts catalyst such as FeCl<sub>3</sub>, SnCl<sub>4</sub>, TiCl<sub>4</sub><sup>2</sup>. In such a reaction, the rubber loses its elasticity and turns into a hard and brittle material. The average size of the cyclical structure formed during the cyclization process was found was not depends on the concentration of the rubber and the catalyst but was depends on the reaction temperature. The double bonds still present in the CNR products are less than 20%<sup>3</sup>.

CNR has poor adhesion properties to polar molecules/surfaces. To improve the adhesion of CNR to the polar surface and its stability it is necessary to modify the chemical structure so that the CNR product can further be utilized in the wider field. Chemical modification by grafting of monomers has been widely performed to produce products following the desired specifications. The technique of grafting is a relatively simple and easy and widely applied technique. Various substances have been used as graft monomers in various types of polymer chains using grafting techniques<sup>4</sup>.

Maleic anhydride (MA) is one of the most widely used monomers to modify polymeric materials to produce high performance, high quality natural and biotechnical (nanoengineering) materials, both natural and synthetic polymers, such as polypropylene<sup>5</sup>, natural rubber<sup>6-8</sup>, paraffin<sup>9</sup> and polybutadiene<sup>10</sup>. The use of MA has improved the properties of thermoplastic polymer graft



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copolymerization such as polyolefins, polystyrene, polyamide and also biodegradable polymers, polysaccharides and natural and synthesis rubber<sup>4</sup>.

Grafting of polar maleate increases the polarity of CNR. The presence of maleic groups is expected to improve the interface adhesion properties and their compatibility to polar and metal polymeric materials and their mixtures. Grafting of AM onto non-polar polymer chain has overcome the weakness of the interface adhesion to the polar surface. This not only increases the hydrophilicity of the polymer surface for printing and coating applications but also the adhesion and compatibility of these polymer to polar polymers such as polyamides, metals, and glass fibers. The maleic functionalized polymer also used as a compatibilizer in polymer blends.<sup>11-12</sup>

Reactive processing in the melt phase using an extruder and/or internal mixer has been developed by many researchers on grafting MA onto polypropylene<sup>4,5,13-16</sup> polyethylene<sup>17-20</sup> polystyrene<sup>21</sup>, natural rubber<sup>7</sup>, cyclized natural rubber<sup>22</sup> in which some succeed in commercially product.

In general, the grafting degree of MA onto the polymer chain is low since MA has a low reactivity due to the lack of dual bond electron density. To increase the grafting degree of MA on the polymer chain some researchers used a comonomer/coagent. The addition of the comonomer is intended as a donor electron to activate the MA monomer in the polymerization reaction of the graft. Trimethylol propane triacrylate is a comonomer that has been used to increase the grafting degree of AM onto polypropylene polymers<sup>23</sup> and natural rubber.<sup>24</sup>

The studies on the grafting of MA onto CNR in the melt phase by using trimethylol propane triacrylate comonomers have not been reported. In this study, we performed the grafting of MA onto CNR in the melt phase in an internal mixer in the absence and presence of a trimethylol propane triacrylate comonomer.

## 2. Experimental

### 2.1 Material

The chemicals used were commercial-grade; ethanol, methanol, xylene, trimethylol propane triacrylate supplied by Merck, Germany; maleic anhydride is supplemented by Riedel-de Haen, Seelze, Germany. CNR produced by Industri Karet Nusantara (Nusantara Rubber Industry) Indonesia.

### 2.2 Procedures

#### 2.2.1 Preparation of Plasticorder Brabender Internal Mixer

Grafting of MA onto CNR were performed in an internal mixer of Brabender Plasticorder PLE 331 Duisberg Germany, with and without trimethylol propane triacrylate comonomers. It was first setting the operational temperature 150°C and the internal rotor speed 80 rpm, following the experimental design of the study to be carried out. The internal mixing device can be used for the grafting process once the chamber temperature is following the experimental design.

#### 2.2.2 Grafting MA onto CNR

In the absence of a trimethylol propane triacrylate comonomer, the 30 grams of CNR loaded into the chamber slowly and left for about 4 minutes until completely melted. Then added some 16 phr (per hundred rubber) MA into the chamber so that it is mixed and undergoes a grafting reaction for 8 minutes. The process is stopped by pressing the STOP button. Furthermore, in hot conditions, the grafting product is removed quickly from the chamber. After it is cool, it is made into granules form. The same procedure was done with the presence of trimethylol propane triacrylate comonomer with Tris/MA mole ratio used are 1: 2; 1: 1 and 2: 1.

## 3. Results and Discussions

Maleic anhydride grafting products on cyclized natural rubber have been produced in the presence of trimethylolpropanetriacrylate comonomer which is processed in an internal mixer with various compositions in accordance with the research design. The graft product is purified of all the graft

products. The graft of maleic anhydride on cyclized natural rubber was confirmed by the absorption of the 1700s wave number in the FT-IR spectrum.<sup>22</sup>The degree of grafting for each graft product is determined by the titration method.

Table 1. Effect of Tris addition on the degree of grafting Maleic Anhydride

Tris (mol ratio)	VolumeNaOH				graftingdegree (%)
	I	II	III	average	
0,5	16,00	16,05	16,05	16,03	3,92
1,0	19,80	19,80	19,85	19,81	4,85
2,0	24,00	24,00	24,00	24,00	5,88

From table 1 it can be seen that the higher the concentration of Tris is added the more maleic anhydride is grafted on cyclized natural rubber.

### 3.1 Effect of adding Tris Comonomers on the degree of AM grafting

From table 1 it can be seen that the addition of Tris comonomer to maleic anhydride grafting on cyclized natural rubber can affect the increase in the degree of grafting on cyclized natural rubber, as figure 1.

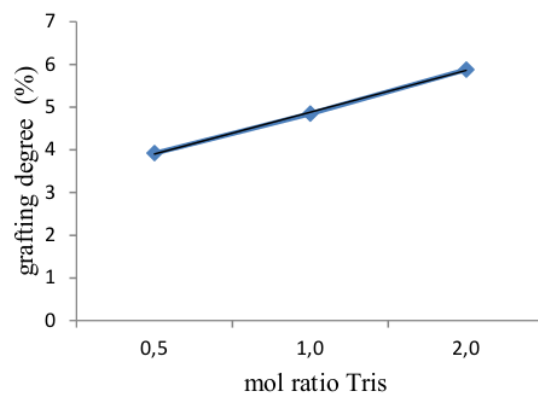


Figure 1. Relationship of Tris concentration to the degree of grafting AM.

In this study, maleic anhydride grafting was performed by adding Tris comonomers. Tris concentration variations namely; 0.5, 1 and 2 phr. So that it can be seen in the figure 1, the more Tris additions, the higher the degree of maleic anhydride grafting grafted on a cyclized natural rubber.

With the addition of the Tris comonomer, it affects the maleic anhydride grafting on cyclized natural rubber. The degree of grafting of maleic anhydride on cyclized natural rubber has increased significantly. This is because Tris acts as a comonomer so that the more Tris comonomers are added the higher the degree of maleic anhydride grafting on the cyclized natural rubber. Eddiyanto<sup>5</sup>, showed that the role of Tris comonomer in the grafting of maleic anhydride in natural rubber significantly increased the degree of grafting obtained at the mole ratio of maleic anhydride and Tris 1: 1. Tris as a donor electron comonomer can interact with maleic anhydride through a complex of charged to form Tris-MA copolymers which can then react to produce a copolymer of MA-c-CNR grafts.

The higher the concentration of maleic anhydride the more grafted maleic anhydride. With the same concentration of maleic anhydride the same tendency was found between the reaction of maleic

anhydride grafting without the presence of Tris and with the presence of Tris. A higher degree of grafting was obtained in the graft reaction in the presence of the Triscomonomer. Tris concentration affects the amount of maleic anhydride that reacts with cyclized natural rubber. In this condition, the higher Tris concentration in the reaction system, the more radicals are formed, the more consequence the macroradical formation which then reacts with maleic anhydride, so that the higher the degree of grafting of maleic anhydride on macroradical cyclized natural rubber. With the presence of Tris, it is increasingly easy to form the main macroradical which then reacts with maleic anhydride to form a graft product on cyclized natural rubber.

#### 4. Conclusions

Grafting of maleic anhydride onto CNR was successfully carried out in the melting phase in the an internal mixer. The addition of trimethylolpropanetriacrylate twice the number of MA molecules increased the degree of grafting. The degree of grafting increases with increasing trimethylol propane triacrylate mole ratio. The highest degree of grafting is obtained in moles ratio of 2: 1 which is to 5.88%

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