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Study on the thermal properties of the grafted product of maleic anhydride onto clylized natural rubber by using thermogravimetric method

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ABSTRACT

This study aims to investigate the thermal properties of grafted products of maleic anhydride onto cyclized natural rubber. The grafting was carried out in the melt phase at an internal mixer of 150 °C and a rotor speed of 80 rpm. A total of 16 phr maleic anhydride was reacted with cyclized natural rubber in the present and absence of divinylbenzene comonomer with various mole ratios: 0.5, 1, and 2. The grafted products were characterized by the thermogravimetric method to investigate their thermal properties. Based on the results of the thermogravimetric analysis, it was shown that the sample increased its thermal stability. The sample decomposes at a higher temperature with the increasing mole ratio of divinylbenzene added. The grafted product with 16 phr maleic anhydride decomposed at 489.41 °C. Then, the graft product samples with the addition of 0.5, 1, and the 2-mole ratio of divinylbenzene comonomers decomposed at: 501.62 °C, 514.39 °C, and 520.82 °C, respectively.

1. Introduction

Indonesia is one of the main producers of natural rubber in the world. There is a natural rubber plantation area with 3.6 million hectares of land and producing 3.630.268 tons. Natural rubber plantations are a leading agricultural sub-sector that supports the Indonesian economy with an export volume of 2.99 million tons and US$ 5.10 billion. In 2016 Indonesia produced 26% of natural rubber in the world, ranking second in the world's natural rubber production after Thailand (Indonesia, 2016). Modification of the molecular structure of natural rubber physically or chemically is important to produce new materials that have unique characteristics for new and broad uses in certain fields (Hayeemasae et al. 2020; Widiarti et al. 2018).

Natural rubber is a cis-poly isoprene natural polymer compound resulting from the addition of 1,4 from isoprene monomer which has a molecular weight of 1-2 million and there are 15,000-20,000 unsaturated bonds in the molecular chain. Natural rubber has properties that are not resistant to ozone, oil, and temperature due to the presence of a carbon-carbon double bond in the chemical structure of cis-1,4-polyisoprene which is the main component of natural rubber (Nakason et al. 2006; Guldogan et al. 2004; Rzayev, 2011). But natural rubber has advantages in terms of resilience, abrasion resistance, stickiness, and plasticity (Saelao & Phinyocheep, 2005).

Cyclized Natural Rubber/CNR is a derivative material of natural rubber which is the leading product in the rubber industry. CNR is a modified natural rubber by cyclization reaction. Cyclization of natural rubber causes a change in the characteristics of natural rubber from being elastic to being thermoplastic that is hard and rigid. CNR still contain unsaturation after cyclization (Nandiyanto et al. 2019; Soleimani et al. 2020).

Modification of CNR by grafting using Maleic Anhydride (AM) monomer has been successfully carried out by several researchers (Zhao et al. 2018; Ritonga et al. 2019). Based on the Fourier Transformed Infra-Red/FTIR spectral data of the grafted product, the maleate group was successfully grafted onto the CNR structure with the appearance of absorption at 1780 cm-1 and 1841 cm-1 which is a typical carbonyl absorption of the maleate group (Sitanggang & Eddyanto, 2019; Eddiyanto, 2007; Siregar et al. 2014; Siregar, 2015; Siregar et al. 2019; Siregar et al. 2021a; Siregar et al. 2021b). To increase the degree of grafting, styrene comonomers (Siregar et al. 2014), divinylbenzene (Siregar et al. 2019; Siregar et al. 2021a; Siregar et al. 2021b) and Trimethylol Propane Triacrylate (Siregar et al. 2019; Siregar et al. 2021) have been used.

Based on the description above, this paper reports on the study of the thermal properties of grafted products of maleic anhydride onto CNR in the molten state in an internal mixer in the presence and absence of divinylbenzene comonomer by using the thermogravimetry (TGA) method.

2. Methods

2.1. Materials

This research uses chemicals produced by Merck, namely 99.5% acetone, 99.9% maleic anhydride (MA), 80% technical divinylbenzene (DVB), xylene p.a. The Cyclized Natural Rubber/CNR used was produced by the Resiprena Factory, PT Industri Karet Nusantara, Sei Bamban, Tebing Tinggi, North Sumatra, Indonesia, in granular form and is a commercial product under the trade name Resiprena 35 (R- 35).

2.2. Equipment

The equipment used in this study were: Mettler Toledo analytical balance, Duisberg Germany Plastograph Brabender internal mixer, Memmert Laboratory Oven type UN 260, filter paper (Whatman) Z241393, pyrex ts joint reflux apparatus 29/32 1 set, and Thermogravimeter Mettler Toledo TGA850.

2.3. General Procedure

This research is a laboratory experiment to produce grafted products in an internal mixer with a temperature of 150 ^{o}C and a rotor speed of 80 rpm, where 16 phr MA was reacted with CNR in the presence and absence of DVB comonomer with various mole ratios of 0,5, 1 and 2 (Siregar, 2014). To investigate the thermal properties of the grafted product, it was characterized by a Mettler Toledo TGA 850 Thermogravimeter.

2.4. Preparation of Internal Mixer

The operating temperature of 150 ^{o}C and the rotational speed of the rotor of 80 rpm, the internal mixer was programmed in accordance with the research design to be carried out. Furthermore, the internal mixer can be used after the chamber temperature matches programmed temperature, which can be seen on the computer monitor screen.

2.5. Grafting Maleic Anhydride onto Cyclized Natural Rubber without Divinylbenzene

The number of 30 gram CNR was slowly put into the chamber and left for about 4 minutes until all melted completely. Then 16 phr MA was added into the chamber without the addition of DVB so that it was mixed and grafting reaction occurs, allowed to continue for 8 minutes. By pressing the STOP button the process is stopped. Furthermore, in a hot state, the reaction products are quickly removed from the chamber. After cooling it is made into pellets/granules and stored.

2.6. Grafting MA onto CNR in the Presence of DVB

With the same procedure as 2.5. After all CNR melted completely, then 16 phr MA was added into the chamber in the presence of a 0.5-mole ratio of DVB so that it was mixed and a grafting reaction occurs. The results are also stored for further treatment. The same was done using 16 phr MA and the addition of DVB with concentrations: 1 and 2-mole ratios.

2.7. Purification of Grafted Products

The number of 1 gram of the grafted product was added into 50 mL of xylene. The mixture was heated at 60 °C while stirring until all the products were completely dissolved. If there are still undissolved solids, they are separated using filter paper. The filtrate is then added slowly into excess acetone to form a precipitate. The precipitate is then separated from the filtrate. Using acetone as a solvent, the precipitate obtained was rinsed 3 times and then dried in an oven at 120 °C for 24 hours.

3. Results and Discussion

3.1. Thermogravimetric Analysis

The grafted products were characterized by using a Thermogravimeter by heating the sample in a special place with a certain temperature and time so that it experienced a reduction in mass. Furthermore, data processing and analysis were done by using Thermogravimetry Analysis (TA Analysis) software to determine the thermal stability of the sample.

3.2. Grafting MA onto CNR

In Figure 1 it can be seen that there was a change in the mass of the sample at a temperature of 121-178 °C, the sample experienced a reduction of 1.4-9.8%. And at a temperature of 179-383 °C, the sample experienced a reduction of 9.8%. This sample reduction occurs due to the evaporation of volatile compounds contained in the sample. Then at a temperature of 424-489 °C, there is a drastic mass reduction in the sample. The sample experienced a reduction of 90.6%. This is thought to be caused by the decomposition of the sample (Bettini & Agnelli, 1999).

3.3. Grafting MA onto CNR in the Presence of 0.5 grams of Divinylbenzene

In Figure 2 it can be seen that the sample experienced a change in mass at a temperature of 107-140 °C, the sample experienced a reduction of 1.8-4%. At a temperature of 141-382 °C the sample experienced a reduction of 4-18.8%. This reduction in sample mass is thought to be due to the evaporation of volatile compounds present in the sample. The presence of moisture in the sample is possible because the sample is stored in a container that can be in contact with air during storage, after being dried in the oven, and before the TGA thermal characterization is carried out. Then at a temperature of 382-471 °C there was a drastic reduction in the mass of the sample. The sample experienced a mass reduction of 90.2%. This is in line with what was reported by previous researcher

(Widiarti et al. 2018). It is suspected that the cause is that the sample undergoes decomposition, the compound decomposes into simpler ones.

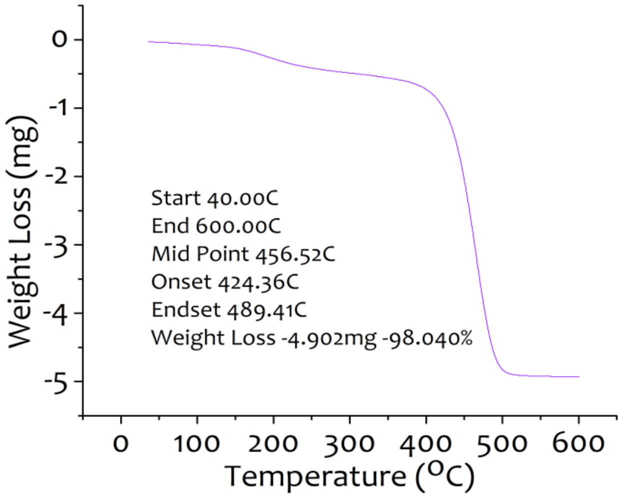

Figure 1. Thermogram of CNR with the addition of AM.

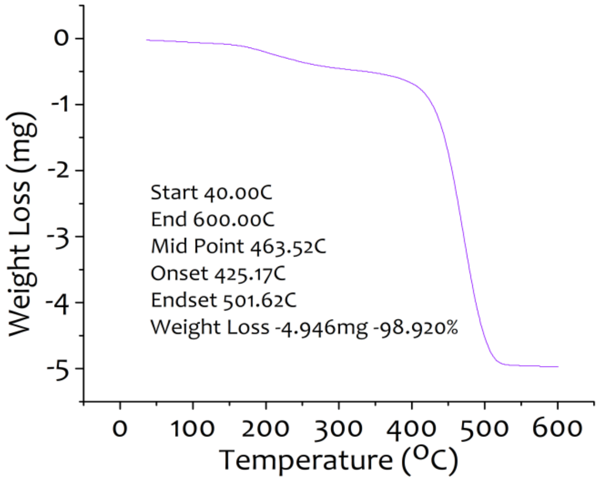

Figure 2. Thermogram of CNR with the addition of MA and 0.5 gram of Divinylbenzene.

In general, it can be said that there is a change in the thermal properties of grafted product with the graft reaction in the internal mixer based on the thermogravimetric characteristics. Grafting of MA onto CNR affects the thermal properties of CNR when viewed from the thermogravimetric curve line and the amount of change in sample content as can also be seen in Figure 1 and Figure 2.

For blank sample, decomposition occurs at a temperature of 424.36 °C (onset) to 489.41 °C (endset). There was an increase in the decomposition temperature of the grafted sample at 16 phr MA, namely at a temperature of 382 °C (onset) to 471 °C (endset). The grafting of the maleate group onto the CNR structure causes a change in the molecular structure of the rubber in which the addition of a new group affects the branch chain formed so that its molecular weight increases. Changes in the structure of CNR cause changes in its thermal properties where the resistance to heat increases as indicated by the increase in the decomposition temperature of the sample (Nakason et al. 2006).

3.4. Grafting of MA onto CNR in the Presence of 1 gram of Divinylbenzene

In Figure 3 it is known that the sample experienced a mass change at a temperature of 100-150 °C, the sample experienced a reduction of 0.2-0.6%. At a temperature of 151-382 °C the samples experienced a reduction of 0.6-8.6%. This sample reduction is thought to be due to the evaporation of volatile compounds (moisture) contain in the sample. The presence of moisture in the sample is possible because the sample is stored in a container that can be in contact with air during storage, after being dried in the oven, and before the TGA thermal characterization is carried out. Then at a temperature of 382-468 °C there was a drastic reduction in the mass of the sample. The sample experienced a mass reduction of 84.2%. This is thought to be caused by the decomposition of the sample.

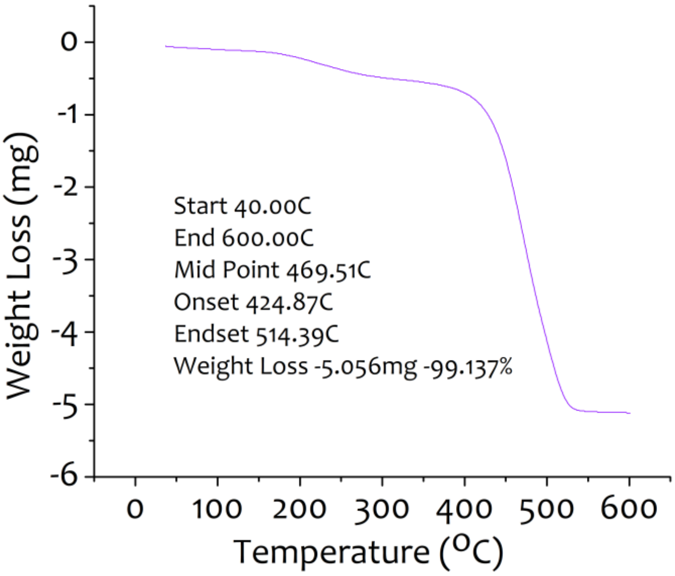

Figure 3. Thermogram of Maleated CNR Product in the Presence of 1 gram of Divinylbenzene.

3.5. Grafting of MA onto CNR in the Presence of 2 grams of Divinylbenzene

In Figure 4 it is known that the sample experienced a mass change at a temperature of 100-200 °C, the sample experienced a reduction of 3.6-7.2%. Temperature at 200-383 °C the sample experienced a reduction of 7.2 to 14.8%. This sample reduction is thought to be due to the evaporation of volatile compounds contain in the sample. The presence of moisture in the sample is possible because the sample is stored in a container that can be in contact with air during storage, after being dried in the oven, and before the TGA thermal characterization was carried out. Then at a temperature of 384-479 °C, there was a drastic mass reduction in the sample. The sample experienced a mass reduction of 82.2%. It is suspected that the sample undergoes decomposition.

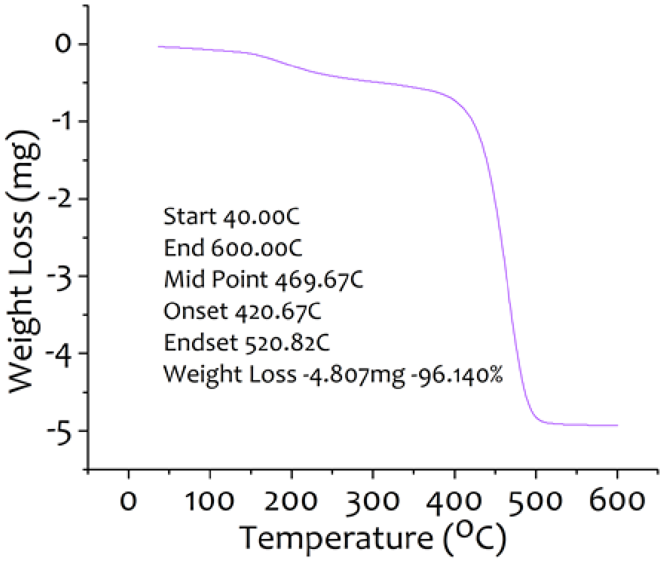

Figure 4. Thermogram of Maleated CNR Product in the Presence of 2 grams of Divinylbenzene.

In Figure 5 and Figure 6 it can be seen that the same trend occurs for all samples. CNR which had undergone a graft reaction with the addition of MA 16 phr and added divinylbenzene (0.5 gams, 1 gram, and 1.5 grams) showed changes in the temperature range and almost the same quantity. Three phases of mass reduction temperature for samples were found: a temperature of 100-200 °C, a temperature of 141-383 °C, and a temperature of 382-489 °C, respectively as can be seen in Table 1.

Table 1. The Phase Change of Sample Mass of Grafted Product.

No	Sample	Phase 1		Phase 2		Phase 3	
		(°C)	Weight Loss (%)	(°C)	Weight Loss (%)	(°C)	Weight Loss (%)
1	CNR+MA	121-178	1.4-9.8	179-383	9,8	424-489	90.6
2	CNR+MA+DVB 0.5	107-140	1.8-4	141-382	4-18.8	382-471	90.2
3	CNR+MA+DVB 1.0	100-150	0.2-0.6	151-382	0.6-8.6	382-468	84.2
4	CNR+MA+DVB 2.0	100-200	3.6-7.2	200-383	7.2-14	384-479	82.2

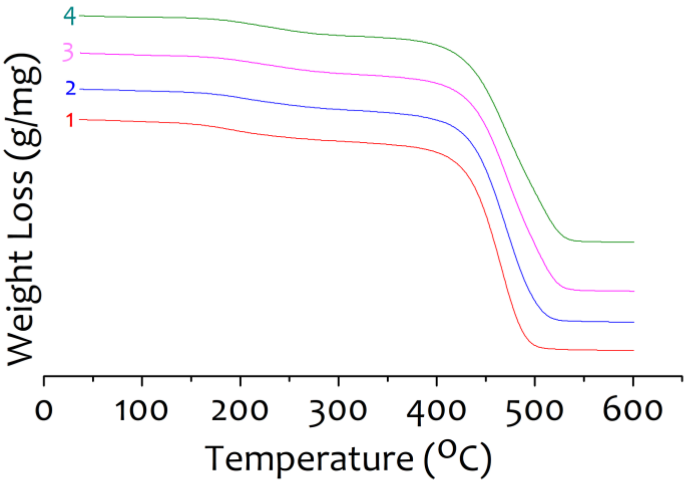

Figure 5. Overlay Thermograms Grafted CNR (1) Grafted CNR and 0.5 gram DVB (2), 1 gram DVB (3), and 2 gram DVB (4).

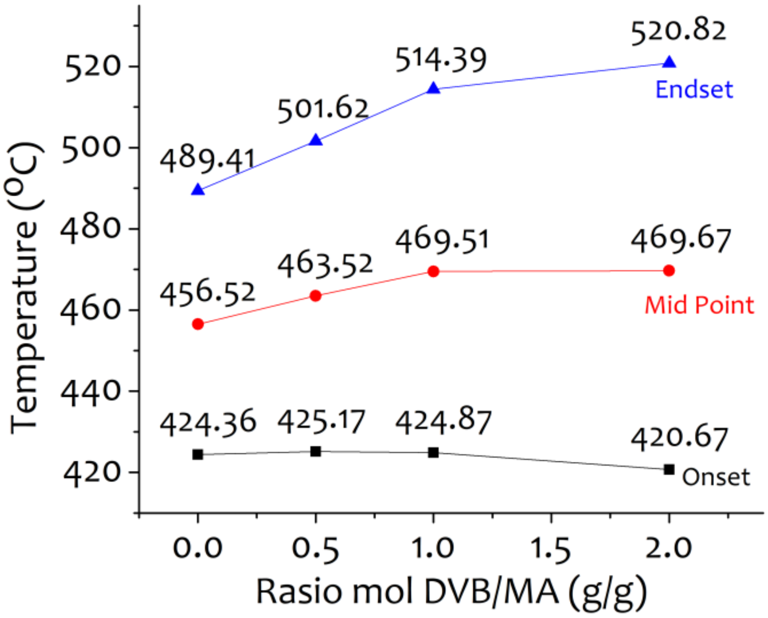

Figure 6. Overlay Mole Ratio-vs-Temperature Graphs: Onset, Midpoint, and Endset.

In phase 1 temperature 100-200 °C there is a reduction in the sample mass of 0.2-9.8%. Then at a temperature of 141-383 °C, there was a reduction in the mass of the sample from 0.6 to 18.8%. Furthermore, at a temperature of 282-489 °C, there was a drastic mass reduction of 82.2-90.6%. In general, it can be said that the thermal properties of maleated grafted CNR with the addition of divinylbenzene have almost the same thermal properties. This is following the statement that divinylbenzene can act as a crosslinking agent which has an impact on increasing the number of MA molecules bonded to the CNR chain.

4. Conclusion

CNR which has undergone a graft reaction with the addition of maleic anhydride affects increasing the thermal stability of CNR. The sample decomposition temperature increased with the increasing mole ratio of added DVB. The grafted product of 16 phr MA onto CNR decomposed at 489.41 °C. Samples of grafted products with the addition of 0.5, 1, and 2 mol ratio divinylbenzene comonomers experienced an increase in the decomposition temperature: 501.62 °C, 514.39 °C, and 520.82 °C, respectively.

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