Grafting Of Maleic Anhydride onto Cyclized Natural Rubber In The Melt Phase: The Effect of Maleic Anhydride Consentrations on the Spesific Weight and Total Acid

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Abstract: The grafting product of maleic anhydride onto cyclized natural rubber have been produced which is processed in an internal mixer 150^{o}C 80 rpm. In this research, the consentrations of maleic anhydride used is 2, 4, 8, 16 phr. All grafted product was purified to determine the spesific weight and total acid for each graft product by the titration method. Specific weights of grafting products by addition of AM 2,4,8,16 is 0.245, 0.276, 0.288, 0.304, and total acid is 3.272, 6.145, 6.145, 10.280 respectively.

Keywords: grafting, cyclized natural rubber, maleic anhydride, specific weight and total acid

Introduction

Cyclized natural rubber (CNR) can be produced through cyclization reaction by treatment natural rubber with hard acids[1] (such as sulfuric acid, p-toluene sulphonic acid) or Friedel-crafts catalyst such as $FeCl_3$, $SnCl_4$, $TiCl_4$[2]. 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%[3].

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[4].

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[5], natural rubber [6,7,8], paraffin[9] and polybutadiene[10]. The use of MA has improved the properties of thermoplastic polymer graft copolymerization such as polyolefins, polystyrene, polyamide and also biodegradable polymers, polysaccharides and natural and synthesis rubber[4].

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 polymers to polar polymers such as polyamides, metals, and glass fibers. The maleic functionalized polymer is also used as a compatibilizer in polymer blends.[11,12]

Reactive processing in the melt phase using an extruder and/or internal mixer has been developed by many researchers on grafting MA onto polypropylene[4,5,13,14,15,16] polyethylene[17,18,19,20] polystyrene[21], natural rubber[7], cyclized natural rubber[22] 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[23] and natural rubber.[24]

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.

Experimenital

Materials and Method

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.

Procedures

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 of trimethylol propane triacrylate comonomers. It was first setting the operational temperature 150^{o}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.

Grafting MA onto CNR

The 30 grams of CNR loaded into the chamber slowly and left for about 4 minutes until completely melted. Then added some 2 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 by addition of 4,8,16 phr.

Results And Discussions

From the results of research and general statistical tests show that Maleic Anhydride affects the observed cyclized natural rubber. Data on the average observations of the influence of Maleic Anhydride can be seen in Table 1.

Table 1. Effects of Addition of Maleic Anhydride onto Cyclized Natural Rubber (CNR) Parameters.

MA Consentration	Specific Weight g/ml	Total Acid mg KOH/g
2 phr	0.245	3.272
4 phr	0.276	6.145
8 phr	0.288	8.443
16 phr	0.304	10.280

Based on table 1, it can be seen that the effect of Maleic anhydride on specific gravity and total acid has increased. Increasing the addition of Maleic Anhydride onto cyclized natural rubber is in line with the increase in specific gravity and total acid.

Specific Weight
Effect of Addition of Maleic Anhydride

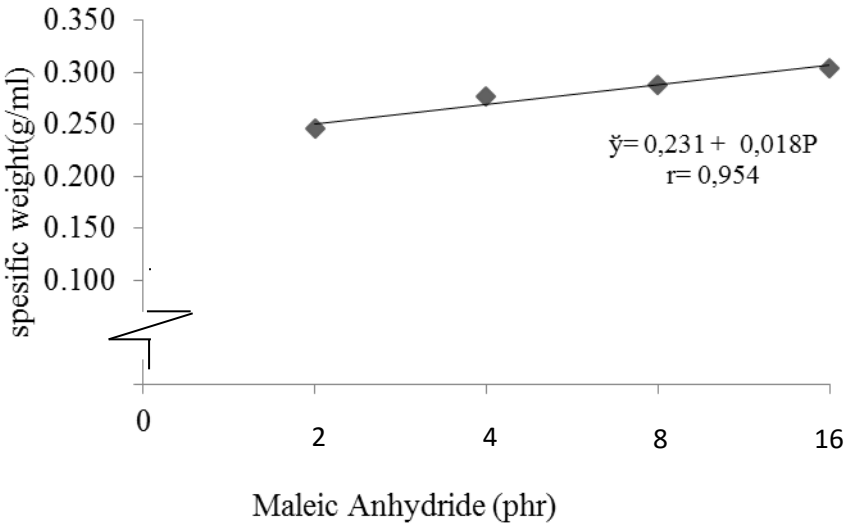

Figure 1. Effect of Maleic Anhydride To Specific Weights

Based on Figure 1, it shows that the addition of MA onto CNR causes an increase in specific gravity. Specific weight is the ratio of the mass of a substance to the mass of water at the same temperature and volume. Specific weight describes the number of components contained in the substance, the size of the specific gravity value is often associated with the weight fraction of the components contained therein (Nur Oktavia et al, 2016). CNR grafted

with MA with levels of MA 2, 4, 8 and 16 phr at a mixing temperature of 150^0C. On mixing it can be seen an increase in specific gravity, at 2 phr the value is 0.245 g / ml and at a maximum addition of 16 phr values 0.304 g / ml.
Nakason et al (2004) who have modified natural rubber with MA 4, 6, 8, 10 and 12 phr at a mixing temperature of 135 ℃ and Zhen Yao et al (1998) who modified natural rubber with MA 5, 10, 15 and 20 phr at a mixing temperature of 150 ℃. The results showed that the higher of MA grafted on the structure of natural rubber, the greater the degree of grafting of natural rubber grafted MA. This is due to differences in molecular weight and nature of the modified natural rubber that affects branch chains that are formed.

Total Acid
Effect of Maleic Anhydride

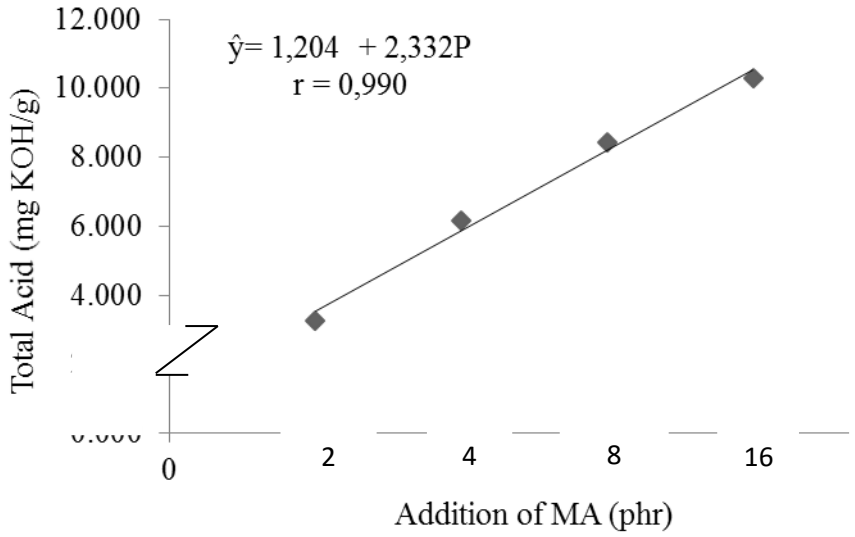

Figure 3. Effect of MA on Total Acid.

Based on Figure 3, it is known that the addition of MA has an increase in total acid. Analysis of total titrated acid is the amount of acid contained in a solution, which in the test refers to the total acid contained in the material (Frazier and Westhoff, 1978). The total titrated acid test was done simply because it wanted to know how much acid was present in anhydrous maleate grafting which was done with natural rubber. The acid present in MA grafting with CNR is formed because the MA reagent used contains acid. Maleic anhydride is made commercially by the oxidation reaction of benzene or other aromatic compounds.

Conclusions
Grafting of maleic anhydride onto CNR was successfully carried out in the melting phase in the an internal mixer. The addition of MA molecules increased the specific weight and total acid of grafting product. Specific weights of grafting products by addition of AM 2,4,8,16 is 0.245, 0.276, 0.288, 0.304, and total acid is 3.272, 6.145, 6.145, 10.280 respectively.

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