



## Grafting of Oleic Acid On Cyclic Natural Rubber Resiprene-35 Using Dicumyl Peroxide Initiator and Divinylbenzene Compatibilizers For Paint Binder In Polyamide Thermoplastics

BARITA ARITONANG<sup>1,2\*</sup>, TAMRIN<sup>2\*</sup>, BASUKI WIRJOSENTONO<sup>2</sup> and EDDIYANTO<sup>3</sup>

<sup>1</sup> Department of Chemistry, University of Sari Mutiara Indonesia, Medan-20123, Indonesia.

<sup>2</sup>Department of Chemistry Doctoral Program, University of Sumatera Utara, Medan-20155, Indonesia.

<sup>3</sup>Department of Chemistry, University of State Medan, Medan-20221, Indonesia.

\*Corresponding author E-mail: baritaaritonang11@gmail.com; thamrinsumut@gmail.com

<http://dx.doi.org/10.13005/ojc/350119>

Received: November 23, 2018; Accepted: January 24, 2019)

### ABSTRACT

In this paper, we reported about modifications of Cyclic Natural Rubber (CNR) with Oleic Acid (OA) and divinylbenzene (DVB) and dicumyl peroxide (DCP). The aim of this research is to improve their compatibility as a paint binder in polyamide thermoplastic substrates. The method of this research is grafting method in order to know grafting process of CNR to generate CNR-g-OA, and its compatibility after being blended with Polyamide (PA). Analysis of CNR-g-OA was carried out by using FTIR and SEM. The results showed that the best compositions ratio of CNR-g-OA are CNR (100 phr), OA (6 phr), DCP (0.5 phr); and DVB (0.5 phr). The FTIR data of CNR-g-OA show that there is a sharp and weak peak at 1700 to 1800 cm<sup>-1</sup>, indicating that is carbonyl (C=O). It is oleic acid. The SEM data of CNR-g-OA is totally difference compare to CNR-g-OA with polyamide after the addition of DVB. It is caused the grafting was succeed to generate CNR-g-AO and compatible with PA.

**Keywords:** Cyclic Natural Rubber, Oleic Acid, Dicumyl Peroxide, Divinylbenzena, Grafting, Polyamide.

### INTRODUCTION

Chemical modification of natural rubber is one of the efforts made to improve the properties of natural rubber so that a new product is obtained, such as modification of natural rubber through cyclization reaction is cyclic natural rubber/resiprene-35. Cyclic natural rubber (CNR) is currently widely used as a resin for the paint, adhesive and printing ink industries because it has the advantages that are

resistant to abrasion (friction strength), resistant to water (corrosion resistant), and has good adhesion to metals, wood, glass and paper<sup>1,2,3</sup>.

Cyclic natural rubber also still has the disadvantages of physical chemical properties in terms of the compatibility of polyamide thermoplastic surfaces. The weak adhesive properties can be caused by low compatibility between CNR as a paint binder with the surface of a polyamide thermoplastic<sup>4,5</sup>.



Blending of cyclic natural rubber with the polyamide thermoplastics is incompatible caused by the properties of polymer materials which have different polarity components. If the two ingredients are blended, a non-polar system is obtained without any chemical bonds between the two polymer materials. Incompatible polymer blends cause the adhesion of cyclic natural rubber are reduced. Besides that, cyclic natural rubber is also susceptible to free radical attacks such as inorganic acid and ozone, due to the presence of carbon double bonds ( $> C = C <$ ) in cyclic carbon chains<sup>5,6,7</sup>.

To overcome the disadvantages of the cyclic natural rubber as well as to improve the performance of the adhesive properties and compatibility with the surface of the polyamide thermoplastic, it is necessary to modify the surface of cyclic natural rubber in order to obtain high adhesive properties so that it can interact with polyamide. The effective method for modifying the surface of cyclic natural rubber is by grafting<sup>8,9,10</sup>.

Previous studies on chemical modification with grafting techniques have been carried out to produce a product as expected. Siregar, *et al.*,<sup>11</sup> conducted research on maleic anhydride grafted on cyclic natural rubber in internal mixers, physical properties and compatibility with polyamide. Based on the results of research, CNR-g-AM products were obtained, where increasing maleic anhydride concentration causes the maleic group grafted on the CNR polymer chain also increases. Grafting products have improved compatibility with polyamide. Nasution *et al.*,<sup>12</sup> conducted research of cyclic natural rubber grafting with methyl methacrylate using dicumyl peroxide initiator. Based on the results of research, CNR-g-MMA products were obtained, which are characterized by the appearance of wave number absorption peaks in the area of  $1731\text{ cm}^{-1}$  (absorption of carbonyl groups) typical for carbonyl ( $C=O$ ) from methyl methacrylate.

Oleic acid is a polar un saturated fatty acid and has a double bond in the carboxylic group. Oleic acid is expected to improve physical and mechanical properties, and compatibility of cyclic natural rubber because oleic acid can be converted into epoxide oil which will be used as a monomer, so that the process of grafting oleic acid monomers in the molecular chain of cyclic natural rubber can

occur. This has been proven by Zhou<sup>13</sup> that the oleic acid monomers was successfully grafted into the main chain of acrylonitrile-butadiene-styrene through grafting process using benzoyl peroxide initiator in 1,2-dichloroethane solution. The results obtained that oleic acid can increase the flexibility, elasticity and stability of the polymer against heat and ultraviolet radiation. Liu<sup>14</sup> explained that oleic acid monomers have been successfully grafted on low density polyethylene in the internal mixer to form copolymers by using dicumyl peroxide initiator. In order to obtain good morphological results for incompatible polymeric materials, a compatibilizers are needed, such as divinylbenzene (DVB)<sup>15,16</sup>.

In this research, it is expected that the addition of DVB compatibility can increase reactivity in CNR interactions with polyamide thermoplastics. Characterization of CNR-g-OA includes morphology test by Scanning Electron Microscopy (SEM), and chemical-physics interaction test by Fourier Transform Infrared (FTIR) spectroscopy.

## EXPERIMENTAL

### Materials

The chemicals used are from E-Merck, namely Acetone, Ethanol, Xylene, Dicumyl Peroxide (DCP), Divinylbenzene (DVB), Oleic Acid, Hydrochloric Acid (HCl), and Polyamide (PA).

Modified material is Cyclic Natural Rubber (CNR)/ Resiprene-35) sourced from PT. Nusantara Rubber Industry (PT. IKN) in the North Sumatera Province which is engaged in processing natural rubber into resin.

### Oleic Acid Grafting Process Onto CNR Using Initiator Dicumyl Peroxide

100 phr (33 g) cyclic natural rubber (CNR) is weighed, then CNR is slowly inserted into the internal mixer, after that the temperature is set to  $160^{\circ}\text{C}$  on the internal mixer, and left for 4 min until the CNR melts perfectly, then added with oleic acid 6 phr (2 g) followed by the addition of DCP initiators using several variations 0.25 phr (0.1 g); 0.5 phr (0.2 g); and 1.0 phr (0.3 g) until homogeneous. The blending process is carried out for 8 min to experience a grafting reaction. After 8 min, the process is stopped. In hot conditions quickly the reaction product is removed from the

internal mixer. The results obtained are then cooled and made into granules/pellets. The same was also carried out for variations of oleic acid 3 phr (1 g),

6 phr (2 g), and 9 phr (3 g) with DCP initiators 0.5 phr (0.2 g). The variations of blends are listed, as in Table 1 and Table 2.

**Table 1: Variation of dicumyl peroxide initiator**

Sample	Cyclic Natural Rubber (CNR)		Oleic Acid (OA)		Dicumyl Peroxide(DCP)	
DCP-0	100 phr	33 g	6 phr	2 g	0.00 phr	0.0 g
DCP-0,25	100 phr	33 g	6 phr	2 g	0.25 phr	0.1 g
DCP-0,5	100 phr	33 g	6 phr	2 g	0.50 phr	0.2 g
DCP-1	100 phr	33 g	6 phr	2 g	1.00 phr	0.3 g

\*phr (Parts per Hundred Rubber)

**Table 2: Variation of oleic acid**

Sample	Cyclic Natural Rubber (CNR)		Oleic Acid (OA)		Dicumyl Peroxide (DCP)	
OA-3	100 phr	33 g	3 phr	1 g	0.50 phr	0.2 g
OA-6	100 phr	33 g	6 phr	2 g	0.50 phr	0.2 g
OA-9	100 phr	33 g	9 phr	3 g	0.50 phr	0.2 g

\* phr (Parts per Hundred Rubber)

Then the result of CNR that has been grafted with oleic acid (CNR-g-OA) are refluxed with 100 mL of xylene with a series of reflux devices which are heating, boiling pumpkin and liebig condenser at 110°C until dissolved. After dissolving, 100 mL of ethanol is added until the precipitate is formed. The precipitate formed is filtered using filter paper which has been connected to a vacuum pump and washed with ethanol repeatedly in order to dissolve the remaining acidic reactions. The precipitate formed was dried in oven at a temperature of 120°C for 24 hours. Specific results were characterized by FTIR.

#### Oleic Acid Grafting Process Onto CNR Using Initiator Dicumyl Peroxide And Compatibilizers Divinylbenzene

100 phr (33 g) Cyclic natural rubber (CNR)

is weighed, then CNR is slowly inserted into the internal mixer, after that the temperature is set to 160°C on the internal mixer, and left for 4 min until the CNR melts perfectly, then added with oleic acid as much as 6 phr (2 g), followed by the addition divinylbenzene 0.25 phr (0.1 g); 0.5 phr (0,2 g); and 1.0 phr (0,3 g) and DCP initiators of 0.5 phr (0.2 g) until homogeneous. The blending process is carried out for 8 minutes to experience a grafting reaction. After 8 min the process is stopped. In hot conditions quickly the reaction product is removed from the internal mixer. The results obtained are then cooled and made into granules/pellets. The variations of blends are listed, as in Table 3.

**Table 3: Variation of Divinylbenzene**

Sample	Cyclic Natural Rubber (CNR)		Oleic Acid (OA)		Dicumyl Peroxide (DCP)		Divinyl Benzene (DVB)	
DVB-0,25	100 phr	33 g	6 phr	2 g	0.50 phr	0.2 g	0.25 phr	0.1 g
DVB-0,5	100 phr	33 g	6 phr	2 g	0.50 phr	0.2 g	0.50 phr	0.2 g
DVB-1	100 phr	33 g	6 phr	2 g	0.50 phr	0.2 g	1.00 phr	0.3 g

\* phr (Parts per Hundred Rubber)

Then the result of cyclic natural rubber that has been grafted with oleic acid (CNR-g-OA) are refluxed with 100 mL of Xylene with a series of reflux devices which are heating, boiling pumpkin and Liebig condenser at 110°C until dissolved. After dissolving, 100 mL of ethanol is added until the precipitate is formed. The precipitate formed is filtered using filter paper which has been connected

to a vacuum pump and washed with ethanol repeatedly in order to dissolve the remaining acidic reactions. The precipitate formed was dried in oven at a temperature of 120°C for 24 hours. Specific results were characterized by FTIR.

#### Compatibility of CNR-g-OA and Polyamide Resin

80 g of polyamide are put into erlenmeyer

and then dissolved with 20 mL of HCl 25% and 2 mL of acetone after that stirred for  $\pm$  20 min until all polyamide resins dissolve completely. 20 g of CNR-g-OA is put into erlenmeyer and then dissolved with 100 mL of xylene, and stirred using a magnetic stirrer for  $\pm$  20 min until it dissolves and homogeneous. Polyamide solution is added to CNR-g-OA solution, then the mixture is stirred using a magnetic stirrer for  $\pm$  20 min until it is mixed homogeneously. The blends is then formed thin layer on the glass using a film forming device, with a thickness of 120 micrometers. The thin layer formed was waited until dry after it was characterized by FTIR and Scanning Electron Microscopy to determine the compatibility of CNR-g-OA with Polyamide. The same procedure was also carried out for CNR-g-OA/ PA using DVB compatibilizer.

## RESULT AND DISCUSSION

### Results of Grafting Oleic Acid on CNR Using Dicumyl Peroxide Initiator

The grafting process of oleic acid on CNR is carried out using the initiator dicumyl peroxide, and the composition refers to Table 1. The results obtained from the dicumyl peroxide variations are shown in Figure 1.

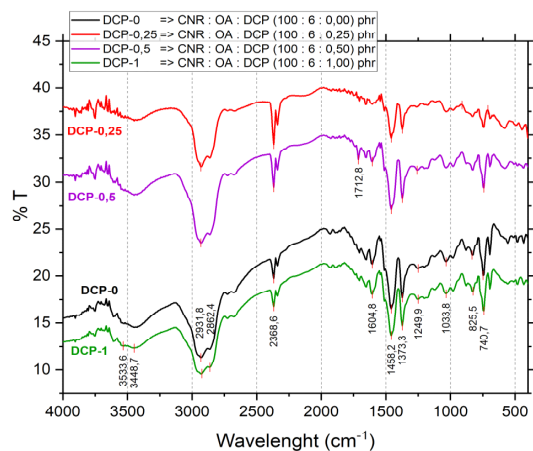


Fig. 1. FTIR of CNR-g-OA (Variation of DCP : 0,25 phr; 0,5 phr; and 1 phr)

Of all the variations, it appears that all peaks with wide absorption and low intensity at 3448.7  $\text{cm}^{-1}$  shows the presence of OH from oleic acid. The presence of absorption at 2931.8  $\text{cm}^{-1}$  and low intensity shows the presence of the aliphatic -CH of CNR. At absorption 1604.8  $\text{cm}^{-1}$  it shows the strain vibration -C=C-. In the area 1500 to 500  $\text{cm}^{-1}$ , there

is a peak at 1458.2  $\text{cm}^{-1}$  indicates a vibration strain  $\text{CH}_2$ , at 1373.3  $\text{cm}^{-1}$  indicates the presence of  $\text{CH}_3$ . At 1033.8  $\text{cm}^{-1}$  indicates the presence of C-O.

Meanwhile, in the variation of DCP-0.5, sharp absorption with very low intensity was seen at 1712.8  $\text{cm}^{-1}$  which indicates the presence of C=O, this means that oleic acid has been grafted on CNR even though the intensity is very low<sup>17</sup>. Furthermore, variations are made for oleic acid (3, 6, and 9) phr, with the composition of the DCP initiator is fixed 0.5 phr, so that the FTIR results are obtained as shown in Figure 1.

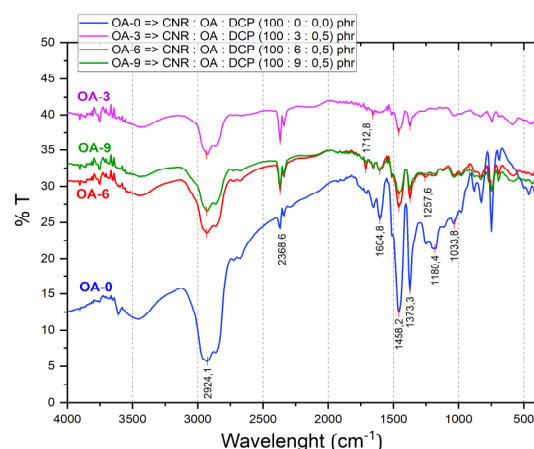


Fig. 2. FTIR of CNR-g-OA (Variation of OA : 3 phr; 6 phr; and 9 phr)

Of all variations of OA-3, OA-6, and OA-9 peak appeared on 3448.7  $\text{cm}^{-1}$ ; 2931.8  $\text{cm}^{-1}$ ; 1604.8  $\text{cm}^{-1}$ ; 1458.2  $\text{cm}^{-1}$ ; 1373.3  $\text{cm}^{-1}$ ; 1033.8  $\text{cm}^{-1}$ . At OA-6 there is a C=O at 1712.8  $\text{cm}^{-1}$  which indicate that oleic acid has been grafted on CNR even though in very small amounts. At OA-0 there is a different spectrum form for CNR without oleic acid with high intensity, as shown at 2924.1  $\text{cm}^{-1}$ ; 1604.8  $\text{cm}^{-1}$ ; 1458.2  $\text{cm}^{-1}$ ; 1373.3  $\text{cm}^{-1}$ ; 1033.8  $\text{cm}^{-1}$ , also in the absorption area of 779.2  $\text{cm}^{-1}$ .

### Results of Oleic Acid Grafting on CNR Using Dicumyl Peroxide Initiator and Divinyl Benzene

The addition of divinylbenzene in the blends as a compatibilizer, so that the bond between CNR and OA becomes stronger than before the additions of DVB, as shown in Figure 3.

Of all variations of DVB-0.25; DVB-0.5; and DVB-1 shows the absorption peak at 3425.6  $\text{cm}^{-1}$ ; 2924.1  $\text{cm}^{-1}$ ; 1604.8  $\text{cm}^{-1}$ ; 1458.2  $\text{cm}^{-1}$ ; 1373.3  $\text{cm}^{-1}$ ; 1080.1  $\text{cm}^{-1}$ . In the variation of DVB-0.5, there was no

peak in absorption of  $3425.6\text{ cm}^{-1}$  which showed the presence of OH bonds. This means that the addition of DVB is able to shift the hydroxyl bonds in blends, so that DVB makes the blends more compatible.

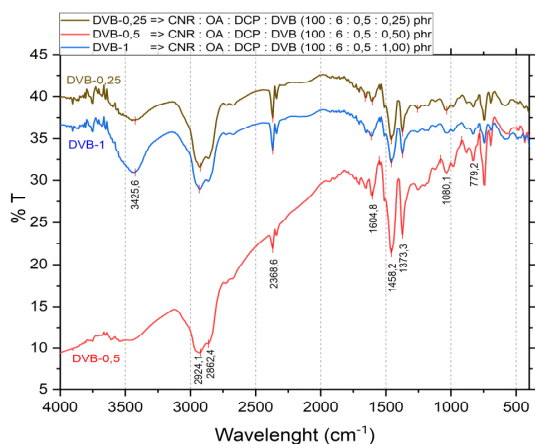


Fig. 3. FTIR of CNR-g-OA/DVB (Variation of DVB : 0,25 phr; 0,5 phr; and 1 phr)

#### Compatibility of CNR-g-OA in Polyamide Resin

Compatibility of CNR-g-OA in polyamide resin was carried out for CNR-g-OA samples with oleic acid variations as shown in Fig. 4, and DCP initiators variations as shown in Figure 5.

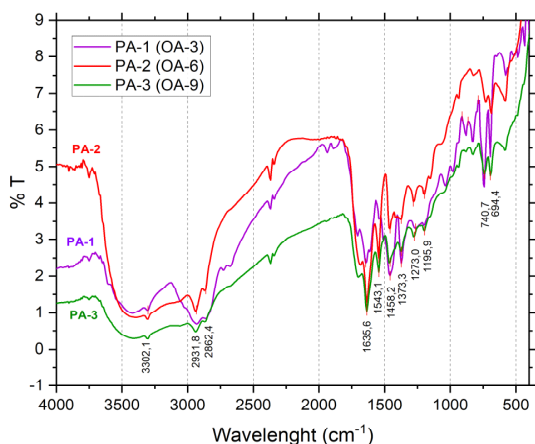


Fig. 4. FTIR of CNR-g-OA/PA (Variation of OA : 3 phr; 6 phr; and 9 phr)

Based on Figure 5, there is an absorption at  $3302.1\text{ cm}^{-1}$  and low intensity which indicating the presence of OH from oleic acid. Absorption at  $2931.8\text{ cm}^{-1}$ , it shows the presence of an aliphatic -CH from CNR. At  $1604.8\text{ cm}^{-1}$ , it shows the strain vibration -C=C-. In the area of  $1500\text{ to }500\text{ cm}^{-1}$ , it shows the absorption at  $1458.2\text{ cm}^{-1}$ ;  $1373.3\text{ cm}^{-1}$ ;

$1033.8\text{ cm}^{-1}$ . While the variation of PA-2 and PA-5 shows sharp absorption and low intensity at  $1712.8\text{ cm}^{-1}$  which indicates the presence of C=O carbonyl bonds, meaning that the blends has been grafted.

The results of SEM characterization for CNR-g-AO/PA with the composition CNR: OA: DCP (100: 6: 0.5) phr as shown in Figure 6.

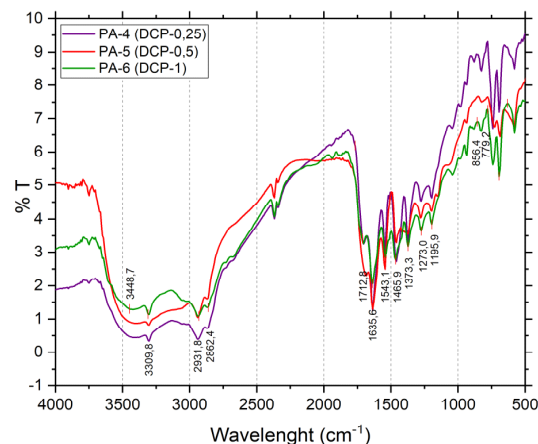


Fig. 5. FTIR of CNR-g-OA/PA (Variation of DCP: 0,25 phr; 0,5 phr; and 1 phr)

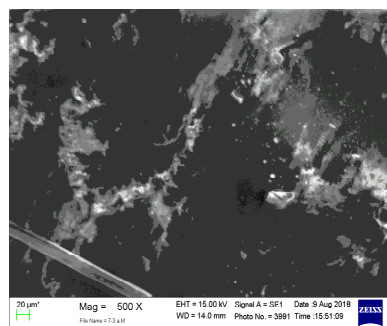


Fig. 6. SEM of CNR-g-OA/ PA

Based on Figure 6 which is the surface structure of CNR-g-OA / PA there is a white surface which is polyamide blended in CNR-g-OA. In figure 6, it appears that the surface structure is a little smoother; the PA material also seems less homogeneous even though it has been dispersed evenly.

#### Compatibility of CNR-g-OA Using Divinylbenzene in Polyamide Resin

Compatibility of CNR-g-OA using divinylbenzene in polyamide resin, as shown in Figure 7.

Of all variations of PA-7, PA-8, and PA-9 in Fig. 7, there was an absorption peak at  $3410.1\text{ cm}^{-1}$ ;

2931.8  $\text{cm}^{-1}$ ; 1643.4  $\text{cm}^{-1}$ ; 1458.2  $\text{cm}^{-1}$ ; 1373.3  $\text{cm}^{-1}$ ; 1080.1  $\text{cm}^{-1}$ . At PA-8, it appears that the absorption peak at 1705.1  $\text{cm}^{-1}$  means that there is a bond of  $\text{-C=O}$ , and also absorption at 1643.4  $\text{cm}^{-1}$  and medium intensity which shows the presence of  $\text{C=C}$ .

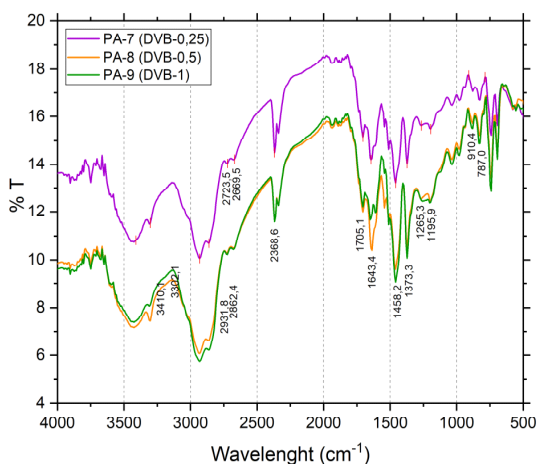


Fig. 7. FTIR of CNR-g-OA/DVB/PA (Variation of DVB : 0,25 phr; 0,5 phr; 1 phr)

Based on the comparison of the FTIR spectrum in Fig. 5 and Fig. 7, there has been a change in FTIR spectrum after the addition of DVB. In Fig. 7, shows an increase in intensity at 1458.2  $\text{cm}^{-1}$  and 1373.3  $\text{cm}^{-1}$  which indicates the presence of  $\text{CH}_2$  and  $\text{CH}_3$ . This is clearly a change in CNR-g-OA after DVB was added. While the decrease in intensity occurs at 1643.4  $\text{cm}^{-1}$  because there is a lot of disconnection in the double bond chain  $\text{C=C}$  after the grafting process occurs.

Similarly, the surface structure as shown in Fig. 8 which is CNR-g-OA/DVB/PA with the composition CNR: OA: DCP: DVB (100: 6: 0.5: 0.5) phr. In Fig. 8 the surface structure of CNR-g-OA/DVB /PA is smooth and PA material is evenly dispersed, and the surface structure also doesn't show any PA material, which

is caused by the presence of DVB which makes the blends more homogeneous and compatible.

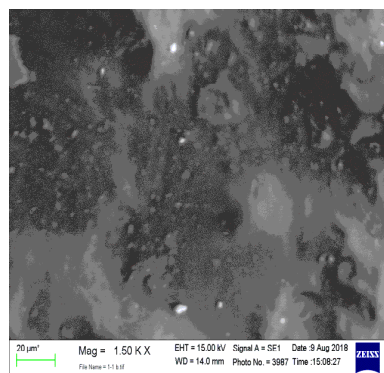


Fig. 8. SEM of CNR-g-OA/DVB/PA

## CONCLUSION

The best compositions ratio of CNR-g-OA products are CNR (100 phr), OA (6 phr), DCP (0.5 phr); and DVB (0.5 phr) with results of grafting formed is CNR-g-OA which indicated by the presence of sharp and weak peaks at 1700 to 1800  $\text{cm}^{-1}$ , indicating that is carbonyl ( $\text{C=O}$ ) (typical for carbonyl) from oleic acid. It is caused the grafting was succeed to generate CNR-g-OA. Blending CNR-g-OA with polyamide after the addition of DVB is difference compare to CNR-g-OA. This indicates that CNR-g-OA is compatible (homogeneous) after blending with PA.

## ACKNOWLEDGEMENT

The authors would like to thank the Directorate of Research and Community Service, Directorate General for Research and Development, Ministry of Research, Technology and Higher Education of the Republic of Indonesia for research funding assistance so as to support the completion of this doctoral dissertation research with research contract number 131/K1.1/LT.1/2018.

## REFERENCES

1. Wongthong, P.; Nakason, C.; Pan, Q.; Rempel, G. L.; Kiatkamjornwong, S., *Eur. Polym. J.*, **2013**, *49*, 4035.
2. Phinyocheep, P., In *Chemistry, Manufacture and Applications of Natural Rubber*; Elsevier., **2014**, 68–118.
3. Siregar, M. S.; Thamrin; Basuki; Eddiyanto; Mendez, J. A., *Chem. Mater. Res.*, **2014**, *6*, 15.
4. Carone Jr., E.; Kopcak, U.; Goncalves, M. C.; Nunes, S. P., *Polymer (Guildf.)*, **2000**, *41*, 5929.
5. Hamid, F.; Akhbar, S.; Halim, K. H. K., *Procedia Eng.*, **2013**, *68*, 418.
6. Narang, J.; Chauhan, N.; Singh, A.; Pundir, C. S., *J. Mol. Catal. B Enzym.*, **2011**, *72*, 276.

7. Wang, Q.; Zhu, J.; Wang, P.; Li, L.; Yang, Q.; Huang, Y., *J. Appl. Polym. Sci.*, **2012**, *124*, 5064.
8. Nakason, C.; Pechurai, W.; Sahakaro, K.; Kaesaman, A., *Polym. Adv. Technol.*, **2005**, *16*, 592.
9. Song, Y.-W.; Do, H.-S.; Joo, H.-S.; Lim, D.-H.; Kim, S.; Kim, H.-J., *J. Adhes. Sci. Technol.*, **2006**, *20*, 1357.
10. Liqun, Z.; Irwan, G. S.; Kondo, T.; Kubota, H., *Eur. Polym. J.*, **2000**, *36*, 1591.
11. Siregar, M. S.; Thamrin, M.; Basuki, W. S., *Agrium.*, **2015**, *17*.
12. Nasution, A. S.; Said, E.; Siregar, M. S., *Agrium.*, **2015**, *19*.
13. Zhou, Z. F.; Huang, H.; Liu, N. C., *J. Appl. Polym. Sci.*, **2002**, *85*, 726.
14. Liu, M.; Liu, Z.; Ding, S.; Li, S.; Zhang, L., *J. Appl. Polym. Sci.*, **2003**, *90*, 3299.
15. Vigo, F.; Canepa, G.; Munari, S., *J. Polym. Sci. Part A1 Polym. Chem.*, **1969**, *7*, 3015.
16. Tank, R.; Gupta, D. C., *J. Porous Mater.*, **2009**, *16*, 387.
17. Kravovich, M. L.; Koenig, J. L., *Rubber Chem. Technol.*, **1998**, *71*, 300.