

Grafting of Maleic Anhydride onto Cyclized Natural Rubber by Reactive Processing: the Effect of Time and Rotor Speeds

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Abstract

Grafting of maleic anhydride onto cyclized natural rubber has been performed in an Internal Mixer with variation of time and rotor speeds. The grafted product were analyzed by Fourier Transformed Infra Red to determine the presence of Maleic Anhydride onto Cyclized Natural Rubber, and Thermogravimetric Analysis to investigate its thermal properties. Fourier Transformed Infra Red spectra confirmed that the grafted product accured by appearance of characteristic band at 1780 cm^{-1} . The optimum time of grafting process was 8 minutes, by means of carbonyl index. The rotor speeds were not significantly effected the grafting degree. Characterization by Thermogravimetric Analysis observed that the thermal properties of grafted product were not significantly different from cyclized natural rubber standard.

Keywords: grafting, cyclized natural rubber, maleic anhydride, time and rotor speed

1. Introduction

Chemical modification by grafting of functional group have been carried out to produce the expected specifications product. Grafting technique is a technique that relatively simple and easy and has many widely performed. Grafting of Maleic Anhydride (MA) onto non-polar backbone of polyolefins and rubbers has overcome the disadvantage of low surface energy of these polymers, improving their surface hydrophilicity for the benefit of printing and coating applications, adhesion with polar polymers, metal, and glass fibers (Zakir M. O. Rzayev, 2011).

MA is one of the most common monomers in the polymer modification. Chemical structure of this monomer can be used in grafting onto synthetic and natural polymers. Grafting of MA onto various polyolefins and rubbers and preparation of high performance engineering materials and nanocomposites by using reactive extruder systems have been significantly developed, some results of which are employed in commercial applications (S. N. Sathe, et al, 1994).

Grafting maleic polar group is intended to increase the polarity of cyclized natural rubber. The presence of maleic group is expected to increase the interfacial adhesion properties and compatibility with polar polymer materials and metals and their alloys. Grafting of MA onto non-polar polymer chain has overcome the weak interfacial adhesion to polar surfaces. It not only increases the hydrophilicity of the polymer surface for printing and coating applications interests but also adhesion and compatibility of these polymers with polar polymers such as polyamides, metal, and glass fiber. Functionalized maleate polymer is also used as compatibilizer in polymer blends (S. Cimmino dkk., 1986 dan Y. Kayano dkk., 1998).

Grafting by reactive processing in an internal mixer and/or extruder has been developed by many researchers in the grafting of MA onto polypropylene (S. N. Sathe et al 1994; S. H. P. Bettini and J. A. M. Agnelli, 1999; Jaehyug Cha dan James L. White, 2001; Yilser Guldogan et al, 2004; B. M. Dorscht and C. Tzoganakis, 2003; Eddyanto, 2007), polyethylene (W. Heinen et al, 1998; N. G. Gaylord and R. Mehta, 1988) and natural rubber (Nakason, C. A. Et al, 2001) where some managed to produce commercially. In the previous paper we have reported that grafting of MA onto cyclized natural rubber. The higher concentration of maleic anhydride reacted the higher of grafting degree of maleic anhydride [Siregar, M.S., et al, 2014].

In this paper we want to report the result obtained on grafting of maleic anhydride onto cyclized natural rubber, the influence of time and rotor speeds.

2. Experimental

2.1. Materials and Methods

CNR used was the commercial grade, Resiprena 35, manufactured by PT Industri Karet Nusantara (Nusantara Rubber Industry), Medan, Indonesia. MA used to prepare the maleated cyclized natural rubber was manufactured by Riedel-deHaen, Seelze, Germany. For the determination of the grafting degree of maleated Cyclized natural rubber used in this work, different reactants were used toluene, acetone were acquired from Merck, Germany Scharlau (Barcelona, Spain), used without any prior purification.

2.1.1. Grafting Procedure

The grafting of MA onto CNR was performed in an internal mixer, Brabender Plasticorder PLE 331 (Duisberg,

Germany) type batch mixer. The amount of 30 g CNR loaded into the chamber slowly. The internal mixer was then used to melted CNR at 150 °C for 4 minutes. The amount of 16 phr MA was then incorporated into the internal mixer. The mixing was continued for 8 min and the process was then stopped by pressing the STOP button. Furthermore, in hot conditions the product quickly removed from the chamber and the product was then granulated. Various of time grafting (i.e. 4, 8 and 12 minutes) were each used to investigate the effect of time. To investigate the effect of rotor speed various rotor speed were each used 70, 80 and 90 rpm.

2.1.2. Purification of grafted products

The amount of 1.0 g crude blend product was first dissolved in 50 ml of toluene. The mixture was heated at 60 °C under reflux condition to complete the solubility. The undissolved solid content was separated out by filtration. Then the product solution was added slowly into the excess acetone to precipitate the grafted product. The solid product obtained was washed with acetone. The product was dried in a vacuum oven at 120 °C for 24 h. The dried and purified grafted product stored in desiccator.

2.2. Characterizations

2.2.1. Fourier Transformed-Infra Red (FT-IR)

The dried and purified grafted product molded into tablets with KBr powder. The Fourier Transformed Infra Red spectra were determined on a GALAXY 5000 Fourier Transformed Infra Red Spectrometer.

2.2.2. Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA) was performed with a Mettler Toledo TGA850 thermal analyzer in nitrogen atmosphere. Samples were heated from 50 to 650 °C at a heating rate of 10 °C min⁻¹.

3. Result and Discussions

3.1. Fourier Transformed-Infra Red (FT-IR)

3.1.1. The effect of grafting time

To investigate the effect of time on the grafting degree of MA onto CNR, we designed an experiment with variations in time are: 6, 8 and 12 minutes using a concentration of MA 16 phr and rotor speed of 80 rpm. FT-IR spectra of the grafting product of MA onto CNR can be shown in Figure 1. From Fig 1. it can be seen that there has been a grafting reaction of MA onto CNR, which can be confirmed by the appearance of absorption band at wave number 1780 cm⁻¹ which is absorption typical carbonyl group (C = O) of Maleate (S.H.P. Bettini and Agnelli, 1999; Demin et al., 2000; C. Nakason et al., 2004; Bhattacharya, A. and B.N. Misra, 2004 and Eddiyanto, 2007).

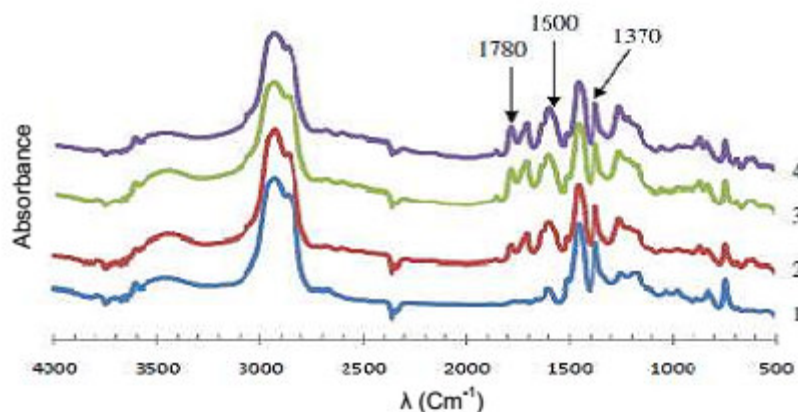


Figure 1. Overlay FT-IR spectra grafted MA-CNR, CN/blank (1), with grafting time: 6 minutes (2), 8 minutes (3) and 12 minutes (4)

Furthermore, by using OMNIC software can be determined a peak area absorption at 1720 cm⁻¹ for each maleated product. Then based on the peak area can be determined Carbonyl Index (CI) for each FT-IR spectra were generated. Carbonyl Index is a peak area at 1720 cm⁻¹ (typical carbonyl absorption) compared with peak reference [Siregar, M.S. et al., 2014]. In Figure 2. CI can be seen for all the time process.

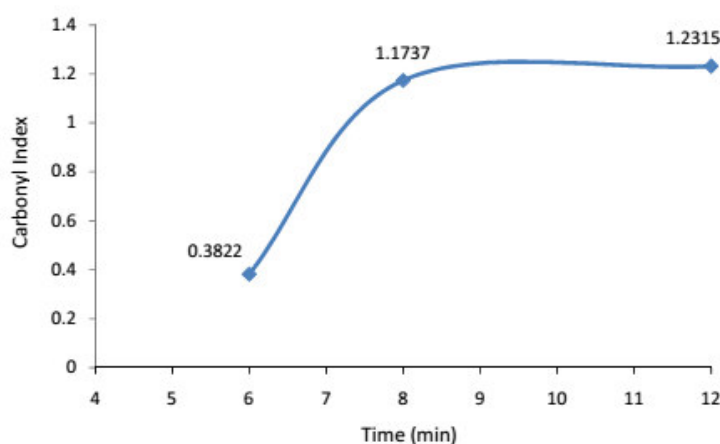
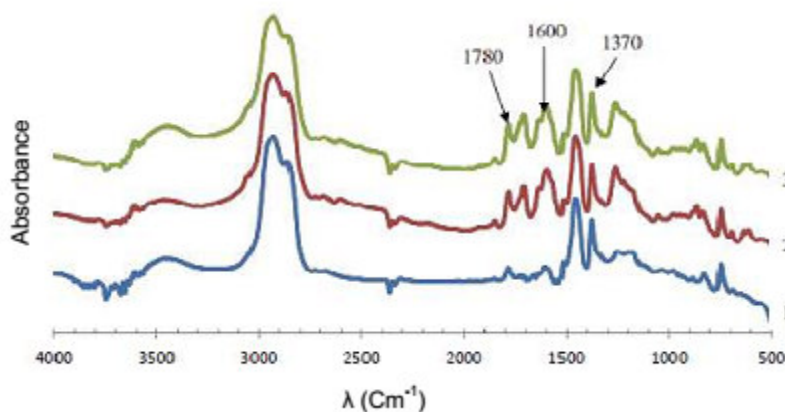


Figure 2. Carbonyl Index versus grafting time

At the 6 minutes reaction time observed that absorption intensity of carbonyl lower than the absorption at the reaction time of 8 and 12 minutes. It is assumed that the grafting MA onto CNR yet optimally. There is still a possibility of reaction but the reaction MA onto CNR has been terminated. When the reaction is carried out longer is 8 minutes then look in the FT-IR spectra in which the intensity of the absorption at 1780 cm^{-1} higher. Addition reaction time till 8 minutes increased the number of MA which graft onto CNR. But the 12-minute reaction time can no longer be observed additional absorption intensity at 1780 cm^{-1} . The intensity of the absorption at 1780 cm^{-1} were not significantly different with increasing reaction time. In the reaction with a time of 8 minutes is alleged to have occurred optimal grafting reaction MA onto CNR. By increasing the reaction time is not longer reaction occurs MA onto CNR.

3.1.2. The effect of rotor speed

To investigate the effect of rotor speed on the degree of grafting MA onto CNR, we designed an experiment with variations in rotor speed are: 70 rpm, 80 rpm and 90 rpm. FT-IR spectrum of the reaction product of grafting MA onto CNR can be shown in Figure 3. From Figure 3, it can be seen that there has been a grafting reaction of MA onto CNR, which can be confirmed by the appearance of absorption band at wave number 1780 cm^{-1} which is absorption typical carbonyl group ($\text{C}=\text{O}$) of Maleate AM (S. H. P. Bettini and Agnelli, 1999; Demin et al., 2000; C. Nakason et al., 2004; Qi et al., 2005 and Eddiyanto, 2007).



Gambar Figure 3. Overlay FT-IR spectra grafted MA-CNR, with rotor speed: 70 rpm (1), 80 rpm (2) and 90 rpm (3)

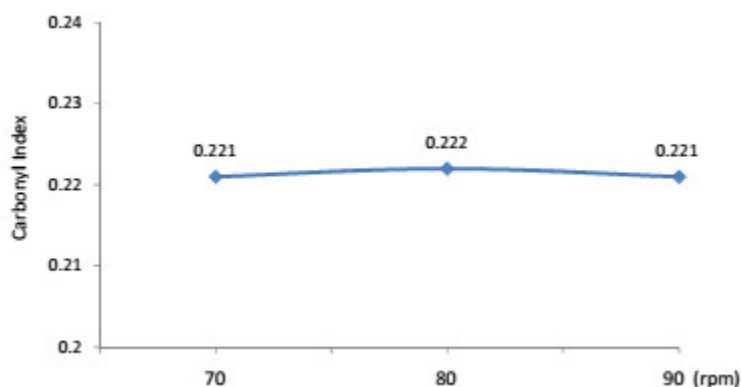


Figure 4. Carbonyl Index versus rotor speed

Based on calculations Carbonyl Index, it can be seen that there is no difference in the degree of grafting MA onto CNR obtained by the rotor speed differences in this study, as can be seen in Figure 4. It can be explained that the rotor function is just to assist the mixing of substances involved in the reaction to produce the product. The higher the rotor speed, the faster the mixing of the substances involved in the reaction. Mixing substances reactants means of collision between the substances involved in the reaction allows the reaction that produces the product. Thus the rotor speed only affects reaction time to form the product as a result of collisions that occur due to mixing aided rotor rotation. In this study the grafting reaction accured for 8 (eight) minutes. By this time the reaction is estimated at low rotor speed, 70 rpm also enough so that the grafting reaction of MA onto CNR takes place optimal.

3.2. Thermogravimetric Analysis TGA

Chromatograms of CNR blank and grafting products AM onto CNR can be seen that there is a change in the sample mass temperature 139-257°C process, there is a decrease of 4% sample mass. This sample mass reduction due to evaporation compounds volatile (mosture) within the sample. Mosture presence in samples is possible because the samples were stored in containers that can be in contact with air during storage, after being dried in the oven and before the thermal characterization TGA. Futhermore, at a temperature of 251°C to 522°C occurred drastic reduction in the mass of the sample, about 95%. The samples undergo decomposition. And at a temperature of 660 OC found the rest of the sample as ash (signal value) about 2%.

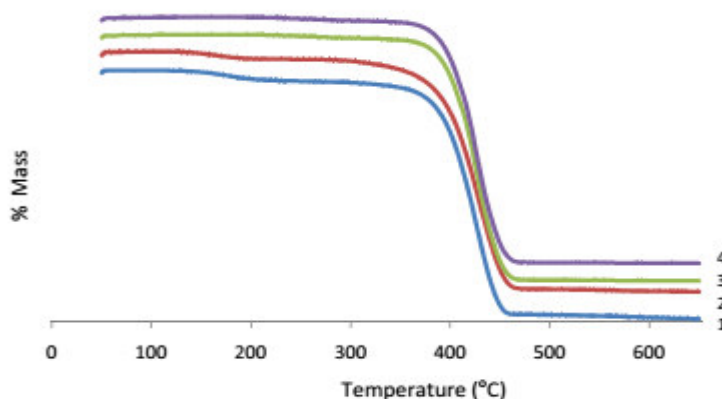


Figure 5. Overlay thermogram grafted product, CNR blank (1), with grafting time: 6 minutes (2), 8 minutes (3) and 12 minutes (4)

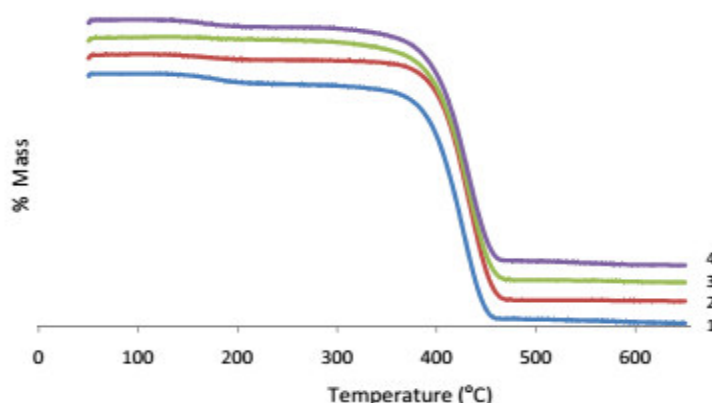


Figure 6. Overlay thermogram grafted product, CNR blank (1), with rotor speed: 70 rpm (2), 80 rpm (3) and 90 rpm (4)

In general it can be said that the thermal properties grafted product does not change significantly compared with the blank CNR. Samples and standards were already experiencing grafting reaction in the internal mixer has the same thermal properties, no thermal properties change with the grafting reaction in the internal mixer. Likewise grafted product samples with different time reacts of AM did not show different thermal properties of the product. Different time reactions were not significantly effect on the thermal properties of grafted CNR, as can also be seen in Figure 5. The same case we observed with different speed of rotor. Different rotor speeds were not significantly effect on the thermal properties of grafted CNR, as can also be seen in Figure 6.

4. Conclusions

Grafting of MA onto CNR can be done by reactive processing in an Internal Mixer at 150°C. Fourier Transformed Infra Red spectra confirmed that the grafted product accrued by appearance of characteristic band at 1780 cm⁻¹. The intensity of the absorption at 1780 cm⁻¹ were not significantly different with increasing reaction time. In the reaction with a time of 8 minutes is alleged to have occurred optimal grafting reaction MA onto CNR. By increasing the reaction time is not longer reaction occurs MA onto CNR. The higher the rotor speed, the faster the mixing of the substances involved in the reaction. The rotor speed only affects reaction time to form the product as a result of collisions that occur due to mixing aided rotor rotation. In this study the grafting reaction accrued for 8 (eight) minutes. By this time the reaction is estimated at low rotor speed, 70 rpm also enough so that the grafting reaction of MA onto CNR takes place optimal. The thermal properties grafted product does not change significantly compared with the blank CNR.

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