# Effects of natural zeolite and ferric oxide to electromagnetic and reflection loss properties of polyurethane nanocomposite

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**Abstract**. Microwave-absorptive polymeric composite materials are becoming important to protect interference of any communication systems due to increasing use of microwave-inducing devices. In this work, the microwave-absorptive polyurethane nanocomposites were prepared using natural zeolites of Sarulla North Sumatra and commercial ferric oxide as fillers. Weight ratios of the polyurethane to natural zeolite and ferric oxide were varied (90%:6%:4%; 80%:12%:8%; 70%:24%:6%) by weight. The fillers were prepared using ball milling technique and characterized for their particle size distributions using Particle Size Analyzer. The nanocomposites, prepared using in-situ reaction of polyethylene glycol, toluene diisocyanate and fillers. The complex permittivity ($\varepsilon'$ and $\varepsilon''$) and complex permeability ($\mu'$ and $\mu''$) as electromagnetic properties were calculated using NRW method after collecting real and imaginary S parameter using Vector Network Analyzer measurement at X band frequency. Results show ratio of the fillers will affect the permeability, permittivity and reflection loss of the materials. The best reflection loss was shown -40.588 dB (>99 % absorption) at ratio for polyurethane : nanozeolite : ferric oxide (80%:12%:8%) by weight observed at 10.92 GHz. According to the measurement and calculation was shown the polyurethane filled with natural nanozeolite and ferric oxide is a good electromagnetic wave attenuation material.

## 1. Introduction

The electromagnetic interference, a specific type of interference environmental pollution, is worsening due to the rapid development and utilization of wireless communications circuit devices and military applications. In the past decades, electromagnetic attenuation materials which comprise dielectric or magnetic fillers and polymer, have been commonly used to minimize the electromagnetic interference. The spinel ferrite have been utilized as the most frequent absorbing materials in various forms. The absorbing characteristics of materials depend on the frequency, layer thickness, complex permeability and complex permittivity. All the real and imaginary parameters of complex permeability and complex permittivity are found to increase with the increased of ferrite contents [1].

Zeolite mineral is a compound of aluminium silicate hydrate with alkali metal which is group of several types of minerals. Zeolite is aluminosilicate with a framework structure enclosing cavities

occupied by a large ions and water molecules, both of which have considerable freedom of movement, permitting ion-exchange and reversible dehydration. Natural zeolite is natural mineral that composed of crystalline silica ($SiO_2$) and alumina ($Al_2O_3$), with cavities of metal ions, which is usually alkali and alkaline or earth metals, and water molecules. Unique characteristic, include very stable with very high adsorption capacity and selectivity and have large active pore structure (microporous) and has a high specific surface area. Natural resources have the potential to be further processed into products that can be used for broad applications, among others, as supporting the catalyst or catalysts, and slow release substances. Zeolite crystal structure of alumina silicate shaped frame (framework) three-dimensional, having cavities and channels as well as containing metal ions such as Na, K, Mg, Ca and Fe as well as water molecules. Sarulla natural zeolite chemical composition analysis using XRF showed the dominant chemical compounds are $SiO_2$ and $Al_2O_3$.

Usually, ferrite composites are used to achieve microwave absorption. The absorbing characteristics and electromagnetic characteristics could be varied by controlling the ferrite filler volume fraction in the composite materials [2]. Studies of either nanoparticles or core-shell nanopowders such as carbonaceous particles and polyurethane as matrix for the application in microwave absorbers were very interesting in the last decades [3,4,5]. However, studies of using nanozeolite as a filler for microwave-absorptive materials were very limited.

In this paper, with the aim finding high microwave absorption in GHz range filled with nanozeolite as an abundant local natural resources and ferric oxide with its strong magnetic characteristic were prepared. We investigate electromagnetic properties and the reflection loss properties due to nanofillers variation of weight. Our experimental results highest reflection loss was -40.588 dB at 10.92 GHz and as the result is polyurethane filled with nanozeolite and ferric oxide are promising for microwave-absorptive materials.

## 2. Materials and Methods

The fillers used for nanocomposite was Sarulla natural zeolite and Sigma Aldrich commercial ferric-oxide ($\alpha$-$Fe_2O_3$) with 99.95% purity. The polyurethane matrix used was Sigma Aldrich commercial type which contains two-part monomers i.e. 60% wt polyethylene glycol has a density 1.01 g/mL and 40% wt toluene diisocyanate has a density 1.22 g/mL.
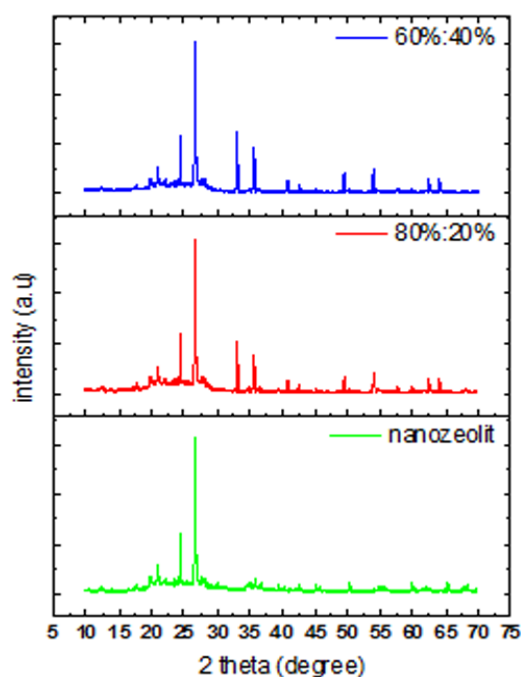
The polyurethane nanocomposites reinforced with natural nanozeolite and ferric-oxide were fabricated with in-situ reaction. The activated natural zeolite prepared using planetary ball mill for 28 h to complete nanozeolite with average particle size distribution < 100 nm. Nanozeolite mixed for 4 h with ferric oxide using planetary ball mill to produce nanofillers. The homogen nanofillers divided into the same ratio and mixed with PPG and TDI for 1 min. Polyethylene glycol and toluene
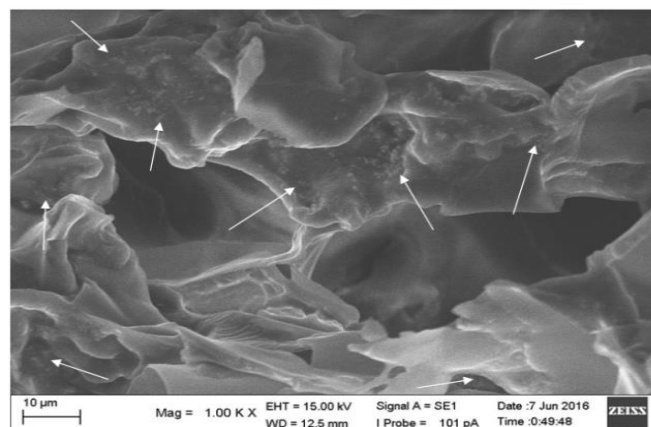
diisocyanate with nanofillers of zeolite and ferric oxide are using in-situ reaction. Both of PPG and TDI with nanofiller mixed for 2 min with in-situ reaction at room temperature. The reaction of PPG and TDI and nanofillers  polyurethane nanocomposites filled with nanozeolite and ferric oxide is hold and pressed for 30 min using iniversal testing machine with 5 mm sample thickness.

The crystal structure of the samples were determined by Shimadzu-700 X-ray Diffractometer (XRD) using Cu Kα radiation (λ = 1.54 Å) operated at 35 kV and 25 mA. The reflection loss of the samples was measured between 8 GHz and 12 GHz  using Vector Network Analyzer Advantest type R 3770 and microstructure of the samples using SEM-EDX Carl Zeiss-Bruker Type MA10.
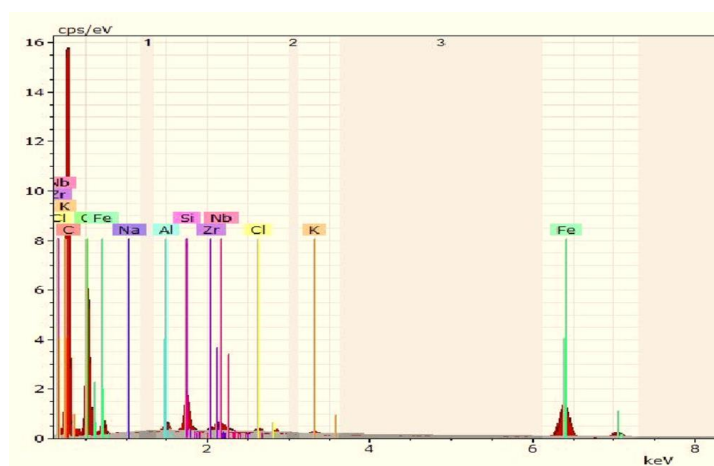
### 3.  Characteristic of Product

Figure 1.a shows the X-Ray Diffraction spectrum of Sarulla natural zeolite. Observed from the XRD spectrum shows intensity at $2\theta$ = 29.76; 27.67 and 27.92. Maximum peak occur at 29.76 with FWHM 0.124 which is at the aluminium silicate phase. Mordenite standard have a high intensity at $2\theta$ = 27; 25.63 and 23. Compare with Sarulla zeolite, it shows that natural zeolite is mordenite, but another peak at natural zeolite at 29.76 shows that crystaline at Sarulla natural zeolit is not only modernit but also mixed with other crystalline and other impurities. Combination of filler varied of nanozeolit and ferric oxide with ratio (80% : 20%) and (60%:40%) by weight, observed from the XRD spectrum shows another high intensity at $2\theta$ = 33.121 and 35.60, which is not occur at the nanozeolite XRD spectrum. The occurance of these intensity due to entrance of ferric oxide.

(b)



(c)

**Figure 1.** (a) XRD pattern of natural zeolite (b) SEM photograph of polyurethane nanocomposite
(c) EDX  polyurethane nanocomposite characterization

From Figure 1.b SEM photograph of polyurethane nanocomposite shows that dark colors are pores or cavities and bright color is polyurethane matrices and arrows show the occurance of agglomeration caused by nanozeolite and ferric oxide. Results of other studies suggest that the materials properties will be compatible with the polymer matrices and influenced by several factors such as filler particle size. The particle size will affect the bond of the filler and the matrix. The amount of surface area will be increased by the presence of a surface porous on the fillers surface as well as with the addition of natural nanozeolite and ferric oxide. Figure 1.c show EDX polyurethane nanocomposite characterization. According to the EDX characterization it was shown that the agglomeration is the effect of the fillers.

## 4. Results and Discussion

Characterization of electromagnetic wave absorption was carried out with a Vector Network Analyzer. From the scattering parameters $S_{11}$ and $S_{21}$ measured by the coaxial method using VNA in the frequency range of 8 - 12 GHz, the relative complex permeability $\mu_r$ ( $= \mu_r' - j\mu_r''$ ) and the relative complex permittivity $\varepsilon_r$  ( $= \varepsilon_r' - j\varepsilon_r''$ ) were calculated using Nicholson Ross Weir model. The electromagnetic properties which is dielectric and magnetic properties of polyurethane nanocomposites will characterize using NRW model.
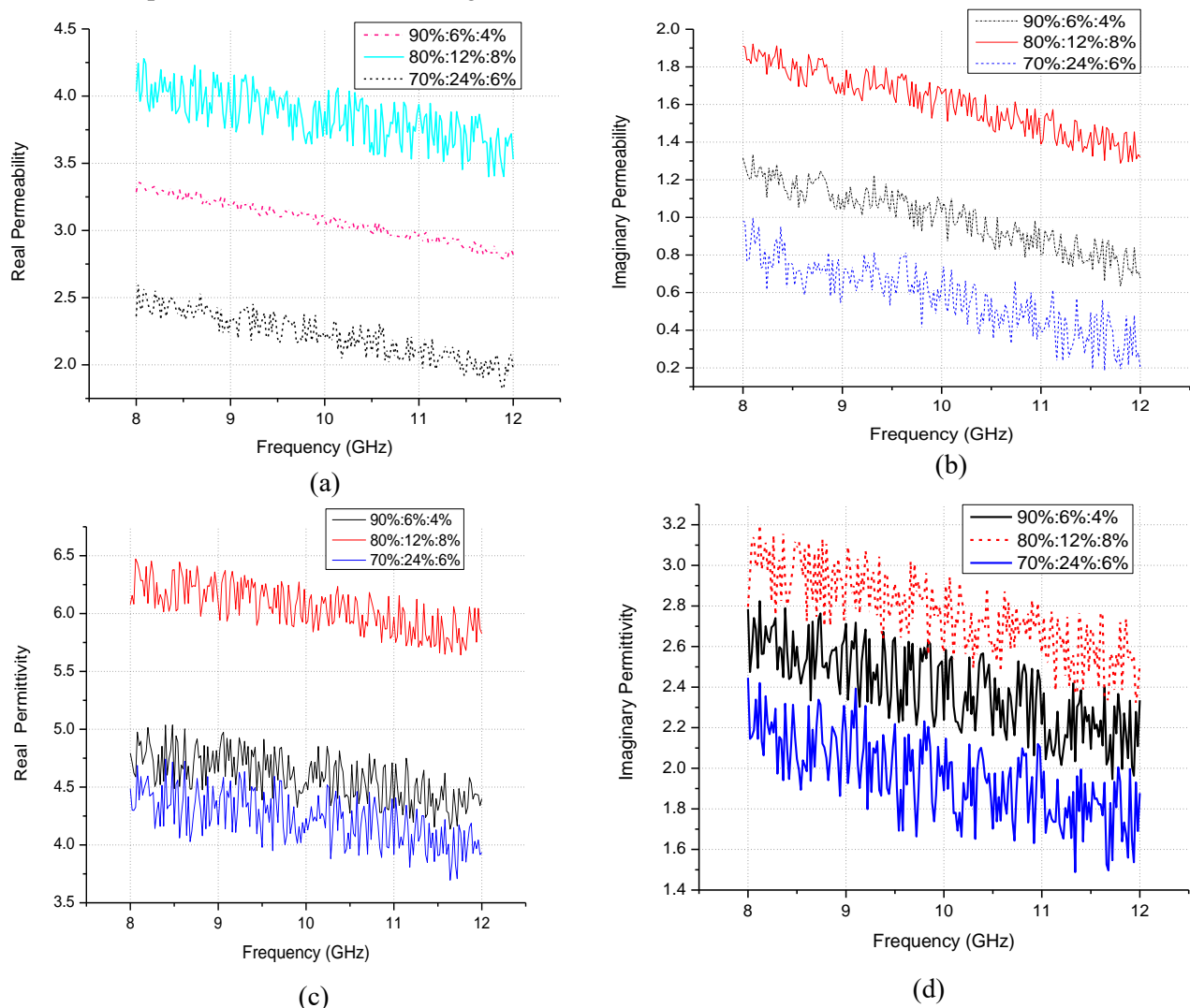


**Figure 2.** (a) Real permeability spectra (b) Imaginary permeability spectra
(c) Real permittivity spectra (d) Imaginary permittivity spectra

From Figure 2 above show how variation of the filler affect the permittivity and permeability of the polyurethane nanocomposite. It is observed that in the lowest frequency region the polyurethane filled with nanozeolite and ferric oxide shows the larger value of real and imaginary for both permittivity and permeability. Dielectric constants depends on two factors, orientation and interfacial polarizations.

In case of polyurethane nanocomposite (80%:12%:8%), the orientation and interfacial polarizations should be high due to ferric oxide. The variation of both real and imaginary parts of permittivity with frequency may be happen due to space charge polarization. Polar-polar reaction between polyurethane and the fillers probably will affected the demagnetizing field. The demagnetizing field generated by the magnetic poles on the surface of magnetic fillers plays a very important and characteristics role in the permeability of material. Both μ' and μ'' shows decreasing trend with increasing of frequency, due to the lower resonance frequency range of the polyurethane nanocomposite. The fluctuation of the permittivity and permeability spectra caused by the pores of polyurethane nanocomposite. As a confirmation for the other research it was shown that trends of permittivity spectra was observed that in the lowest frequency region shows the larger value of real and imaginary permittivity [5].

The enhanced μ' and μ'' values will improve the microwave absorbing effect by transferring electromagnetic energy into heat energy. Magnetic losses, as the important phenomena in absorptive materials, are caused by the time lag of the magnetization vector behind the magnetic field vector [6]. The change of the magnetization vector is generally brought about by rotation of the magnetization or the domain wall displacement. These motions lag behind the change of the magnetic field and contribute to μ''. The smaller the particle size, the weaker the spins coupling at the surface of the nanozeolite and ferric oxide, which makes the magnetic relaxation behaviour more complex.

The magnetic and dielectric particles filled into the polyurethane matrix can act as a large number of charge domains and can contribute to increase the dielectric constant values due to interfacial polarization [7]. The dielectric loss mechanism occur due to the permanent and dominant polarization and their associated relaxation phenomena. The nanocomposite materials showed the microwave absorption properties according to their dielectric loss values. Polyurethane filled with nanozeolite and ferric oxide  (80% : 12% : 8%) have better dielectric loss value than other nanocomposites and it achieved better microwave absorbing properties.

Reflection loss measurement using Vector Network Analyzer for polyurethane nanocomposites reinforcement with ratio of polyurethane : nanozeolite : ferric oxide = (90% : 6% : 4%); (80% : 12%: 8%) and (70% : 24% : 6%) by weight as a function of frequency in X-band  (8-12 GHz) shows in Figure 3. Polyurethane nanocomposites with ratio (80% : 12% : 8%) have the optimum reflection loss of  -40.588 dB at 10.92 GHz. The reflection loss of less than -40 dB means the microwave absorption more than 99% [8]. The microwave absorption being dependent on the ratio of $SiO_2$ and $Al_2O_3$ which is to dominant compounds of natural zeolite and ferric-oxide, the content of ferric-oxide in natural zeolite will modify the reflection loss and microwave absorption of the nanocomposite and will affect the complex permittivity and complex permeability of the nanocomposite. To satisfy the zero-reflection condition where maximum absorption would occur. Ferrite itself usually present

electromagnetic characteristics of complex permeability less than complex permittivity. Minimum loss occurs when the thickness is about an odd multiple of one quarter of the wavelength of the incident frequency.
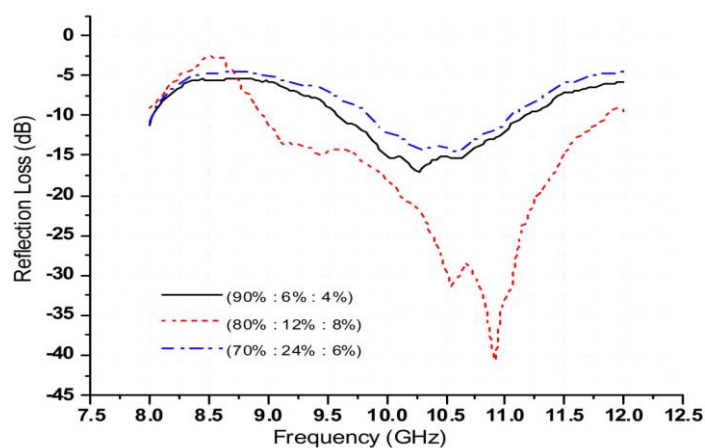


**Figure 3.** Reflection loss measurement of polyurethane nanozeolite and ferric oxide nanocomposites

## 5. Conclusion

Natural zeolite and ferric oxide ratio as a filler in polyurethane matrices will modify permeability and permittivity of the nanocomposite, by the addition of the the filler will cause a different effect in electromagnetic properties and microwave absorption due to material reflection loss. The nanocomposite absorb microwave at X band frequency for > 99 % absorption. This is due to the effect of aluminum silicate and ferric oxide binding with polar - polar reaction between filler and matrices. These reaction cause difference in input impedance and this will make a difference in the resonance at high frequency. Ferrite-oxide particle have a great microwave absorption characteristic, but in this case, the ratio between zeolite and ferric-oxide will affect the best microwave absorption. The unique properties of nanozeolite and polyurethane provide an important foundation for developing the materials with strong microwave absorption in wide applications prospects.

## References

[1]　Abbas SM *et al* 2006 Composites :Part A 37 2148-2154.
[2]　Kong I *et al* 2010 *J Magnetism Magnetic Mat* **322** 3401-3409.
[3]　Peng C H *et al* 2004 *J. Magnetic Mater* **284** 113-119.
[4]　F. Qin and C. Brosseau 2012 *J. Appl. Phys* 111, 061301.
[5]　Esfahani *et al* 012 *Preparation and Characterization of Foamed Polyurethane/Silicone Rubber/Graphite Nanocomposite as Radio Frequency Wave Absorbing Material : The Role of Interfacial Compatibilization,* J. Compscitech.
[6]　Pawar R P *et al* 2013 *Proc. and Appl. Ceramics* **7** [1]: 1-7.
[7]　Jamal E.M *et al* 2009 *Mater. Sci. and Eng. B* **156** 24-31.
[8]　Kato Y *et al* 2002 *Materials Transactions M* **43** 406-409.