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# Dynamic mechanical properties of enhanced filler dispersion polyethylene-glycol/q-SiO<sub>2</sub> composites

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**Abstract.** In this work, polyethylene-glycol (PEG)/q-SiO<sub>2</sub> (silica quartz) composites were prepared by dispersing q-SiO<sub>2</sub> in various fractions, i.e., 0, 20, and 40 wt.%. We elaborated the silica dispersion in the polymer matrix from the previously reported solid method (reported in [1]) and a liquid method. In the latter, the dispersion of q-SiO<sub>2</sub> in the matrix was done by a stirring process in the liquefied polyethylene glycol with temperature control. The filler content and mixing method were selected to optimize the dynamic mechanical properties of composites, especially, the shear moduli ( $G'$ ) from the Dynamic Mechanical Analyzer (DMA) instrument. The maximum shear modulus value was found with 40 wt.% q-SiO<sub>2</sub> by the liquid method, which showed 46% increment as compared to 40 wt.% q-SiO<sub>2</sub> by the solid method. We showed in this work that the dynamic mechanical properties are tightly related with the dispersion of the filler in the matrix. The quantitative analysis of filler dispersion was done using *PixelProfile* software and dispersibility characterization from SEM-EDX images. We analyzed each image in three regions by RGB (*Red-Green-Blue spectrum*). The lower the dispersibility index ( $I_{dispersibility}$ ), the better the filler dispersion. By applying the liquid method, the dispersibility indices were 0.357 for 20 wt.% and 0.705 for 40 wt.%, better than solid method.

## 1. Introduction

In the past several decades, polymer composites have been very rapidly developed since their worldwide applications like in aerospace, packaging, cosmetics, automobile and some industrial applications [1–5]. The composites can be designed according to the usage. Some important aspects that affect the properties of composites are (1) type of filler, (2) filler concentration, and (3) filler morphology. Furthermore, the filler dispersion will have a critical role in the composites' properties, besides the properties of its structural components. The effectiveness of filler particles dispersion surely influences the final composites performance such as strength, stiffness, modulus, electrical/thermal conductivity, etc. [6]. Therefore, a well-defined method for improving the filler dispersion is required.

Several attempts have been introduced to increase the distribution of filler in composites, such as ultrasonic dispersion [7], melting blending [8], microemulsion [9], and the assistance of surfactants [10]. Therefore, one should choose the most effective method to optimize the filler distribution in the composite. In most studies, however, the distribution of fillers in composites was presented qualitatively. For instance, Jamil *et al.* [11] observed the nanofiller in polyetherimide (PEI) with various modified montmorillonite (f-Mt) using EDX mapping and qualitatively analyze the distribution of the filler. Moreover, the study of non-covalent functionalization of carboxylated ionic liquid (IL) for improving filler dispersion has been studied by Jiang *et al.* [12] using TEM images to analyze the distribution of carboxylated multi-walled carbon nanotubes composites (MWCNT). Interestingly, a quantitative approach has been proposed by Glaskova *et al.* [6] where a mathematical model was used to describe the quality of filler dispersions. The model worked well only in nanocomposites systems, and therefore imperative to examine it in other systems.



In this work, we examined the filler distribution in composite systems, which involved the melt of a commercial polyethylene-glycol (PEG) as a matrix. The liquid method may give rise to silica dispersion and, consequently, improve the dynamic mechanical properties of the composites, especially, the shear moduli ( $G'$ ) as compared to the previously reported solid method. All compounds acquired by melt blending were characterized through their morphological images to obtain the quantitative information about the silica dispersion in the polymer matrix.

## 2. Methods

### 2.1. Composites preparation

In this research, quartz powder is obtained from purified silica sand. The silica sand comes from Tanah Laut, Pelaihari, South Kalimantan. Polyethylene glycol (PEG) 4000 was purchased from Merck Schuchardt OHG (Hohenbrunn, Germany) and used as the matrix. The purifying process has been reported elsewhere [1,13–15]. The phases present in the quartz powder ( $q\text{-SiO}_2$ ) was identified using X-Ray Diffractometer (XRD). There are two ways of making composite samples in this study: liquid processes and solid processes. Making composite with a liquid process is carried out using  $q\text{-SiO}_2$  powder (20 wt.% and 40 wt.%) which acts as a filler, was mixed into the melted PEG then casted into the pellet shape (SQ 20-L and SQ 40-L). Meanwhile, the solid process is done using  $q\text{-SiO}_2$  powder that was mixed with PEG then formed into pellets (SQ 20-S and SQ 40-S) [1,14].

### 2.2. Scanning electron microscopy

To determine the dispersion of the  $q\text{-SiO}_2$  filler in the PEG matrix, the microstructure images were taken by Scanning Electron Microscopy (SEM) from all SQ pellets while the element mapping data were collected from the same samples using the embedded EDX. The observations were set in the same condition to ensure compatible relative intensity ratios. The intensity of the SEM-EDX images was obtained using *PixelProfile* software. The dispersion of the filler was determined using equation (1) as follow [16] :

$$I_{dispersibility} = \frac{S_{intensity}}{\bar{x}_{intensity}} \quad (1)$$

where  $S_{intensity}$  is the standard deviation of intensity, and  $\bar{x}_{intensity}$  indicates the average intensity.

### 2.3. Dynamic mechanical behavior measurement

All samples were formed in (5 mm × 5 mm) sizes and 1 mm thick in according to the sample holder on the DMA testing for shear mode. The detailed sample preparation has been explained elsewhere [1,14,17]. DMA/SDTA861·Mettler Toledo instrument was the thermo mechanical analyzer. In this experiment, all samples were measured at a temperature range of 25 °C up to 80 °C. Storage modulus ( $G'$ ) was the output of DMA, which becomes the parameter related to the homogeneity of the silica filler in the PEG matrix.

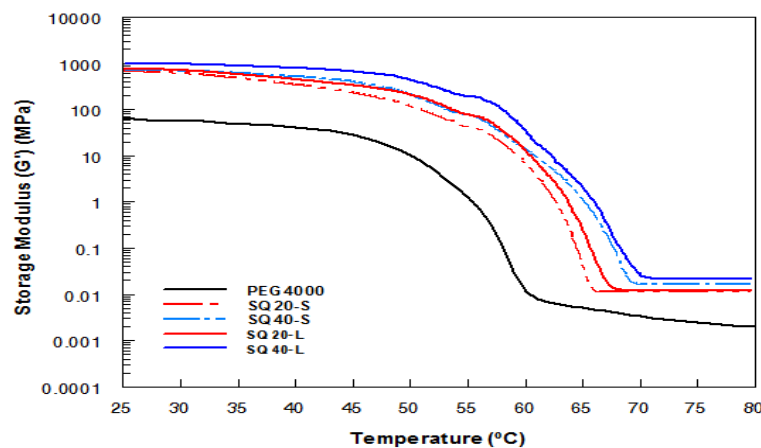
## 3. Results and discussion

Figure 1 provides the results obtained from the DMA measurement as a function of temperature for all PEG/ $q\text{-SiO}_2$  composites, i.e., at different silica weight fraction and preparation method (liquid and solid methods). The pure PEG plot is also presented and shows the lowest storage modulus at room temperature belongs to pristine PEG among all samples. The figure also shows a significant increase in such  $G'$  values from the SQ composites by both liquid and solid methods.  $G'$  for the 40 wt.%  $q\text{-SiO}_2$  by liquid method sample exhibits a 46% increase as compared to the 40 wt.%  $q\text{-SiO}_2$  by solid method sample. Meanwhile, the increase for the 20 wt.% was approximately 25%. It is obvious that the liquid method was more effective in increasing silica dispersion than the solid one. The correlation between silica dispersion and storage modulus will be discussed in detail later.

Furthermore, as  $T$  increases, the pure PEG and the composite samples exhibit a different decreasing trend. However, no significant difference trend between the two methods was evident. Faster drop in storage moduli values was observed in the SQ composites with 20 wt.% filler compared with 40 wt.%, generally for liquid and solid method. Drop rate of moduli in the glassy region (start from room temperature to around 55 °C) can be interpreted regarding polymer transition processes, where the large-scale chain slippage occurs and then initiated to melt. The presence of hard and rigid filler inhibited the movement of the polymer chains in the process of polymer chains transition and material

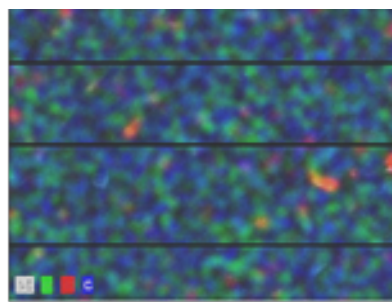
**Table 1.** Reinforcement factor  $G'/G_0$  as a function of silica weight fractions of the SQ composites.

Silica wt%	Solid	Liquid
20	7.19	8.25
40	7.85	10.88

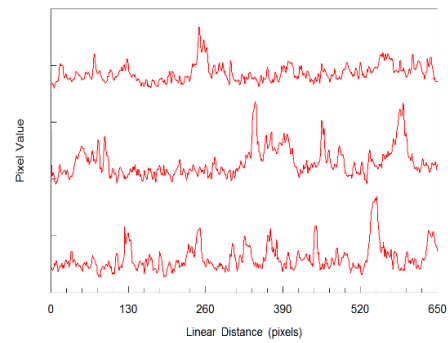
**Figure 1.** Shear storage moduli ( $G'$ ) of SQ with various silica content of 0, 20, and 40 wt% by solid and liquid method.

melt. Also, the melting temperature ( $T_m$ ) shifts to the higher values as the filler was added, i.e., 47° and 51 °C for SQ 20-S and SQ 40-S, 48° and 51°C for SQ 20-L and SQ 40-L respectively. The limited PEG chain movement due to the presence of silica filler acts as the barrier which results in the shift of  $T_m$  [18]. Further analysis shows that the reinforcement effect can be observed clearly at a higher temperature. At  $T > 65$  °C, PEG has entered the liquid region which is indicated a very low moduli values as compared to that at room temperature. The  $G'$  value in the liquid region increases with silica content. This effect can be explained by the reinforcement factor from silica (see table 1). The evolution of  $G'/G_0$  (where  $G'$  is the storage modulus value in room temperature, and  $G_0$  is the storage modulus value of pure PEG) presents the significant deviation from the dynamic response when the increasing silica weight fraction as filler. For example, in 20 wt.%, q-SiO<sub>2</sub> added in the composite, almost 4% of the total composite volume is filled by the silica particles, and 19 vol% for 40 wt.% q-SiO<sub>2</sub>. From previous research [19], this  $G'/G_0$  is related to the filler connectivity threshold which is observed between the polymer chain and the filler. As a comparison, SQ 40-L has the higher reinforcement factor value than SQ 40-S. It means that, for the high reinforcement, the filler/polymer interaction in the liquid process is more dominant than the solid one.

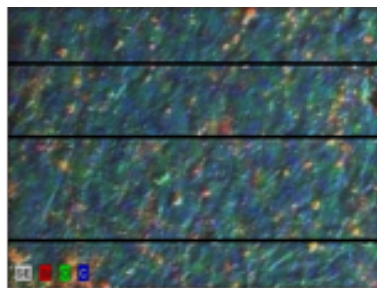
The correlation of dynamic results above was supported by the microstructure observation. The SEM-EDX images of the four blends and the associated elemental mappings are presented in figure 2. The red color represents silicon element, while green and blue are for oxygen and carbon respectively. Qualitatively, one can observe that the liquid process improves the silica dispersion in the PEG matrix. The silica agglomeration was observed for SQ 40-S (see figure 2c). Silica distribution in SQ 20-L and SQ 40-L are more homogenous than in SQ 20-S and SQ 40-S. This observation proves that the liquid method restrains the silica agglomeration in the PEG matrix. Liquid process combined with stirring in the polymer melted matrix will bring up the electrostatic force which plays an important role in enhancing the distribution of silica filler [20]. The electrostatic force occurred due to the interaction between the silica surface and PEG during stirring process. Meanwhile, the temperature treatment was the driving force for the homogenization process. By considering figure 1 and figure 2, consequently, the excellent dispersion of silica in PEG matrix can increase  $G'$  values of the composites.



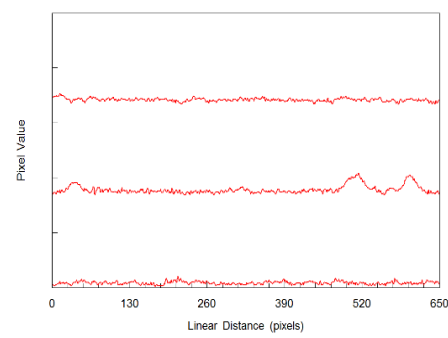
(a)



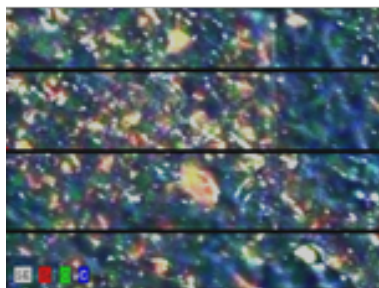
(b)



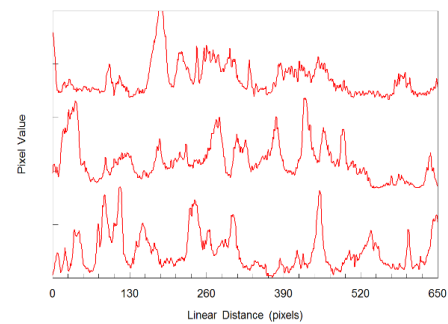
(c)



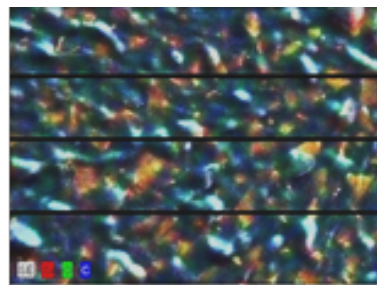
(d)



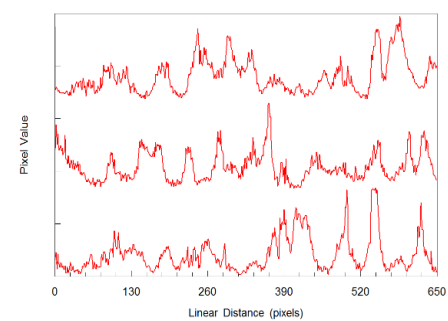
(e)



(f)



(g)



(h)

**Figure 2.** SEM-EDX and *PixelProfile* spectrum of (a) 20 wt.%-S (b) 20 wt.%-L (c) 40 wt.%-S (d) 40 wt.%-L composites.

**Table 2.** The dispersibility index ( $\bar{I}_{\text{dispersibility}}$ ) of the SQ composites

		Solid		Liquid	
		20	40	20	40
$\bar{x}_{\text{intensity}}$	1	12.813	58.429	79.993	70.483
	2	17.268	77.019	93.246	63.299
	3	12.438	74.613	89.711	61.413
$S_{\text{intensity}}$	1	4.415	45.881	38.346	47.734
	2	11.250	54.134	38.346	40.436
	3	4.211	52.789	33.617	49.004
$I_{\text{dispersibility}}$	1	0.345	0.785	0.285	0.677
	2	0.652	0.703	0.411	0.639
	3	0.339	0.707	0.374	0.798
$\bar{I}_{\text{dispersibility}}$		0.445	0.732	0.374	0.705

Quantitatively, the SEM-EDX images from figure 2 have been analyzed using the *PixelProfile* software. Table 1 shows the values of  $\bar{I}_{\text{dispersibility}}$  from all composites. The liquid process yields a lower  $\bar{I}_{\text{dispersibility}}$  value as compared to the solid process. This result confirmed the SEM-EDX images. The lower the  $\bar{I}_{\text{dispersibility}}$ , the better the dispersion (see table 2). The SEM-EDX images by the solid process show large silica agglomerations, which well confirmed by the increase of  $\bar{I}_{\text{dispersibility}}$  values from SQ 20-S and SQ 40-S. Thus, the agglomeration is responsible for determining the composite properties, especially its storage moduli.

A liquid process can be alternative for increasing filler dispersion in the polymer matrix [8]. In this process, the interaction between PEG chains and silica particles leads to the decreasing of polymer mobility. Additionally, the existence of electrostatic force is also responsible for enhancing the silica dispersion. This result can be used for further studies on how to improve the dispersion of the filler in polymer composites.

#### 4. Conclusions

This work demonstrated how filler dispersion could be improved in the PEG/silica composites by the liquid method. The quantitative parameter,  $I_{\text{dispersibility}}$ , can be used to measure the degree of dispersibility of the filler. Lower  $I_{\text{dispersibility}}$  implies better filler distribution. The 20 wt.% of SQ-L sample exhibited the lowest  $I_{\text{dispersibility}}$  value at 0.357. We have shown that particle dispersibility has a positive correlation with storage shear modulus. The storage shear modulus of the liquid method was higher than that of the solid method, i.e., by 25% for the SQ 20-L sample and by 46% for the SQ 40-L sample.

#### Acknowledgements

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