

The effect of comonomer styrene on the grafting of maleic anhydride onto cyclized natural rubber

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ABSTRACT

The grafting degree of maleic anhydride onto cyclized natural rubber is generally still low. This is due to the lack of electron density of the maleic anhydride double bond so that its reactivity is low. This research aims to increase the grafting degree by the addition of a styrene comonomer. Grafting of maleic anhydride onto cyclized natural rubber had been performed in an internal mixer 150 oC and 80 rpm in the presence of styrene comonomer. The grafted product was analyzed by Fourier Transform Infra-Red to determine the presence of maleic groups and Differential Scanning Calorimetry and Thermalgravimetric to investigate its thermal properties. Fourier Transform Infra-Red spectra confirmed that the grafted product of maleic anhydride onto Cyclized Natural Rubber formed with absorption at 1700 cm⁻¹, 1850 cm⁻¹ and 700 cm⁻¹. The higher concentration of maleic anhydride reacted the higher of grafting degree of maleic anhydride with the high intensity of absorption at 1700 cm⁻¹ and 1850 cm⁻¹. Differential Scanning Calorimetry spectra showed that the glass transition temperature of maleated Cyclized Natural Rubber products increases, the more comonomer are added the higher the glass transition temperature of the product. Generally, based on the Thermalgravimetric spectra, the thermal properties of grafted product does not change significantly compared to the blank sample.

Introduction

Cyclized Natural Rubber (CNR) can be produced through cyclization reaction by treatment natural rubber with hard acids (Hayemasae et al., 2020) (such as sulfuric acid, p-toluene sulphonic acid) or Friedel-Crafts catalyst (such as FeCl₃, SnCl₄, TiCl₄). In such a reaction (Mirzataheri, 2000), 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 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% (Riyajan and Saktapippanich, 2006).

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 in accordance with 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 (Sitanggang and Eddiyanto, 2019).

Maleic Anhydride (MA) is one of the most widely used monomers to modify polymeric materials to produce high performance, high quality natural and biotechnical (nano-engineering) materials, both natural and synthetic polymers, such as polypropylene (Tanrattanakul et al., 2020), natural rubber (Eddiyanto et al., 2024), paraffin (Krump et al., 2005), and polybutadiene (Ferrero, 2005). 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 (Mahendra et al., 2019; Coudane et al., 2022).

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 (Ritonga et al., 2019; Aritonang et al., 2020). Grafting of MA onto a 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 the purposes of 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 (Fatimah et al., 2015).

Reactive processing in the melt phase using an extruder and/or internal mixer has been developed by many researchers on grafting MA onto polypropylene (Nitiyah et al., 2024; Coudane et al., 2022) polyethylene (Heinen and Duin, 1998; Gaylord et al., 1992; Yang et al., 2002; Dorscht and Tzoganakis, 2002), polystyrene (Moad, 2002), natural rubber (Wongthong et al., 2013; Wongthong et al., 2013), cyclized natural rubber (Siregar et al., 2019; Siregar et al., 2021; Siregar et al., 2022) 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. Styrene is a comonomer that has been used to increase the grafting degree of MA onto polypropylene polymers (De Roover et al., 1995) and natural rubber (Saelao and Phinyocheep, 2005).

The studies on the grafting of MA onto CNR in the melt phase by using styrene comonomer have not been reported. In this study, we performed the grafting of MA onto cyclized natural rubber in the melt phase in an internal mixer in the presence of a styrene comonomer.

Methods

Materials

The chemicals used were commercial-grade; ethanol, methanol, xylene, styrene supplied by Merck, Germany; maleic anhydride is supplemented by Riedel-deHaen, Seelze, Germany. CNR produced by PT. Industri Karet Nusantara, Indonesia. The equipment used consists of Glassware, Agrimsa pelletizer Sant Adria` de Besos, Spain, Brabender Internal Mixer PLE 331 Duisburg Germany, Differential Scanning Calorimetry (DSC) Model: Q INSTRUMENTS Q2000, Thermo Scientific™, Fourier Transformed Infra-Red (FT-IR) spectrometer, Mettler Toledo Analytical Balance, Memmert Oven, PMC Heating Tools and Thermogravimetry Analysis (TGA).

Preparation of Internal Mixer

Grafting of MA onto CNR was performed in an internal mixer of Brabender Plasticorder PLE 331 Duisberg Germany, with and without styrene comonomer. It was first setting the operational temperature and the internal rotor speed in accordance with 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 in accordance with the experimental design (Table 1).

Table 1. Experimental design

No	CNR (g)	Maleic Anhydride (MA)		Styrene (St)		Rotor speed (rpm)	T (°C)	t (min)
		(phr)	(g)	(mol ratio/MA)	(g)			
1	30	-	-	-	-	60	150	8
2	30	16	4.8	0.5	2.55	80	150	8
3	30	16	4.8	1.0	5.11	80	150	8
4	30	16	4.8	2.0	10.22	80	150	8

Grafting MA in the Absence of Styrene Comonomer

The 30 grams of CNR loaded into the chamber slowly and left for about 4 minutes until completely melted. Then added a number of 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 a hot condition, the grafting product is removed quickly from the chamber. After it is cool, it is made into granules form.

Grafting MA in the Presence of Styrene Comonomer

The 30 grams of CNR loaded into the chamber slowly and left for about 4 minutes until completely melted. Then added a number of 16 phr MA and a certain amount of styrene (mole ratio of St/MA) into the chamber so that it is mixed and undergoes a grafting reaction for 8 minutes, and then the process is stopped. Furthermore, in a hot condition, the grafting product is removed quickly from the chamber. After it is cool, it is made into granules. The St/MA mole ratio used is 1: 2; 1: 1 and 2: 1.

Results and Discussion

Fourier Transform Infra Red Analysis

To determine the effect of styrene comonomer on the grafting degree of MA onto CNR, experiments were carried out with MA 16 phr and the addition of styrene comonomer with variations in the mole ratio. The amount of styrene used is expressed by the mole ratio. The mole ratio of styrene to MA used in this study is 1: 2, 1: 1, and 2: 1, respectively. The overlay of the FT-IR spectra of the products resulting from grafting with the addition of styrene is shown in Fig-1.

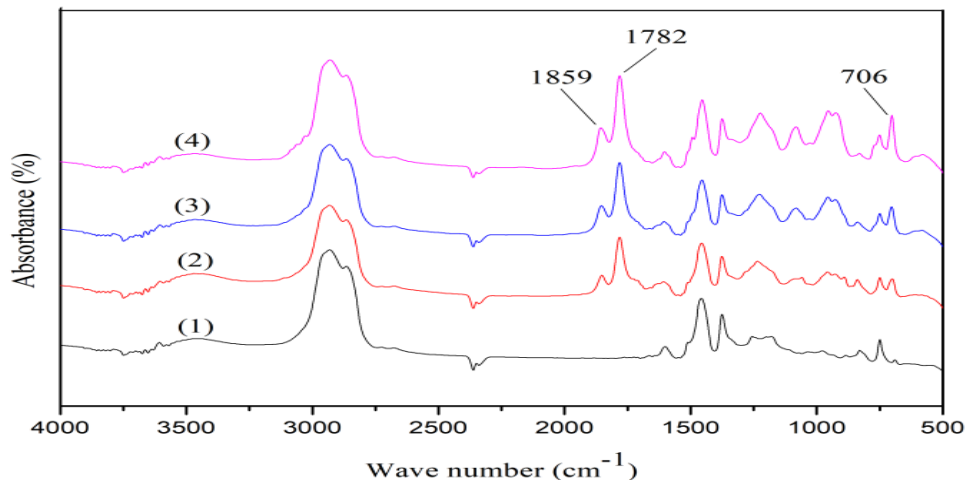


Fig-1. FT-IR overlay spectra of maleated CNR in the presence of St: blank (1), St/MA = 1: 2 (2), 1: 1 (3), and 2: 1 (4) mole ratios

Fig-1 shown that the CNR maleated product has been successfully obtained. This can be confirmed by the appearance of absorption bands at wave numbers 1720-1780 cm^{-1} and 1854 cm^{-1} , which are typical of carbonyl groups ($\text{C}=\text{O}$) and succinic rings of maleate molecules (Krump et al., 2005; Tanrattanakul et al., 2020; Siregar et al., 2022). The more styrene is added, the higher the absorption intensity at wave numbers 1720-1780 cm^{-1} and 1854 cm^{-1} .

Furthermore, Fig-1. also shows a new wave number at 700 cm^{-1} which is a typical phenyl of styrene (De Roover et al., 1995). The intensity wave number area at 700 cm^{-1} also showed that increases with the increase in the amount of styrene in the reaction. Increasing the intensity in the area of 1720-1780 cm^{-1} is proportional to the increase in absorption intensity at wave numbers at 700 cm^{-1} (Siregar et al., 2014).

This is related to the amount of macro radical CNR-St that is formed. The more styrene comonomer are added, the more macro radical CNR-St is formed. Furthermore, there are more possibilities to form macro radical CNR-St and produced the final product of CNR-St-MA. Reaction mechanism proposed in Fig-2.

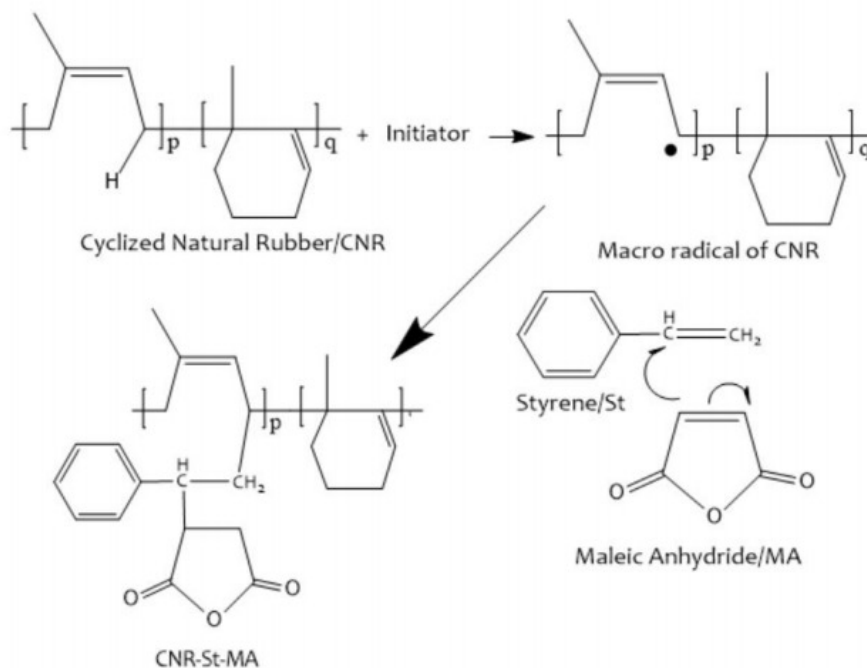


Fig-2. Reaction of grafting of Maleic Anhydride onto Cyclized Natural Rubber in the presence of Styrene

Styrene is reported to be used as a donor electron to activate MA in graft polymerization reactions in polyethylene and polypropylene. Styrene has a higher ability to polymerize compared to MA directly in the polypropylene chain. Styrene comonomer can act as a medium to bridge between macro radical of cyclized natural rubber and MA (Sitanggang and Eddyanto, 2019).

Differential Scanning Calorimetry (DSC) Analysis

The overlay DSC thermogram of maleated CNR is shown in Fig-3. From Fig-3. it can be seen that the maleated CNR with the addition of styrene comonomer mol ratio at 1: 2; 1: 1 and 2: 1 have the glass transition temperatures (T_g) of 80.33°C, 81.03°C, and 87.25°C, respectively.

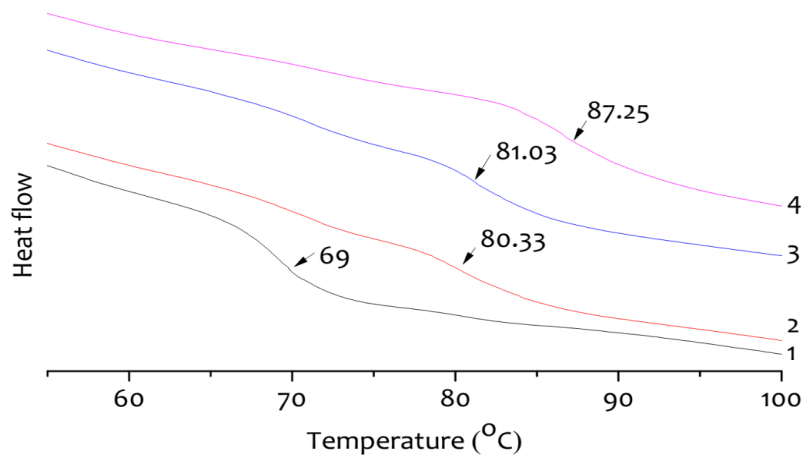


Fig-3. The overlay DSC thermogram of maleated CNR product with styrene addition namely: blank (1), mole ratio St/MA = 1: 2 (2), 1: 1 (3) and 2: 1 (4)

The glass transition temperature (T_g) has a tendency to increase with the occurrence of MA onto CNR. The glass transition temperature of maleated CNR products with the addition of styrene comonomer increases compared to T_g of blank CNR, 69°C. Likewise, the more comonomer are added the higher the glass transition temperature of the product.

Increasing MA concentration is seen to increase the glass transition temperature (T_g) of maleated CNR products. This also shows that the maleate functional group grafted onto the CNR chain. The more maleate groups are grafted, the CNR product becomes bulkier or more rigid, polar, and increased molecular mass. The bulky structure and increasing polar properties and increasing molecular mass of a substance will increase the glass transition temperature of the substance (Sitanggang and Eddyanto, 2019).

Thermogravimetric Analysis (TGA)

The overlay TGA thermogram product of maleated CNR for all variations of the St/MA mole ratio is shown as in Figure 4. In Figure 4 we can see that the same trend occurred for all samples. The samples without MA and samples that grafted product by addition of comonomer St show changes in the same temperature and quantity range. Two phases of temperature were found in the mass loss: temperatures of 100°C to 300°C and temperatures of 300°C to 500°C.

At temperatures of 113°C to 289°C, there is a loss mass of 2.3% to 3.4%. Then at 301°C to 532°C, there was 95% to 96%. Furthermore, at 661°C the residual sample (signal value) was found to be 2.6% to 3.1%. The sample's loss mass at temperatures of 113°C to 289°C is due to evaporation of the volatile compounds/moisture contained in the sample. The presence of moisture in the sample is possible because of stored in containers that can be in contact with air during storage, after being dried in the oven, and before TGA characterization.

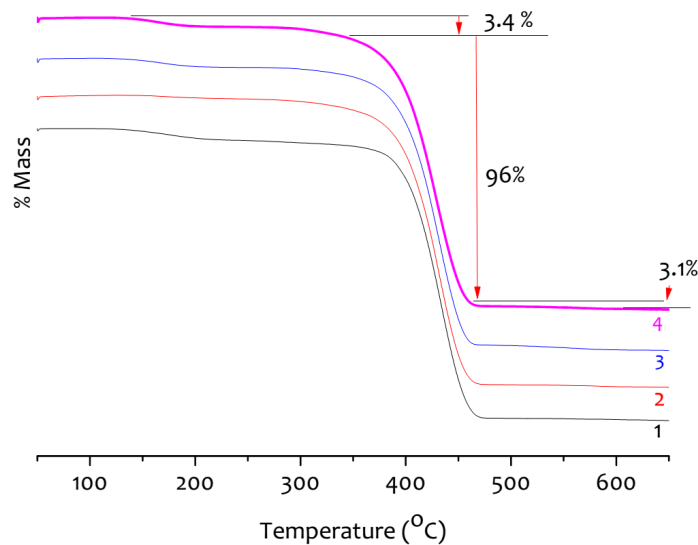


Fig-4. The overlay thermogram TGA of MA grafted product by addition of styrene: blank (1), mole ratio St/MA = 1: 2 (2), 1: 1 (3), and 2: 1 (4)

Then at temperatures of 310°C to 532°C, there was a drastic loss mass in all samples, 95% to 96%. All samples have been decomposed. And at 661°C the remaining samples were found as ash (signal value) for all samples, each 2.6% to 3.1%. Generally, it can be said that the thermal properties of MA grafted product does not change significantly compared to the blank sample. Blank samples and grafted products have similar thermal properties, there is no change in thermal properties.

Thermal properties of MA grafted product with the addition of comonomer styrene has also similar thermal properties. Different moles of St/MA ratios do not have a significant effect on the thermal properties of MA grafted products, as can also be seen in Fig-4.

Conclusion

Grafting of Maleic Anhydride onto CNR was successfully carried out in the melting phase in the Internal Mixer. The amount of Maleic Anhydride grafted onto CNR increases with an increasing mole ratio of Maleic Anhydride/Styrene. The glass transition temperature of maleated CNR products with the addition of styrene comonomer increases, the more comonomer are added the higher the glass transition temperature of the product. Meanwhile, the stability thermal properties of grafted product does not change significantly compared to the blank sample.

Conflict of Interests

The author(s) declares that there is no conflict of interest in this research and manuscript.

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