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#31799 Summary

SUMMARY | REVIEW | EDITING

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Round 1

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PEER REVIEW
ROUND 1
REVIEWER A

1 **Study on the thermal properties of the grafted**
2 **product of maleic anhydride onto cyclized natural**
3 **rubber by using thermogravimetric method**

4
5
6 **Abstract**

7 This study aims to investigate the thermal properties of grafted products of maleic
8 anhydride onto cyclized natural rubber. The grafting was carried out in the melt phase at an
9 internal mixer of 150 °C and a rotor speed of 80 rpm. A total of 16 phr maleic anhydride was
10 reacted with cyclized natural rubber in the present and absence of divinylbenzene
11 comonomer with various mole ratios: 0,5, 1, and 2. The grafted products were characterized
12 by the thermogravimetric method to investigate their thermal properties. Based on the
13 results of the thermogravimetric analysis, it was shown that the sample increased its
14 thermal stability. The sample decomposes at a higher temperature with the increasing mole
15 ratio of divinylbenzene added. The grafted product with 16 phr maleic anhydride
16 decomposed at 489.41 °C. Then, the graft product samples with the addition of 0.5, 1, and
17 the 2-mole ratio of divinylbenzene comonomers decomposed at: 501.62 °C, 514.39 °C, and
18 520.82 °C, respectively.

19 **Keywords:** cyclized natural rubber, maleic anhydride, divinylbenzene, thermamogravimetric

20 **1. Introduction**

21 Indonesia is one of the main producers of natural rubber in the world. There is a
22 natural rubber plantation area with 3.6 million hectares of land and producing
23 3,630,268 tons. Natural rubber plantations are a leading agricultural sub-sector that

Comment [U1]: Separate with a period (.)

24 supports the Indonesian economy with an export volume of 2.99 million tons and
25 US\$ 5.10 billion. In 2019 Indonesia produced 26% of natural rubber in the world,
26 ranking second in the world's natural rubber production after Thailand (Indonesia,
27 2019). Modification of the molecular structure of natural rubber physically or
28 chemically is important to produce new materials that have unique characteristics for
29 new and broad uses in certain fields (Hayeemasae et al., 2020), (Widiarti et al., 2018).

Comment [U2]: (..... et al. 2018; et al. 2020)

30 Natural rubber is a cis-poly isoprene natural polymer compound resulting from the
31 addition of 1,4 from isoprene monomer which has a molecular weight of 1-2 million
32 and there are 15,000-20,000 unsaturated bonds in the molecular chain. Natural
33 rubber has properties that are not resistant to ozone, oil, and temperature due to the
34 presence of a carbon-carbon double bond in the chemical structure of cis-1,4-
35 polyisoprene which is the main component of natural rubber (Nakason et al., 2006),
36 (Guldogan et al., 2004), (Rzayev, 2011). But natural rubber has advantages in terms of
37 resilience, abrasion resistance, stickiness, and plasticity (Saelao & Phinyocheep,
38 2005).

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

45 Modification of CNR by grafting using Maleic Anhydride (AM) monomer has been
46 successfully carried out by several researchers (Zhao et al., 2018), (Ritonga et al.,
47 2019). Based on the Fourier Transformed Infra-Red/FTIR spectral data of the grafted
48 product, the maleate group was successfully grafted onto the CNR structure with the
49 appearance of absorption at 1780 cm⁻¹ and 1841 cm⁻¹ which is a typical carbonyl
50 absorption of the maleate group (Sitanggang & Eddyanto, 2019) (Eddiyanto, 2007),
51 (Siregar, M.S. et al., 2014, 2015, 2019, 2021, 2021). To increase the degree of grafting,

52 styrene comonomers (Siregar, M.S. et al., 2014), divinylbenzene (Siregar, M.S. et al.,
53 2019, 2021, 2021) and Trimethylol Propane Triacrylate (Siregar, M.S. et al., 2019, 2021)
54 have been used.

Comment [U3]: (Siregar et al. 2014)

Comment [U4]: (Siregar et al. 2019; Siregar et al. 2021a; Siregar et al. 2021b)

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

59

60 2. Methods

Comment [U5]: Patented methods must include the source

61 2.1 Materials

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

67 2.2 Equipment

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

72

73 2.3 General Procedure

Comment [U6]: Patented methods must include the source

74 This research is a laboratory experiment to produce grafted products in an
75 internal mixer with a temperature of 150°C and a rotor speed of 80 rpm, where 16
76 phr MA was reacted with CNR in the presence and absence of DVB comonomer with
77 various mole ratios of 0, 0.5, 1 and 2. To investigate the thermal properties of the
78 grafted product, it was characterized by a Mettler Toledo TGA 850
79 Thermogravimeter.

80

81 2.4. Preparation of Internal Mixer

82 The operating temperature of 150 oC and the rotational speed of the rotor of 80
83 rpm, the internal mixer was programmed in accordance with the research design to
84 be carried out. Furthermore, the internal mixer can be used after the chamber
85 temperature matches programmed temperature, which can be seen on the
86 computer monitor screen.

Comment [U7]: 150 oC or 150 °C?

87

88 2.5. Grafting MA onto CNR without DVB

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

Comment [U8]: What are MA, CNR and DVB?

95

96 2.6. Grafting MA onto CNR in the presence of DVB

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

102

103 2.7. Purification of grafted products

104 The number of 1 gram of the grafted product was added into 50 mL of xylene.
105 The mixture was heated at 60°C while stirring until all the products were completely
106 dissolved. If there are still undissolved solids, they are separated using filter paper.
107 The filtrate is then added slowly into excess acetone to form a precipitate. The

108 precipitate is then separated from the filtrate. Using acetone as a solvent, the
109 precipitate obtained was rinsed 3 times and then dried in an oven at 120°C for 24
110 hours.

111

112 3. Results and Discussion

113 3.1. Thermogravimetric Analysis (TGA)

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

119

120 3.2. Grafting MA onto CNR

121 In Figure 11 (a), it can be seen that there was a change in the mass of the sample
122 at a temperature of 121-178 °C, the sample experienced a reduction of 1.4-9.8%. And at
123 a temperature of 179-383 °C, the sample experienced a reduction of 9.8%. This sample
124 reduction occurs due to the evaporation of volatile compounds contained in the
125 sample. Then at a temperature of 424-489 °C, there is a drastic mass reduction in the
126 sample. The sample experienced a reduction of 90.6%. This is thought to be caused by
127 the decomposition of the sample (Bettini & Agnelli, 1999).

128

129 3.3. Grafting MA onto CNR in the presence of 0.5 grams of divinyl benzene

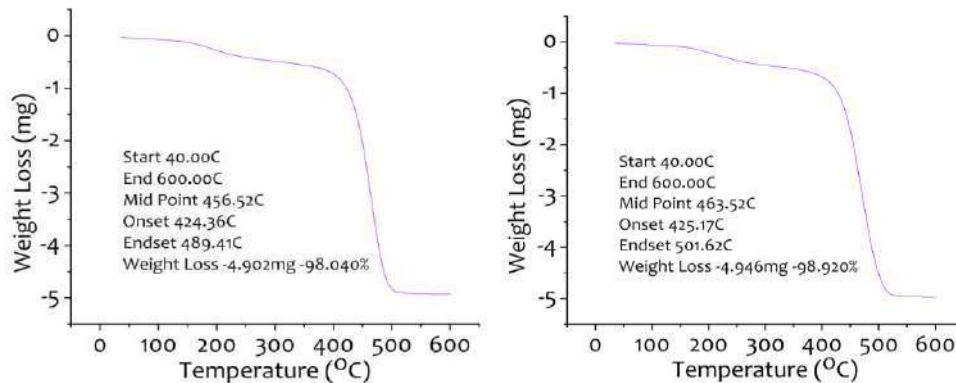
130 In Figure 11 (b) it can be seen that the sample experienced a change in mass at a
131 temperature of 107-140 °C, the sample experienced a reduction of 1.8-4%. At a
132 temperature of 141-382 °C the sample experienced a reduction of 4-18.8%. This
133 reduction in sample mass is thought to be due to the evaporation of volatile
134 compounds present in the sample. The presence of moisture in the sample is possible
135 because the sample is stored in a container that can be in contact with air during

Comment [U9]: Why abbreviate if not used

Comment [U10]: Figure 1 or Figure 11?

Comment [U11]: Figure 2 or Figure 11?

136 storage, after being dried in the oven, and before the TGA thermal characterization is
137 carried out. Then at a temperature of 382-471 °C there was a drastic reduction in the
138 mass of the sample. The sample experienced a mass reduction of 90.2%. This is in line
139 with what was reported by previous researcher (Widiarti et al., 2018).



140

141 **Figure 11.** Thermogram of CNR with the addition of AM (a) and the addition of MA

142 and 0.5 gram of divinyl benzene (b).

143

144 It is suspected that the cause is that the sample undergoes decomposition, the
145 compound decomposes into simpler ones.

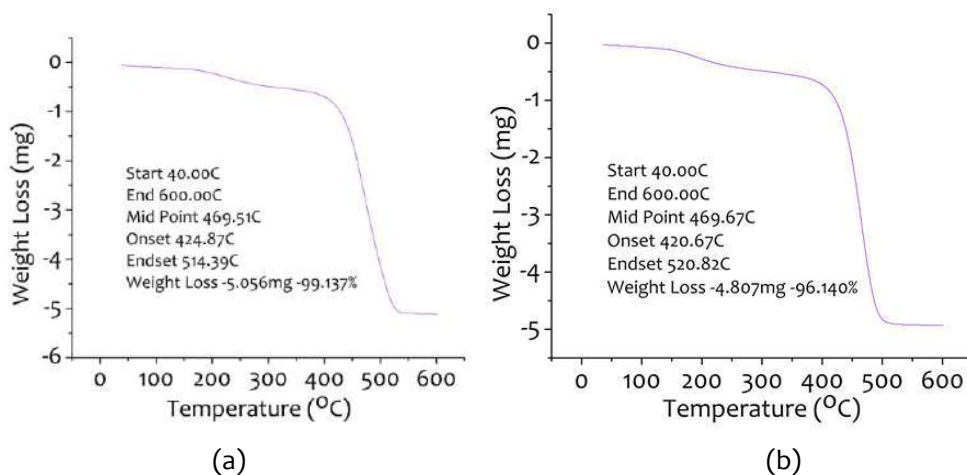
146 In general, it can be said that there is a change in the thermal properties of
147 grafted product with the graft reaction in the internal mixer based on the
148 thermogravimetric characteristics. Grafting of MA onto CNR affects the thermal
149 properties of CNR when viewed from the thermogravimetric curve line and the
150 amount of change in sample content as can also be seen in **Figures 11 (a) and (b)**.

151 For blank sample, decomposition occurs at a temperature of 424.36 °C (onset) to
152 489.41 °C (endset). There was an increase in the decomposition temperature of the
153 grafted sample at 16 phr MA, namely at a temperature of 382 °C (onset) to 471 °C
154 (endset). The grafting of the maleate group onto the CNR structure causes a change
155 in the molecular structure of the rubber in which the addition of a new group affects
156 the branch chain formed so that its molecular weight increases. Changes in the

Comment [U12]: Figure 1 -10 where?

Comment [U13]: Figure 1 and Figure 2 or Figure 11 (a) and (b)?

157 structure of CNR cause changes in its thermal properties where the resistance to heat
158 increases as indicated by the increase in the decomposition temperature of the
159 sample (Nakason et al., 2006).



160
161

162 **Figure 12.** Thermogram of maleated CNR product in the presence of 1 gram of
163 divinylbenzene (a) and the presence of 2 grams of divinylbenzene (b).

Comment [U14]: Figure ??

164

165 3.4. Grafting of MA onto CNR in the presence of 1 gram of divinylbenzene

166 In **Figure 12(a)**, it is known that the sample experienced a mass change at a
167 temperature of 100-150 °C, the sample experienced a reduction of 0.2-0.6%. At a
168 temperature of 151-382 °C the samples experienced a reduction of 0.6-8.6%. This
169 sample reduction is thought to be due to the evaporation of volatile compounds
170 (moisture) contain in the sample. The presence of moisture in the sample is possible
171 because the sample is stored in a container that can be in contact with air during
172 storage, after being dried in the oven, and before the TGA thermal characterization is
173 carried out. Then at a temperature of 382-468 °C there was a drastic reduction in the
174 mass of the sample. The sample experienced a mass reduction of 84.2%. This is
175 thought to be caused by the decomposition of the sample.

Comment [U15]: Figure ?

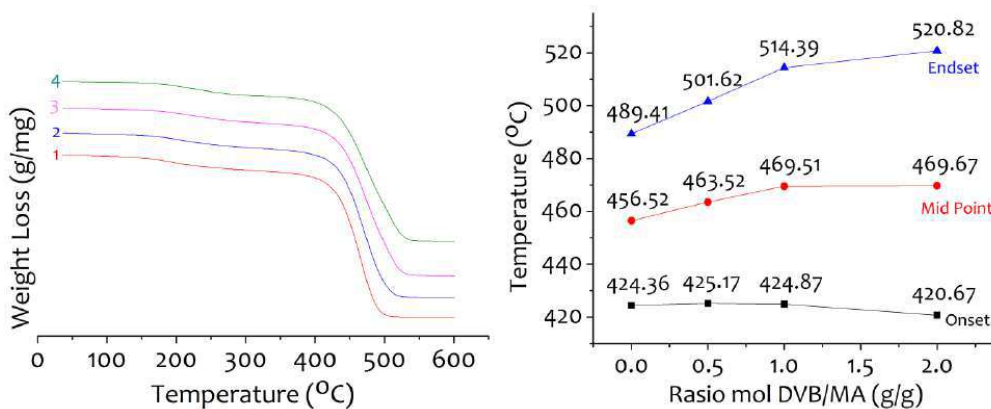
176

177 3.5. Grafting of MA onto CNR in the presence of 2 grams of divinylbenzene

178 In Figure 12(b), it is known that the sample experienced a mass change at a
 179 temperature of 100-200 °C, the sample experienced a reduction of 3.6-7.2%. And at a
 180 temperature of 200-383 °C the sample experienced a reduction of 7.2 to 14.8%. This
 181 sample reduction is thought to be due to the evaporation of volatile compounds
 182 contain in the sample. The presence of moisture in the sample is possible because the
 183 sample is stored in a container that can be in contact with air during storage, after
 184 being dried in the oven, and before the TGA thermal characterization was carried out.
 185 Then at a temperature of 384-479 °C, there was a drastic mass reduction in the
 186 sample. The sample experienced a mass reduction of 82.2%. It is suspected that the
 187 sample undergoes decomposition.

Comment [U16]: Figure ?

Comment [U17]: The beginning of the sentence should not use 'And'



188
 189 **Figure 13.** Overlay thermograms grafted CNR (1) grafted CNR and 0.5 gram DVB (2), 1
 190 gram DVB (3), and 2 gram DVB (4) and overlay mole ratio-vs-temperature
 191 graphs: onset, midpoint, and endset.

192
 193 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

Comment [U18]: Separate with a period (.)

194

195 In Figure 13 (a) it can be seen that the same trend occurs for all samples. CNR
 196 which had undergone a graft reaction with the addition of MA 16 phr and added
 197 divinylbenzene (0.5 gams, 1 gram, and 1.5 gram) showed changes in the temperature
 198 range and almost the same quantity. Three phases of mass reduction temperature
 199 for samples were found: a temperature of 100-200 °C, a temperature of 141-383 °C,
 200 and a temperature of 382-489 °C, respectively as can be seen in Table 1.

201 In phase 1 temperature 100-200 oC there is a reduction in the sample mass of 0.2-
 202 9.8%. Then at a temperature of 141-383 °C, there was a reduction in the mass of the
 203 sample from 0.6 to 18.8%. Furthermore, at a temperature of 282-489 °C, there was a
 204 drastic mass reduction of 82.2-90.6%. In general, it can be said that the thermal
 205 properties of maleated grafted CNR with the addition of divinylbenzene have almost
 206 the same thermal properties. This is following the statement that divinylbenzene can
 207 act as a crosslinking agent which has an impact on increasing the number of MA
 208 molecules bonded to the CNR chain.

209

Comment [U19]: We recommend that the image numbers are sorted from Figure 1, Figure 2, and so on

210 4. Conclusion

211 CNR which has undergone a graft reaction with the addition of maleic anhydride
 212 affects increasing the thermal stability of CNR. The sample decomposition
 213 temperature increased with the increasing mole ratio of added DVB. The grafted
 214 product of 16 phr MA onto CNR decomposed at 489.41 °C. Samples of grafted
 215 products with the addition of 0.5, 1, and 2 mol ratio divinylbenzene comonomers
 216 experienced an increase in the decomposition temperature: 501.62 °C, 514.39 °C, and
 217 520.82 °C, respectively.

218

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223 Karet Nusantara (Nusantara Rubber Industry) for providing Resiprena 35.

Comment [U20]: It's better to write down the research contract number

224

225 References

- 226 Bayu, A., Nandiyanto, D., Oktiani, R., & Ragadhita, R. (2019). How to Read and
227 Interpret FTIR Spectroscopy of Organic Material. *Indonesian Journal of Science &*
228 *Technology*, 4(1), 97–118.
- 229 Bettini, S. H. P., & Agnelli, J. A. M. (1999). Grafting of Maleic Anhydride onto
230 Polypropylene by Reactive Processing. I. Effect of Maleic Anhydride and Peroxide
231 Concentrations on the Reaction. *Journal of Applied Polymer Science*, 74, 2706–
232 2717. <https://doi.org/10.1002/app.10705>
- 233 Eddiyanto. (2007). *Functionalisation of Polymers: Reactive Processing, Structure and*
234 *Performance Characteristics*. In Aston University.
- 235 Guldogan, Y., Egri, S., Rzaev, Z. M. O., & Piskin, E. (2004). Comparison of maleic
236 anhydride grafting onto powder and granular polypropylene in the melt by
237 reactive extrusion. *Journal of Applied Polymer Science*, 92(6), 3675–3684.
238 <https://doi.org/10.1002/app.20304>
- 239 Hayeemasae, N., Sensem, Z., Sahakaro, K., & Ismail, H. (2020). Maleated Natural
240 Rubber / Halloysite. *Processes*, 1–13.
- 241 Indonesia, B. S. (2019). *Indonesian Rubber Statistics*.
- 242 Nakason, C., Saiwaree, S., Tatun, S., & Kaesaman, A. (2006). Rheological, thermal and
243 morphological properties of maleated natural rubber and its reactive blending
244 with poly(methyl methacrylate). *Polymer Testing*, 25(5), 656–667.
245 <https://doi.org/10.1016/j.polymertesting.2006.03.011>
- 246 Ritonga, A. H., Aritonang, B., & Siahaan, M. A. (2019). *MODIFICATION OF CYCLIC*

247 NATURAL RUBBER WITH COMONOMER OF ANHYDRIDE MALEIC AND OLEIC ACID
248 THROUGH GRAFTING METHOD WITH REFLUX TECHNIQUE USING BENZOYL PEROXIDE
249 INITIATOR. 17(November), 37–44.

250 Rzayev, Z. M. O. (2011). Graft Copolymers of Maleic Anhydride and Its Isostructural
251 Analogues: High Performance Engineering Materials. 3(March), 153–215.
252 <http://arxiv.org/abs/1105.1260>

253 Saelao, J., & Phinyocheep, P. (2005). Influence of styrene on grafting efficiency of
254 maleic anhydride onto natural rubber. *Journal of Applied Polymer Science*, 95(1),
255 28–38. <https://doi.org/10.1002/app.20810>

256 Said Siregar, M., Ardilla, D., Eddiyanto, & Nasution, A. S. (2021). Grafting of Maleic
257 Anhydride onto Cyclized Natural Rubber in the Melt Phase: The Effect of
258 Trimethylol Propane Triacrylate. *Journal of Physics: Conference Series*, 1764(1).
259 <https://doi.org/10.1088/1742-6596/1764/1/012200>

260 Siregar, M. S. (2015). Grafting Product Of Maleic Anhydride Onto Cyclized Natural
261 Rubber In An Internal Mixer: Physical Properties And Compatibility With
262 Polyamide. *Agrium ISSN 0852-1077 (Print) ISSN 2442-7306 (Online)*, 19(2), 176–181.

263 Siregar, M. S., Ardilla, D., Eddiyanto, & Nasution, A. S. (2021). Grafting of Maleic
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266 <https://doi.org/10.1088/1742-6596/1764/1/012200>

267 Siregar, M. S., Ardilla, D., & Nasution, A. S. (2019). Grafting of Maleic Anhydride onto
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269 Triacrylate. *Proceeding International Seminar on Islamic Studies*, 1(1), 10–15.
270 <https://doi.org/10.1088/1742-6596/1764/1/012200>

271 Siregar, M. S., Astuti, R. P., Fuadi, M., Ardilla, D., Masyura, M. D., Nasution, A., &
272 Eddiyanto. (2021). GRAFTING OF MALEIC ANHYDRIDE ONTO CYCLIZED NATURAL
273 RUBBER: THE PRESENCE OF DIVINYLBENZENE TO INCREASE THE GRAFTING

274 DEGREE. *Jurnal Riset Teknologi Industri*, 15(2), 222–230.

275 Siregar, M. S., Thamrin, Basuki, Eddiyanto, & Mendez, J. A. (2014). Grafting of Maleic
276 Anhydride onto Cyclized Natural Rubber by Reactive Processing : the Effect of
277 Maleic Anhydride Concentrations. *Chemistry and Material Research*, 6(11), 15–21.

278 Sitanggang, B. C., & Eddyanto, E. (2019). Functionalization of cyclic natural rubber
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281 <https://doi.org/10.24114/jpkim.v11i3.15736>

282 Soleimani, S. M., Faheiman, A., & Mowaze, Z. (2020). The Effects of Using Crumb
283 Rubber Modified Binder in an Asphalt Pavement. *American Journal of Engineering
284 and Applied Sciences*, 13(2), 237–253. <https://doi.org/10.3844/ajeassp.2020.237.253>

285 Widiarti, L., Wirjosentono, B., & Eddyanto2. (2018). ANALYSIS OF THERMAL
286 PROPERTIES AND SOLUBILITY TEST OF CYCLIC NATURAL RUBBER AND CYCLIC LIQUID
287 NATURAL RUBBER. 14, 139–143.

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291

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

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.

Keywords: cyclized natural rubber, maleic anhydride, divinylbenzene, thermogravimetric

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

24 supports the Indonesian economy with an export volume of 2.99 million tons and
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26 ranking second in the world's natural rubber production after Thailand (Indonesia,
27 2019). Modification of the molecular structure of natural rubber physically or
28 chemically is important to produce new materials that have unique characteristics for
29 new and broad uses in certain fields (Hayeemasae et al. 2020; Widiarti et al. 2018).

30 Natural rubber is a cis-poly isoprene natural polymer compound resulting from the
31 addition of 1,4 from isoprene monomer which has a molecular weight of 1-2 million
32 and there are 15,000-20,000 unsaturated bonds in the molecular chain. Natural
33 rubber has properties that are not resistant to ozone, oil, and temperature due to the
34 presence of a carbon-carbon double bond in the chemical structure of cis-1,4-
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39 Cyclized Natural Rubber/CNR is a derivative material of natural rubber which is the
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41 cyclization reaction. Cyclization of natural rubber causes a change in the
42 characteristics of natural rubber from being elastic to being thermoplastic that is
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47 Based on the Fourier Transformed Infra-Red/FTIR spectral data of the grafted
48 product, the maleate group was successfully grafted onto the CNR structure with the
49 appearance of absorption at 1780 cm^{-1} and 1841 cm^{-1} which is a typical carbonyl
50 absorption of the maleate group (Sitanggang & Eddyanto, 2019; Eddyanto, 2007;
51 Siregar et al. 2014; Siregar, 2015; Siregar et al., 2019; Siregar et al. 2021a; Siregar et al.,

52 2021b). To increase the degree of grafting, styrene comonomers (Siregar et al. 2014),
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54 Trimethylol Propane Triacrylate (Siregar et al. 2019; Siregar et al. 2021) have been
55 used.

56 Based on the description above, this paper reports on the study of the thermal
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58 an internal mixer in the presence and absence of divinylbenzene comonomer by
59 using the thermogravimetry (TGA) method.

60

61 **2. Methods** (M. S. Siregar, 2014)

62 2.1 Materials

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

68 2.2 Equipment

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

73

74 2.3 General Procedure

75 This research is a laboratory experiment to produce grafted products in an
76 internal mixer with a temperature of 150°C and a rotor speed of 80 rpm, where 16
77 phr MA was reacted with CNR in the presence and absence of DVB comonomer with
78 various mole ratios of 0,5, 1 and 2 (M. S. Siregar, 2014). To investigate the thermal

79 properties of the grafted product, it was characterized by a Mettler Toledo TGA 850
80 Thermogravimeter.

81

82 2.4. Preparation of Internal Mixer

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

88

89 2.5. Grafting maleic anhydride onto cyclized natural rubber without divinylbenzene

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

96

97 2.6. Grafting MA onto CNR in the presence of DVB

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

103

104 2.7. Purification of grafted products

105 The number of 1 gram of the grafted product was added into 50 mL of xylene.
106 The mixture was heated at 60°C while stirring until all the products were completely

107 dissolved. If there are still undissolved solids, they are separated using filter paper.
108 The filtrate is then added slowly into excess acetone to form a precipitate. The
109 precipitate is then separated from the filtrate. Using acetone as a solvent, the
110 precipitate obtained was rinsed 3 times and then dried in an oven at 120°C for 24
111 hours.

112

113 3. Results and Discussion

114 3.1. Thermogravimetric Analysis

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

120

121 3.2. Grafting MA onto CNR

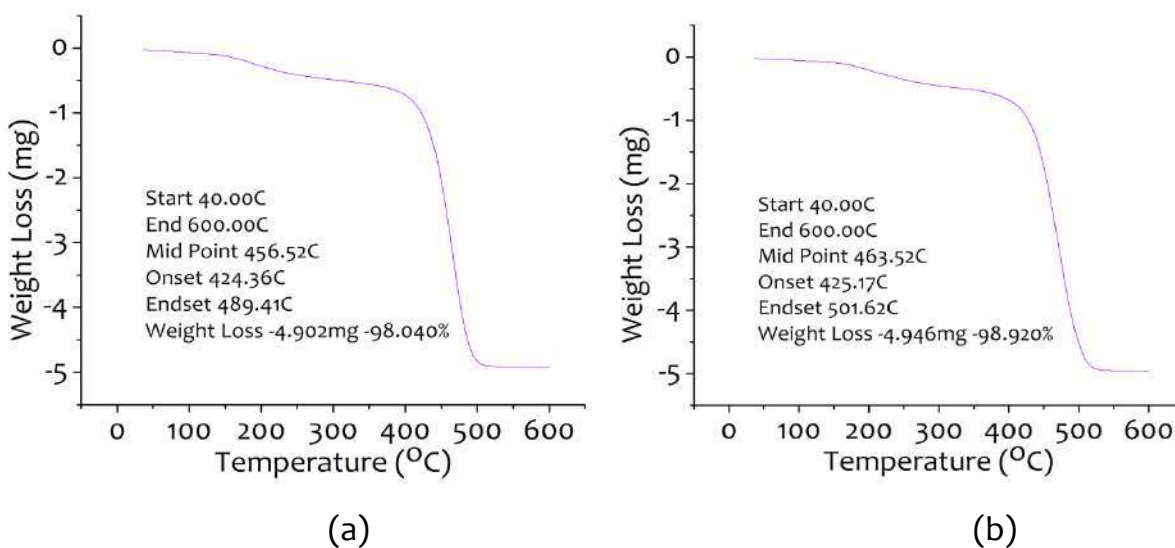
122 In [Figure 1 \(a\)](#), it can be seen that there was a change in the mass of the sample at
123 a temperature of 121-178 °C, the sample experienced a reduction of 1.4-9.8%. And at a
124 temperature of 179-383 °C, the sample experienced a reduction of 9.8%. This sample
125 reduction occurs due to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

129

130 3.3. Grafting MA onto CNR in the presence of 0.5 grams of divinyl benzene

131 In [Figure 1 \(b\)](#) it can be seen that the sample experienced a change in mass at a
132 temperature of 107-140 °C, the sample experienced a reduction of 1.8-4%. At a
133 temperature of 141-382 °C the sample experienced a reduction of 4-18.8%. This
134 reduction in sample mass is thought to be due to the evaporation of volatile

135 compounds present in the sample. The presence of moisture in the sample is possible
136 because the sample is stored in a container that can be in contact with air during
137 storage, after being dried in the oven, and before the TGA thermal characterization is
138 carried out. Then at a temperature of 382-471 °C there was a drastic reduction in the
139 mass of the sample. The sample experienced a mass reduction of 90.2%. This is in line
140 with what was reported by previous researcher (Widiarti et al., 2018).



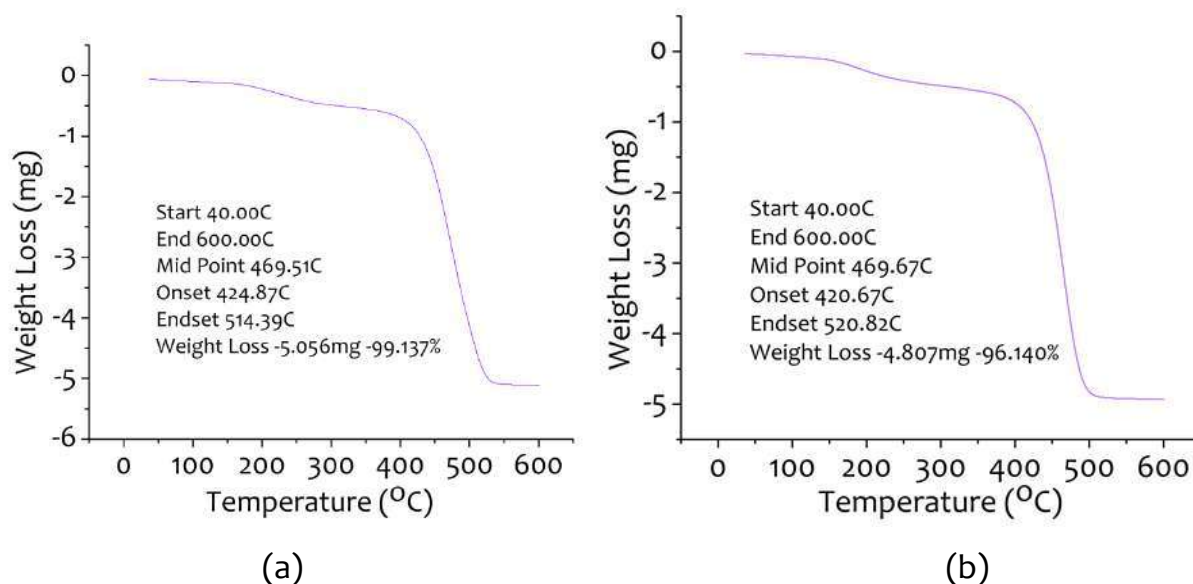
141
142 (a) (b)
143 **Figure 1.** Thermogram of CNR with the addition of AM (a) and the addition of MA and
144 0.5 gram of divinyl benzene (b).

145
146 It is suspected that the cause is that the sample undergoes decomposition, the
147 compound decomposes into simpler ones.

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

153 For blank sample, decomposition occurs at a temperature of 424.36 °C (onset) to
154 489.41 °C (endset). There was an increase in the decomposition temperature of the
155 grafted sample at 16 phr MA, namely at a temperature of 382 °C (onset) to 471 °C

156 (endset). The grafting of the maleate group onto the CNR structure causes a change
157 in the molecular structure of the rubber in which the addition of a new group affects
158 the branch chain formed so that its molecular weight increases. Changes in the
159 structure of CNR cause changes in its thermal properties where the resistance to heat
160 increases as indicated by the increase in the decomposition temperature of the
161 sample (Nakason et al., 2006).



162
163 (a) (b)
164 **Figure 2.** Thermogram of maleated CNR product in the presence of 1 gram of
165 divinylbenzene (a) and the presence of 2 grams of divinylbenzene (b).

167 3.4. Grafting of MA onto CNR in the presence of 1 gram of divinylbenzene

168 In **Figure 2(a)**, it is known that the sample experienced a mass change at a
169 temperature of 100-150 °C, the sample experienced a reduction of 0.2-0.6%. At a
170 temperature of 151-382 °C the samples experienced a reduction of 0.6-8.6%. This
171 sample reduction is thought to be due to the evaporation of volatile compounds
172 (moisture) contain in the sample. The presence of moisture in the sample is possible
173 because the sample is stored in a container that can be in contact with air during
174 storage, after being dried in the oven, and before the TGA thermal characterization is
175 carried out. Then at a temperature of 382-468 °C there was a drastic reduction in the

176 mass of the sample. The sample experienced a mass reduction of 84.2%. This is
177 thought to be caused by the decomposition of the sample.

178

179 3.5. Grafting of MA onto CNR in the presence of 2 grams of divinylbenzene

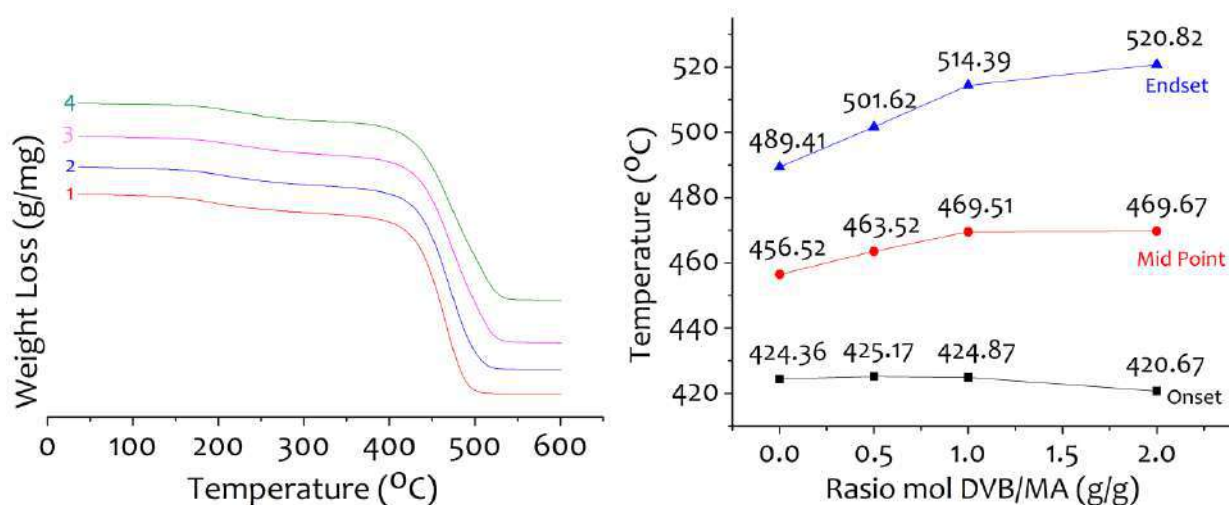
180 In Figure 2(b), it is known that the sample experienced a mass change at a
181 temperature of 100-200 °C, the sample experienced a reduction of 3.6-7.2%.

182 Temperature at 200-383 °C the sample experienced a reduction of 7.2 to 14.8%. This
183 sample reduction is thought to be due to the evaporation of volatile compounds

184 contain in the sample. The presence of moisture in the sample is possible because the
185 sample is stored in a container that can be in contact with air during storage, after

186 being dried in the oven, and before the TGA thermal characterization was carried out.
187 Then at a temperature of 384-479 °C, there was a drastic mass reduction in the

188 sample. The sample experienced a mass reduction of 82.2%. It is suspected that the
189 sample undergoes decomposition.



190

191 **Figure 3.** Overlay thermograms grafted CNR (1) grafted CNR and 0.5 gram DVB (2), 1
192 gram DVB (3), and 2 gram DVB (4) and overlay mole ratio-vs-temperature
193 graphs: onset, midpoint, and endset.

194

195 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

196

197 In Figure 3 it can be seen that the same trend occurs for all samples. CNR which
 198 had undergone a graft reaction with the addition of MA 16 phr and added
 199 divinylbenzene (0.5 gams, 1 gram, and 1.5 gram) showed changes in the temperature
 200 range and almost the same quantity. Three phases of mass reduction temperature
 201 for samples were found: a temperature of 100-200 °C, a temperature of 141-383 °C,
 202 and a temperature of 382-489 °C, respectively as can be seen in Table 1.

203 In phase 1 temperature 100-200 oC there is a reduction in the sample mass of 0.2-
 204 9.8%. Then at a temperature of 141-383 °C, there was a reduction in the mass of the
 205 sample from 0.6 to 18.8%. Furthermore, at a temperature of 282-489 °C, there was a
 206 drastic mass reduction of 82.2-90.6%. In general, it can be said that the thermal
 207 properties of maleated grafted CNR with the addition of divinylbenzene have almost
 208 the same thermal properties. This is following the statement that divinylbenzene can
 209 act as a crosslinking agent which has an impact on increasing the number of MA
 210 molecules bonded to the CNR chain.

211

212 4. Conclusion

213 CNR which has undergone a graft reaction with the addition of maleic anhydride
 214 affects increasing the thermal stability of CNR. The sample decomposition
 215 temperature increased with the increasing mole ratio of added DVB. The grafted
 216 product of 16 phr MA onto CNR decomposed at 489.41 °C. Samples of grafted

217 products with the addition of 0.5, 1, and 2 mol ratio divinylbenzene comonomers
218 experienced an increase in the decomposition temperature: 501.62 °C, 514.39 °C, and
219 520.82 °C, respectively.

220

221 **Acknowledgment**

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223 Education, the Republic of Indonesia for their financial support through Penelitian
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226 (Nusantara Rubber Industry) for providing Resiprena 35.

227

228 **References**

- 229 Bettini, S. H. P., & Agnelli, J. A. M. (1999). Grafting of Maleic Anhydride onto
230 Polypropylene by Reactive Processing. I. Effect of Maleic Anhydride and Peroxide
231 Concentrations on the Reaction. *Journal of Applied Polymer Science*, 74, 2706–
232 2717. <https://doi.org/10.1002/app.10705>
- 233 Eddiyanto. (2007). Functionalisation of Polymers: Reactive Processing, Structure and
234 Performance Characteristics. In *Aston University*.
- 235 Guldogan, Y., Egri, S., Rzaev, Z. M. O., & Piskin, E. (2004). Comparison of maleic
236 anhydride grafting onto powder and granular polypropylene in the melt by
237 reactive extrusion. *Journal of Applied Polymer Science*, 92(6), 3675–3684.
238 <https://doi.org/10.1002/app.20304>
- 239 Hayeemasae, N., Sensem, Z., Sahakaro, K., & Ismail, H. (2020). Maleated Natural
240 Rubber / Halloysite. *Processes*, 1–13.
- 241 Indonesia, B. S. (2019). *Indonesian Rubber Statistics*.
- 242 Nakason, C., Saiwaree, S., Tatun, S., & Kaesaman, A. (2006). Rheological, thermal and
243 morphological properties of maleated natural rubber and its reactive blending

244 with poly(methyl methacrylate). *Polymer Testing*, 25(5), 656–667.
245 <https://doi.org/10.1016/j.polymertesting.2006.03.011>

246 Nandiyanto, Asep Bayu, D., Oktiani, R., & Ragadhita, R. (2019). How to Read and
247 Interpret FTIR Spectroscope of Organic Material. *Indonesian Journal of Science &*
248 *Technology*, 4(1), 97–118.

249 Ritonga, A. H., Aritonang, B., & Siahaan, M. A. (2019). *Modification Of Cyclic Natural*
250 *Rubber With Comonomer Of Anhydrtaes Maleic And Oleic Acid Through Grafting*
251 *Method With Reflux Technique Using Benzoyl Peroxide Initiator*. 17(November),
252 37–44.

253 Rzayev, Z. M. O. (2011). *Graft Copolymers of Maleic Anhydride and Its Isostructural*
254 *Analogues: High Performance Engineering Materials*. 3(March), 153–215.
255 <http://arxiv.org/abs/1105.1260>

256 Saelao, J., & Phinyocheep, P. (2005). Influence of styrene on grafting efficiency of
257 maleic anhydride onto natural rubber. *Journal of Applied Polymer Science*, 95(1),
258 28–38. <https://doi.org/10.1002/app.20810>

259 Siregar, M. S. (2014). *Modifikasi dan Karakterisasi Karet Alam Siklis Dengan Anhidrida*
260 *Maleat Sebagai Substituen Bahan Pengikat Cat Sintetis*. University of Sumatera
261 Utara.

262 Siregar, M. S. (2015). Grafting Product Of Maleic Anhydride Onto Cyclized Natural
263 Rubber In An Internal Mixer: Physical Properties And Compatiblity With
264 Polyamide. *Agrium ISSN 0852-1077 (Print) ISSN 2442-7306 (Online)*, 19(2), 176–181.

265 Siregar, M. S., Ardilla, D., Eddiyanto, & Nasution, A. S. (2021). Grafting of Maleic
266 Anhydride onto Cyclized Natural Rubber in the Melt Phase: The Effect of
267 Trimethylol Propane Triacrylate. *Journal of Physics: Conference Series*, 1764(1).
268 <https://doi.org/10.1088/1742-6596/1764/1/012200>

269 Siregar, M. S., Ardilla, D., & Nasution, A. S. (2019). Grafting Of Maleic Anhydride onto
270 Cyclized Natural Rubber In The Melt Phase: The Effect of Maleic Anhydride

271 Concentrations on the Specific Weight and Total Acid. *Proceeding International*
272 *Seminar on Islamic Studies*, 1(1), 10–15. <https://doi.org/10.1088/1742->
273 [6596/1764/1/012200](https://doi.org/10.1088/1742-6596/1764/1/012200)

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288 *And Solubility Test Of Cyclic Natural Rubber And Cyclic Liquid Natural Rubber*. 14,
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4
5
6 **Abstract**

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Comment [U1]: et al.

Comment [U2]: et al.

Comment [U3]: et al.

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Comment [U4]: et al.

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60

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Comment [U5]: Letakkan di tahapan metode yang merujuk sumber ini

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66 Nusantara, Sei Bamban, Tebing Tinggi, North Sumatra, Indonesia, in granular form
67 and is a commercial product under the trade name Resiprena 35 (R- 35).

68 2.2 Equipment

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

73

74 2.3 General Procedure

75 This research is a laboratory experiment to produce grafted products in an
76 internal mixer with a temperature of 150°C and a rotor speed of 80 rpm, where 16
77 phr MA was reacted with CNR in the presence and absence of DVB comonomer with
78 various mole ratios of 0,5, 1 and 2 (M. S. Siregar, 2014). To investigate the thermal

Comment [U6]: Pastikan cara mengutip sudah benar, lihat contoh

79 properties of the grafted product, it was characterized by a Mettler Toledo TGA 850
80 Thermogravimeter.

81

82 2.4. Preparation of Internal Mixer

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

88

89 2.5. Grafting maleic anhydride onto cyclized natural rubber without divinylbenzene

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

96

97 2.6. Grafting MA onto CNR in the presence of DVB

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

103

104 2.7. Purification of grafted products

105 The number of 1 gram of the grafted product was added into 50 mL of xylene.
106 The mixture was heated at 60°C while stirring until all the products were completely

107 dissolved. If there are still undissolved solids, they are separated using filter paper.
108 The filtrate is then added slowly into excess acetone to form a precipitate. The
109 precipitate is then separated from the filtrate. Using acetone as a solvent, the
110 precipitate obtained was rinsed 3 times and then dried in an oven at 120°C for 24
111 hours.

112

113 3. Results and Discussion

114 3.1. Thermogravimetric Analysis

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

120

121 3.2. Grafting MA onto CNR

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

129

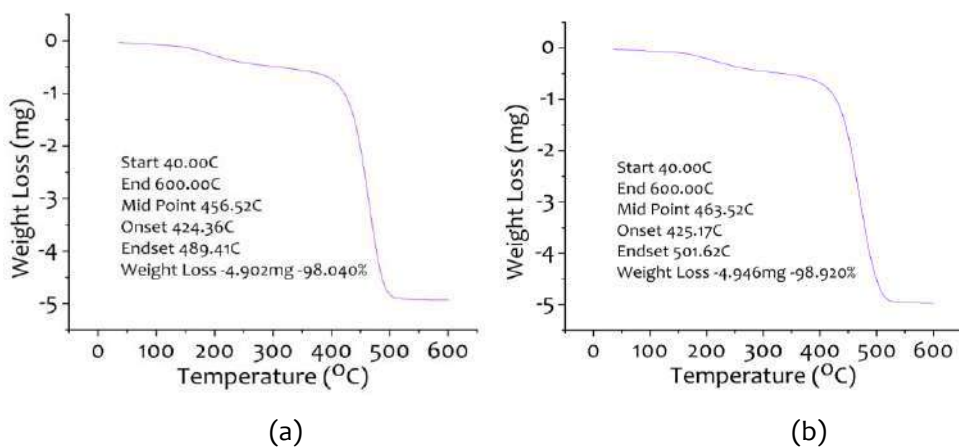
130 3.3. Grafting MA onto CNR in the presence of 0.5 grams of divinyl benzene

131 In **Figure 1 (b)** it can be seen that the sample experienced a change in mass at a
132 temperature of 107-140 °C, the sample experienced a reduction of 1.8-4%. At a
133 temperature of 141-382 °C the sample experienced a reduction of 4-18.8%. This
134 reduction in sample mass is thought to be due to the evaporation of volatile

Comment [U7]: Make it as Figure 1 instead of Figure 1(a)

Comment [U8]: Make it as Figure 2 instead of Figure 1(b)

135 compounds present in the sample. The presence of moisture in the sample is possible
136 because the sample is stored in a container that can be in contact with air during
137 storage, after being dried in the oven, and before the TGA thermal characterization is
138 carried out. Then at a temperature of 382-471 °C there was a drastic reduction in the
139 mass of the sample. The sample experienced a mass reduction of 90.2%. This is in line
140 with what was reported by previous researcher (Widiarti et al., 2018).



143 Figure 1. Thermogram of CNR with the addition of AM (a) and the addition of MA and
144 0.5 gram of divinyl benzene (b).

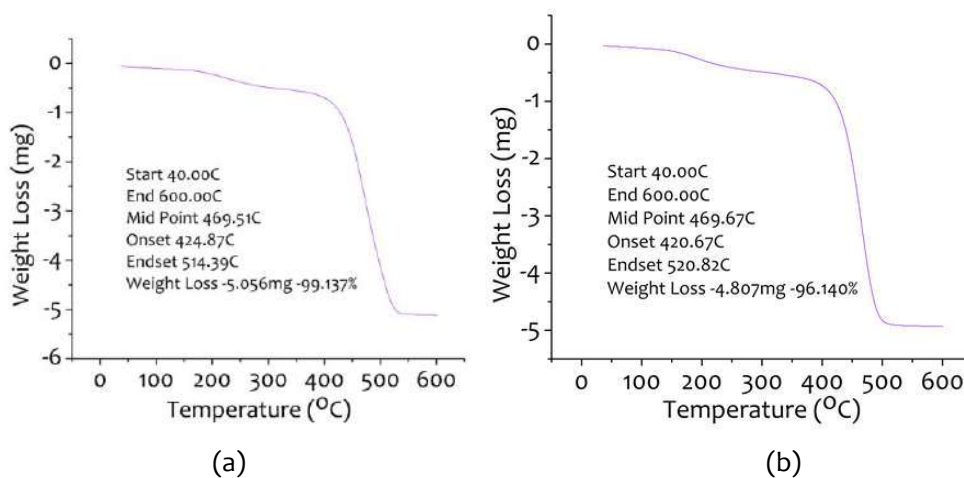
145
146 It is suspected that the cause is that the sample undergoes decomposition, the
147 compound decomposes into simpler ones.

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

153 For blank sample, decomposition occurs at a temperature of 424.36 °C (onset) to
154 489.41 °C (endset). There was an increase in the decomposition temperature of the
155 grafted sample at 16 phr MA, namely at a temperature of 382 °C (onset) to 471 °C

156 (endset). The grafting of the maleate group onto the CNR structure causes a change
157 in the molecular structure of the rubber in which the addition of a new group affects
158 the branch chain formed so that its molecular weight increases. Changes in the
159 structure of CNR cause changes in its thermal properties where the resistance to heat
160 increases as indicated by the increase in the decomposition temperature of the
161 sample (Nakason et al., 2006).

Comment [U9]: et al.



162

163

164 Figure 2. Thermogram of maleated CNR product in the presence of 1 gram of
165 divinylbenzene (a) and the presence of 2 grams of divinylbenzene (b).

166

167 3.4. Grafting of MA onto CNR in the presence of 1 gram of divinylbenzene

168 In Figure 2(a), it is known that the sample experienced a mass change at a
169 temperature of 100-150 °C, the sample experienced a reduction of 0.2-0.6%. At a
170 temperature of 151-382 °C the samples experienced a reduction of 0.6-8.6%. This
171 sample reduction is thought to be due to the evaporation of volatile compounds
172 (moisture) contain in the sample. The presence of moisture in the sample is possible
173 because the sample is stored in a container that can be in contact with air during
174 storage, after being dried in the oven, and before the TGA thermal characterization is
175 carried out. Then at a temperature of 382-468 °C there was a drastic reduction in the

Comment [U10]: Make it as Figure 3 instead of Figure 2(a)

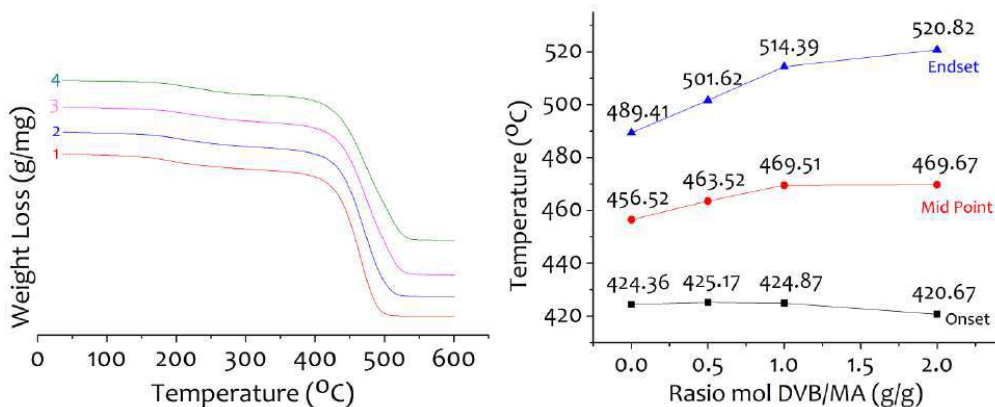
176 mass of the sample. The sample experienced a mass reduction of 84.2%. This is
177 thought to be caused by the decomposition of the sample.

178

179 3.5. Grafting of MA onto CNR in the presence of 2 grams of divinylbenzene

180 In Figure 2(b), it is known that the sample experienced a mass change at a
181 temperature of 100-200 °C, the sample experienced a reduction of 3.6-7.2%.
182 Temperature at 200-383 °C the sample experienced a reduction of 7.2 to 14.8%. This
183 sample reduction is thought to be due to the evaporation of volatile compounds
184 contain in the sample. The presence of moisture in the sample is possible because the
185 sample is stored in a container that can be in contact with air during storage, after
186 being dried in the oven, and before the TGA thermal characterization was carried out.
187 Then at a temperature of 384-479 °C, there was a drastic mass reduction in the
188 sample. The sample experienced a mass reduction of 82.2%. It is suspected that the
189 sample undergoes decomposition.

Comment [U11]: Make it as Figure 4 instead of Figure 2(b)



190

191 Figure 3. Overlay thermograms grafted CNR (1) grafted CNR and 0.5 gram DVB (2), 1
192 gram DVB (3), and 2 gram DVB (4) and overlay mole ratio-vs-temperature
193 graphs: onset, midpoint, and endset.

Comment [U12]: Figure 3 has two, not one.

194

195

196

197 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

198

199 In Figure 3 it can be seen that the same trend occurs for all samples. CNR which
 200 had undergone a graft reaction with the addition of MA 16 phr and added
 201 divinylbenzene (0.5 gams, 1 gram, and 1.5 gram) showed changes in the temperature
 202 range and almost the same quantity. Three phases of mass reduction temperature
 203 for samples were found: a temperature of 100-200 °C, a temperature of 141-383 °C,
 204 and a temperature of 382-489 °C, respectively as can be seen in Table 1.

Comment [U13]: Figure 3 has two, not one.

205 In phase 1 temperature 100-200 oC there is a reduction in the sample mass of 0.2-
 206 9.8%. Then at a temperature of 141-383 °C, there was a reduction in the mass of the
 207 sample from 0.6 to 18.8%. Furthermore, at a temperature of 282-489 °C, there was a
 208 drastic mass reduction of 82.2-90.6%. In general, it can be said that the thermal
 209 properties of maleated grafted CNR with the addition of divinylbenzene have almost
 210 the same thermal properties. This is following the statement that divinylbenzene can
 211 act as a crosslinking agent which has an impact on increasing the number of MA
 212 molecules bonded to the CNR chain.

213

214 4. Conclusion

215 CNR which has undergone a graft reaction with the addition of maleic anhydride
 216 affects increasing the thermal stability of CNR. The sample decomposition
 217 temperature increased with the increasing mole ratio of added DVB. The grafted

218 product of 16 phr MA onto CNR decomposed at 489.41 °C. Samples of grafted
219 products with the addition of 0.5, 1, and 2 mol ratio divinylbenzene comonomers
220 experienced an increase in the decomposition temperature: 501.62 °C, 514.39 °C, and
221 520.82 °C, respectively.

222

223 **Acknowledgment**

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225 Education, the Republic of Indonesia for their financial support through Penelitian
226 Dasar Unggulan Perguruan Tinggi/DUPT year 2017 under contract number 327/II.3-
227 AU/UMSU/LP2M/C/2017 and also to Mr. Suprianto, PT. Industri Karet Nusantara
228 (Nusantara Rubber Industry) for providing Resiprena 35.

229

230 **References**

- 231 Bettini, S. H. P., & Agnelli, J. A. M. (1999). Grafting of Maleic Anhydride onto
232 Polypropylene by Reactive Processing. I. Effect of Maleic Anhydride and Peroxide
233 Concentrations on the Reaction. *Journal of Applied Polymer Science*, 74, 2706–
234 2717. <https://doi.org/10.1002/app.10705>
- 235 Eddiyanto. (2007). Functionalisation of Polymers: Reactive Processing, Structure and
236 Performance Characteristics. In *Aston University*.
- 237 Guldogan, Y., Egri, S., Rzaev, Z. M. O., & Piskin, E. (2004). Comparison of maleic
238 anhydride grafting onto powder and granular polypropylene in the melt by
239 reactive extrusion. *Journal of Applied Polymer Science*, 92(6), 3675–3684.
240 <https://doi.org/10.1002/app.20304>
- 241 Hayemasae, N., Sensem, Z., Sahakaro, K., & Ismail, H. (2020). Maleated Natural
242 Rubber / Halloysite. *Processes*, 1–13.
- 243 Indonesia, B. S. (2019). *Indonesian Rubber Statistics*.
- 244 Nakason, C., Saiwaree, S., Tatun, S., & Kaesaman, A. (2006). Rheological, thermal and

245 morphological properties of maleated natural rubber and its reactive blending
246 with poly(methyl methacrylate). *Polymer Testing*, 25(5), 656–667.
247 <https://doi.org/10.1016/j.polymeresting.2006.03.011>

248 Nandiyanto, Asep Bayu, D., Oktiani, R., & Ragadhita, R. (2019). How to Read and
249 Interpret FTIR Spectroscopy of Organic Material. *Indonesian Journal of Science &
250 Technology*, 4(1), 97–118.

251 Ritonga, A. H., Aritonang, B., & Siahaan, M. A. (2019). Modification Of Cyclic Natural
252 Rubber With Comonomer Of Anhydrides Maleic And Oleic Acid Through Grafting
253 Method With Reflux Technique Using Benzoyl Peroxide Initiator. 17(November),
254 37–44.

255 Rzayev, Z. M. O. (2011). Graft Copolymers of Maleic Anhydride and Its Isostructural
256 Analogues: High Performance Engineering Materials. 3(March), 153–215.
257 <http://arxiv.org/abs/1105.1260>

258 Saelao, J., & Phinyocheep, P. (2005). Influence of styrene on grafting efficiency of
259 maleic anhydride onto natural rubber. *Journal of Applied Polymer Science*, 95(1),
260 28–38. <https://doi.org/10.1002/app.20810>

261 Siregar, M. S. (2014). *Modifikasi dan Karakterisasi Karet Alam Siklis Dengan Anhidrida
262 Maleat Sebagai Substituen Bahan Pengikat Cat Sintetis*. University of Sumatera
263 Utara.

264 Siregar, M. S. (2015). Grafting Product Of Maleic Anhydride Onto Cyclized Natural
265 Rubber In An Internal Mixer: Physical Properties And Compatibility With
266 Polyamide. *Agrium ISSN 0852-1077 (Print) ISSN 2442-7306 (Online)*, 19(2), 176–181.

267 Siregar, M. S., Ardilla, D., Eddiyanto, & Nasution, A. S. (2021). Grafting of Maleic
268 Anhydride onto Cyclized Natural Rubber in the Melt Phase: The Effect of
269 Trimethylol Propane Triacrylate. *Journal of Physics: Conference Series*, 1764(1).
270 <https://doi.org/10.1088/1742-6596/1764/1/012200>

271 Siregar, M. S., Ardilla, D., & Nasution, A. S. (2019). Grafting Of Maleic Anhydride onto

272 Cyclized Natural Rubber In The Melt Phase: The Effect of Maleic Anhydride
273 Concentrations on the Specific Weight and Total Acid. *Proceeding International*
274 *Seminar on Islamic Studies*, 1(1), 10–15. [https://doi.org/10.1088/1742-](https://doi.org/10.1088/1742-6596/1764/1/012200)
275 [6596/1764/1/012200](https://doi.org/10.1088/1742-6596/1764/1/012200)

276 Siregar, M. S., Thamrin, Basuki, Eddiyanto, & Mendez, J. A. (2014). Grafting of Maleic
277 Anhydride onto Cyclized Natural Rubber by Reactive Processing : the Effect of
278 Maleic Anhydride Concentrations. *Chemistry and Material Research*, 6(11), 15–21.

279 Siregar, M S., Astuti, R. P., Fuadi, M., Ardilla, D., Masyura, M. D., Nasution, A., &
280 Eddiyanto. (2021). Grafting Of Maleic Anhydride Onto Cyclized Natural Rubber:
281 The Presence Of Divinyl Benzene To Increase The Grafting Degree. *Jurnal Riset*
282 *Teknologi Industri*, 15(2), 222–230.

283 Sitanggang, B. C., & Eddyanto. (2019). Functionalization of cyclic natural rubber
284 grafted maleic anhydride (cnr-g-ma) with variation of ma concentration, inisiator
285 and reaction time. *Jurnal Pendidikan Kimia*, 11(3), 87–94.

286 Soleimani, S. M., Faheiman, A., & Mowaze, Z. (2020). The Effects of Using Crumb
287 Rubber Modified Binder in an Asphalt Pavement. *American Journal of Engineering*
288 *and Applied Sciences*, 13(2), 237–253. <https://doi.org/10.3844/ajeassp.2020.237.253>

289 Widiarti, L., Wirjosentono, B., & Eddyanto, E. (2018). *Analysis Of Thermal Properties*
290 *And Solubility Test Of Cyclic Natural Rubber And Cyclic Liquid Natural Rubber*. 14,
291 139–143.

292 Zhao, Y., Ma, C., Cheng, S., Xu, W., Du, Y., Bao, Y., & Xiao, Z. (2018). Maleic anhydride-
293 grafted isotactic polybutene-1 and modified polyamide 6. *Polymers*, 10(8), 1–12.
294 <https://doi.org/10.3390/polym10080872>

Comment [U14]: Adapt to the cited article

(Siregar, 2021a)?

(Siregar, 2021b)?

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KOMENTAR PENGULAS:

- 300 1. Semua referensi harus dikutip dalam artikel
- 301 2. Beberapa kutipan tidak ada dalam daftar referensi (missal: Siregar, 2021a dan
302 Siregar, 2021b)
- 303 3. Gambar 1(a) sebaiknya berdiri sendiri menjadi Gambar 1, tidak disatukan
304 dengan Gambar 1(b), sebab kedua gambar berbeda subjudul kegiatan. Jika
305 mau disatukan menjadi Gambar 1(a) dan Gambar 1(b), maka kedua subjudul
306 harus disatukan. Demikian dengan Gambar 2(a), dst...
- 307 4. Gambar 3 justru terdiri dari dua Gambar, namun didalam artikel dibuat menjadi
308 satu gambar, perbaiki ini....
- 309 5. Cara mensitasi, lihat panduan penulisan

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

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.

Keywords: cyclized natural rubber, maleic anhydride, divinylbenzene, thermogravimetric

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

24 supports the Indonesian economy with an export volume of 2.99 million tons and
25 US\$ 5.10 billion. In 2019 Indonesia produced 26% of natural rubber in the world,
26 ranking second in the world's natural rubber production after Thailand (Indonesia,
27 2019). Modification of the molecular structure of natural rubber physically or
28 chemically is important to produce new materials that have unique characteristics for
29 new and broad uses in certain fields (Hayeemasae et al. 2020; Widiarti et al. 2018).

30 Natural rubber is a cis-poly isoprene natural polymer compound resulting from the
31 addition of 1,4 from isoprene monomer which has a molecular weight of 1-2 million
32 and there are 15,000-20,000 unsaturated bonds in the molecular chain. Natural
33 rubber has properties that are not resistant to ozone, oil, and temperature due to the
34 presence of a carbon-carbon double bond in the chemical structure of cis-1,4-
35 polyisoprene which is the main component of natural rubber (Nakason et al. 2006;
36 Guldogan et al. 2004; Rzayev, 2011). But natural rubber has advantages in terms of
37 resilience, abrasion resistance, stickiness, and plasticity (Saelao & Phinyocheep,
38 2005).

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

45 Modification of CNR by grafting using Maleic Anhydride (AM) monomer has been
46 successfully carried out by several researchers (Zhao et al. 2018; Ritonga et al. 2019).
47 Based on the Fourier Transformed Infra-Red/FTIR spectral data of the grafted
48 product, the maleate group was successfully grafted onto the CNR structure with the
49 appearance of absorption at 1780 cm^{-1} and 1841 cm^{-1} which is a typical carbonyl
50 absorption of the maleate group (Sitanggang & Eddyanto, 2019; Eddyanto, 2007;
51 Siregar et al. 2014; Siregar, 2015; Siregar et al. 2019; Siregar et al. 2021a; Siregar et al.

52 2021b). To increase the degree of grafting, styrene comonomers (Siregar et al. 2014),
53 divinylbenzene (Siregar et al. 2019; Siregar et al. 2021a; Siregar et al. 2021b) and
54 Trimethylol Propane Triacrylate (Siregar et al. 2019; Siregar et al. 2021) have been
55 used.

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

60

61 2. Methods

62 2.1 Materials

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

68 2.2 Equipment

69 The equipment used in this study were: Mettler Toledo analytical balance,
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71 type UN 260, filter paper (Whatman) Z241393, pyrex ts joint reflux apparatus 29/32 1
72 set, and Thermogravimeter Mettler Toledo TGA850.

73

74 2.3 General Procedure

75 This research is a laboratory experiment to produce grafted products in an
76 internal mixer with a temperature of 150°C and a rotor speed of 80 rpm, where 16
77 phr MA was reacted with CNR in the presence and absence of DVB comonomer with
78 various mole ratios of 0,5, 1 and 2 (Siregar, 2014). To investigate the thermal

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80 Thermogravimeter.

81

82 2.4. Preparation of Internal Mixer

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

88

89 2.5. Grafting maleic anhydride onto cyclized natural rubber without divinylbenzene

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

96

97 2.6. Grafting MA onto CNR in the presence of DVB

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

103

104 2.7. Purification of grafted products

105 The number of 1 gram of the grafted product was added into 50 mL of xylene.
106 The mixture was heated at 60°C while stirring until all the products were completely

107 dissolved. If there are still undissolved solids, they are separated using filter paper.
108 The filtrate is then added slowly into excess acetone to form a precipitate. The
109 precipitate is then separated from the filtrate. Using acetone as a solvent, the
110 precipitate obtained was rinsed 3 times and then dried in an oven at 120°C for 24
111 hours.

112

113 **3. Results and Discussion**

114 3.1. Thermogravimetric Analysis

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

120

121 3.2. Grafting MA onto CNR

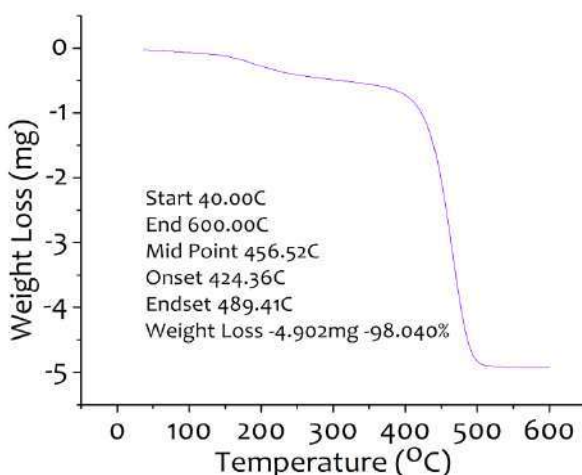
122 In [Figure 1](#) it can be seen that there was a change in the mass of the sample at a
123 temperature of 121-178 °C, the sample experienced a reduction of 1.4-9.8%. And at a
124 temperature of 179-383 °C, the sample experienced a reduction of 9.8%. This sample
125 reduction occurs due to the evaporation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

129

130 3.3. Grafting MA onto CNR in the presence of 0.5 grams of divinyl benzene

131 In [Figure 2](#) it can be seen that the sample experienced a change in mass at a
132 temperature of 107-140 °C, the sample experienced a reduction of 1.8-4%. At a
133 temperature of 141-382 °C the sample experienced a reduction of 4-18.8%. This
134 reduction in sample mass is thought to be due to the evaporation of volatile

135 compounds present in the sample. The presence of moisture in the sample is possible
136 because the sample is stored in a container that can be in contact with air during
137 storage, after being dried in the oven, and before the TGA thermal characterization is
138 carried out. Then at a temperature of 382-471 °C there was a drastic reduction in the
139 mass of the sample. The sample experienced a mass reduction of 90.2%. This is in line
140 with what was reported by previous researcher (Widiarti et al., 2018).



141

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

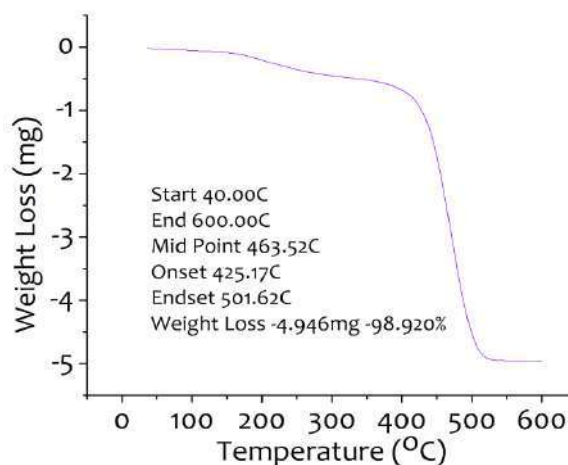


Figure 2. Thermogram of CNR with the addition of MA and 0.5 gram of divinyl benzene.

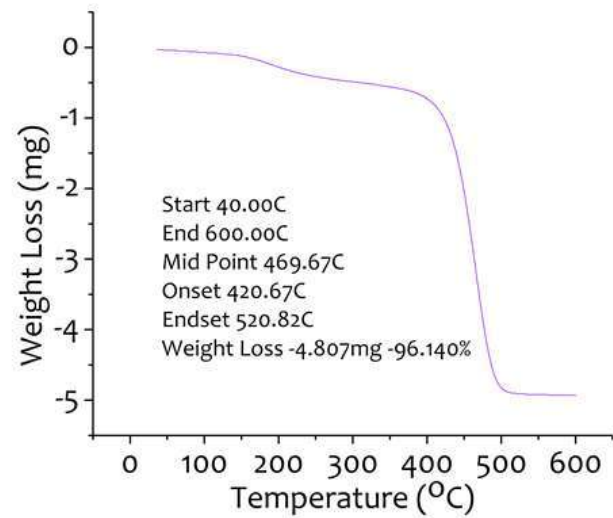
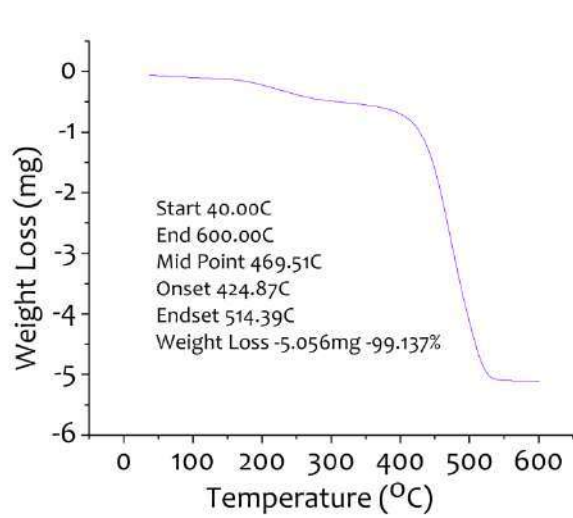
142

143 It is suspected that the cause is that the sample undergoes decomposition, the
144 compound decomposes into simpler ones.

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

150 For blank sample, decomposition occurs at a temperature of 424.36 °C (onset) to
151 489.41 °C (endset). There was an increase in the decomposition temperature of the
152 grafted sample at 16 phr MA, namely at a temperature of 382 °C (onset) to 471 °C
153 (endset). The grafting of the maleate group onto the CNR structure causes a change

154 in the molecular structure of the rubber in which the addition of a new group affects
155 the branch chain formed so that its molecular weight increases. Changes in the
156 structure of CNR cause changes in its thermal properties where the resistance to heat
157 increases as indicated by the increase in the decomposition temperature of the
158 sample (Nakason et al. 2006).



159

Figure 3. Thermogram of maleated CNR product in the presence of 1 gram of divinylbenzene.

Figure 4. Thermogram of maleated CNR product in the presence of 2 grams of divinylbenzene.

160

161 3.4. Grafting of MA onto CNR in the presence of 1 gram of divinylbenzene

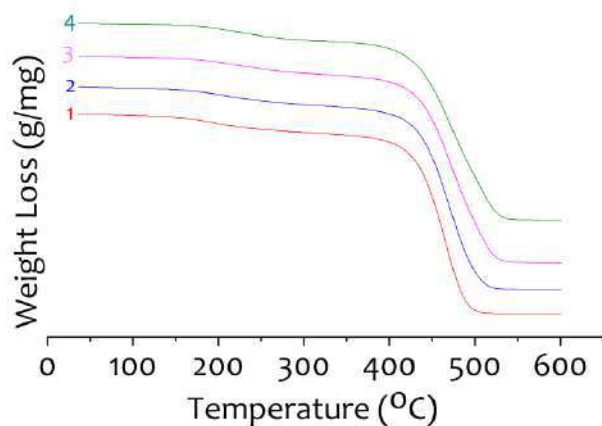
162 In Figure 3 it is known that the sample experienced a mass change at a
163 temperature of 100-150 °C, the sample experienced a reduction of 0.2-0.6%. At a
164 temperature of 151-382 °C the samples experienced a reduction of 0.6-8.6%. This
165 sample reduction is thought to be due to the evaporation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

172

173 3.5. Grafting of MA onto CNR in the presence of 2 grams of divinylbenzene

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

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



190

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

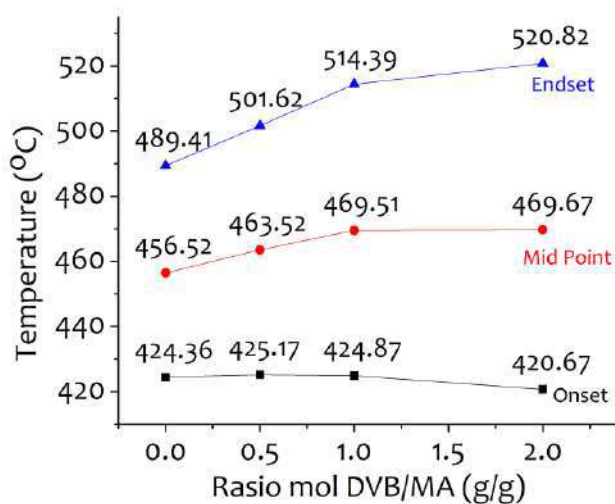


Figure 6. Overlay mole ratio-vs-temperature graphs: onset, midpoint, and endset.

191 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

192

193 In phase 1 temperature 100-200 oC there is a reduction in the sample mass of 0.2-
 194 9.8%. Then at a temperature of 141-383 °C, there was a reduction in the mass of the
 195 sample from 0.6 to 18.8%. Furthermore, at a temperature of 282-489 °C, there was a
 196 drastic mass reduction of 82.2-90.6%. In general, it can be said that the thermal
 197 properties of maleated grafted CNR with the addition of divinylbenzene have almost
 198 the same thermal properties. This is following the statement that divinylbenzene can
 199 act as a crosslinking agent which has an impact on increasing the number of MA
 200 molecules bonded to the CNR chain.

201

202 4. Conclusion

203 CNR which has undergone a graft reaction with the addition of maleic anhydride
 204 affects increasing the thermal stability of CNR. The sample decomposition
 205 temperature increased with the increasing mole ratio of added DVB. The grafted
 206 product of 16 phr MA onto CNR decomposed at 489.41 °C. Samples of grafted
 207 products with the addition of 0.5, 1, and 2 mol ratio divinylbenzene comonomers
 208 experienced an increase in the decomposition temperature: 501.62 °C, 514.39 °C, and
 209 520.82 °C, respectively.

210

211

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219 **References**

- 220 Bettini, S. H. P., & Agnelli, J. A. M. (1999). Grafting of Maleic Anhydride onto
221 Polypropylene by Reactive Processing. I. Effect of Maleic Anhydride and Peroxide
222 Concentrations on the Reaction. *Journal of Applied Polymer Science*, 74, 2706–
223 2717. <https://doi.org/10.1002/app.10705>
- 224 Eddiyanto. (2007). Functionalisation of Polymers: Reactive Processing, Structure and
225 Performance Characteristics. In *Aston University*.
- 226 Guldogan, Y., Egri, S., Rzaev, Z. M. O., & Piskin, E. (2004). Comparison of maleic
227 anhydride grafting onto powder and granular polypropylene in the melt by
228 reactive extrusion. *Journal of Applied Polymer Science*, 92(6), 3675–3684.
229 <https://doi.org/10.1002/app.20304>
- 230 Hayeemasae, N., Sensem, Z., Sahakaro, K., & Ismail, H. (2020). Maleated Natural
231 Rubber / Halloysite. *Processes*, 1–13.
- 232 Indonesia, B. S. (2019). *Indonesian Rubber Statistics*.
- 233 Nakason, C., Saiwaree, S., Tatun, S., & Kaesaman, A. (2006). Rheological, thermal and
234 morphological properties of maleated natural rubber and its reactive blending
235 with poly(methyl methacrylate). *Polymer Testing*, 25(5), 656–667.
236 <https://doi.org/10.1016/j.polymertesting.2006.03.011>
- 237 Nandiyanto, Asep Bayu, D., Oktiani, R., & Ragadhita, R. (2019). How to Read and
238 Interpret FTIR Spectroscopy of Organic Material. *Indonesian Journal of Science &*

239 Technology, 4(1), 97–118.

240 Ritonga, A. H., Aritonang, B., & Siahaan, M. A. (2019). *Modification Of Cyclic Natural*
241 *Rubber With Comonomer Of Anhydrides Maleic And Oleic Acid Through Grafting*
242 *Method With Reflux Technique Using Benzoyl Peroxide Initiator*. 17(November),
243 37–44.

244 Rzaev, Z. M. O. (2011). *Graft Copolymers of Maleic Anhydride and Its Isostructural*
245 *Analogues: High Performance Engineering Materials*. 3(March), 153–215.
246 <http://arxiv.org/abs/1105.1260>

247 Saelao, J., & Phinyocheep, P. (2005). Influence of styrene on grafting efficiency of
248 maleic anhydride onto natural rubber. *Journal of Applied Polymer Science*, 95(1),
249 28–38. <https://doi.org/10.1002/app.20810>

250 Siregar, M. S. (2014). *Modifikasi dan Karakterisasi Karet Alam Siklis Dengan Anhidrida*
251 *Maleat Sebagai Substituen Bahan Pengikat Cat Sintetis*. University of Sumatera
252 Utara.

253 Siregar, M. S. (2015). Grafting Product Of Maleic Anhydride Onto Cyclized Natural
254 Rubber In An Internal Mixer: Physical Properties And Compatibility With
255 Polyamide. *Agrium ISSN 0852-1077 (Print) ISSN 2442-7306 (Online)*, 19(2), 176–181.

256 Siregar, M. S., Ardilla, D., Eddiyanto, & Nasution, A. S. (2021a). Grafting of Maleic
257 Anhydride onto Cyclized Natural Rubber in the Melt Phase: The Effect of
258 Trimethylol Propane Triacrylate. *Journal of Physics: Conference Series*, 1764(1).
259 <https://doi.org/10.1088/1742-6596/1764/1/012200>

260 Siregar, M S., Astuti, R. P., Fuadi, M., Ardilla, D., Masyura, M. D., Nasution, A., &
261 Eddiyanto. (2021b). Grafting Of Maleic Anhydride Onto Cyclized Natural Rubber:
262 The Presence Of Divinyl Benzene To Increase The Grafting Degree. *Jurnal Riset*
263 *Teknologi Industri*, 15(2), 222–230.

264 Siregar, M. S., Ardilla, D., & Nasution, A. S. (2019). Grafting Of Maleic Anhydride onto
265 Cyclized Natural Rubber In The Melt Phase: The Effect of Maleic Anhydride

266 Concentrations on the Specific Weight and Total Acid. *Proceeding International*
267 *Seminar on Islamic Studies*, 1(1), 10–15. <https://doi.org/10.1088/1742->
268 [6596/1764/1/012200](https://doi.org/10.1088/1742-6596/1764/1/012200)

269 Siregar, M. S., Thamrin, Basuki, Eddiyanto, & Mendez, J. A. (2014). Grafting of Maleic
270 Anhydride onto Cyclized Natural Rubber by Reactive Processing : the Effect of
271 Maleic Anhydride Concentrations. *Chemistry and Material Research*, 6(11), 15–21.

272 Sitanggang, B. C., & Eddyanto. (2019). Functionalization of cyclic natural rubber
273 grafted maleic anhydride (cnr-g-ma) with variation of ma concentration, inisiator
274 and reaction time. *Jurnal Pendidikan Kimia*, 11(3), 87–94.

275 Soleimani, S. M., Faheiman, A., & Mowaze, Z. (2020). The Effects of Using Crumb
276 Rubber Modified Binder in an Asphalt Pavement. *American Journal of Engineering*
277 *and Applied Sciences*, 13(2), 237–253. <https://doi.org/10.3844/ajeassp.2020.237.253>

278 Widiarti, L., Wirjosentono, B., & Eddyanto, E. (2018). *Analysis Of Thermal Properties*
279 *And Solubility Test Of Cyclic Natural Rubber And Cyclic Liquid Natural Rubber*. 14,
280 139–143.

281 Zhao, Y., Ma, C., Cheng, S., Xu, W., Du, Y., Bao, Y., & Xiao, Z. (2018). Maleic anhydride-
282 grafted isotactic polybutene-1 and modified polyamide 6. *Polymers*, 10(8), 1–12.
283 <https://doi.org/10.3390/polym10080872>

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Acceptance Letter

Date: 29/ 03/ 2022

Dear, M. Said Siregar

We are glad to inform you that your manuscript, entitled:

JPKim-31799: Study on the thermal properties of the grafted product of maleic anhydride onto cyclized natural rubber by using thermogravimetric method

M. Said Siregar, Dian Arsita Fitri, Muhammad Iqbal Nusa, Desi Ardilla, Masyura M.D, Asmarasari Nasution and Eddiyanto

has been reviewed and subsequently accepted for publication in Jurnal Pendidikan Kimia. The paper will be published in Jurnal Pendidikan Kimia, **Vol. 14, No. 1, 2022** issue of the journal.

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Study on the thermal properties of the grafted product of maleic anhydride onto cyclized 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 (Hayemasae 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 (Sitanggung & Eddyanto, 2019; Eddyanto, 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 °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 °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.

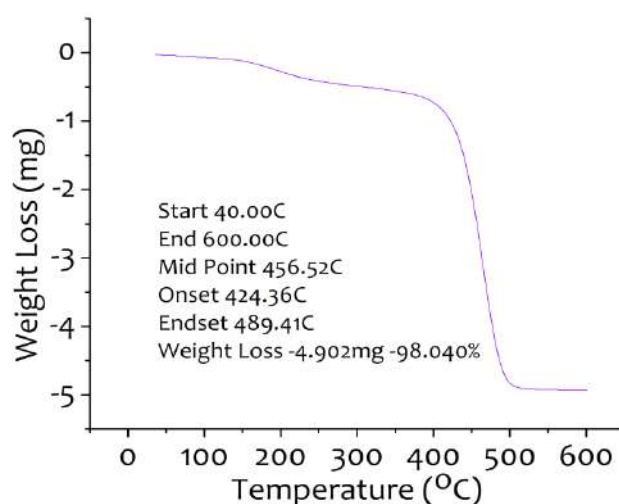


Figure 1. Thermogram of CNR with the addition of AM.

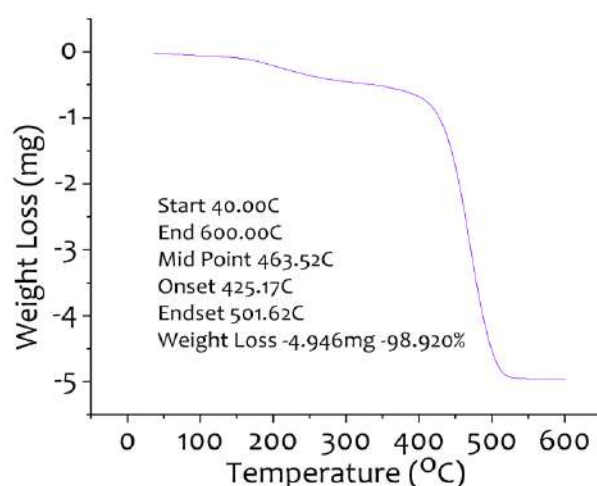


Figure 2. Thermogram of CNR with the addition of MA and 0.5 gram of Divinylbenzene.

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.

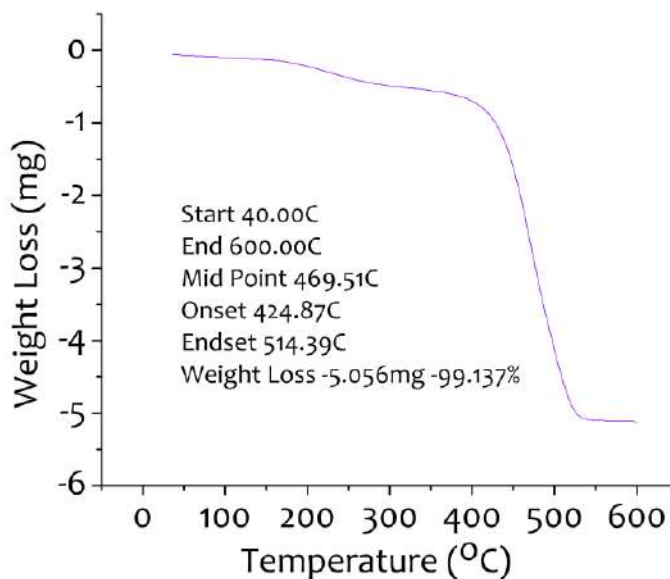


Figure 3. Thermogram of Maleated CNR Product in the Presence of 1 gram of Divinylbenzene.

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.

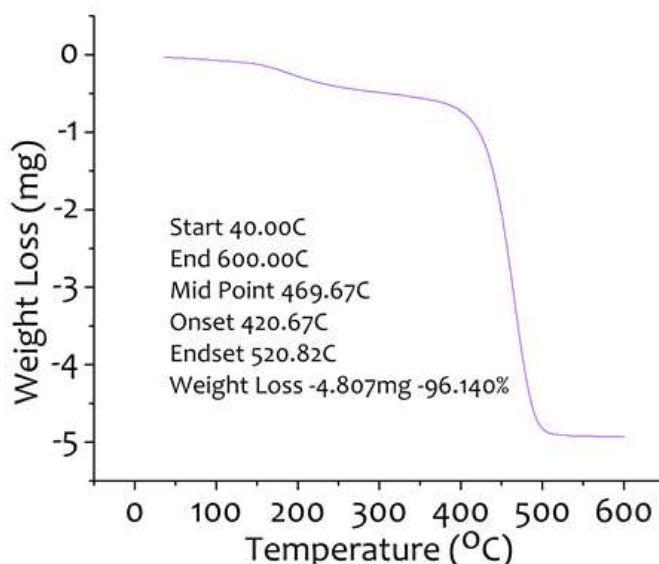


Figure 4. Thermogram of Maleated CNR Product in the Presence of 2 grams of Divinylbenzene.

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 grams, 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

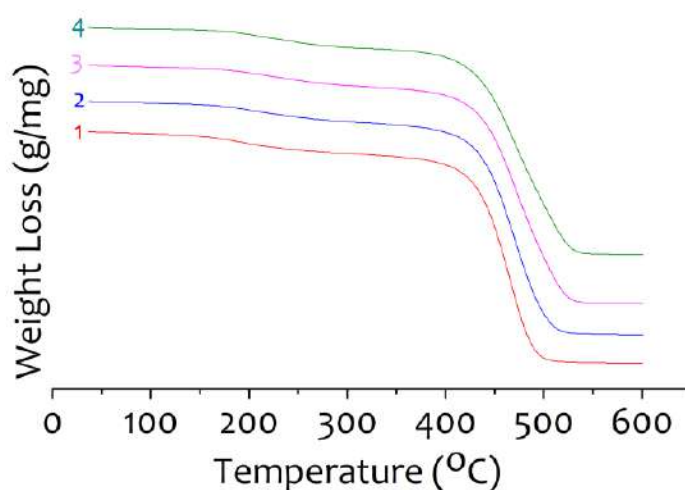


Figure 5. Overlay Thermograms Grafted CNR (1) Grafted CNR and 0.5 gram DVB (2), 1 gram DVB (3), and 2 gram DVB (4).

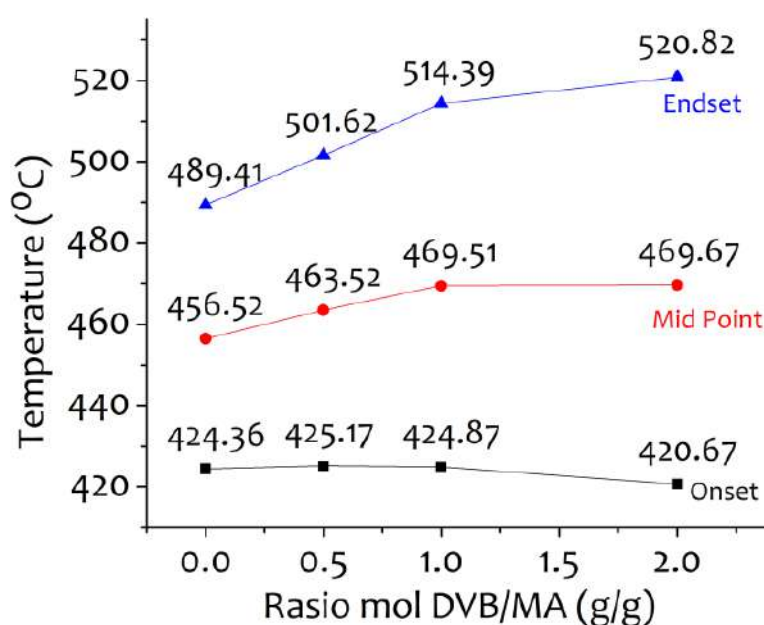


Figure 6. Overlay Mole Ratio-vs-Temperature Graphs: Onset, Midpoint, and Endset.

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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References

- Bettini, S. H. P., & Agnelli, J. A. M. (1999). Grafting of maleic anhydride onto polypropylene by reactive processing. I. effect of maleic anhydride and peroxide concentrations on the reaction. *Journal of Applied Polymer Science*, 74, 2706–2717. <https://doi.org/10.1002/app.10705>
- Eddiyanto. (2007). Functionalisation of polymers: Reactive processing, structure and performance characteristics. Thesis (Ph.D.), Aston University.
- Guldogan, Y., Egri, S., Rzaev, Z. M. O., & Piskin, E. (2004). Comparison of maleic anhydride grafting onto powder and granular polypropylene in the melt by reactive extrusion. *Journal of Applied Polymer Science*, 92(6), 3675–3684. <https://doi.org/10.1002/app.20304>
- Hayemasae, N., Sensem, Z., Sahakaro, K., & Ismail, H. (2020). Maleated natural rubber/halloysite nanotubes composites. *Processes*, 8(3), 286. <https://doi.org/10.3390/pr8030286>
- Nakason, C., Saiwaree, S., Tatun, S., & Kaesaman, A. (2006). Rheological, thermal and morphological properties of maleated natural rubber and its reactive blending with poly(methyl methacrylate). *Polymer Testing*, 25(5), 656–667. <https://doi.org/10.1016/j.polymertesting.2006.03.011>
- Nandiyanto, Asep Bayu, D., Oktiani, R., & Ragadhita, R. (2019). How to read and interpret FTIR spectroscopy of organic material. *Indonesian Journal of Science & Technology*, 4(1), 97–118. <https://doi.org/10.17509/ijost.v4i1.15806>
- Ritonga, A. H., Aritonang, B., & Siahaan, M. A. (2019). Modifikasi karet alam siklis dengan komonomer maleat anhidrat dan asam oleat melalui metode pencangkokan dengan teknik refluks menggunakan inisiator benzoil peroksida. *Jurnal Kimia Mulawarman*, 17(1), 37-44.
- Rzayev, Z. M. O. (2011). Graft copolymers of maleic anhydride and its isostructural analogues: High performance engineering materials. *Int. Rev. Chem. Eng.*, 3(2), 153-215. <https://doi.org/10.48550/arXiv.1105.1260>
- Saelao, J., & Phinyocheep, P. (2005). Influence of styrene on grafting efficiency of maleic anhydride onto natural rubber. *Journal of Applied Polymer Science*, 95(1), 28–38.

<https://doi.org/10.1002/app.20810>

- Siregar, M. S. (2014). Modifikasi dan karakterisasi karet alam siklis dengan anhidrida maleat sebagai substituen bahan pengikat cat sintetis. Disertasi, University of Sumatera Utara.
- Siregar, M. S. (2015). Grafting product of maleic anhydride onto cyclized natural rubber in an internal mixer: Physical properties and compatibility with polyamide. *Agrium: Jurnal Ilmu Pertanian*, 19(2), 176–181. <http://dx.doi.org/10.30596%2Fagrium.v19i2.376>
- Siregar, M. S., Ardilla, D., Eddiyanto., & Nasution, A. S. (2021a). Grafting of maleic anhydride onto cyclized natural rubber in the melt phase: The effect of trimethylol propane triacrylate. *Journal of Physics: Conference Series*, 1764 012200. <https://doi.org/10.1088/1742-6596/1764/1/012200>
- Siregar, M. S., Astuti, R. P., Fuadi, M., Ardilla, D., Masyura, M. D., Nasution, A., & Eddiyanto. (2021b). Pencangkakan anhidrida maleat pada karet alam siklis: Penambahan divinil benzen untuk meningkatkan derajat pencangkakan. *Jurnal Riset Teknologi Industri*, 15(2), 222–230. <http://dx.doi.org/10.26578/jrti.v15i2.6973>
- Siregar, M. S., Ardilla, D., & Nasution, A. S. (2019). grafting of maleic anhydride onto cyclized natural rubber in the melt phase: The effect of maleic anhydride concentrations on the specific weight and total acid. *Proceeding International Seminar on Islamic Studies*, 1, 10–15.
- Siregar, M. S., Thamrin, Basuki, Eddiyanto, & Mendez, J. A. (2014). Grafting of maleic anhydride onto cyclized natural rubber by reactive processing: The effect of maleic anhydride concentrations. *Chemistry and Materials Research*, 6(11), 15–21.
- Sitanggang, B. C., & Eddyanto, E. (2019). Functionalization of cyclic natural rubber grafted maleic anhydride (cnr-g-ma) with variation of ma concentration, inisiator and reaction time. *Jurnal Pendidikan Kimia*, 11(3), 87-94. <https://doi.org/10.24114/jpkim.v11i3.15736>
- Statistics Indonesia (2016). "Indonesian Rubber Statistics 2015." Statistics Indonesia.
- Soleimani, S. M., Faheiman, A., & Mowaze, Z. (2020). The effects of using crumb rubber modified binder in an asphalt pavement. *American Journal of Engineering and Applied Sciences*, 13(2), 237–253. <https://doi.org/10.3844/ajeassp.2020.237.253>
- Widiarti, L., Wirjosentono, B., & Eddyanto, E. (2018). Analisis sifat termal dan uji kelarutan dari karet alam siklis dan karet alam cair siklis. *Jurnal Kimia Mulawarman*, 16(1), 32-35. <https://doi.org/10.30872/jkm.v16i1.481>
- Zhao, Y., Ma, C., Cheng, S., Xu, W., Du, Y., Bao, Y., & Xiao, Z. (2018). Maleic anhydride-grafted isotactic polybutene-1 and modified polyamide 6. *Polymers*, 10(8), 1–12. <https://doi.org/10.3390/polym10080872>