Activation energy determination in multi-frequency dynamic molecular interaction analysis of PEG 4000-Cristobalite composites using DMA

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Abstract. Degradation activation energy of PEG-Cristobalite composites was investigated using Dynamic Mechanical Analysis (DMA) instrument at multi-frequency shear mode. The applied frequencies were 1, 10, 100, and 200 Hz. The cristobalite of as much as 20% and 40% by weight was used as the filler of the composites, while PEG 4000 was the matrix. Results showed that additional of cristobalite improved the storage modulus ($G'$) of the composites almost five times of the pure PEG 4000. Moreover, such addition and higher applied frequency shifted glass transition temperature ($T_g$) to higher values. Furthermore, the multi-frequency measurement provided the degradation activation energy of the samples, where the highest value was reached by the 40% sample, i.e. 571.4 kJ. This result implied that there was a certain energetic barrier from the filler that the structural units of polymer need to surmount collectively before its viscous flow occured.

1. Introduction
Research focus in modern polymeric materials includes thermal stability as well as physical and mechanical properties at high temperature. The thermal stability of polymers is connected not only with the initial degradation temperature ($T_d$) [1], but also, with dislocations due to mechanic and thermal treatment [2]. In particular, the apparent activation energy ($E_a$) is of great importance aspect of degradation of such materials [3].

DMA technique is useful in characterizing polymer degradation as a function of frequency, temperature, time, stress or a combination of these parameters [4-6]. The dynamic mechanical responses of degradation are usually observed at temperatures near (or, in some cases, above) the melting point. As a result, the lifetime predictions based on these measurements can be determined. DMA response also depends on the physical or structural arrangement of phases such as interface, morphology and the nature of the constituents [4,5]. In particular, the effect of filler, fibre content, fibre orientation in fibre-reinforced composite materials has been extensively studied [7,8].

Cristobalite is a metastable silica polymorph. It exists at room temperature but easily transformed into quartz at high temperature. There is no study on the utilization of cristobalite as a filler in a composite system. This phase is very unique since it exhibits a negative Poisson’s ratio [9-12]. Materials with a negative Poisson’s ratio (called auxetic material) have a counterintuitive behaviour of becoming wider when stretched and thinner when compressed [12]. This behaviour has many beneficial effects on the materials’ macroscopic properties (e.g., increased indentation resistance, a
natural ability to form “dome-shaped” surfaces) that make them superior in many practical applications [10-11].

Research on polyethylene glycol (PEG)-based functional polymer-ceramic composites is relatively extensive. For example, SiO$_2$–PEG–3-isocyanato-propyltrietoxysilane nanocomposite was prepared as hydrophilic films [13]. Qian et. al. [14] also reported green shape-stabilized composite phase change material (PCM) of PEG/SiO$_2$ with enhanced thermal performance based on oil shale ash via temperature-assisted sol–gel method. They did not, however, determine the crystalline phase of SiO$_2$ in their studies. In our previous work, we reported the effect of quartz content on the PEG 4000-quartz composites using DMA in shear mode [15]. Quartz is a polymorph of silica which is chemically stable and exhibits positive Poisson’s ratio. The dynamic mechanical responses using multi-frequency DMA of such composites are reported elsewhere [16]. However, the multi-frequency DMA measurements for PEG 4000-cristobalite composites have not been investigated yet.

In this report, we describe thermal degradation experiments of PEG 4000-cristobalite composites. The low melting point PEG 4000, i.e. $T_m= 60$–$63$ ºC [15], [17] was used as the matrix, while cristobalite which was processed from natural silica sand was the filler. The activation energy determination was investigated through DMA measurements in shear mode at various frequency.

2. Experimental

2.1. Sample preparation

Cristobalite powder was prepared by purifying silica sand from Tanah Laut, Pelaihari, South Kalimantan. Polyethylene Glycol 4000 (Merck Schuchardt OHG 85662 Hohenbrunn, Germany) was used as matrix in this composite. Magnetic separation and immersion with HCl 2M was done to purify silica sand and get SiO$_2$ quartz powder. Next step, precursor quartz powder was copresipited by using NaOH. In order to get SiO$_2$ crystobalite (SC), copresipited powder was calcined at 950ºC under the air for 8 hours. All of those phases were identified by using X-Ray Diffractometer (XRD). The composite samples were prepared by mixing SC powder (as much as 20% and 40% by weight) as the filler in PEG 4000 and then followed by casting in pellet forms. A pure PEG 4000 sample was also prepared for comparison.

2.2. DMA measurement

Composite samples were casted in small-dimension, 1 mm thickness and (5 mm $\times$ 5 mm) square which were compatible with the geometry and dimensions for DMA testing in shear mode. The experiment has been described elsewhere [15]. For each composite sample was heated at 50ºC to increase samples necking after considering the theoretical melting point of PEG 4000. The mechanical properties of composite samples were measured using DMA Mettler Toledo instrument. From our initial experiments, the range temperature was about 25ºC until 80ºC with multi-frequency as oscillation responses (1, 10, 100, and 200 Hz). This range required to investigated dynamic responses from composites.

3. Results and discussion

Figures 1, 2, and 3 show comparative storage moduli ($G'$) of the composite samples at various frequencies as a function of temperature, as well as those for pure PEG samples. In general, $G'$ drops as temperature increases. The decline is very sharp around 50-65ºC for all samples. A decline in $G'$ is often associated with a reduction in viscosity and resistance of the materials toward deformation. In glassy region (see figure 1) is often related to the toughness with high viscosity. As increasing temperature continues increasing free motion of polymer chain. As heating continues, it will reach $T_g$ (glass transition). In this region, $T_g$ presents a major transition for drastically from glassy region to rubbery state. For thermoplastic, degradation continues after $T_g$ because of light cross-links in polymer chain (it can be seen in rubbery plateau from figure 1) [18].
As can be compared from figures 1, 2, and 3, the highest $G'$ is achieved by 40 wt% cristobalite. Its $G'$ value is five times of that of pure PEG. This phenomenon can be attributed to crosslinking between PEG and cristobalite. The effects of crosslinking on the various regions of the DMA curve are visible in the rubbery and glass transition regions. However, the effect is not visible in the glassy region. Thus, highly cross-linked thermoplastic polymer has much larger storage modulus indicating the tighter network structure and higher stiffness while that with light cross-links shows a considerably smaller storage modulus [7,19].

When various frequencies are applied, $G'$ drop shifts to higher temperature for all samples – as shown by solid arrows in figures 1-3. The shift therefore indicates changes in $T_g$. The higher the frequency the higher $T_g$. $T_g$ values for all samples are presented in table 1. The shift to higher temperature is a direct consequence of polymer to achieve (rubbery) equilibrium state. The polymer chain motions are constrained at high frequency but become more liberated at low frequency [18,20]. Consequently, higher $T_g$ is required for a sample to achieve a mechanical equilibrium state at high frequency load.
Table 1. $T_g$ value of PEG 4000-cristobalite in multi-frequency

|            | 1 Hz  | 10 Hz | 100 Hz | 200 Hz |
|------------|-------|-------|--------|--------|
| PEG 4000   | 43.00 | 45.50 | 47.70  | 54.98  |
| SC 20      | 47.00 | 49.34 | 53.75  | 57.56  |
| SC 40      | 48.00 | 51.87 | 53.95  | 56.60  |

The resulting set of experimental $T_g$ data (table 1) was used to determine the apparent activation energy ($E_a$) of material degradation. Using Arrhenius equation [21],

$$\ln f = \frac{E_a}{RT}$$

(1)

where $f$ = applied frequency, $R$ = general gas constant, and $T$ = degradation temperature (here we used $T_g$), plots between $\ln(f)$ and $1000/T$ for all samples are presented in figure 4. $E_a$ can be obtained from the slope of the plots. The $E_a$ value for each sample is shown in figure 4, where in general increases with cristobalite content. Higher $E_a$ value implies higher energy to initiate degradation [20]. The presence of cristobalite crystals inhibits the degradation in the composite. In particular, cristobalite prevents the free motions of the PEG polymer chains.

Figure 4. $E_a$ value of composites 20 and 40 wt% cristobalite.

4. Conclusion
Since this study we can investigate dynamic mechanical behaviour by using multi-frequency DMA. Minimum degradation material energy ($E_a$) can be obtained by using arrennius equation. The highest $E_a$ value was reached by 40 wt% cristobalite. Adding cristoballite as filler is highly effective to increase degradation temperatur of composites.

Acknowledgements
The author acknowledges to Ministry of Research Technology and High Education of the Republic of Indonesia and LPPM ITS to support finance through program PUPT-2016 No. 01751/IT2.11/PN.08/2016. Also a great thanks to Departement of Physics, Institute of Technology Sepuluh Nopember (ITS) to support this work.

References
[1] Kissinger H E 1957 Anal. Chem. 29(11) 1702–6
[2] Malyshev C 2014 Annals of Physics 351 22–34
[3] Freeman E S and Carol B 1958 J. Phys. Chem. 62(4) 394–7
[4] Jawaid M and Khalil H P S A 2011 BioResources 6 2309–22
[5] Sreekala M S and Thomas S G G P 2005 Polym. Compos. 26 388–400
[6] Khonakdar H A 2015 *Compos. Part B* **76** 343-53
[7] Saba N, Jawaid M, Aloothman O Y and Paridah M T 2016 *Constr. Build. Mater.* **106** 149–59
[8] Sreenivasan V S, Rajini N, Alavudeen A and Arumugaprabu V 2015 *Compos. Part B* **69** 76–86
[9] Heimann R B 2010 *Classic and Advanced Ceramics* (Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA) pp 71–81, 507–20
[10] Kimizuka H, Ogata S and Shibutani Y 2007 *Phys. Status Solidi B* **244** 900–9
[11] Yeganeh-Haeri A, Weidner D J and Parise J B 1992 *Science* **257** 650–2
[12] Grima J N, Gatt R, Alderson A and Evans K E 2006 *Mat. Sci. Eng. A* **423** 219–24
[13] Burunkaya E, Kesmez Ö, Kiraz N, Çamurlu H E, Asiltürk M and Arpaç E 2012 *Thin Solid Films* **522** 238–46
[14] Qian T, Li J, Ma H and Yang J 2015 *Sol. Energ. Mat. Sol. C.* **132** 29–39
[15] Fauziyah N A, Musyarofah M, Triwikantoro T, Mashuri M, Firdaus S and Pratapa S 2015 *Adv. Mater. Res.* **1112** 385–8
[16] Fadly T A, Fauziyah N A, Rosyidi A and Pratapa S 2016 *Experimental Approach to Activation Energy of Polymer Composites PEG 4000-Quartz by Using Dynamic Mechanical Analyser (DMA)*, AIP, submitted in ICESNANO conference
[17] Li J, Li S, Fan C and Yan Z 2012 *Colloids Surf., B* **89** 203–10
[18] Menard K P 2008 *Dynamic Mechanical Analysis (Second edition)* (USA: CRC Press (Taylor Francis Group))
[19] Goertzen W K and Kessler M R 2007 *Compos. Part B* **38** 1-9
[20] Chartoff R P, Menczel J D and Dillman S H 2009 *Dynamic Mechanical Analysis (DMA)* eds J. D. Menczel and R. B. Prime (USA: John Wiley & Sons, Inc.)
[21] Baboo M, Dixit M, Sharma K and Saxena N S 2010 *Thermochim. Acta* **502**(1-2) 47–50