Analysis of structural and functional groups on the magnetic composite rubber – Lanthanum Manganite modification

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\textbf{Abstract.} The synthesis and characterization of composite rubber – lanthanum manganite modification have been performed. The composite was prepared by rubber elastomer thermoplastics, stearic acid, ZnO, n-cyclohexyl-2-benzothiazyl sulphenamide (CBS), sulfur, and magnetic powder of La\textsubscript{0.8}Ba\textsubscript{0.2}(Fe, Mn, Ti)O\textsubscript{3}. The raw material was mixed by open two-roll mixing for 32 min and then pressed at temperature of 140 °C for 30 min. The element analysis showed that the sample contained carbon, oxygen, sulfur, zinc, lanthanum, barium, manganese, titanium and iron. The refinement results of x-ray diffraction pattern show that the sample is semi-crystalline with the crystallinity of 46%. The sample consist of the matrix is amorphose phase and the filler is crystalline phase. The filler consist of two phases, namely ZnO and La\textsubscript{0.8}Ba\textsubscript{0.2}(Fe, Mn,Ti)O\textsubscript{3} phases. The functional groups analysis show that the sulfur addition modified the polymer by forming crosslink (bridges) between individual polymer chains and bonding between magnetic filler and rubber matrix. We concluded that this study has been successfully made a composite of rubber – La\textsubscript{0.8}Ba\textsubscript{0.2}(Fe, Mn,Ti)O\textsubscript{3} for microwave absorber sheet application.

1. Introduction

Elastomer Thermoplastic (ETP) is one of polymer that had the quality both elastic and thermoplastic. ETP is generally used in the automotive industry until household appliances. At this time the ETP is also a target for the electronics industry utilization. Recently introduced a product of electromagnetic absorbing can provide a relatively easy solution to reduce unwanted RF noise in electronic equipment, namely absorber sheet materials. Absorber sheet is a product of a composite material with magnetic particles embedded in the ETP. The composite has good noise attenuation performance from hundreds of MHz to several GHz.

The primary objective of this study is to develop a composite material based on natural rubber that can be used to absorb the electromagnetic waves. Indonesia is one of the biggest rubber producers in the world with a total production of about 1.4 million tons per years. Natural rubber is an elastomer, it has a relatively high molecular weight and the potential for the manufacture of elastomer thermoplastic (ETP). Use of ETP from natural rubber-based is increasing every year because it has many advantages namely the process is easy and simple, the manufacturing process is faster and can be recycled [1]. The filler used magnetic material which was able to absorb the electromagnetic
waves. Previous study has been carried out on the development of magnetic absorber material Ba-Sr hexaferrite by substituting Fe ions with Mn and Ti [2]. Recent development of other magnetic material that serves as an absorber material is modification of hexaferrite systems [3-5] and ABO$_3$ perovskite [6-9]. The combination of both materials is expected to obtain superior composite materials that can be used for electromagnetic waves absorber and is of flexible nature.

However to make a good composite materials is not that simple and straightforward, because the process is influenced by several factors. The composite manufacturing process begins with the termination of the polymer chain. The step is called by mastication process to facilitate the mixing process between rubber, magnetic powder and other chemicals. The second step is vulcanization process to create a crosslink (bridges) between individual polymer chains. The filler of magnetic material must be homogeneous and blended with the polymer matrix. Temperature- and time of heating control must be precise. Therefore the result and discussions have focused on the synthesis result and structural characterization and functional groups analysis of the composite. So the aim of this study is to synthesize a composite material from a combination of rubber and lanthanum manganite modification method, and to understand the microstructure, the crystal structure, and the bonding mechanism of the composite.

### 2. Materials and Methods

The synthesis of La$_{0.8}$Ba$_{0.2}$(Fe, Mn,Ti)O$_3$ material was performed by using the solid reaction method. This magnetic material was prepared by oxide materials as starting materials, namely BaCO$_3$, Fe$_2$O$_3$, MnCO$_3$, TiO$_2$, and La$_2$O$_3$. The raw materials were obtained from Merck product with a purity of more than 99%. The raw materials are mixed by using a high-energy milling (HEM) apparatus of the type Spex 8000 for 10 hours at room temperature. The finely mixed powder was compacted at 5000 psi into pellets and sintered in the electric chamber furnace THERMOLYNE at 1000°C for 10 hour in the air at atmospheric pressure. The synthesis of composite material is started with the weighing of La$_{0.8}$Ba$_{0.2}$(Fe, Mn,Ti)O$_3$ material and then the mixing process is carried out by using an open two-roll mixer (model: HF-2RM, series: 2394). The mixing process consists of mastication, vulcanization, pressing, and heat treatment. Vulcanization usually used sulfur and additive. These additives include accelerators, activators like zinc oxide and stearic acid and n-cyclohexyl-2-benzothiazyl sulphenamide (CBS). Accelerators can increase the rate of cure by catalyst the addition of sulfur chains to the rubber molecules. Formulation of the composite material is showed in Table 1.

| No. | Material                                | Fraction (per hundred rubber) |
|-----|-----------------------------------------|-------------------------------|
| 1.  | Rubber (ETP)                            | 100.0                         |
| 2.  | Stearic acid                            | 2.0                           |
| 3.  | Zinc oxide (ZnO)                        | 5.0                           |
| 4.  | (La$_{0.8}$Ba$_{0.2}$Fe$_{0.3}$(Mn,Ti)$_{0.3}$O$_3$) | 20.0                          |
| 5.  | n-cyclohexyl-2-benzothiazyl sulphenamide (CBS) | 1.4                           |
| 6.  | Sulfur                                  | 2.5                           |

### 3. Results and Discussion

The composite is prepared by rubber elastomer thermoplastics, stearic acid, ZnO, n-cyclohexyl-2-benzothiazyl sulphenamide (CBS), sulfur, and magnetic powder of La$_{0.8}$Ba$_{0.2}$(Fe,Mn,Ti)O$_3$. Fig. 1 is showing the results of the elementary analysis by using energy dispersive spectroscopy method on the composite material.
The energy dispersive spectrum as shown in Fig. 1 shows that the dominant elements are carbon (C), oxygen (O), sulfur (S), zinc (Zn), lathanum (La), barium (Ba), manganese (Mn), titanium (Ti) and iron (Fe). This means that the sample is iron rich. The detailed content of the sample is shown in Table 2.

### Table 2. The result of elementer analysis of the iron sand sample

| No. | Unsure         | Content (wt%) |
|-----|----------------|---------------|
| 1.  | Iron (Fe)      | 1.80 ± 0.06   |
| 2.  | Titanium (Ti)  | 0.46 ± 0.07   |
| 3.  | Manganese (Mn)| 0.80 ± 0.09   |
| 4.  | Lanthanum (La)| 6.03 ± 1.85   |
| 5.  | Barium (Ba)    | 1.42 ± 0.50   |
| 6.  | Zinc (Zn)      | 5.60 ± 1.73   |
| 7.  | Oxygen (O)     | 13.07 ± 1.65  |
| 8.  | Sulfur (S)     | 3.00 ± 0.25   |
| 9.  | Carbon (C)     | 67.82 ± 0.21  |

The SEM micrograms of the sample show that the filler of magnetic particles are embedded in the ETP matrix and are distributed homogeneously through out the sample’s surface. And the results of elemental analysis have shown that all of the elements contained in the composite have emerged. So that, a further confirmation about phases formed in the sample is needed which is achieved by using XRD method as is shown in Fig. 2.
The refinement result of XRD pattern on the sample has produced an excellent quality of fitting with the reliability factor R being very small. And the goodness of fit value $\chi^2$ (chi-squared) is in good agreement with the standard value allowed in the Rietveld analysis [10]. The sample is semicrystalline with the crystallinity of 46%. The sample consists of an amorphous phase matrix and a crystalline phase filler. The filler consists of two phases, namely ZnO and $\text{La}_{0.8}\text{Ba}_{0.2}(\text{Fe,Mn,Ti})\text{O}_3$ phases. $\text{La}_{0.8}\text{Ba}_{0.2}(\text{Fe,Mn,Ti})\text{O}_3$ phase had monoclinic structure, space group of $\text{I} \overline{1} 2 / a$, the lattice parameters of $a = 5.543(1)$ Å, $b = 5.587(1)$ Å and $c = 7.822(1)$ Å, $\alpha = \gamma = 90^\circ$ and $\beta = 89.73(3)^\circ$, $V = 242.3(1)$ Å$^3$, and $\rho = 6.414$ gr.cm$^{-3}$. ZnO phase had hexagonal structure, space group of $\text{P} 63 \text{mc}$, the lattice parameters of $a = 3.2487(9)$ Å, $b = 3.2487(9)$ Å and $c = 5.204(1)$ Å, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, $V = 47.56(3)$ Å$^3$, and $\rho = 5.467$ gr.cm$^{-3}$. The phase identification referred to COD of No. 1001820 and No. 9011662 for LaMnO$_3$ and ZnO phases, respectively. This result is evidenced by the calculation results of the mass fraction as shown in Table 3.

### Table 3. Mass fraction of the samples

| Sample    | Phase                          | Mass fraction (%) | wRp | $\chi^2$ (chi-squared) |
|-----------|--------------------------------|-------------------|-----|------------------------|
| Composite | $\text{La}_{0.8}\text{Ba}_{0.2}(\text{Fe,Mn,Ti})\text{O}_3$ | 94.20             | 5.84 | 1.196                  |
|           | ZnO                            | 5.80              |      |                        |

However, the XRD results could not explain the bonding mechanism, including the formation of crosslink (bridges) between individual polymer chains in the composite so that it is needed further confirmation by using FTIR equipment as shown in Fig. 3.

![Fig. 3. The FTIR transmittance spectrum of the sample.](image)

Fig. 3 represented the FTIR spectrum between 4000 to 400 cm$^{-1}$ of the composite sample. Transmittance peaks of the FTIR spectra on the composite sample indicate the presence of vibration of La–O, O–H, C–H, C=C, C–O, C–O, C=CH, Mn–O, Fe–O, C–S bond [11-14]. Natural rubber consists of suitable polymers of the organic compound isoprene with minor impurities of other organic compounds and water. Forms of polyisoprene that are useful as natural rubbers are classified as elastomers. Chemical structure of cis-polyisoprene as the main constituent of natural rubber was showed in Fig. 4.

![Figure 4. Chemical structure of cis-polyisoprene as the main constituent of natural rubber](image)
The functional groups analysis results obtained by using the FTIR method, have shown that transmittance peaks of the rubber appear at wave numbers around 2849-2959, 1373 cm\(^{-1}\), 1539 cm\(^{-1}\), and 843 cm\(^{-1}\) that indicated the presence of the C–H, C=C, and C=CH bond vibrations, respectively. Meanwhile transmittance peaks of the \(\text{La}_{0.8}\text{Ba}_{0.2}\text{Fe}_{0.3}(\text{Mn,Ti})_{0.35}\text{O}_3\) appear at wave numbers of 3694 cm\(^{-1}\), 613 cm\(^{-1}\) and 576 cm\(^{-1}\) attributed to the La–O, Mn–O, and Fe–O bond vibrations, respectively. The composite manufacturing process needs to be supplemented by a vulcanization process to create a crosslink (bridges) between individual polymer chains. A cross-link is a bond that links one polymer chain to another. They can be covalent bonds or ionic bonds. Vulcanization process usually used sulphur in the process. Both of these contain a sulphur atom in the molecule that initiates the reaction of the sulphur chains with the rubber. The chemical process of vulcanization is a type of cross-linking so that it is expected that the C–S bond would materialize as shown in Fig. 5.

![Figure 5. Schematic presentation of two polymer chains cross-linked after the vulcanization](image)

The functional groups analysis showed that transmittance peaks of the crosslink appeared at a wave number of around 590 cm\(^{-1}\) that indicates the presence of the C–S bond vibrations. However, it has also been found that transmittance peaks of the samples appear at wave numbers around 1728 cm\(^{-1}\) and 1146 cm\(^{-1}\) that indicate the presence of C=O and C–O, bond vibrations, respectively. It is suspected that there was a bonding between the magnetic filler and the rubber matrix.

### 4. Conclusion

The synthesis and characterization of composite rubber – lanthanum manganite modification have been carried out using chemical process. Microstructure of the sample showed that the filler of magnetic particles are embedded in the ETP matrix and are distributed homogeneously on the sample’s surface. The elemental analysis shows that the sample contains carbon, oxygen, sulfur, zinc, lanthanum, barium, manganese, titanium and iron. The refinement results of x-ray diffraction pattern showed that the sample is semicrystalline with the crystallinity of 46%. The sample consist of the matrix was amorphous phase and the filler was crystalline phase. The filler consist of two phases, namely \(\text{ZnO}\) and \(\text{La}_{0.8}\text{Ba}_{0.2}(\text{Fe,Mn,Ti})_{0.35}\text{O}_3\) phases. The functional groups analysis showed that the sulfur addition modified the polymer by forming crosslink (bridges) between individual polymer chains and bonding between magnetic filler and rubber matrix. This study has been successfully synthesized composite rubber–lanthanum manganite modification and has been understood changes in the microstructure, crystal structure and bonding mechanism of the composite.

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