

Modification and Characterization Natural Cycle Rubber (Resipren-35) with Oleat Acid using Dicumyl Peroxide and Divinilbenzena as Compatibility

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Abstract: Modification of cyclic natural rubber with oleic acid using initiator diumil peroxide and divinilbenzene as a compositer through the melting phase in the internal mixer using the copolymer grafting method at 160 oC for 8 minutes at 80 rpm was carried out with the aim of increasing its compatibility as a paint binder. Variations in the concentration of oleic acid were used 3, 6 and 9 phr while the initiator concentrations of dicumyl peroxide 0.5 phr and divinilbenzena 1.0 phr. Determination of the degree of grafting was carried out by titration method and FT-IR spectra analysis to determine the presence of oleic acid grafting in the cyclic natural rubber chain. The results showed that the process of transplanting oleic acid into the chain of cyclic natural rubber molecules with the presence of initiators dicumyl peroxide and divinylbenzene was successfully carried out marked the emergence of new absorption peaks at wave number 1705.07 cm⁻¹ which is a typical uptake of oleic acid indicating the presence of bond vibrations C=O carbonyl group asymmetry derived from oleic acid. The maximum percentage grafting degree is 0.2630% at 9 phr oleic acid monomer concentration. The degree of grafting increases with increasing concentration of oleic acid. The transition temperature of cyclic natural rubber glass before being grafted with oleic acid is 102.86 OC but after the transplanting process using the initiator diumil peroxide and divinylbenzene the glass transition temperature (T_g) decreases to 83.98 OC this proves that the process of transplanting oleic acid into the cyclic natural rubber molecule chain has been successfully carried out with the formation of the new CNR-g-AO product.

1 INTRODUCTION

Natural rubber is a renewable polymer containing carbon atoms (C) and hydrogen atoms (H) obtained from *Hevea brasiliensis* trees which have good tensile strength and tear resistance, and have a fairly good stickiness so that they can be widely used as adhesives in the coating / coating industry (Khan et al., 2011; Hirata et al., 2014).

However, as unsaturated polymers, natural rubber has the limitation that it will experience gradual degradation at high temperatures when exposed to oxygen, ozone or ultraviolet, and its solubility in hydrocarbon solvents thus affecting the quality of natural rubber itself (Grassie et al., 1988; Wypych, 2015).

One of the efforts made to overcome the weakness of natural rubber is chemical modification through cyclization reaction using Lewis acid catalyst. The aim of the chemical modification of natural rubber is to improve the properties of natural rubber so that new products are produced that are more useful, economical and have superior properties, so that they can be applied in various types of rubber products (Tanaka et al., 2004; Saelao et al., 2005).

Cyclic natural rubber (CNR) is a chemical modification of natural rubber through cyclization reaction using Lewis acid catalyst, has considerable potential to be applied as an adhesive, printing ink and paint industry because it has abrasion resistance properties (friction), resistant to corrosion and has good adhesion to

metals, wood, rubber, leather, textiles and paper (Siregar et al., 2014; Eddiyanto et al., 2015; Aritonang et al., 2018; Ritonga et al., 2018; Barita Aritonang et al., 2019).

However, cyclic natural rubber has a very weak adhesion to the polar surface. This is because cyclic natural rubber is a nonpolar polymer which is very vulnerable to oxidation degradation reactions by ozone, oxygen or ultraviolet (uv) compounds and has a double bond in the polymer chain and its surface energy is very weak, causing interface interactions and the adhesion is weak when mixed with polar polymers. To overcome this problem, it is necessary to do chemical modifications to the structure of cyclic natural rubber using the method of grafting (copolymer grafting). An effective method for modifying cyclic natural rubber is the copolymer grafting technique, so that cyclic natural rubber can be functionalized according to the desired properties without affecting the basic structure of cyclic natural rubber.

Oleic acid is a polar unsaturated fatty acid that can be used as a monomer to increase CNR compatibility, reactivity and adhesive strength because the double bonds in AO provide an opportunity to be able to modify the CASH structure through a copolymer grafting process and the same acid composition can react with hydroxyl groups. This has been proven by Zhou et al. (2002), that through oleic acid monomer polymerization (AO) grafting process successfully grafted the main acrylonitrile-butadiene-styrene (ABS) chain using benzoyl peroxide (BPO) initiator in 1.2 solution -dichloroethane. The result is that AO can increase the flexibility, elasticity and stability of polymers against heat and ultraviolet radiation.

Preliminary research that has modified cyclic natural rubber using the copolymer grafting method, Siregar Said et al (2014) modified cyclic natural rubber using monomer maleic anhydride in the presence of benzoyl peroxide through melting techniques in mixer internal mixers using the copolymer grafting method. The results of the study obtained AM-g-CNR products. The higher the concentration of maleic anhydride, the more maleic anhydride groups are grafted on the CNR polymer chain. Transplant products have physical properties that do not experience significant changes except the glass transition temperature, where there is an increase. Nasution et al. (2015) modified cyclic natural rubber using monomer methyl methacrylate with the presence of the initiator diumil peroxide.

The results of the study obtained CNR-g-MMA products, which are characterized by the appearance of wave number absorption peaks in the area of 1731 cm^{-1} (absorption of carbonyl groups) typical for carbonyl (C = O) from metal methacrylate.

2 MATERIALS AND METHODS

The materials used consisted of Acetone, ethanol ($\text{C}_2\text{H}_5\text{OH}$), commercial cyclic natural rubber (CNR) production of PTPN-3, dicumyl peroxide (DKP), oleic acid (OA), divinil benzene (DVB), hydrochloric acid (HCl), xylene. Glassware, Mettler Toledo Analytical Balance, Memmert Oven, Thermo haake polydrive mixer Shimadzu FT-IR Spectrophotometer, Shimadzu Differential Scanning Calorimetry (DSC).

Grafting of oleic acid in cyclic natural rubber with heat initiation, without dicumyl peroxide As many as 33 grams of cyclic natural rubber are put into the chamber slowly and left for about 4 minutes until all of them melt perfectly. Then add 6 phr oleic acid into the chamber so that it mixes and undergoes a copolymerization reaction. After 8 minutes, the process is stopped by pressing the STOP button. Furthermore, in rapid heat conditions the copolymerization product is removed from the chamber. After the cold is made in the form of pellets / granules.

2.1 Grafting Oleic Acid in Cyclic Natural Rubber using Dicumyl Peroxide

Cyclic natural rubber is weighed as much as 33 grams (100 phr), after which the Thermo mixer internal mixer temperature is set haake polydrive at 160°C , then slowly cyclic natural rubber is inserted into the internal chamber mixer and allowed to last for approximately 4 minutes until cyclic natural rubber melts perfectly, then added with oleic acid as much as 6 phr, followed by the addition of initiator dicumyl peroxide as much as 0.5 phr until mixed homogeneously. The mixing process is carried out for 8 minutes to experience the grafting reaction. After 8 minutes, the process is stopped. In hot conditions quickly the reaction product is removed from the chamber. The products produced are then chilled and made in the form of granules / pellets. Variations in the concentration of oleic acid used 3, 6 and 9 phr.

2.2 Purification Process of Cyclic Grafted Natural Rubber Products Oleic Acid

Oleic acid which has been grafted on cyclic natural rubber (CNR-g-OA) is weighed as much as 1 gram and refluxed with 100 ml of xylene with a series of reflux devices namely heating, boiling pumpkin and liebig condenser at 110°C until dissolved, 100 ml added after dissolving ethanol to form deposits. The

precipitate formed is filtered with Whatman filter paper No.42 which is connected with a vacuum pump and washed with ethanol repeatedly with the aim of dissolving the remaining acidic reactions. The precipitate formed was dried in an oven at a temperature of 120°C for 24 hours, then determined percent degree of grafting. Determination of the degree of grafting is done using the following formula:

$$(\%) \text{ DG} = \frac{N (\text{eq/L}) [(V_0 - V) \text{ ml}] \text{ BMAO } g/\text{eq}}{BS \times 1000 \text{ mg}/g} \times 100 \quad (1)$$

Where,

N = KOH concentration (0.05 N)

V = ml of KOH titration used on CNR-g-AO samples modified

V₀ = ml of KOH titration used on he CNR sample blank is not modified

BM oleic acid = 282.47 g / mol

BS = sample weight

1000 = Conversion factor of carboxylic groups from oleic acid molecules

3 RESULTS AND DISCUSSIONS

Analysis of CNR-g-AO FT-IR without dicumyl Peroxide Initiator To determine the success or failure of the oleic acid grafting process into the cyclic natural rubber molecule chain with and without the presence of the initiator dicumyl peroxide after being purified, it can be seen from the analysis of the spectroscopic Fourier Transformed-Infra Red shown in Figure 1.



Figure 1: Spectrum of CNR-g-AO FT-IR without DKP Initiator.

Seen in Figure 1 (b) the FT-IR spectrum of CNR-g-AO before being purified new functional groups appear with sharp absorption peaks and high intensity wave numbers 1712.79 cm⁻¹, after purification there is a shift in peak absorption of wave numbers and

changes in intensity shown in Figure 1 (c) FT-IR spectrum CNR-g-AO, obtained a weak absorption peak with low intensity wave number 1700 cm⁻¹ shows the existence of strain vibration C = O carbonyl group derived from oleic acid. This is in accordance with the results of previous studies which explained that absorption peaks with spectral regions 1760-1665 cm⁻¹ showed the presence of a group C = O carbonyl derived from oleic acid (Liu Mingzhu et al., 2003; Zhou et al., 2002; Boonyod et al., 2017; Wirjontono et al., 2018; Barita Aritonang et al., 2019).

The emergence of new functional groups in CNR-g-AO samples after being grafted in the mixer internal mixer through heat initiation without using an initiator before and after being purified at the peak wave number 1700 cm⁻¹ and 1712.79 cm⁻¹ indicates the presence of carbonyl groups (C = O) which is a typical absorption derived from oleic acid (AO), has proven that the process of transplanting oleic acid in cyclic natural rubber in the mixer internal mixer has been successfully carried out.

3.1 Analysis of CNR-g-AO FT-IR with Dicumyl Peroxide Initiator

The FT-IR analysis test was carried out on CN-g-AO samples without initiator in bulk peroxide by comparing CNR-g- [AO / DKP] samples with the presence of initiators in wax peroxide after being purified by looking at the absorption peaks in the CNR spectrum and CNR spectrum- g- [AO / DKP] especially in the area of wave number which is an indication of the existence of C = O and C-O bonds from oleic acid. The FT-IR CNR-g- [AO / DKP] spectrum with the dicumyl peroxide initiator is shown in Figure 2.

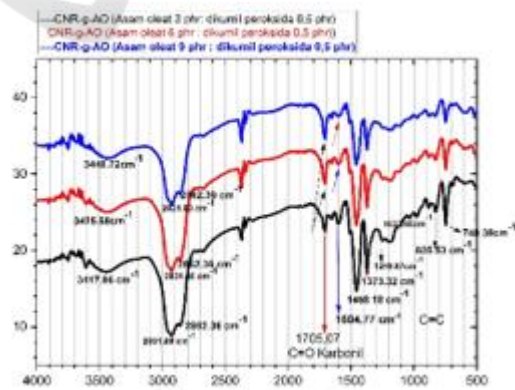


Figure 2: CNR-g-AO FT-IR Spectrum Using DKP Initiator.

Figure 2 analysis of CNR-g-AO FT-IR spectra shows that there has been a chemical interaction between CNR, AO and DKP, this can be proven from

the results of the copolymer grafting of oleic acid into cyclic natural rubber with a new absorption peak at wave number 1705,07 cm⁻¹ which is a typical uptake of AO indicates a vibration of the C = O carbonyl group asymmetry which originates from oleic acid, and is also supported by the presence of CO bonds at wave number 1257.59 cm⁻¹. At 3448.72 cm⁻¹ wave number obtained the peak of the widening and strong absorption band with high intensity shows the presence of a hydroxyl group O-H vibration vibration originating from CNR. The typical strong and sharp absorption peak with high intensity derived from CNR appears at wave number 2931.80 cm⁻¹ which is a stretching vibration of C-H methyl group, at wave number 2862.36 cm⁻¹ is stretching vibration of CH₃ methylene group. At the peak of wave number 1458.18 cm⁻¹ shows the vibration of CH₂ methylene group strain and at the peak of wave number absorption band 1373.32 cm⁻¹ shows the presence of methyl-CH₃ group amplified by vibrations of swing group -CH₂ methylene at peak wave number 719 cm⁻¹. At the peak of absorption wave number 1257.59 cm⁻¹ with a spectrum area of 1080-1300 cm⁻¹ indicates the presence of vibrations of C-O bonds. Based on the FT-IR spectrum analysis data described above it can be concluded that the copolymerization process of grafting AO into the CNR molecular chain has been successfully carried out.

3.2 Determination of Grafting of CNR-g-AO Products

The purpose of refining CNR-g-AO products is to find out how much oleic acid is grafted on a cyclic natural rubber polymer chain. Determination of the degree of grafting of CNR-g-AO products after purification was determined by the acid-base titration method. Based on the results of the research that has been done, the percentage of grafting for CNR-g-AO products before being purified can be seen in table 1.

$$\begin{aligned}
 (\%) \text{ DG} &= \frac{0,05 \text{ (eq/L)} [(0,42 \text{ ml} - 0,29 \text{ ml})] 282,47 \text{ g/eq}}{1,0162 \times 1000 \text{ mg/1g}} \\
 &= \frac{1,8361}{1016,2} \\
 &= 0.1807
 \end{aligned}$$

Table 1: Effect of Oleic Acid Concentration on Grafting Degrees.

	CNR phr	AO phr	DKP phr	Grafting degree (%)
CNR-g-OA	100	3	0,50	0,1807
	100	6	0,50	0,2074
	100	9	0,50	0,2630

The effect of monomer concentration on percent degree of grafting is shown in Figure 3.

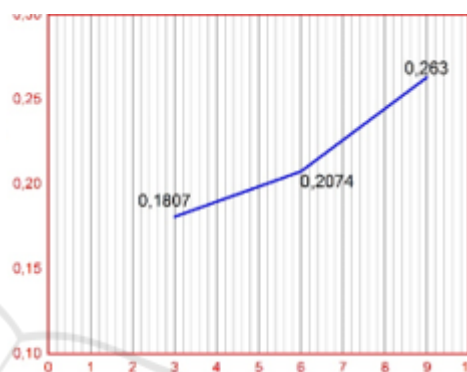


Figure 3: Graph of the Effect of Oleic Acid Concentration on Degrees of Grafting.

Figure 3 clearly shows that percent degree of grafting, in this case the amount of oleic acid that is grafted (attached / grafted) to CNR increases with increasing concentration of oleic acid monomers. Percentage of minimum grafting degree was obtained at 0.1807% at 3 phr oleic acid monomer concentration, at 6 phr oleic acid monomer concentration obtained percent degree of grafting at 0.2074%, for percent grafting maximum degree obtained at 0.2630% at acid monomer concentration oleat 9 phr, this shows that percent degree of grafting is increasing gradually with increasing concentration of oleic acid monomers used, even though the increase is not too significant. Even though the percentage of grafting obtained is very small, but can change the surface of non-polar CNR to be polar hydrophilic, this proves that oleic acid has been successfully grafted into the molecular chain of CNR. This data is supported based on the results of research conducted by Kang and Liaw (1999) reporting that even though the percent of grafting obtained is very small, it has been able to change the nonpolar surface of the polymer to be polar.

3.3 Analysis of Thermal Properties of Pure CNR before and after Grafting with Oleic Acid using Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimeter (DSC) analysis is one of the tools of the Thermal Analyzer that is used to study phase transitions, such as melting temperature (T_m), glass transition temperature (T_g), or exothermic decomposition, and to analyze the stability of oxidation and heat capacity of a material. Glass transition temperature (T_g) is the temperature when the polymer changes from the glass state to rubber. Where when the outside temperature approaches the glass transition temperature, a polymer undergoes a change from a rigid hard state to a soft rubber. Melting temperature (T_m) is the temperature at which solids turn into liquids at a pressure of one atmosphere, in other words, the melting temperature is the temperature when the solid and liquid phases are equally in equilibrium. Based on the results of the research that has been done while the glass transition temperature (T_g) of pure CNR before copolymerized grafts (copolymer grafting) can be seen in Figure 4.

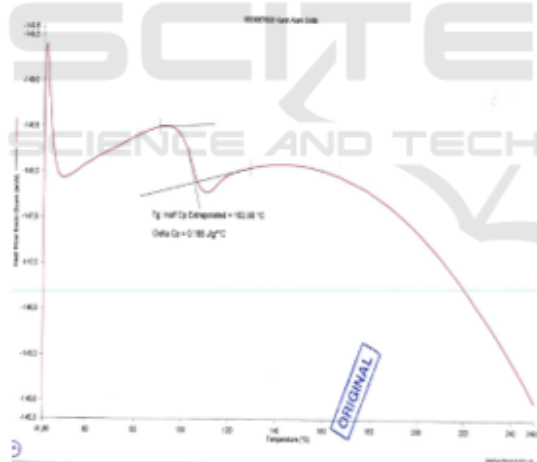


Figure 4: DSC Pure Cyclic Natural Rubber Thermogram.

Based on Figure 4 the results of the DSC thermogram of pure CASH samples before copolymer grafting had a temperature of glass transition temperature (T_g) 102.86 °C and enthalpy change (ΔH) of 0.188 J / g °C. The higher the glass transition temperature (T_g) shows the polymer is increasingly brittle.

3.4 Analysis of Thermal Properties of Grafted Differential Scanning Calorimetry CNR with Dicumyl Peroxide Initiator

The product formed from the oleic acid grafting reaction into the CNR molecular chain using the dicumyl peroxide initiator (DKP) in the mixer internal mixer is CNR-g-AO. The CNR-g-AO product formed was then characterized by Differential Scanning Calorimetry (DSC) to determine the glass transition temperature (T_g) and melting temperature (T_m). The results of the analysis of thermal properties in the form of DSC thermograms of CNR-g-AO products that have been grafted using dicumyl peroxide initiator (DKP) after purification can be seen in Figure 5.

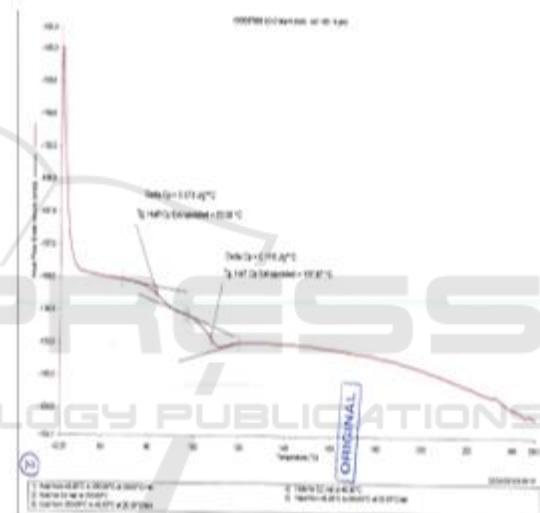


Figure 5: CNR-g-AO DSC Thermogram Using Dicumyl Peroxide Initiator.

Based on Figure 5 the results of research that have been carried out from the DSC thermogram curve obtained out from the DSC thermogram curve obtained two glass transition temperatures (T_g) which were observed at temperatures of 83.98 °C and 107.67 °C. Based on the results of the DSC thermogram curve analysis in Figure 5, there has been a decrease in glass transition temperature (T_g) in cyclic natural rubber before being grafted with oleic acid. The transition temperature of cyclic natural rubber glass before being grafted with oleic acid is 102.86 °C but after the transplanting process using the initiator diumil peroxide and divinylbenzene the glass transition temperature (T_g) decreases to 83.98 °C this proves that the process of transplanting oleic acid into the cyclic natural rubber molecule chain has been successfully carried out with the formation of the new CNR-g-AO product. According to Yang et al, (2003) the main

trigger for transplanted reactions (copolymerization grafting) is when the initiator decomposes into free radicals and there are one or more unpaired electrons. The oleic acid (AO) grafting process (AO) into the cyclic natural rubber molecule chain can occur when AO monomers attach and form covalently branching to the main chain of cyclic natural rubber molecules when the polymer becomes radical by the presence of an initiator. In the early stages of initiator dicumyl peroxide (DKP) will form free radicals that will attack the CNR polymer chain, so that cyclic natural rubber free radicals will be formed, then the cyclic natural rubber free radicals that form will initiate the process of transplanting oleic acid into the natural rubber molecule chain cyclical.

4 CONCLUSIONS

Based on the results of the research that has been done, a conclusion can be drawn as follows:

- a) Modification of cyclic natural rubber with oleic acid using dicumyl peroxide and divinylbenzene in an internal mixer with a temperature of 160 oC and a rotor speed of 80 rpm using the graft copolymer method has been successfully carried out. This can be proven from the results of FT-IR spectra analysis of emerging new absorption peaks at wave number 1705.07 cm⁻¹ which is a typical absorption of oleic acid indicating the presence of vibrations of the C=O bond of asymmetric carbonyl groups originating from oleic acid.
- b) The amount of oleic acid grafted on cyclic natural rubber increases with increasing concentration of oleic acid monomers in the presence of dicumyl peroxide initiators and the addition of divinylbenzene comonomers. The maximum percent degree of grafting is 0.2630 % at the concentration of oleic acid monomers 9 phr.
- c) The transition temperature of cyclic natural rubber glass before grafted with oleic acid was 102.86 °C but after the graft process was carried out using the initiator dicumyl peroxide and divinylbenzene the glass transition temperature decreased to 83.98 °C this proves that the graft process of oleic acid into the chain of cyclic natural rubber molecules has been successfully carried out with the formation of a new product CNR-g-AO

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