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Effect of NR-g-cellulose coupling agent into NR-cellulose composite dispersibility and its physical properties

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Abstract. Natural rubber and cellulose are two materials with very different compatibility, so it is difficult to produce homogenous composite without using coupling agent. Natural rubber is nonpolar while cellulose is polar. The combination of natural rubber with cellulose is expected to produce composite with higher strength. The reinforcement concept of polymeric materials, such as natural rubber with cellulose as filler, results from increased rubber-filler interactions. This study aims to determine the effect of NR-g-Cellulose as coupling agent on the dispersibility of the composite and its physical properties. Hexamine/resorcinol and silane were used as a reference for a commercial coupling agent. Cellulose material was mixed in two-roll open mill together with natural rubber and other chemicals using three types of coupling agents, hexamine/resorcinol, silane, and NR-g-Cellulose. The FESEM result of the surface of composite indicated that composite with NR-g-Cellulose as coupling agent showed homogeneously dispersed compared to two other types of coupling agent but it is lower in physical properties, especially in tensile strength, tear strength, compression set, and rebound resilience of the composite. It may be caused by the NR-g-Cellulose coupling agent not working optimally and therefore it needs a high temperature to optimize the coupling agent to react with natural rubber and cellulose.

1. Introduction

Composites, the wonder materials are becoming an essential part of today's materials due to the several advantages such as low weight, corrosion resistance, high fatigue strength, and faster assembly [1]. Polymer composites are the name given to composite materials in which different polymers (binders) are used as the matrix; here, the second strengthening component (the filler) can be of any nature, including polymeric. The components of composite materials possess a clear phase boundary, while the properties of composite materials are formed by the volume combination of components and differ considerably from the properties of the individual components [2].

Natural rubber (NR) contains the high molecular weight, which is based on cis-1,4-polyisoprene. It has excellent mechanical and physical properties such as tensile strength, tensile modulus, tear



strength, and hardness. However, NR has poor chemical resistance and processing ability. The combination of its unique morphology, physical properties, cost-effectiveness, and environmental friendliness make natural rubber an appealing constituent for many materials and applications [3].

Natural fibres (NF) have been studied as reinforcement in composites due to its availability, environmentally benign, and renewable [4]. One of NF that widely applied in many applications is palm oil Empty Fruit Bunch (EFB). Empty Fruit Bunch (EFB) is a biomass waste produced by oil palm industries (about 25-26%). The empty fruit bunch of palm oil contains cellulose up to 36.67% [5]. The cellulose could be extracted using the pre-treatment process. The purified cellulose would then undergo acid hydrolysis to break the cellulose structure into nano-sized. Nano-sized cellulose that has been formed is fibrous and nanofibrillated [6]. The nanosize of the cellulose (Cellulose Nano Fibre, CNF) provides excellent properties such as high crystalline content, good optical properties, and excellent mechanical properties [7].

In composite preparation, natural rubber (NR) is a material commonly used as matrix [8]. The mechanical properties of bio filler filled rubbers depend on several factors of which most important ones are dispersion level, interfacial strength, and type of filler used [9]. The combination of NR and cellulose is good to improve tear strength. The reinforcement concept of polymeric materials, such as natural rubber with cellulose as filler, result from increased rubber-filler interactions [10]. To improve interfacial bonding and mechanical properties, compatibilizer was commonly added [5].

NR and MFC cannot disperse well because of the differences in polarity. To disperse better, an appropriate coupling agent must be used. One kind compatibilizer or coupling agent for natural rubber (NR)-cellulose composite is synthesized by grafting copolymerization between cellulose and natural rubber resulting in NR-*g*-cellulose; this is the novelty of this research. This research aims to study the effect of its synthesized coupling agent and two commercial coupling agents as comparison into NR-cellulose composite dispersibility and its physical properties. The composite was produced using two roll open mill. The composite samples were vulcanized, and its physical properties were analyzed. The effects of coupling agent on sample morphology were observed using Scanning Electron Microscopy (SEM).

2. Materials and Methods

2.1 Materials

The materials used in this study include Natural rubber (NR), *Standard Indonesia Rubber* (SIR) 20 obtained from local suppliers, and also technical quality rubber compounding chemicals from local suppliers. The rubber compounding chemicals include Sulphur as vulcanization agent, stearic acid and zinc oxide as an activator, hexamine/resorcinol and silane Si-69 as commercial coupling agent, and TBBS as an accelerator.

2.2 Preparation of microfibrillated cellulose (MFC)

Microfibrillated Cellulose (MFC) and coupling agent NR-*g*-MFC were produced by ITI. The initial microcrystalline cellulose (MCC) sample was prepared from oil palm Empty Fruit Bunches (EFB) by grinding and crushing to resulting powder form. The MFC was obtained chemically from MCC by delignification process using sodium hydroxide with high-pressure and bleaching using magnesium oxide and hydrogen peroxide. The dry nano-powder was obtained by being evaporated in vacuum at 80 °C and finally dried at 50 °C up to constant weight [11]. The characterization of MFC was analyzed using Particle Size Analyzer (PSA), Scanning Electron Microscopy (SEM), and Simultaneous Thermal Analysis (STA).

2.3 Preparation of NR-*g*-MFC

The coupling agent between natural rubber and MFC was synthesized via copolymerization reaction by Atomic Transfer Radical Polymerization (ATRP) method using macroinitiator MCF-Bromide in an autoclave [12]. The characterization of the copolymer was analyzed using Fourier Transform Infrared Spectroscopy (FTIR).

2.4 Synthesized of natural rubber/MFC composite

Natural rubber and MFC are mixed with other ingredients in the two-roll open mill according to the compound formula. The addition of chemicals uses a unit of phr (per hundred rubbers). This is used for calculating formulas where other chemicals are calculated as parts per 100 weight of rubber. Compound was formulated with variations in 3 types of coupling agent, as seen in Table 1. Natural rubber/cellulose composites were made without coupling agent as a control. The compounds were then tested for physical properties.

Table 1. The formula of natural rubber/cellulose composite with varied kinds of coupling agents

Materials	Dosage (per hundred rubber, phr)			
	A	B	C	D
NR	100	100	100	100
MFC	25	25	25	25
NR-g-MFC	-	-	3	-
Silane Si-69 (<i>bis-triethoxy silyl propyl-tetrasulfide</i>)	1.5	3	-	-
Hexamine (hexamethylenetetramine)	1.5	-	-	-
Resorcinol (1,3-isomer from benzenediol)	1.5	-	-	-
Zinc Oxide	5	5	5	5
Stearic Acid	2	2	2	2
TBBS (N- tert-butyl-benzothiazole sulphonamide)	0.7	0.7	0.7	0.7
Sulphur	2.25	2.25	2.25	2.25

3. Results and Discussion

3.1 Preparation of microfibrillated cellulose (MFC)

The morphology of the MFC structure was analyzed using Scanning Electron Microscopy (SEM); the results showed a cellulose structure in the form of fibrils with a relatively wide diameter (Figure 1). Based on the PSA analysis, MFC has polydispersity 2.174 with size $4.625.5 \pm 18.862.9$ nm. These results indicate that the synthesized MFC still has various particle sizes that need to be refined and homogenized again to reach smaller size particles. Meanwhile, the thermal properties of MFC based on the STA diagram analysis (Figure 2) show good thermal resistance as evidenced by high degradation temperatures (> 300 °C).

3.2 Preparation of NR-g-MFC

The NR-g-MFC that were successfully synthesized can be proven through FTIR analysis. Figure 3 shows the results of the FTIR spectrum of MFC before and after the synthesis of MFC graft copolymers with natural rubber. Based on Figure 3, it can be seen that the aromatic ring at wave number 1593.12 has disappeared which indicates that the aromatic ring breaks up and binds to the double bond carbon group (C = C) and with the side groups of natural rubber form a double bond and carbonyl group. A Double bond carbon and carbonyl group form can be seen at wavenumbers 1661.77 and 1737.47 which are the characteristic for the absorption of carbon groups C = C and C = O.

3.3 Synthesized of natural rubber/MFC composite

An amount of four NR/MFC composite formulas according to Table 1 have been made compound and cured on a press machine to produce vulcanized rubber as can be seen in Figure 4. Visually based on Figure 4, it can be seen that mixing of natural rubber with MFC and other materials in the two rolls open mill did not result in homogeneous dispersion, the particles of cellulose are still visible on the surface, not well dispersed with natural rubber. This is evidenced by the results of SEM analysis for three composites A, B, and C while SEM results for D composites are still tested (Figure 5).

From the results of SEM analysis, it can be seen that the mixing process has not produced a composite with uniform dispersion. In composite A, cellulose particles still appear on the surface, which is characterized by the appearance of white spots. This indicates that the MFC particles have not completely filled in the natural rubber matrix. In composite B, white spots appear more than composite A, while in composite C, white spots look less than composites A and B. This indicates that

the mixing of materials in composite C using NR-g-MFC as coupling agent is relatively more homogeneous compared to the other two composites.

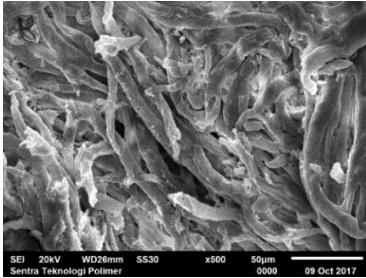


Figure 1. SEM micrograph of microfibrillated cellulose (MFC)

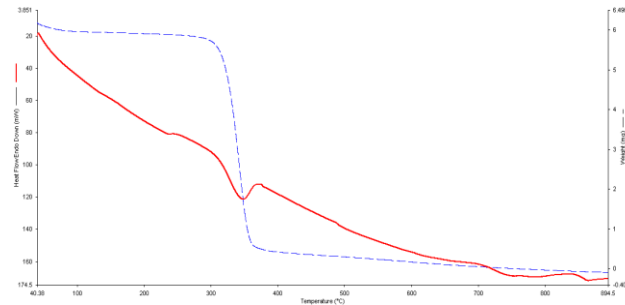


Figure 2. Thermal analysis of microfibrillated cellulose (MFC)

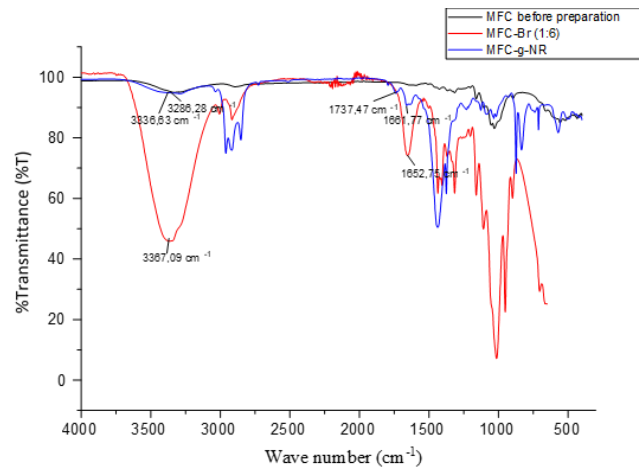


Figure 3. FTIR spectra of MFC before and after synthesis of graft copolymers with natural rubber

3.4 Physical properties of the composite.

The addition coupling agent into natural rubber/MFC composites affected the physical and mechanical properties of the composites. The results of physical properties testing for all vulcanized composites can be seen in Table 2.

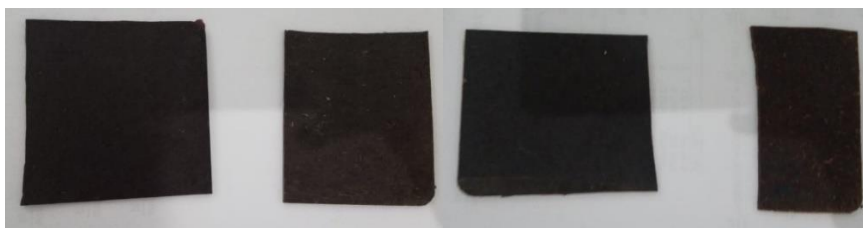


Figure 4. Visualization of composite A-D (from left to right)

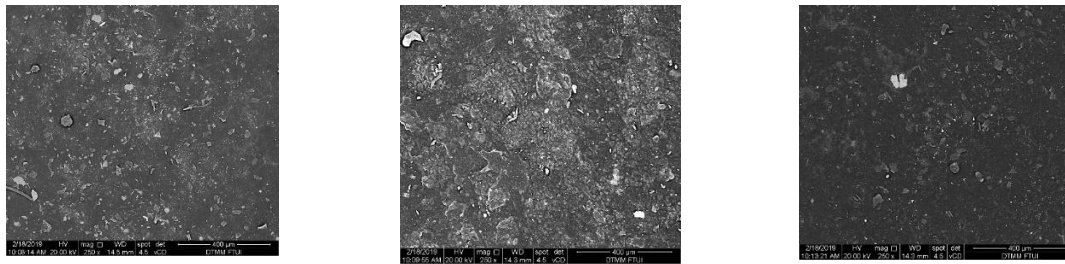


Figure 5. SEM micrograph of composite A, B, and C (from left to right)

Table 2. Physical properties of natural rubber/MFC composite with varied kinds of coupling agent

Physical Properties	Vulcanized			
	A	B	C	D
Hardness (Shore A)	75	67	65	63
Tensile strength (MPa)	4.4	4.3	2.4	5.1
Elongation at break (%)	350	520	420	560
Tear strength (MPa)	35.8	27.3	22.6	27
Compression set, temp. 27±2 °C (%)	9.89	12.64	43.23	13.64
Compression set, temp. -5±2 °C (%)	2.61	5.08	23.14	7.52
Rebound resilience (%)	69	58	51	64

3.5 Effect on hardness

The addition of combinations coupling agent, hexamine/resorcinol and silane, increases the hardness up to 12 shores A compared to D composites, which did not use coupling agent. Meanwhile, the addition of a single coupling agent, silane, increases the hardness by 4 shore A and the addition of NR-g-MFC increases the hardness by 2 shore A. This can be caused by the coupling agent that increases the interaction of natural rubber-filler (NR-MFC interaction) so that the composite structure becomes compact and solid as a result of increased composite hardness.

3.6 Effect on tensile strength

Composites without coupling agent (composite D) provide better tensile strength compared to other composites that using coupling agent. This is probably due to the fact that the coupling agent used is not suitable with the NR/MFC composite so that the addition of the material weakens the NR-MFC interaction which result to the decrease of the elasticity of the NR/MFC composite.

3.7 Effect on elongation at break

Composites without coupling agent (composite D) provide better elongation at break than other composites that using coupling agent. The decrease in elongation at break can be caused by the function of coupling agent to increase NR-MFC interaction so that the intermolecular interactions of natural rubber decrease. It caused decreasing in the elasticity of natural rubber, so the composites with coupling agent become easier to break than composite without coupling agent.

3.8 Effect on tear strength

Composite A, which uses a combination coupling agent, hexamine/resorcinol and silane, gives better tear strength than other composites. The increase in tear strength can be caused by the addition of coupling agent to strengthen the NR-MFC interaction, thus increasing the strength of the NR/MFC composite. Composite B, which uses a single coupling agent, silane, has better tear strength compared to composite D (without coupling agent). However, the tear strength of composite C using NR-g-MFC as coupling agent is lower than other composites. It can be caused that NR-g-MFC is not suitable with NR/MFC composites so that the addition of material weakens the NR-MFC interaction resulting to the decrease of the strength of NR/MFC composite.

3.9 Effect on compression set

Composite A, which uses a combination coupling agent, hexamine/resorcinol and silane, provides better compression set than other composites. The greater compression set value shows that after compressed, rubber elasticity is decreased [13]. Composite B, which uses a single coupling agent, silane, provides better compression set than composite D (without coupling agent). Whereas composite C, which uses NR-g-MFC as coupling agent, has the worst compression set than other composites. This can be caused the NR-g-MFC is not suitable with NR/MFC composites so that the filler-filler interaction of the MFC used is greater than NR-MFC interaction. This shows that the intermolecular interaction of MFC is stronger than the NR-MFC interaction so that when the composite is compressed in high pressure at certain temperature and time, its elasticity will drastically decrease.

3.10 Effect on rebound resilience

Composite C, which uses NR-g-MFC as coupling agent, provides better rebound resilience than other composites. This can be caused by the addition of NR-g-MFC increasing intermolecular interactions of natural rubber so that the elasticity of composites is better than other composites. The lower value of rebound resilience indicates that the composite is more resistant to impact.

4. Conclusions

The uses of NR-g-MFC as a coupling agent for NR/MFC composite could increase the dispersibility of MFC into natural rubber matrix in process compounding. On the other hand, the addition of NR-g-MFC decreases almost all physical properties except rebound resilience. To optimize the function of NR-g-MFC as coupling agent, the temperature of mixing should be increased so the reaction of the coupling agent with natural rubber and MFC will be optimum.

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