Preparation and Characterization of Microwave-absorption of Sarulla North Sumatra Zeolite and Ferric Oxide-filled Polyurethane Nanocomposites

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Abstract

Microwave-absorptive polymeric composite materials are becoming important to protect interference of any communication systems due to the increase in the use of microwave-inducing devices. In this work, the microwave-absorptive polyurethane composites are prepared using natural zeolites of Sarulla North Sumatra and commercial ferric-oxide as fillers. Weight ratio of the natural zeolite to ferric oxide were varied (18:2; 16:4; 14:6; 12:8 and 10:10) by weight. The fillers are prepared using ball milling technique and characterized using Particle Size Analyzer for particle size distribution. The nanocomposites, prepared using in-situ reaction of polyethylene glycol and toluene diisocyanate, is characterized for physical and mechanical properties using tensile strength, thermal properties with TGA techniques, as well as morphological and chemical properties using scanning electron microscopy. Composition and loading of the nanofillers against polyurethane matrices is 20\% by weight. Microwave-absorption properties of the nanocomposites is characterized using 8-12 GHz frequency. Tensile strengths of the natural zeolite-ferric oxides polyurethane nanocomposites shows higher values when matrices filled with lower ferric-oxide, which could be due to the nanozeolites have functioned as reinforcement for the polyurethane matrix through polar-polar interaction between the filler surfaces with the matrices. The microwave absorption properties, which investigated by Vector Network Analyzer, of the nanocomposites filled in polyurethane with the ratio of nanozeolite to ferric oxide filler of 12:8 shows reflection loss of – 13.2 dB. This condition was observed at 11.1 GHz.

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1. Introduction

Electromagnetic interference is worsening with the rapid development of wireless communications and circuit devices. The high frequency electromagnetic wave is drawing more attention, due to the explosive growth in the utilization of telecommunication devices in industrial, medical and military application.\(^1\)\(^2\)

In the past decades, 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 permittivity (\(\varepsilon_r\)) and complex permeability (\(\mu_r\)). All the parameters \(\varepsilon', \varepsilon'', \mu'\) and \(\mu''\) are found to increase with the increased of ferrite contents and it is found that the absorption properties in the composites are greatly improved with the increasing of ferrite contents in the polymer matrix.\(^4\) But in other side, it will increase the mass of the absorbing materials. Conducting polymer composites with micro/nanostructured have attracted a significant academic and technological attention because of their unique physical properties and potential applications.\(^5\)\(^-\)\(^8\)

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\(_2\)O\(_3\)), 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\(_2\)O\(_3\) as shown in Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>% wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(_2)O</td>
<td>1.76</td>
</tr>
<tr>
<td>P(_2)O(_5)</td>
<td>0.61</td>
</tr>
<tr>
<td>MgO</td>
<td>0.12</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>14.19</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>80.3</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>1.45</td>
</tr>
<tr>
<td>CaO</td>
<td>0.14</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>0.52</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>0.91</td>
</tr>
</tbody>
</table>

In this paper in-situ reaction of polyethylene glycol and toluene diisocyanate with nanofillers of zeolite and ferric oxide is used to fabricate PU nanocomposites. The effect of alumino silica as the higher compound in natural zeolite combined with ferric oxide as the most frequent absorbing materials were observed as microwave absorption.

2. Experimental

The fillers used for nanocomposite fabrication are natural zeolite and commercial ferric-oxide (\(\gamma\)-Fe\(_2\)O\(_3\)). The polyurethane matrix used was a commercial type which contains two-part urethane monomers i.e. 60% wt polyethylene glycol and 40% wt toluene diisocyanate.

The PU nanocomposites reinforced with natural zeolite and ferric-oxide were fabricated with in-situ reaction. The activated natural zeolite crushed to the size of 74 \(\mu\)m using planetary ballmill for 10 hours. Natural zeolite and ferric-oxide with ratio of 18:2; 16:4; 14:6; 12:8 and 10:10 by weight were mixed for 4 hours using planetary ballmill. Nanofillers of natural zeolite and ferric oxide is 20 % wt of the Polyurethane. The homogen nanofillers divided into the same ratio and mixed with PPG and TDI for 1 minute. Polyethylene glycol and toluene diisocyanate with nanofillers of zeolite and ferric oxide are using in-situ reaction. Polyurethane, with the sample thickness of 5 mm, is hold and pressed for 30 minutes.
3. Result and Discussion

Fig. 1 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 crystalline at Sarulla natural zeolite is not only modernite but also mixed with other crystalline and other impurities.

![Fig. 1. X-Ray diffraction of Sarulla natural zeolite.](image)

![Fig. 2. (a) SEM micrograph of Sarulla natural nanozeolite; (b) SEM micrograph of PU filled zeolite and ferric oxide 50 x magnification; (c) SEM micrograph of PU filled zeolite and ferric oxide 500 x magnification.](image)
Fig.2(a) above shows the surface of the zeolite have a crystal lattice in the form of pores of the zeolite surface, this is in-line with the report stating that zeolite microporous crystalline solid is hollow and grooved and has a pore size of 3 to 10Å called as molecular sieves. SEM photograph shows that dark colors are pores or cavities and a bright color is a natural zeolite nanoparticles, particle size of > 50 nm stated that zeolite is the mordenite type. Fig.2(b) show the PU nanocomposites foams distribution and Fig.2(c) shows where zeolite and ferric oxide distributed in PU matrices.

Based on the measurement data, it is shows that the best mechanical properties of tensile strength at 3.23 MPa with natural zeolite to ferric oxide ratio is 18:2, larger ferric oxide ratio will affect to the tensile strength degradation. This is probably due to the polar to polar interaction between nanozeolite and PU matrices. The layer silicates in nanometer-sized natural zeolites can be dispersed randomly and evenly that give structure to the nano composites. Silicate layers that exist in scattered individual zeolite has a large surface contact area which caused to a strong bind with the matrix PPG and TDI and further gives effect to the increase in tensile strength.

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Termogram (TGA) curve analysis shows samples of PU with no filler, PU with ratio of nanozeolite and ferric-oxide of 16:4 (PU A-2) and PU with ratio of nanozeolite and ferric-oxide of 10:10 (PU A-5) have lost its weight when the temperature increased, all samples will release the water in the compounds at the temperature of 200°C. Decomposition of PU at 336°C and 410°C will lose its weight of 27.07% and 40.68% respectively. PU A-2 is decomposed at 335°C and 406°C and the weight is reduced of 23.17% and 28.74 % respectively. After heating to the temperature of 680°C, PU will have 16.44% residue, PU A-2 with 29.03 % residue and PU A-5 with 30.18 % residue. Thermal stability will increase according to the increase of ferrite oxide content in the composite.
Reflection loss measurement using Vector Network Analyzer for polyurethane nanocomposites reinforcement with 20% wt nanofillers of natural zeolite and ferric-oxide ratio of 18:2; 16:4; 14:6; 12:8 and 10:10 as a function of frequency in X-band (8-12 GHz) shows in Fig.5 PU nanocomposites with ratio of natural zeolite and ferric-oxide ratio of 12:8 fillers have the optimum reflection loss of -13.2 dB at 11.1 GHz. The reflection loss of less than -10 dB means the microwave absorption more than 90%. The microwave absorption being dependent on the ratio of SiO₂ and Al₂O₃ 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, the impedance of the composite should be 1 to prevent reflection. This can be ideally achieved when the materials present complex permittivity equal to complex permeability. Ferrite itself usually presents 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 4.

![Fig.5. Reflection loss of polyurethane natural zeolite and ferric oxide nanocomposites](image)

4. Conclusion

Polyurethane filled nanozeolite and ferric-oxide has prepared using in-situ reaction. Natural zeolite and ferric oxide ratio as a filler in PU matrices will cause a different effect in mechanical properties and microwave absorption properties. Tensile strength properties show a better value when matrices filled with larger ratio of natural zeolite. Binding of zeolite with PU will increase the mechanical properties. The nanocomposite absorb microwave at X band frequency for > 90 % 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.

References


