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by Nurdin Bukit

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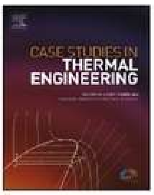

Microstructure and thermal properties of natural rubber compound with palm oil boilers ash for nanoparticle filler

Eva Marlina Ginting [a,**], Nurdin Bukit [a,*], Erna Frida [b], Bunga Fisikanta Bukit [c]

[a] Department of Physics, Universitas Negeri Medan, 20221, Medan, Indonesia
[b] Faculty of Engineering, Universitas Quality, 12345, Medan, Indonesia
[c] Department of Physics, Universitas Quality Berastagi, 22153, Berastagi Sumatera Utara, Indonesia

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ABSTRACT

This study aims to determine the properties of natural rubber compounds by varying the Oil Palm Boiler Ash (OPBA) nanoparticles with variations (0,2,4,6 and 8) wt%. The preparation method for natural rubber compounds uses Open Mill by mixing Indonesian Rubber Standard-20 (SIR-20) with anti-oxidants, activators, preservatives, accelerators, and OPBA nanoparticle fillers. The results showed thermal properties with Differential Scanning Calorimetric (DSC) increased melting point and the presence of cross bonds with increasing OPBA composition compared without filler. The distribution of compounds occurs even with the addition of OPBA filler. The results of the XRD diffraction pattern analysis of natural rubber composites without fillers amorphously shaped, but with the addition of OPBA fillers, the diffraction pattern showed a crystal structure. The FTIR graph shows that there is no significant difference between compounds with and without fillers.

1. Introduction

Indonesia, Malaysia, and Thailand are the countries producing palm oil [1]. Palm oil has many uses, not only the fruit but also almost all parts of the tree can be used. Scientific and technological advances have increased yields. Palm oil products now also function as raw materials for the manufacture of various synthetic materials, medicines, and household materials [2]. An example of palm oil waste is oil palm crust ash originating from a boiler. Oil Palm Boiler Ash (OPBA) is ash from shells and fruit fibers that have been crushed and burned at a temperature of 500–700°C in a boiler furnace. OPBA is an environmental problem because it is a waste of the palm oil mill industry. OPBA is biomass with silica content (SiO_2), so it has the potential to be used. OPBA contains silica chemical elements (SiO_2) 49.50%, Al_2O_3 5.45%, and Fe_2O_3 5.73%. OPBA can replace carbon black as a filler in the manufacture of natural rubber compounds [3–8]. Alumina is a ceramic oxide material that has the potential to be used in various engineering products [9].

OPBA is a hydrophilic inorganic compound. Therefore, to produce compatibility with polymers, it is necessary to modify OPBA before synthesizing it into nanocomposites. Modifying the OPBA surface using NaOH and HCl solutions, and changing its size to nano by coprecipitation method is a simple method.

Natural rubber is an isoprene polymer (C_5H_8) which has a molecular weight. Hevea rubber derived from the Hevea Brasiliensis tree is a natural form of 1,4 - polyisoprene. The use of cis - 1.4 polyisoprene is more than 90% in the rubber industry. Natural rubber is one

* Corresponding author.
** Corresponding author.
E-mail addresses: eva.marlina@unimed.ac.id (E.M. Ginting), nurdinbukit5@gmail.com (N. Bukit).

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Table 1
The Formula Used for Preparation of Natural Rubber Compound with OPBA filler.

No	Materials	S_0	S_1	S_2	S_3	S_4	Function
1	NR SIR-20	100	98	96	94	92	Binder
2	Wax	1.5	1.5	1.5	1.5	1.5	Antilux
3	Filler (OPBA)	0	2	4	6	8	Filler
4	ZnO	5	5	5	5	5	Activator
5	Stearic acid	2	2	2	2	2	Activator
6	Sulfur	3	3	3	3	3	Curing agent
7	IPPD	2	2	2	2	2	Antioxidant
8	TMTD	1.5	1.5	1.5	1.5	1.5	Accelerator
9	MBTS	2.5	2.5	2.5	2.5	2.5	Accelerator

Table 2
Melting point natural rubber compound with OPBA filler.

Sample (wt %)	Onset (C)	Peak (C)	Endset (C)	Heat Area (mJ)	Heat Delta (J/g)
0	370.44	374.44	384.14	65.29	8.37
2	346.10	366.77	387.44	439.59	56.36
4	341.69	369.68	380.00	423.14	50.37
6	333.40	363.48	382.41	485.52	57.80
8	333.01	360.64	375.70	446.55	57.25

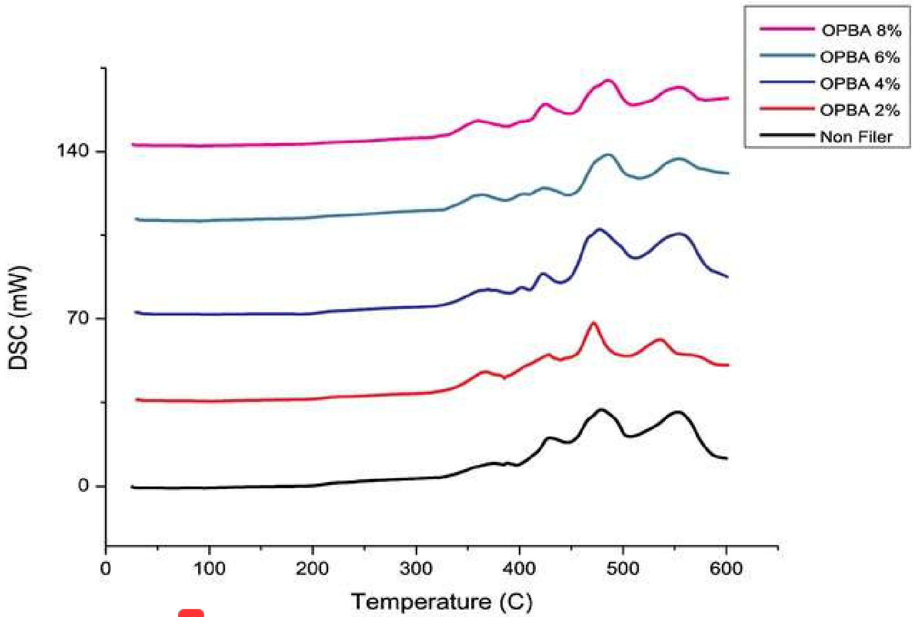

Fig. 1. DSC Thermogram of natural rubber compound with OPBA filler (0–8)wt%.

of the most useful materials in engineering applications. This is because rubber has a natural softness and elasticity. Even so, the use of fillers is also useful to get the desired product [10,11].

To increase the value and the production of natural rubber, it needs to be modified. One type of modification natural rubber is by adding fillers. To improve the quality of rubber, the technique used in rubber is by adding a laxative to the compound. Almost all rubber compounds use carbon black (CB) as a filler. The filler functions as a reinforcement, enlarge the volume, and improve the physical properties of rubber goods and strengthen the volcanic. The resulting rubber compound is useful in making shoe soles, gloves, vehicle tires, and others. Generally, natural rubber which has a non-polar chain is modified first, so that compatibility and reactivity of natural rubber are increased in mixing. The rubber modification method that has been used is halogenation [12].

This study aims to examine the effect of the composition of OPBA nanofiller particles on natural rubber compounds as a substitute for carbon black. Characterization of thermal properties, functional groups, diffraction patterns, and morphology was carried out to determine the results.

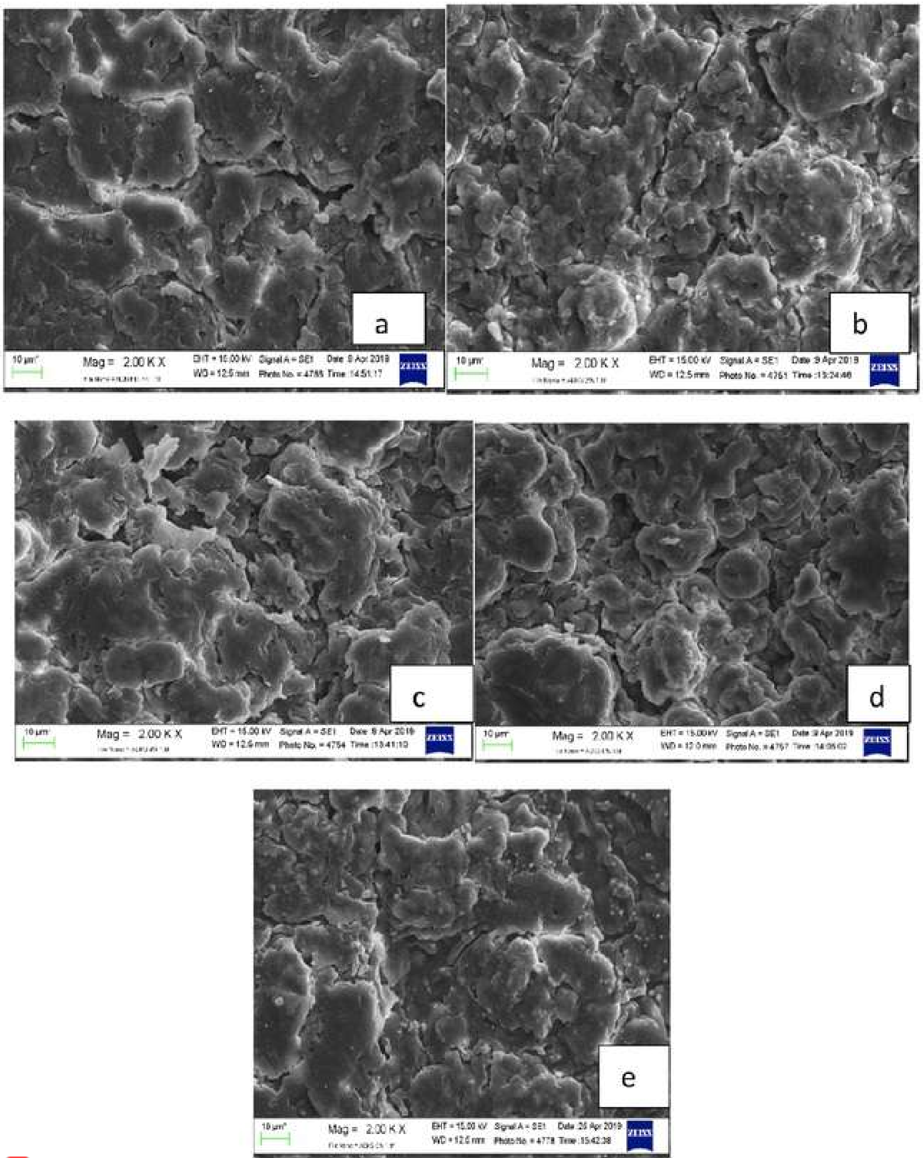

Fig. 2. Morphology of natural rubber compound with OPBA filler (a) 2 wt%, (b) 4 wt%, (c) 6 wt% (d) 8 wt%, (e) non filler.

2. Materials and methods

2.1. Material

Indonesian Standard Ruber-20 natural rubber (SIR-20), nanoparticle OPBA size 56.31 nm research results [9], Zinc Oxide (ZnO), Stearic Acid, Wax, N-Isopropyl-N' - Phenyl-p-phenylenediamine (IPPD), Tetra Methyl Thiura Disulfarat (TMTD), Marcapto Benzhoathizole Disulfide (MBTS), Sulfur.

2.2. Rubber compound preparation

Preparation of rubber compounds using Open mill tools. Materials such as SIR-20 natural rubber, zinc oxide (ZnO), stearic acid, nanoparticle OPBA, Wax, IPPD, TMTD, MBTS are mixed. Table 1 shows the variation of OPBA filler compositions. All ingredients blended using two roll mixing mill, then ground until the rubber is completely solid. While the rubber grinding process is running, the ingredients are inserted one by one in stages into the rheometer.

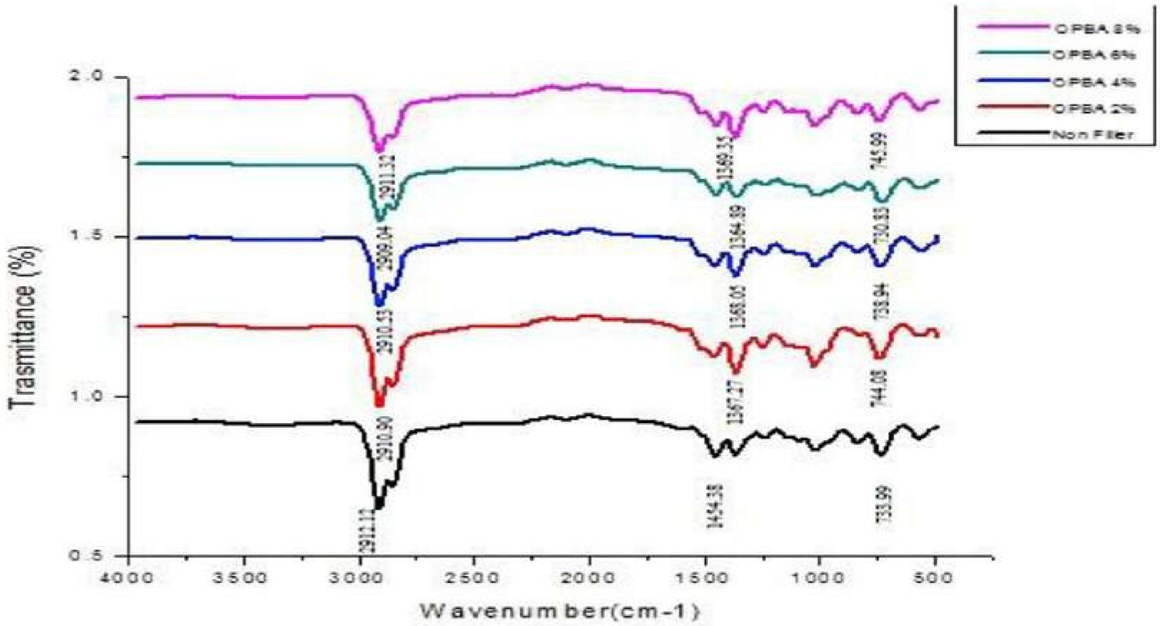

Fig. 3. FTIR Natural rubber compound with OPBA filler (0–8) wt%.

3. Results and discussion

3.1. Analysis of Differential Scanning Calorimetric (DSC)

The sample weight is 10–15 mg. Determine heat vulcanization by integrating the area under the exothermic calorimetry signal. DSC testing with a temperature range of 25 °C–600 °C, where the heating rate setting is at 5 °C/min. DSC test results are thermogram curves that are useful for determining the melting temperature. According to its classification, calorimetry is a technique for determining the amount of heat absorption or released by a substance undergoing physical or chemical changes. At constant pressure, internal energy functions as the enthalpy of H. The peak area of the DSC is useful for estimating the enthalpy of transition, ΔH. In general, this DSC analysis can be used to determine the enthalpy by measuring the differential heat flow needed to keep the sample material and the inert reference at the same temperature. One of the information obtained in semi-crystalline polymers is the material's crystallinity. Both the mechanical, physical, and chemical properties of the sample depend on the composition of the mixture and crystallization conditions such as temperature, pressure, orientation weight, molecule, and diluent [13]. The melting point is a parameter for polymeric materials because it represents the minimum temperature for processing. The melting point is dependent on the chemical structure of the material, the size, and the regularity of crystallization [14].

Table 2 and Fig. 1 show, the melting point of natural rubber compound with OPBA filler, where the heated area is increases with increasing filler composition from 0 wt% to 8 wt%. Where in the composition of 0 wt% is obtained 65.29 mJ and 6 wt% is 485.52 mJ. This is due to the increased silica content present in the natural rubber compound so that it increases the melting point when compared to without silica at 0 wt%. Whereas the melting point from the initial temperature of 333.10C to the final temperature of 387.44C changes in the peak temperature there is little change with the increase in the composition of OPBA from fillers from 2 to 8 wt% from 360.64C to 366.77C.

3.2. Scanning Electron Microscope (SEM) analysis

3.2.1. Morphological analysis of natural rubber compound with OPBA filler

Micrograph SEM blends NR/OPBA with a weight ratio (0,2,4,6,8) wt% vulcanized using sulfur 3 phr is shown in Fig. 2. The magnification scale that will be used for this research is 2000 magnification. The micrograph shows the distribution and particle size of OPBA dispersed in the NR matrix, which is influenced by OPBA composition and vulcanization. Increased OPBA composition results in a more evenly distributed and smaller particle size distribution. Differences in particle distribution cause the mechanical properties of the blend to also be different. The distribution and size of the phase are also influenced by the stress history that occurs during the mixing process. Stress history acts to interact with OPBA particles and distribute them into the NR matrix. Natural rubber and its composites show the presence of nano-sized particles which can improve the mechanical properties of the compound [15].

From Fig. 2a–e, it can be seen that the spread of filler is evenly distributed, due to the good interaction between the filler and rubber. this indicates that rubber and filler interactions indicate improved mechanical properties compared without fillers or OPBA.

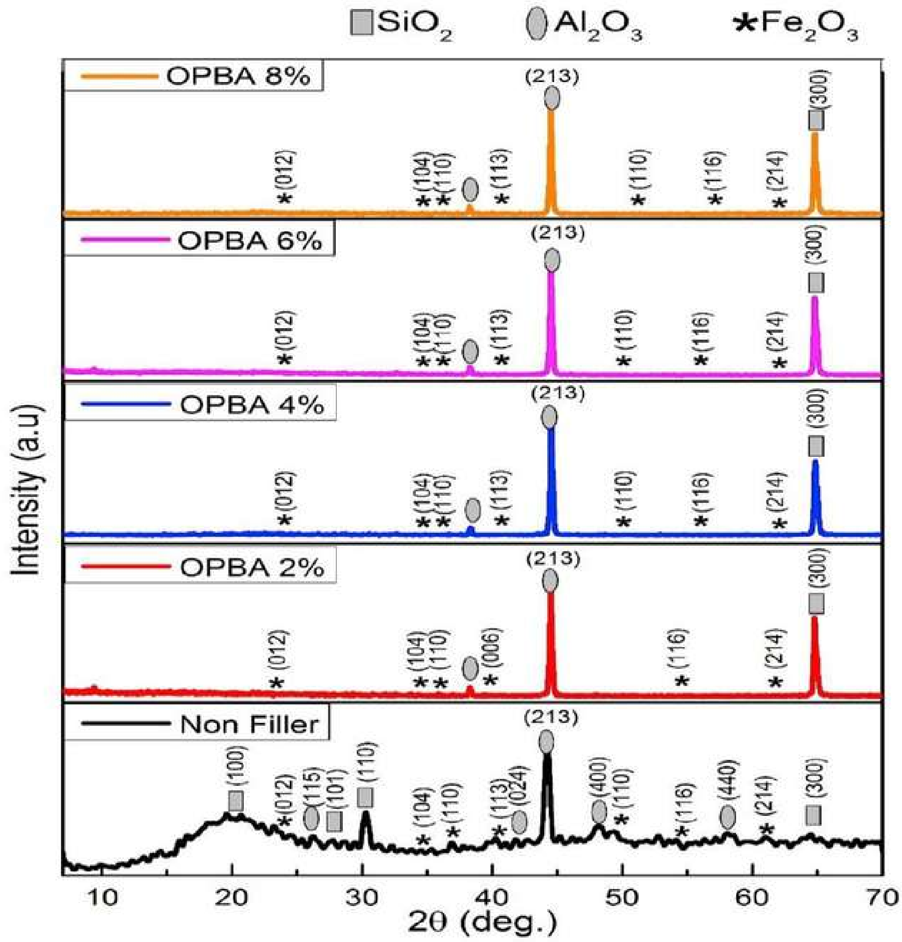

Fig. 4. Diffraction Patterns of natural rubber compound with OPBA filler (0–8)% by weight.

Empty cavities occur because of the OPBA tendency to form agglomeration due to silica in having a hydroxyl group that will try to help hydrogen bond with silica molecules or other chemical materials that are polar and do not show a de-adhesion phenomenon that occurs at the interface of the natural rubber matrix and fillers such as discovered by Ref. [16].

3.3. *Analysis of Fourier Transform Infra-Red (FTIR)*

FTIR spectra use the PerkinElmer System Spectrum One Fourier-transform infrared spectrophotometer. FTIR spectrophotometer is a tool to identify compounds, especially organic compounds, both qualitatively and quantitatively. Conduct analysis by looking at the shape of the spectrum by looking at specific peaks that indicate the type of functional group possessed by this compound. Whereas quantitative analysis uses standard compounds whose spectrum is made at various concentrations. Fig. 3 shows the FTIR graph between nanocomposites with the addition of OPBA fillers and without fillers. The main function of infrared spectrometry is to recognize (explain) the structure of molecules, especially functional groups such as OH, C = O, C = C. The most useful area to recognize the structure of a compound is in the region of 1–25 μm or 10,000 - 400 cm^{-1}.

The results of FTIR characterization on nanocomposite samples with OPBA filler indicate the existence of several vibrational bonds. The C–H bond with hydrogen is attached to the absorbing carbon in the region between 2853 and 2962 cm^{-1}. Peak 1475-1300 also shows C–H bending. Peak 1000–650 shows C = C–H, Ar–H bending. The FTIR graph between nanocomposites with the addition of OPBA fillers and without fillers shows that there is no significant difference. This is confirmed by the results of previous studies [17].

3.4. *X-Ray Diffraction (XRD) analysis*

XRD (X-Ray Diffraction) testing is done to get diffraction patterns of crystalline structures. The XRD used was Shimadzu 6100 (40 kV, 30 mA) with a wavelength of Cu-K_{a1} = 1.5405 Å, at a rate of 2°/min in the angular range of 2Θ = 5°–70°.

Fig. 4 shows the XRD diffraction pattern for natural rubber compounds by adding OPBA to the polymer matrix with a composition of (0,2,4,6,8) wt%. At an angle of $2\theta = 20^0$ at d_{hkl}, 100 for rubber compound without filler. Compound without filler has a maximum intensity and amorphous structure. The addition of OPBA filler composition intensity decreases the diffraction pattern of natural rubber compounds to a crystal pattern. Likewise, the angle $2\theta = 30^0$ at d_{hkl}110. This change shows that there is an intercalation between natural rubber polymers and OPBA. With the increasing of OPBA in natural rubber compounds, the SiO_2 content at $d_{hkl}30^0$ at an angle of $2\theta = 65^0$ is seen to increase. The addition of OPBA filler with Al_2O_3 intensity at d_{hkl} 213 angles $2\theta = 45^0$ can change the amorphous phase to the crystalline phase as a consequence of molecular diffusion during treatment [16]. OPBA has an amount of silica according to the results of the study [18]. From these characteristics, the addition of OPBA can improve mechanical properties [15,19,20].

4. Conclusion

The results showed that the thermal properties of natural rubber compounds increased the melting point and cross-linking with an increase in OPBA composition. Morphology shows a homogeneous mixture. The XRD pattern shows that the mixture without filler has an amorphous structure, whereas, with the addition of OPBA, the diffraction pattern becomes crystal. The FTIR graph shows that there is no significant difference between compounds with and without fillers.

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