Synthesis and thermomechanical characterization of peg/zircon composites

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Abstract. Poly(ethylene) glycol (PEG)/ZrSiO₄ composites have been prepared and their thermomechanical properties have been characterized using a dynamic mechanical analyzer (DMA). PEG 4000 was used as the matrix and a ZrSiO₄ powder, extracted from puya sand Kereng Pangi, Central Kalimantan, was used as the filler. ZrSiO₄ weight fractions of 0, 5, 10 and 20% were employed. The composites were made by a liquid method, where the matrix and the filler were mixed at a temperature when PEG was in a liquid phase. Characterization of FTIR and XRD was used to confirm the absence of any new phase and the composites were formed. The composites were subjected to DMA measurement in a shear mode at a frequency of 1 Hz. Results showed that, in general, the storage modulus of the composites has been improved by the addition of ZrSiO₄. The highest storage modulus was achieved by the composite with 20% ZrSiO₄, i.e., nine times of the pure PEG. The 20% ZrSiO₄ composite also exhibited the largest damping factor (the widest width of $\tan \delta$ peak) and the highest melting temperature ($T_m$), i.e., $57.1 \degree C$, increasing $14.1 \degree C$ from that of pure PEG.

1. Introduction
Poly(ethylene) glycol (PEG) is a versatile polymer material [1] that has a great potential in advanced technology. In the medical field, the research had resulted that PEG can be used as a biomaterial for dental implants and orthopedic. In building industry, PEG was applied as a PCM material for temperature control and heat energy storage [2]. The broad applications were due to the characteristics of PEG such as biocompatible, non-toxic, low vapor pressure, and relatively chemically and thermally stable [3]. Unfortunately, PEG has a relatively low tensile modulus of approximately 100 MPa [4]. Therefore, in its applications, blending PEG with reinforcement materials, such as ceramic [5], is required.

Zircon (ZrSiO₄) is an interesting filler for PEG to form composites. Zircon offers supporting physical, mechanical, thermal, and optical properties [6] to improve the applicability of PEG. Zircon has a tetragonal structure with lattice parameters $a = 6.607(1) \ \text{Å}$, $c = 5.982(1) \ \text{Å}$, and $Z = 4$ and space group of $I4_1/amd$ [7]. Zircon has a low thermal conductivity (5.1 W/m °C at room temperature and 3.5 W/m °C at 1000 °C), a relatively low thermal expansion coefficient (4.1×10⁻⁶ °C⁻¹ in range 25 and 1400 °C) and a high mechanical resistance to heat (more than 1400 °C) [8], [9]. Moreover, the shear modulus of zircon is much greater than pure PEG, i.e. 109 GPa [10]. Research on the use of zircon as a filler of polymer-based composites had not been found in the literature. Therefore, it would be interesting to study the characteristics of such composites with PEG 4000 as the matrix and zircon powder as the filler.
In addition, the availability of zircon minerals in Indonesia is abundant, especially in Kalimantan and Sumatra. The utilization of zircon as a filler is expected to increase its economy value and support the development of advanced materials.

One of interesting aspects on the application of a polymer-ceramic composite is its thermomechanical behavior, which describes the response of the material under simultaneous mechanical and thermal loadings. Dynamical Mechanical Analyzer (DMA) is an appropriate tool to study the behaviour. If shear mode is used, a sinusoidal shear stress loading is applied on the sample and the sample generates two types of modulus (response), i.e. storage and loss moduli. They are related through the measured complex shear modulus (\(G^*\)) according to

\[
G^* = G' + iG''
\]

and through the damping factor \[11\]

\[
\tan \delta = \frac{G''}{G'}
\]

In addition to the mechanical loading, DMA also shows a material response to thermal loading. The material response to the thermal loading varies, so that the dependence of the viscoelastic property of the material can be examined. In the shear mode, the storage modulus (\(G'\)) measures the stored energy, while the loss modulus (\(G''\)) measures the energy loss as heat.

This paper reported the shear modulus and \(\tan \delta\) characters of PEG/zircon composites. From the measurements, the thermomechanical properties of PEG 4000/ZrSiO\(_4\) were revealed.

2. Experimental method

The materials used were zircon and PEG-4000 powders. The zircon powder was synthesized from puya sand of Kereng Pangi, Central Kalimantan. The extraction process of puya sand consists of washing, magnetic separation, milling, and HCl 2M immersion. The immersion was followed by a hydrothermal process using sodium hydroxide (NaOH) 7M to remove quartz and produce pure zircon powder.

The matrix of the composite was poly(ethylene) glycol 4000 (Merck Schuchardt OHG 85662 Hohenbrunn, Germany) or PEG 4000. The mixing of matrix and filler used a liquid method. The PEG was melted at 60 °C. When the PEG melted, a dispersant (\(\text{C}_{12}\text{H}_{25}\text{NaO}_{4}\text{S}\)) was added to increase the particle distribution of the zircon powder. After stirring for 15 minutes, the zircon powder was poured to and mixed with the melt at various compositions (i.e. 0, 5, 10 and 20% wt zircon), and then stirred for 30 minutes. Then, the composites were molded and pressed. The nomenclature of the samples was denoted as L-PZR0, L-PZR5, L-PZR10 and L-PZR20 following the zircon content. The mixture was cast with a square-shaped sample holder of 5\(\times\)5 mm\(^2\) and thickness of 1 mm. The composites were confirmed for the absence of new phases during the synthesis process so that Fourier Transform Infrared (FTIR) Spectroscopy and X-Ray Diffraction (XRD) tests were performed.

In the Dynamic Mechanical Analysis (DMA), the experiment was in a shear mode. The DMA was Mettler Toledo SDTA 861e. Measurements of the modulus were carried out in the temperature range of 25 °C to 75 °C at 1 Hz frequency with 1 μm displacement.

3. Results and discussion

Figures 1 and 2 show the XRD and FTIR patterns from the pure PEG, pure zircon and the three composite samples. Figure 1 clearly reveals the formation of the composites. The XRD patterns (Figure 1) exhibited no new peaks than those of PEG4000 and ZrSiO\(_4\)(PDF# 6-266). The XRD patterns also impart the differences in the level of crystallinity in the composites, as indicated by background level and peak intensity. Composites with more zircon content exhibited improved peak intensity indicating the increase of crystallinity level. Furthermore, the FTIR patterns (Figure 2) show the absence of the new absorption peaks. The peaks are belong to only two compounds, namely PEG and zircon. From the FTIR pattern, peaks A, B, and C are the absorbance peak of pure PEG. The peaks are still dominant in the composite L-PZR5, L-PZR10 and L-PZR20 due to the percentage of PEG is more than zircon. If more precise, there is a slight change in peak C more pointed on all composites. That’s combined a peak
of PEG and peak of zircon. For the absorption peak D of zircon is slightly visible on L-PZR20, although in L-PZR5 and L-PZR10 are not observable. A largest percentage of zircon (20 wt%) in LPZR20 causes the zircon absorption peak to be observed. The absence of other phase can then be concluded that the testing materials were PEG/ZrSiO$_4$ composites.

The DMA plots of the PEG/ZrSiO$_4$ composites can be seen in Figure 3. In Figure 3(a), the $G'$ curve of the composites decreases with increasing temperature. The reason for the decreases is that the molecular motion of the free polymer sequences caused the reduction of the stored energy [12]. At temperatures around 60 °C, the curves decreased significantly. The decrease indicated that, at the designated temperature, the polymer melted or had reached the melting temperature ($T_m$), so that the carbon-bond on the polymer group weakened.

In general, the absolute value of $G'$ composite increased with the addition of the filler. This phenomenon was caused by the shear modulus value ($G'$) of ZrSiO$_4$ which reached 109 GPa [13], a much greater value than that of pure PEG. In theory, when zircon powder mixed with PEG, it fills the space at polymer chains and the surface of zircon powder interacts with them. The presences of zircon and surface interacting in PEG matrix were reducing the freedom of movement of the PEG 4000 polymer chains when the sample was given shear load. This interaction will increase the mechanical strength of the composites well above the polymer strength [14]. The $G'$ values for the 5, 10 and 20 wt%-added samples were 545.5, 642.9, and 837.3 MPa. Fadly et al. (2016) studied the storage modulus of PEG/quartz composites and resulted in the storage modulus of PEG/quartz with 40 wt% filler was 730.6 MPa [5]. Therefore, zircon is more effective in increasing the storage modulus of the composite than quartz.

![Figure 1. XRD patterns (CuKα radiation) of PEG/ZrSiO$_4$ (L-PZR) composites. P=PEG, Z=ZrSiO$_4$.](image)

The $\tan \delta$ characteristics of the samples can be described from Figure 3(b). The highest $\tan \delta$ value was achieved by the pure PEG sample. The $\tan \delta$ is the damping factor suffered by the composite material due to the irregularities of chain motion in the polymer functional group. When the composites were given a shear load, the movement of polymer chain was damped by the filler. One possible explanation is that this damping results from friction at the interface between filler and matrix [15]. An increase in filler content made fewer polymer chain movements of the figure also shows that the $\tan \delta$ peak decreased with filler content. Meanwhile, the peak position of $\tan \delta$ plot describes the melting
temperature \((T_m)\) [16]. From the figure, one can observe that the addition of zircon causes a shift of the \(\tan \delta\) peak to the right. It was because the melting temperature of the polymer was lower than the zircon. When a composite was given the heat treatment, the movement of the polymer molecule was inhibited by the zircon molecule. As a result, the polymer in the sample melts at a higher temperature. Further observation shows that the melting temperatures of L-PZR5, L-PZR10, and L-PZR20 are 54.9, 55.8, and 57.1 °C, respectively. The addition of zircon improved the melting temperature of the composite, since \(T_m\) for PEG4000 is 43 °C [5].

![Figure 2. FTIR spectrum of PEG/ZrSiO\(_4\) (L-PZR) composites.](image)

\(A = B = C = \) the absorbance peak of pure PEG; \(D = \) the absorbance peak of zircon.

![Figure 3.](image)

(a) Storage modulus and (b) \(\tan \delta\) plots for the PEG/ZrSiO\(_4\) (L-PZR) composites as a function of applied temperature.
4. Conclusion
Zircon-reinforced poly(ethylene)glycol (PEG4000) composites were successfully prepared using a liquid method. The addition of zircon significantly improved the storage modulus and the melting temperature of the composite as shown by the DMA tests. The storage modulus of PEG/zircon composite improved substantially in the addition of zircon filler, i.e., six times and up to nine times of that of pure PEG for 5% and 20%wt zircon-added respectively. Meanwhile, the presence of zircon also increased the melting temperature in the composites by 11.9, 12.8, and 14.1 °C for the 5, 10, and 20 %wt composites.

5. Acknowledgment
The authors are thankful to Kemenristek-Dikti of the Republic of Indonesia and LPPM ITS for the financial support through Competency Based Research provided to SP under contract scheme of PBK-2017 No. 528/PKS/ITS/2017.

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