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Original Article

Effect of filler particle characteristics on yield stress and viscosity of fresh sulfur composites

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ABSTRACT

The amount and properties of fillers greatly affect the workability of sulfur composites. In addition, modified sulfur has fluidity only above approximately 115 °C, and its rheology may depend on the temperature. This study aimed to mainly quantify the effects of mixing temperature and filler particle characteristics on the yield stress and viscosity of fresh sulfur composites by applying suspension rheology theory. Sulfur composites containing mineral fillers, such as different blends of fly ash and Portland cement, were examined. The test results revealed that the yield stress of the sulfur composites was influenced by both the type and volumetric ratio of fillers, whereas the viscosity was governed by the specific surface area of filler particles. At 140 °C, the sulfur composites attained a higher yield stress and viscosity than at 120 °C. In addition, the intrinsic viscosity of the sulfur composites was dependent on the filler type and not on its volume ratio. The sulfur composites were well described by conventional yield and viscosity models commonly applied for suspension materials, when the filler volume ratio was less than 30%.

1. Introduction

Elemental sulfur is one of the byproducts of petroleum and natural gas refineries. However, the demand for surplus sulfur is limited, which causes considerable social and environmental problems [1]. As a promising solution, sulfur modified with several chemical additives, such as dicyclopentadiene, cyclopentadiene, and dipentene, has been developed as a construction material in sewer pipes, tetrapods, and roadway paving, to name a few, owing to its low price and unique properties [2].

Modified sulfur composites, which are generally composed of modified sulfur, mineral fillers, and aggregates, use modified sulfur as the binder without water (i.e., no cement hydration) instead of cement paste. Modified sulfur, which is a thermoplastic material, attains plasticity at high temperatures over about 115 °C, and its allotropic change induces a

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rapid strength development under curing. After the modified sulfur polymer is liquified, it is mixed with mineral fillers preheated in advance. Meanwhile, filler particles remain intact at a mixing temperature above roughly 120 °C While Portland cement concrete requires at least 28 days to obtain approximately 90% of its maximum strength, modified sulfur composites generally attain a significantly high strength in a few days after casting. Moreover, they have superior resistance to chemical environments containing strong acids and alkalis as well as low water permeability, compared with normal concrete [2–5].

According to the sulfur concrete mix design reported by Makenya [6], sulfur concrete is required to have an optimal viscosity. On the one hand, sulfur composites with a high sulfur content have issues such as thermal expansion and severe micro-cracking during curing. On the other hand, sulfur composites with a low sulfur content exhibit poor workability. To address these issues, the optimal sulfur content should be determined for the mix design. Because sulfur composites become flowable only at high temperatures, strict conditions and methods are required to evaluate the workability of sulfur composites.

While the slump test has been traditionally used to determine the workability of normal concrete [7], several rheological methods have been recently proposed [8]. The rheological properties, such as yield stress and viscosity, which can be determined using a rheometer, can represent the workability of fresh concrete more quantitatively and accurately. In general, a lower yield stress and viscosity correspond to a lower workability. Rheological methods for suspension materials determine the relation between the suspended particles (e.g., aggregates) and suspending fluid (e.g., cement paste) [9].

To the best of the authors' knowledge, Gwon and Shin [10] is the only study that applied rheological models to sulfur composites. They examined the effect of mixing temperature and micro-filler characteristics on the rheological properties of fresh sulfur composites [10]. Although they suggested a meaningful guideline for casting sulfur concrete, there is still a lack of theoretical studies or quantitative recommendations on the workability of modified sulfur concrete.

A fresh sulfur composite can be considered as a suspension of filler particles, where the modified sulfur and fillers act as a suspending fluid and suspended particles, respectively. According to the suspension theory, the amounts and properties of modified sulfur, mineral fillers, and aggregates influence the workability of modified sulfur composites. Mineral fillers may improve the workability and strength of modified sulfur, allowing its use as a more stable binder [11,12]. The addition of mineral fillers affects the viscosity of the sulfur composite, allowing the mitigation of material segregation. Fillers replace the portion of modified sulfur, which reduces thermal shrinkage caused by the allotropic transition of sulfur during curing. Fly ash, silicate flour, and cement (as a self-healing agent) are commonly used mineral fillers [2,13].

Given the concerns, this study explores the effects of filler characteristics on the workability of fresh sulfur composites as the first step for applying suspension rheology theory to sulfur composites. The properties of the suspended particles, prepared in different blends of fillers (fly ash and/or cement), were characterized by their amount and particle size distribution, which were primarily represented by the total surface area of the filler particles per unit sulfur composite volume. The rheometer testing was performed at two different temperatures, 120 or 140 °C. The rheological test results of the fresh sulfur composites were discussed and analyzed in reflection of conventional yield stress and viscosity models.

2. Rheological approaches

Several theoretical models are introduced for evaluating the rheological properties of modified sulfur composites, including the constitutive, yield stress, and viscosity models.

2.1. *Constitutive model*

For the quantitative evaluation of the workability of fresh concrete, rheological approaches have been investigated based on theoretical and experimental studies [8, 9, 14]. In the theory of rheology, the flow behavior of a material can be described by its rheologica l properties, such as yield stress and viscosity. Multiple constitutive models have been proposed to determine the rheological properties of freshly mixed concrete [15, 16]. Among them, the Bingham model and Herschel–Bulkley model are known to fit experimental data well [17–19]. Because freshly mixed concrete and fresh sulfur composites are suspensions, the same constitutive models can describe the behavior of fresh sulfur composites. Based on the Bingham model, the shear stress beyond a certain level (i.e., yield stress) is assumed to be linearly proportional to the shear strain rate:

$$\tau = \tau_0 + \eta\dot{\gamma} \tag{1}$$

where the constant rate of change of the shear stress (τ) to the shear strain rate ($\dot{\gamma}$) is the plastic viscosity (η), and the minimum shear stress required for the material to start to flow is the yield stress (τ_0).

In the Herschel–Bulkley model, the shear stress, when it is greater than the yield stress, is defined as a power growth function of the shear strain rate:

$$\tau = \tau_0 + a\dot{\gamma}^b \tag{2}$$

where the power growth of the shear stress is expressed by the model constants a and b. Note that the constant a is equivalent to the viscosity (η) when the constant b is equal to unity.

The Bingham and Herschel–Bulkley models were applied to the sulfur composites in this study. The rheological approaches are based on the concept of suspension, which consists of a fluid and suspended particles. Freshly mixed concrete, mortar, and cement paste are classified as suspensions. Concrete is a suspension containing water, cement, coarse aggregate, and fine aggregate, and cement paste is a suspension made of water and cement (or cementitious materials) only [20]. Fresh sulfur composites are also a suspension with melted sulfur and filler particles, such as aggregates and fly ash. Therefore, it is assumed that the rheological

models developed for suspension materials can be applied to fresh sulfur composites.

2.2. Yield stress model

The yield stress is one of the factors that control the rheological behavior (or flowability) of particle-fluid suspension systems. A suspension with a high solid particle volume ratio behaves like a non-Newtonian fluid with a yield stress, whereas a dilute suspension behaves like a Newtonian fluid without a yield stress [21]. Regarding the interaction between solid particles, the behavior of a less concentrated suspension is hydrodynamic. If the concentration of solid particles exceeds a transition point, the frictional interaction between particles becomes substantial and influences the rheology of the suspension [22]. The solid particle volume ratio at the transition point, where the yield stress first appears, is called the percolation threshold [23], which is 0.29 for equally sized spherical particles [24].

Walsh and Saar [23] suggested that the relationship between the yield stress and solid particle volume ratio of a suspension can be expressed as a power growth function:

$$\tau_0 \propto (\phi - \phi_c)^{\beta} \tag{3}$$

where τ_0 is the yield stress, ϕ is the solid particle volume ratio, ϕ_c is the percolation threshold, and β is a model constant. This relationship was numerically derived for crystal-melt suspensions, where the crystals form a crystal network connecting macroscopic samples (i.e., suspended particles), causing the development of yield stress. For crystal-melt suspensions, the exponent β varies between 2.5 and 3.5 [23]. In addition, cement pastes with different amounts of fly ash, in which the water-to-cement ratio was 0.35 by mass and the volume fraction of fly ash ranged between 0 and 60% of the mixture by weight, were fitted by a power growth function with $\beta = 4.5$ and $\phi_c = 0$ [25].

2.3. Viscosity model: Krieger–Dougherty model

The viscosity of suspensions depends on the volume fraction and/or concentration of solid particles. In general, as the solid particle volume fraction increases, the viscosity of a suspension increases [26]. The relationship between the viscosity and solid particle volume ratio of suspensions can be expressed by the Krieger–Dougherty equation [27]:

$$\eta_r = \frac{\eta_s}{\eta_c} = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \tag{4}$$

where η_r is the relative viscosity, defined as the ratio of the suspension viscosity η_s to the viscosity of the continuous fluid η_c, which refers to the fluid phase excluding the solid particles; ϕ indicates the volumetric ratio occupied by solid particles; ϕ_m is the maximum packing density of the solid particles, which expresses how much volume can be occupied only by the solid particles in a unit volume; and $[\eta]$ is the intrinsic viscosity of the solid particles, which expresses how much the solid particles influence the rheological properties of the suspension and by how much they vary with the shape and size distribution of particles. Eq. (4) is a semi-empirical equation, originally derived based on experimental data for suspensions of mono-sized spherical latex particles. Because the Krieger–Dougherty equation was derived using suspensions of mono-sized spherical particles, it generally agrees well with suspensions of the same shaped particles. The intrinsic viscosity primarily depends on the shape of solid particles; for spherical, equally distant, and rod or fiber particles, $[\eta]$ is 2.5, 3–5, and 4–10, respectively. The intrinsic viscosity of dispersed cement paste with a superplasticizer and equally distant particles is approximately 5 [28]. The maximum packing density is also affected by the shape and size distribution of solid particles [27].

3. Raw materials and sample preparation

This section introduces the raw materials and test methods used to quantity the rheological properties (i.e., yield stress and viscosity) of various mix proportions of fresh sulfur composites.

3.1. Raw materials

Modified sulfur was used as the binder in the tested sulfur composites. The modified sulfur was produced from the reaction of elemental sulfur with 3.3 wt.% dicyclopentadiene in the form of yellow powder by Micro Powder, Inc., Korea [10]. Type-I Portland cement and class-F fly ash were employed as the fillers. Table 1 lists the oxide compositions of all the raw materials obtained from an X-ray fluorescence (XRF) analysis. Table 2 reports the specific gravity, particle size range, and mean particle size of the fillers. Because modified sulfur was used in the molten state, at a temperature more than 115 °C, only the specific gravity was reported.

Table 2 – Physical properties of all the raw materials.

Material	Specific gravity	Maximum particle size (μm)	Mean particle size (μm)
Modified sulfur	1.91	–	–
Cement	3.14	150	11.93
Fly ash	2.22	255	18.22

Table 1 – Oxide compositions of all the raw materials obtained from an XRF analysis (unit: wt.%).

Material	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	Na_2O
Modified sulfur	0	0	0	0	99.8	0	0	0
Cement	60.8	21.1	4.7	3.2	2.7	2.1	0.9	0.3
Fly ash	6.2	52.3	22.6	9.1	–	1.8	1.8	1.8

3.2. Mix proportions

Table 3 lists the mix proportions of twenty tested sulfur composites. The mix proportions were designed in a volumetric ratio, as recommended by ACI committee 548 [29]. The volume ratio of a certain filler blend was 20, 25, 30, or 35% of the total volume of the sulfur composite. For each filler ratio, five blends of cement and fly ash were prepared at relative ratios of cement to fly ash equal to 1:0, 0.75:0.25, 0.5:0.5, 0.25:0.75, and 0:1, which resulted in different particle size distributions; the five filler blends were labeled as C100, C75F25, C50F50, C25F75, and F100, respectively.

Fig. 1 shows the cumulative particle size distributions of the five filler blends measured using a laser diffraction particle size analyzer (Sympatec HELOS, Germany). From the figure, it can be seen that an increasing ratio of cement in the filler blends resulted in a smaller mean particle size ranging from 18.2 to 11.9 μm.

The particle size distributions were used to quantify the total surface area of the filler particles in each sulfur composite. The following assumptions were made for computational simplification: (1) all the particles have a spherical shape; (2) because the discrete particle size was measured by the laser diffraction particle size analyzer, their diameters are equal to the average of adjacent discrete particle sizes; (3) the specific gravity is identical regardless of the particle size. The total surface area of filler particles in each sulfur composite was calculated considering the volumes and specific gravities of cement and fly ash [30]. Table 3 summarizes the total surface area of filler particles per unit sulfur composite volume, and Table 4 presents the total surface areas of the five filler blends with a 20% filler ratio as an example. With the same filler ratio in the sulfur composites, the total surface area of filler particles got larger as the cement ratio increased.

3.3. Sample preparation

Fig. 2 describes the sample preparation steps for the rheometer tests explained in the next section. Modified sulfur, fly ash, and cement were prepared with the mix proportions reported in Table 3. Fly ash and cement were heated in an oven at 150 °C for approximately 24 h. Modified sulfur was melted in a high-temperature mixing bowl at 140 °C. Once the sulfur gained perfect plasticity, the heated fly ash and cement were poured into the bowl with molten sulfur. The whole mixture was agitated for 15 min using a mechanical mixer at 100 rpm. The surface temperature of homogenized sulfur composite was approximately 140°C until it was loaded in the rheometer. A more detailed explanation for the sample preparation can be found in our previous paper [10].

4. Test methods

4.1. Rheometer tests

The rheological properties of the sulfur composites were measured using a HAKKE MARS rheometer (Thermo Scientific, USA). Fig. 3 shows photographs of the rheometer. A sulfur composite sample was loaded between two parallel plates with a diameter equal to 35 mm. The size of gap between the two plates was 1 mm, considering the maximum diameter of the filler particles (approximately 0.25 mm). The furnace shown in Fig. 3(a) controlled the temperature of the loaded sample at 120 or 140 °C with hot air conditioning during the measurement. Only the upper plate rotated at a specified rate. The rheometer recorded the shear stress induced by the applied shear strain rate. The relationship between the shear strain rate and shear stress represents the flow behavior of the sulfur composite.

Table 3 – Mix proportions of tested sulfur composites.

Filler volume ratio (%)	Filler blend	Modified sulfur (g/cm^3)	Cement (g/cm^3)	Fly ash (g/cm^3)	Total surface area of filler particles per unit sulfur composite volume (m^2/cm^3)
20	20C100	1.528	0.628	0	0.186
	20C75F25		0.471	0.111	0.177
	20C50F50		0.314	0.222	0.169
	20C25F75		0.157	0.333	0.158
	20F100		0	0.444	0.150
25	25C100	1.433	0.785	0	0.233
	25C75F25		0.589	0.139	0.222
	25C50F50		0.393	0.278	0.212
	25C25F75		0.196	0.416	0.198
	25F100		0	0.555	0.187
30	30C100	1.337	0.942	0	0.279
	30C75F25		0.707	0.167	0.266
	30C50F50		0.471	0.333	0.254
	30C25F75		0.236	0.500	0.237
	30F100		0	0.666	0.225
35	35C100	1.242	1.099	0	0.326
	35C75F25		0.824	0.194	0.311
	35C50F50		0.550	0.389	0.297
	35C25F75		0.275	0.538	0.277
	35F100		0	0.777	0.262

Table 4 – Total surface area of filler particles per unit sulfur composite volume with filler ratio of 20% (for example, 40 cm^3 of fillers in 200 cm^3 of sulfur composite).

Filler blend	Total surface area of filler particles in 40 cm^3 of fillers (m^2)	Total surface area of filler particles per unit sulfur composite volume (m^2/cm^3)
C100	37.2	0.186
C75F25	35.5	0.177
C50F50	33.9	0.169
C25F75	31.7	0.158
F100	30.0	0.150

Table 5 – Maximum packing densities of the filler blends (initial volume before packing: 37.5 cm^3).

Filler blend	Volume of the centrifuged filler blend including voids (cm^3)	Volume of the particles only (cm^3)	Maximum packing density
C100	26.3	12.7	0.485
C75F25	27.5	13.8	0.500
C50F50	28.1	14.9	0.531
C25F75	30.0	16.3	0.545
F100	30.8	18.0	0.585

Fig. 4 displays the time history of the applied shear strain rate. Each test continued for 150 s. For the first 30 s, a low shear rate of 1 1/s was exerted to warrant a sound contact between the sample and plates. After 30 s, the shear strain rate increased by 5 1/s every 20 s from 5 to 30 1/s. The rheometer tests were performed at least two times for each mixture reported in Table 3.

4.2. *Maximum packing density*

The maximum packing density (ϕ_m) of filler particles is one of the factors affecting the behavior of a suspension as per the Krieger–Dougherty equation (Eq. (4)). It indicates how many particles can be stored in a unit volume of a container. In this study, the maximum packing density of each filler blend was measured using a centrifuge (FLETA 40, HANIL SCIENCE CO., Korea), as shown in Fig. 5(a) [25]. The filler blend was centrifuged at 3000 rpm for 10 min after the cement and fly ash particles were well mixed. The volume of the centrifuged filler blend, including voids and the bulk volume, were measured. Then, the volume occupied only by the filler particles was calculated from the density of the blends, which was determined using the laser diffraction particle analyzer. The volume of solid particles in the bulk volume gives the maximum packing density.

Fig. 5 shows the volume reductions of the two filler blends (C75F25 and C25F75) packed completely after the centrifuge operation. Table 5 summarizes the maximum packing densities of the five different blends of cement and fly ash; the initial volume before packing was 37.5 cm^3. As can be seen from the table, a higher cement ratio induced a lower maximum packing density. This indicates that the cement itself owns a lower maximum packing density owing to its narrower particle size distribution compared to that of fly ash (Fig. 1).

5. Test results and discussions

5.1. *Flow curve analysis*

Fig. 6 shows the shear strain rate and shear stress behaviors of several selected sulfur composites obtained from the rheometer tests. Figs. 6(a–c) show the effects of the mixing temperature, filler volumetric ratio, and cement ratio, respectively. As shown in the figure, in all the tested composites, an increase in the shear strain rate brings an increase in the shear stress, as expected. As shown in Fig. 6(a), the

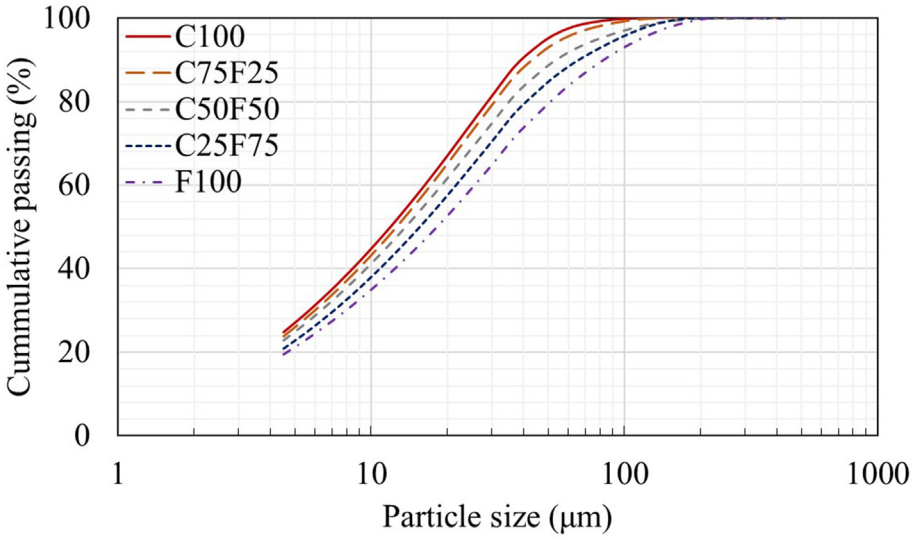


Fig. 1 – Cumulative particle size distributions of the five blends of cement and fly ash obtained with the laser diffraction particle size analyzer.

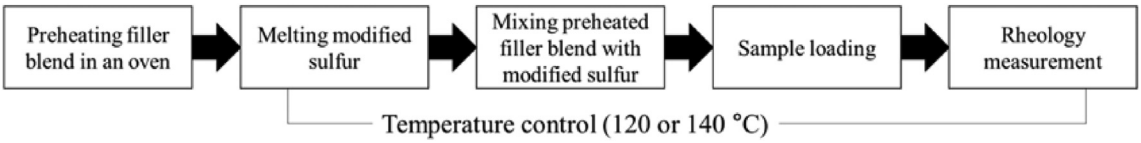


Fig. 2 – Sample preparation steps for the rheology measurement of sulfur composites.

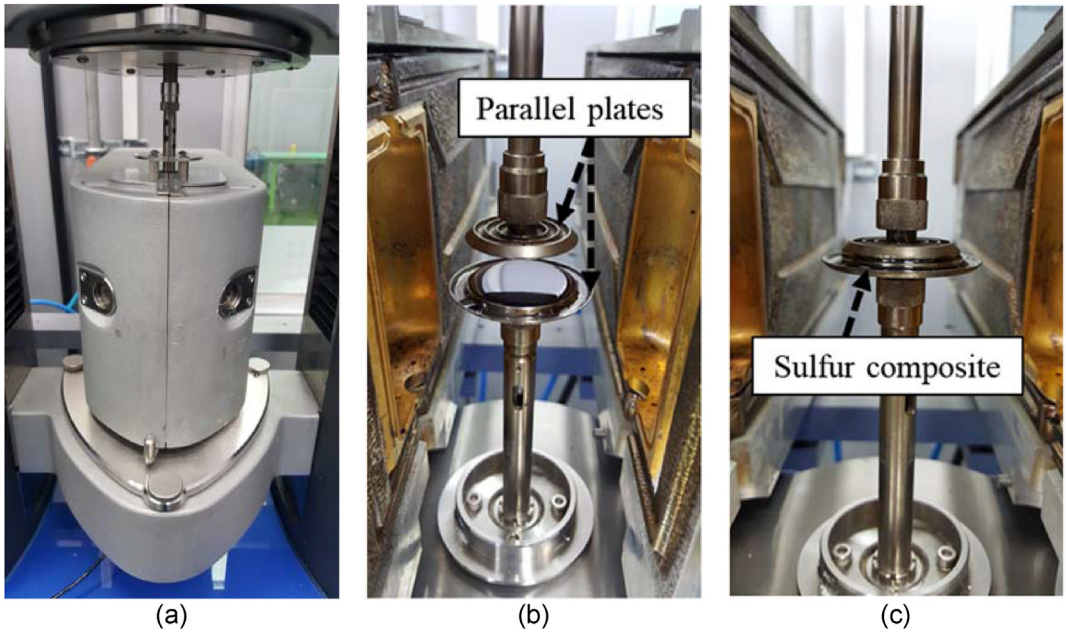


Fig. 3 – Photographs of the rheometer: (a) furnace controlling the sample temperature; (b) parallel plates in the furnace after loading a sulfur composite; (c) parallel plates during the test.

higher temperature (140 °C) induces a higher shear stress at every shear strain rate in all the mixtures; for C75F25, the shear stress at 140 °C is approximately seven times larger than that at 120 °C. As shown in Fig. 6(b), with the same temperature and type of filler blend, the shear stress increases with increasing amount of fillers. On the other hand, as shown in Fig. 6(c), with the same temperature and filler ratio, a higher cement ratio in the filler blend causes a higher shear stress.

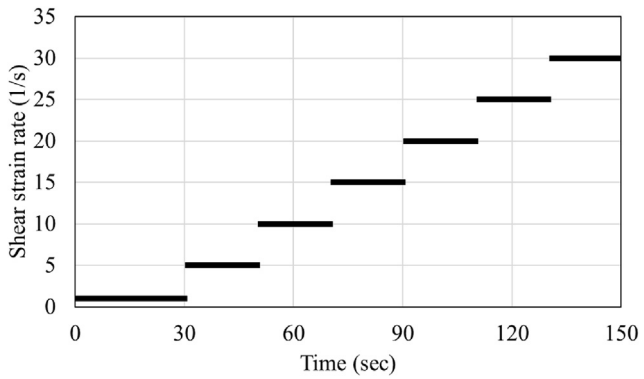


Fig. 4 – Applied shear strain rate history.

When the amount of fillers and/or cement ratio is relatively small, the shear stress and shear strain rate generally show a linear correlation. This is also the case when the temperature of sulfur composites is 120 °C (Fig. 6(a)). On the contrary, the relationship becomes nonlinear as the amount of fillers and/or cement ratio increases and when the temperature is 140 °C, especially for shear strain rates lower than 10 1/s.

For the sulfur composites with a linear relationship between the shear stress and shear strain rate, the Bingham model (Eq. (1)) shows a better fitting (solid line in Fig. 6). Meanwhile, for the mixtures with a nonlinear relationship, the tangential slope of the flow curve rapidly decreases at lower shear strain rates, and the Herschel–Bulkley model (Eq. (2)) fits better to the test results (dotted line in Fig. 6). Therefore, both models should be used to represent the flow curves of the sulfur composites. In the following sections, the yield stress and viscosity decided by the Bingham model are used for comparison. Note that only the shear stress data at 10, 15, and 20 1/s were used for the Bingham model to increase the R-squared value.

5.2. *Effect of total surface area of filler particles on yield stress*

Fig. 7 shows plots of the yield stress of all the tested mixtures as a function of the total surface area of filler particles per unit sulfur composite volume (referred to as the "filler surface area density" hereafter). The sulfur composites with identical filler blend were grouped together; for example, 20C100, 25C100, 30C100, and 35C100 were categorized as C100. As seen in Fig. 7, the yield stress increases as the filler surface area density increases with a higher filler ratio, regardless of the mixing temperature. The relationship between the yield stress and filler surface area density for each filler blend is characterized by a power law distribution. The yield stress at 140 °C (Fig. 7(b)) increases significantly compared with that at 120 °C (Fig. 7(a)), and the difference in the exponents affected by the filler blend type is smaller at 140 °C than at 120 °C.

In Fig. 8, the yield stresses of the sulfur composites with the same filler ratio were grouped together. The yield stress rapidly increases as the filler surface area density increases with a higher cement ratio. For each filler ratio, the yield stress and filler surface area density also show a power law correlation, but the exponents were much larger than those for each filler blend in Fig. 7.

It is noted that the positive correlation between the filler surface area density and the yield stress has a considerable variation. For example, 30C100 and 35C25F75 have similar filler surface area densities (0.279 and 0.277 m^2/cm^3, respectively), but the yield stress of 35C25F75 is much lower than that of 30C100. This suggests that both the filler surface area density and the shape or cohesion of the particles influence the yield stress of the sulfur composites.

5.3. *Effect of total surface area of filler particles on viscosity*

Fig. 9 shows plots the change of viscosity in relation to the filler surface area density in all the tested sulfur composites. The viscosity exhibits an exponential growth with increasing filler surface area density. Considering all the mixtures, the viscosity (Fig. 9) presents a much stronger correlation with the filler surface area density than the yield stress (Figs. 7 and 8). This suggests that the viscosity of the sulfur composites is primarily governed by the filler surface area density, not the shape or cohesion of the fillers. Regarding the effect of the mixing temperature, all the sulfur composites attain a much greater viscosity at 140 °C than at 120 °C.

6. Application to rheological models

6.1. *Application of the conventional yield stress model*

According to Eq. (3), the yield stress of a suspension is proportional to the volume fraction of solid particles in the suspension, and their relationship can be represented by a power law distribution. For the sulfur composites with the same filler blend, the correlation between the filler volumetric ratio and the yield stress was expressed as a power law distribution. Then, the power law function was transformed into a linear function by taking common logarithm on both the yield stress and filler ratio, as shown in Fig. 10. The regression function for each filler blend well represents the test results, which means that the yield stress model has potential to be applicable to the sulfur composites. However, the model cannot describe the change in yield stress originating from the different types of filler blends.

6.2. *Application of the conventional viscosity model*

According to the Krieger–Dougherty equation (Eq. (4)), the relative viscosity (η_r) is the ratio of the viscosity of the suspension (i.e., sulfur composite) (η_s) to the viscosity of the continuous fluid (i.e., modified sulfur itself) (η_c). For the tested sulfur composites, the volume ratio of solid particles (i.e., filler ratio) was set in the mix design, and the maximum packing density of each filler blend was measured by a

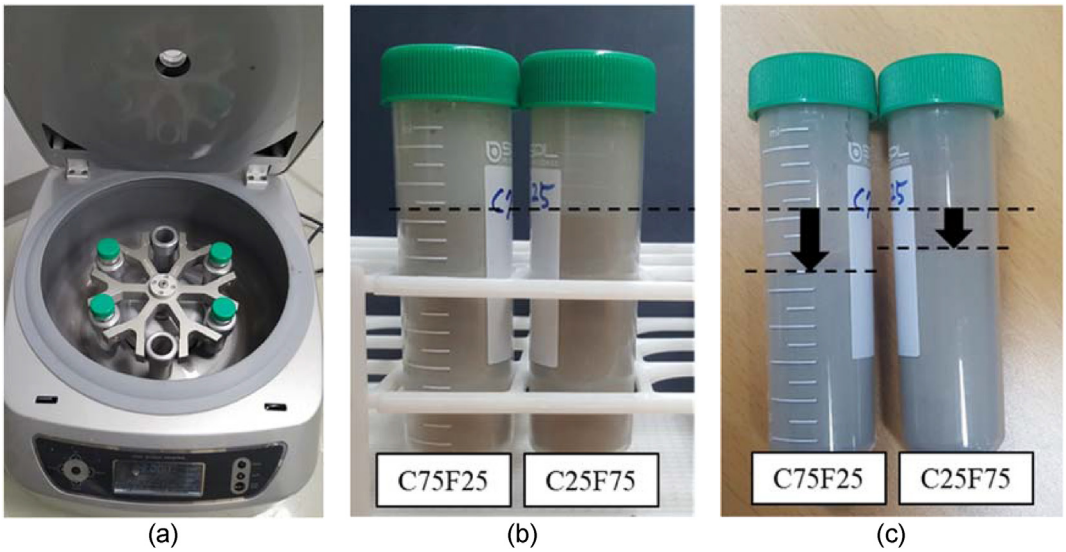
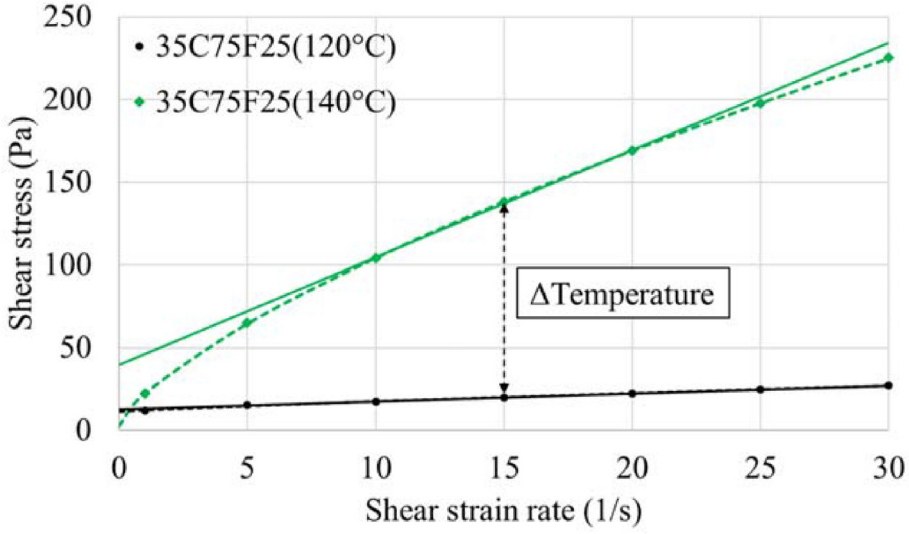
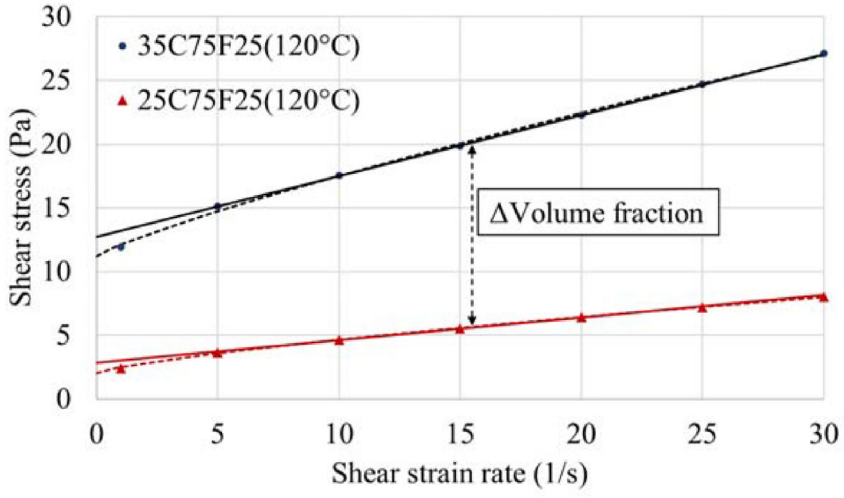


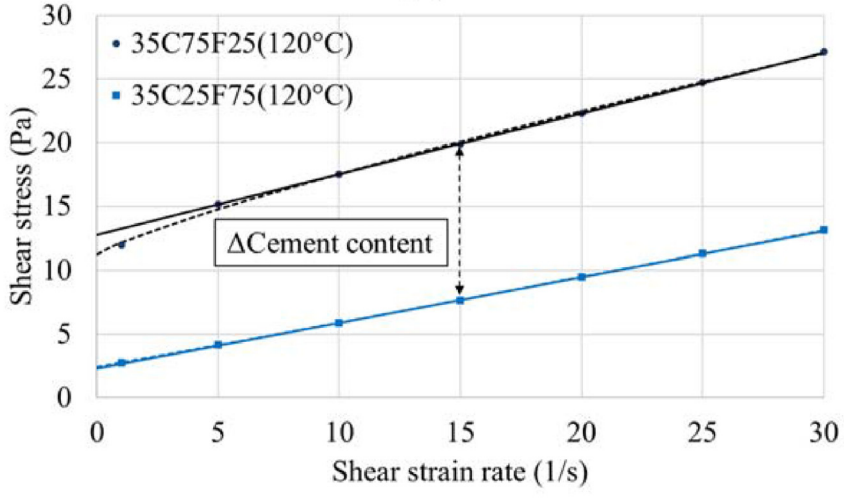
Fig. 5 – Photographs of the (a) centrifuge and C75F25 and C25F75 samples (b) before and (c) after packing.



(a)



(b)



(c)

Fig. 6 – Flow curves of sulfur composites: (a) same mixture at different temperatures; (b) mixtures with different filler volumes; (c) mixtures with different cement ratios.

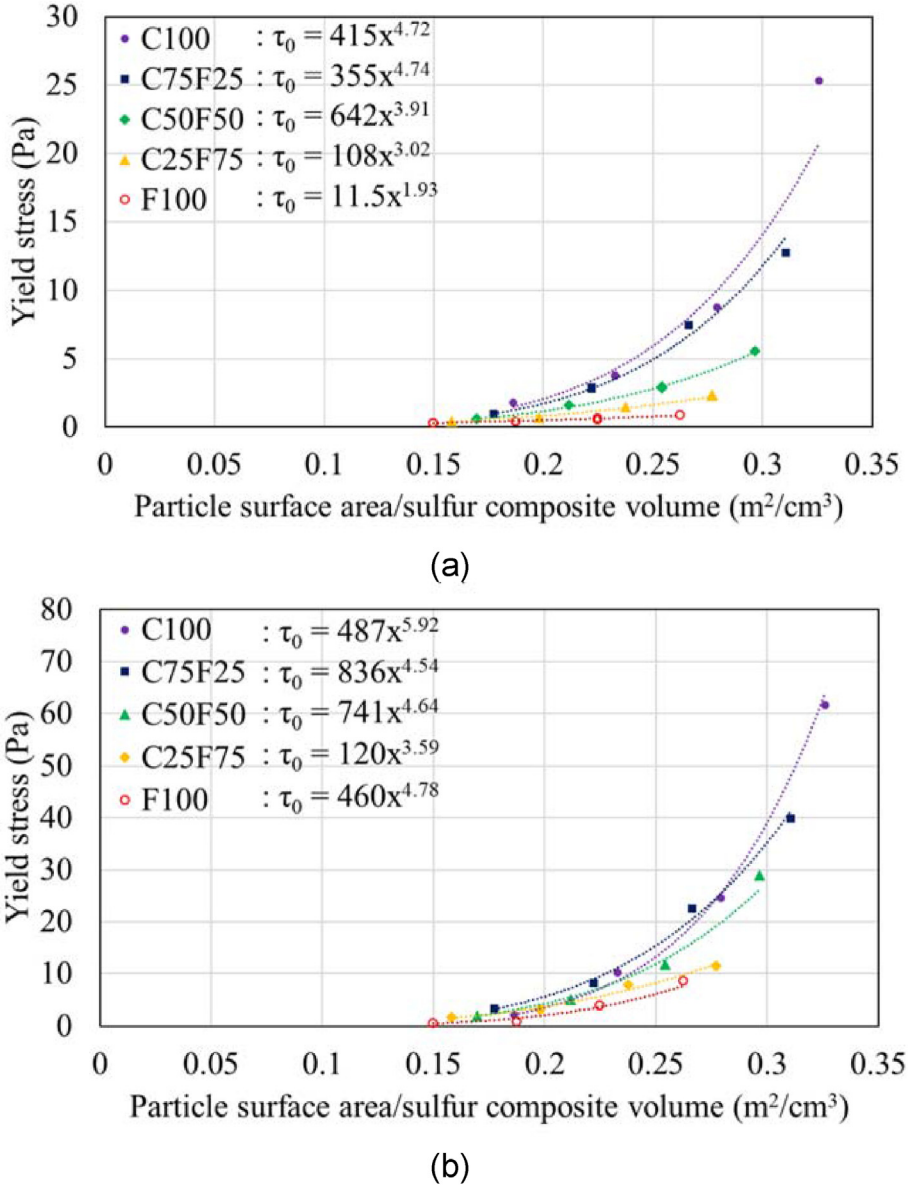


Fig. 7 – Relationship between yield stress and filler surface area density, grouped by filler blend type: (a) 120 °C; (b) 140 °C.

centrifuge. The only unknown parameter in Eq. (4) is the intrinsic viscosity. Table 6 shows the intrinsic viscosities of the fly ash and cement used in this study obtained by fitting the rheometer test results (F100 and C100) to Eq. (4); the relative viscosity was experimentally determined twice for each filler ratio, η_{r1} and η_{r2}. Regardless of the filler ratio, the intrinsic viscosities obtained from the mixtures with the same filler blend (i.e., F100 or C100) are similar to each other. Thus, the intrinsic viscosity of fly ash or cement was taken to be equal to the average of those from the four filler ratios (Table 6).

The intrinsic viscosity of a filler blend consisting of cement and fly ash can be calculated by considering the volume fraction and intrinsic viscosity of each material as follows [27]:

$$[\eta] = \frac{V_{CE}}{V_{CE}+V_{FA}}[\eta]_{CE} + \frac{V_{FA}}{V_{CE}+V_{FA}}[\eta]_{FA} \quad (6)$$

where $[\eta]_{CE}$, $[\eta]_{FA}$, and $[\eta]$ are the intrinsic viscosity of cement, fly ash, and filler blend, respectively; V_{CE} and V_{FA} are the volume fractions of the cement and fly ash in the blend, respectively. Based on the intrinsic viscosities of fly ash and cement reported in Table 6, the intrinsic viscosities of the other filler blends were calculated using Eq. (6), and the results are reported in Table 7.

Fig. 11 compares the calculated relative viscosity per the Krieger–Dougherty equation using the calculated intrinsic viscosity in Table 7 with the measured relative viscosity in all the tested mixtures. As shown in the figure, at 120 °C, the

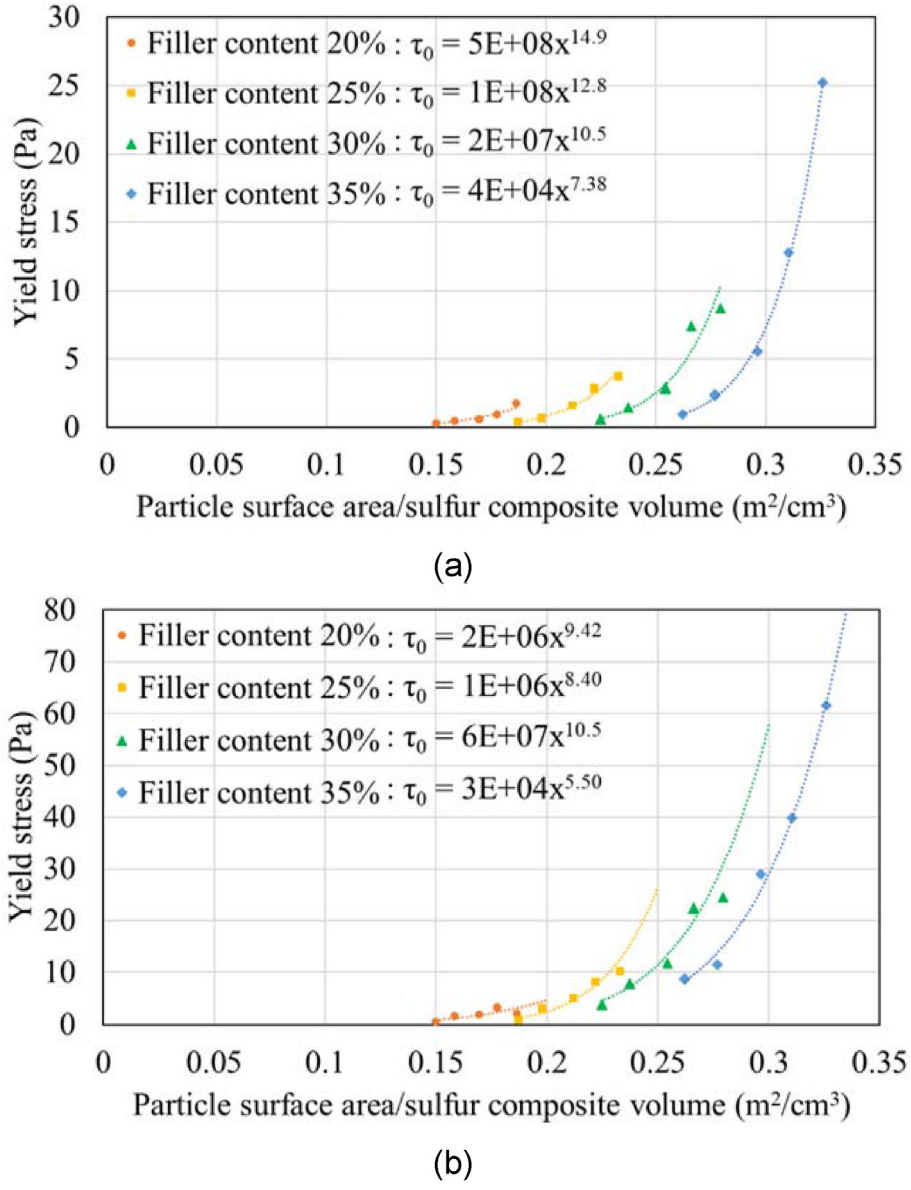


Fig. 8 – Relationship between yield stress and filler surface area density, grouped by filler volume ratio: (a) 120 °C; (b) at 140 °C.

measured relative viscosity of 30C100 is 20.23% lower than the calculated one; those of 35C25F75, 35C50F50, and 35C75F25 are 12.42%, 29.69%, and 25.13% lower than the calculated one, respectively (Fig. 11(a)). For the other mixtures with relative viscosity equal to or lower than 8, the measured relative viscosities are similar to the calculated one. At 140 °C, the measured relative viscosities of 30C75F75, 35C25F75, 35C50F50, 35C75F25, and 35C100 are 20.38%, 37.03%, 37.49%, 19.54%, and 19.93% larger than the calculated one, respectively (Fig. 11(b)). For the other mixtures with a relative viscosity equal to or lower than 5, the measured and calculated relative viscosities matched well.

6.3. *Effects of excessive use of filler on the rheology of sulfur composite*

6.3.1. *Sedimentation of filler particles in sulfur composite*

Fig. 11(a) reveals that the mixtures with the relative viscosity above 8 have a smaller relative viscosity than the calculated one. The overall yield stress and viscosity at 140 °C were distinctly higher than those at 120 °C. This is because an increase in temperature induces a higher concentration of longer polymers (i.e., a consequent formation of additional high molecular weight polysulfides) in fresh modified sulfur [2,31]. The rheology of the suspending fluid, which is liquid

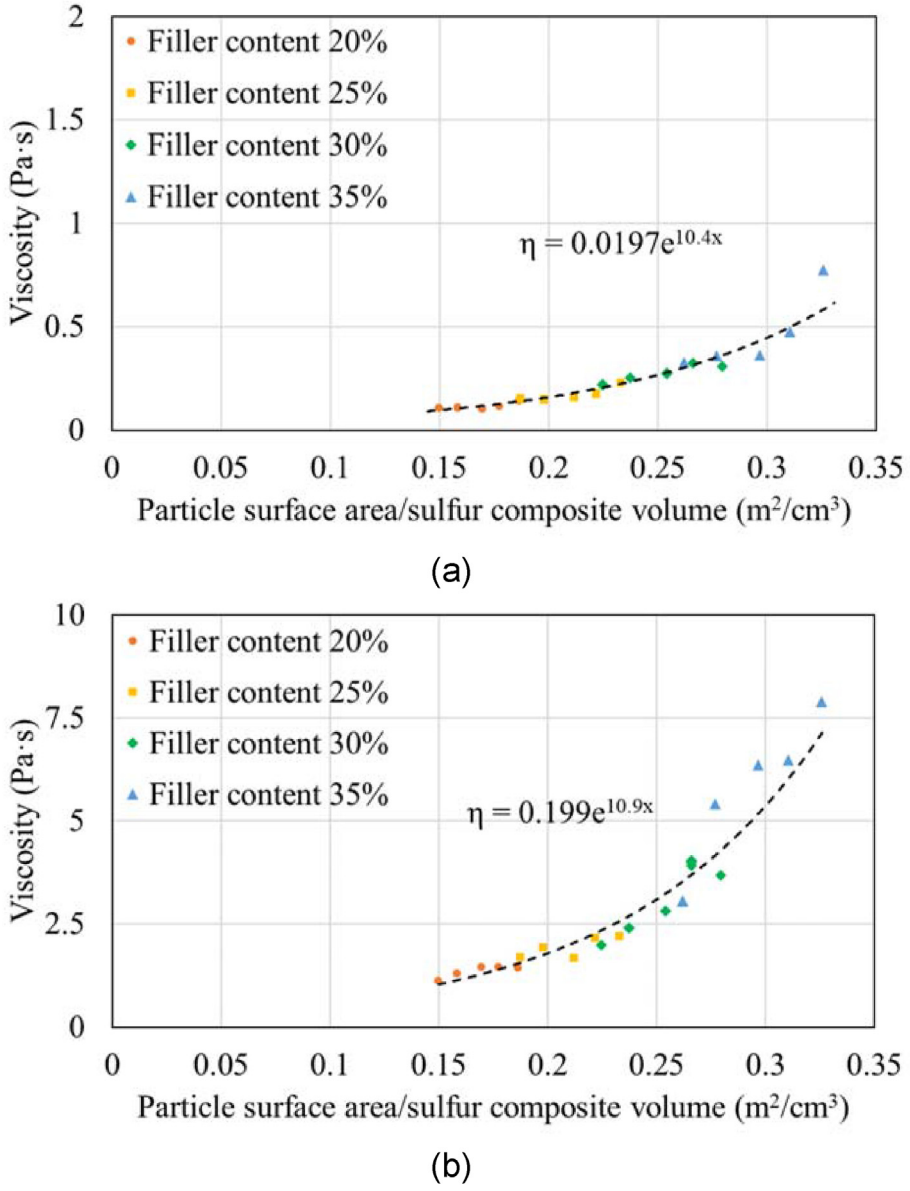


Fig. 9 – Relationship between viscosity and filler surface area density: (a) 120 °C; (b) at 140 °C.

Table 6 – Intrinsic viscosities of cement and fly ash obtained by fitting to the Krieger–Dougherty equation.

Temp.	Label	ϕ	η_{s1}	η_{s2}	ϕ_m	η_c	η_{r1}	η_{r2}	$[\eta]_1$	$[\eta]_2$	$[\eta]$
120 °C	F100	0.20	0.11	0.11	0.59	0.04	2.53	2.45	3.79	3.66	3.80
		0.25	0.15	0.15			3.47	3.52	3.81	3.86	
		0.30	0.22	0.22			5.15	5.02	3.90	3.84	
		0.35	0.32	0.32			7.36	7.58	3.74	3.80	
	C100	0.20	0.14	0.14	0.49	0.04	3.33	3.27	4.66	4.60	4.54
		0.25	0.23	0.23			5.28	5.27	4.74	4.73	
		0.30	0.30	0.29			7.10	6.76	4.19	4.09	
		0.35	0.76	0.77			17.6	18.0	4.62	4.66	
140 °C	F100	0.20	1.11	1.13	0.59	0.6	1.86	1.89	2.52	2.59	2.85
		0.25	1.43	1.70			2.38	2.83	2.66	3.19	
		0.30	1.99	2.13			3.32	3.55	2.86	3.01	
		0.35	2.82	3.07			4.70	5.12	2.90	3.06	
	C100	0.20	1.44	1.57	0.49	0.6	2.41	2.61	3.41	3.72	3.80
		0.25	2.14	2.21			3.56	3.68	3.62	3.71	
		0.30	3.48	3.69			5.81	6.15	3.76	3.89	
		0.35	7.94	7.90			13.2	13.2	4.17	4.16	

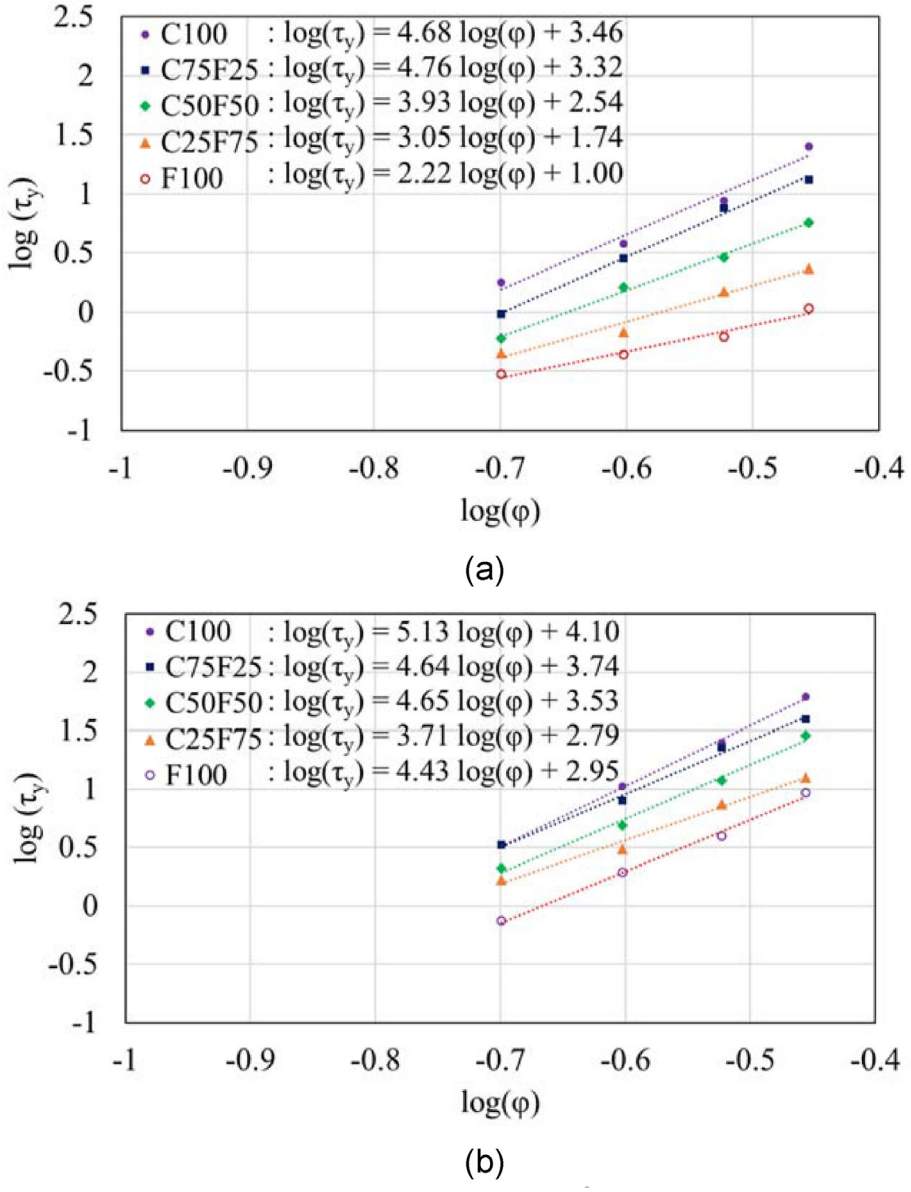


Fig. 10 – Relationship between yield stress and filler ratio in common logarithm scale: (a) at 120 °C and (b) at 140 °C.

modified sulfur in this study, affects the degree of sedimentation of the filler particles [32]. Fresh modified sulfur at 120 °C has a weaker capability to suspend the filler particles than at 140 °C, which causes partial sedimentation of the filler particles. The sedimentation refers to the separation of suspended particles and continuous fluid. Accordingly, some portion of the particles may sink to the bottom owing to gravity. Because the parallel plates measure the shear stress at the top surface of the sample, the sedimentation makes the upper part of the loaded sample more dilute, which reduces the effect of the particles on the rheological properties.

Table 7 – Intrinsic viscosity of each filler blend calculated using Eq. (6).

Label	[η] for 120 °C	[η] for 140 °C
F100	3.799	2.850
C25F75	3.983	3.088
C50F50	4.168	3.327
C75F25	4.353	3.565
C100	4.537	3.804

6.3.2. *Frictional and hydrodynamic interaction between particles in suspension*

In the suspension system, the mechanism of interaction between the suspended particles changes according to the shear strain rate and volume fraction of suspended particles [33]. For example, the yield stress of the freshly mixed normal concrete with different volume fractions of aggregates varies depending on the volume fraction. As the volume fraction of aggregates increases, the frictional effect of particles becomes dominant over the hydrodynamic effects. An increasing

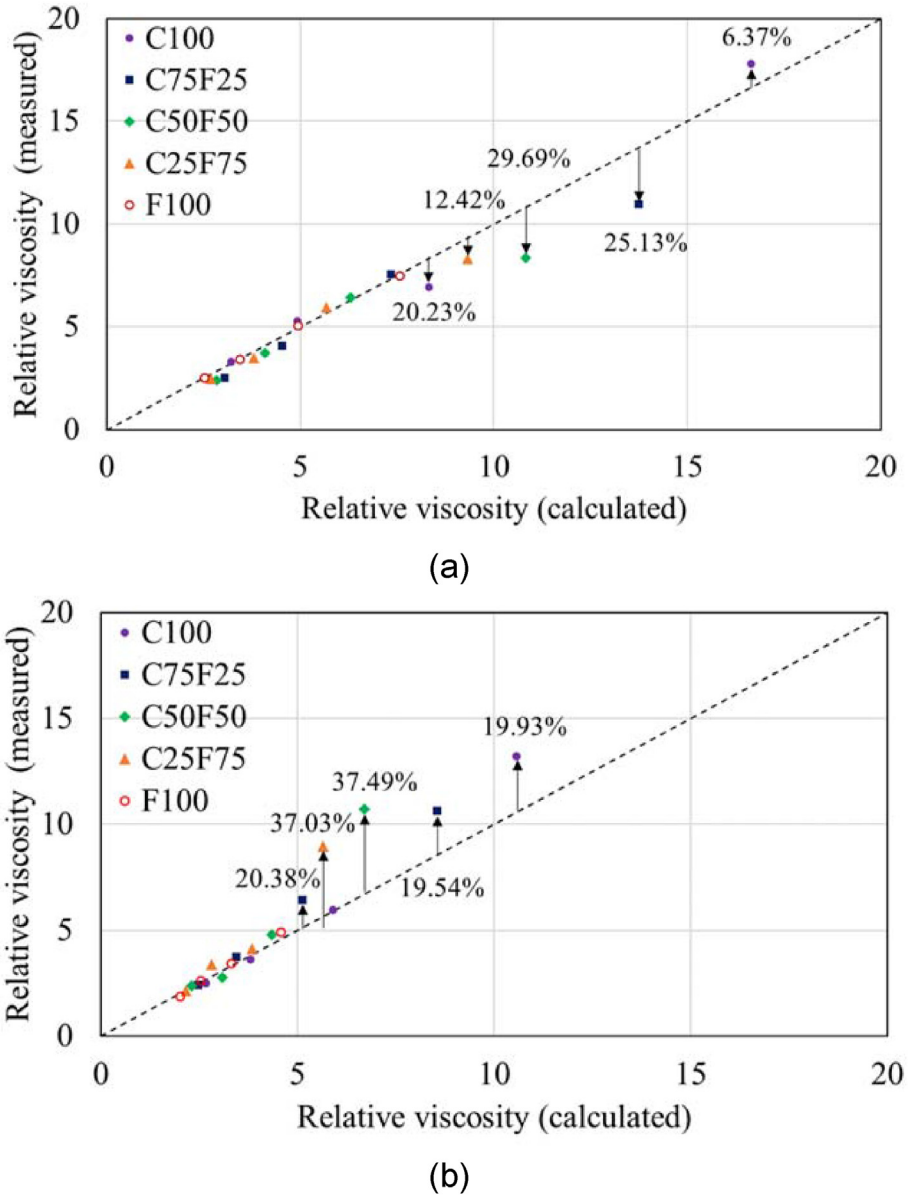


Fig. 11 – Comparison of the relative viscosity calculated using the Krieger–Dougherty equation with the measured relative viscosity at (a) 120 °C and (b) 140 °C.

friction between the particles, which is primarily due to the increase of the total surface area of filler particles per unit composite volume, induces the growth of both the yield stress and viscosity. In Fig. 11(b), the mixtures with relative viscosity above 5, most of which have 35% filler, show a higher relative viscosity than the calculated one. This is because the Krieger–Dougherty equation is derived without considering the frictional effect of particles and has been verified for soft suspensions, which have a lower volume fraction of particles. The sedimentation of filler and the frictional effect, which occurred mostly in suspensions with 35% filler, were likely to cause errors in the measurements of the rheology of the sulfur composites; the viscosity appears to be either overestimated or underestimated by 10–30%.

7. Conclusion

This study examined the effect of filler particle characteristics on the rheological behavior of fresh sulfur composites at 120 and 140 °C with a fundamental approach for the quantitative evaluation of the workability of sulfur concrete. The findings and conclusions can be summarized as follows.

1. The development of both the yield stress and viscosity of sulfur composites was mainly governed by the mixing temperature, filler volume, and cement ratio in the filler blend (mixture of fly ash and/or cement). Of them, the

temperature was the most influential on the rheology of sulfur composites.
2. With a certain surface area of the fillers, a higher ratio of cement in the filler blend induced a higher yield stress. However, the viscosity was mainly dependent on the total surface area of filler particles per unit volume of sulfur composite, and was not much affected by the cement ratio.
3. With the same filler type, the yield stress varied logarithmically with the filler volume ratio. The model constant of yield stress depended on the filler type. It was demonstrated that both the filler volume ratio and the filler type significantly affected the yield stress of sulfur composites.
4. The intrinsic viscosity of the filler blend composed of two types of fillers (i.e., fly ash and cement) was estimated using the Krieger–Dougherty model considering the volumetric ratio and intrinsic viscosity of each filler. The calculated and measured viscosities of the sulfur composites with the filler volume ratio equal to or less than 30% were in good agreement at both 120 and 140 °C.
5. The yield stress and viscosity at 140 °C were larger than at 120 °C, likely due to the increase of the concentration of longer sulfur polymers at 140 °C. With a filler ratio above 35%, however, the rheological properties of sulfur composites were less dependent on the mixing temperature. At 120 °C, the fresh modified sulfur had a weaker capability to suspend the filler particles, followed by a partial sedimentation of the filler particles. At 140 °C, the friction between the filler particles in the sulfur composites became substantial, causing an abrupt rise in both the yield stress and viscosity.
6. The conventional models for the rheological properties of suspension materials were well applicable to the sulfur composites with filler ratio below 30%. In addition, it appears that various suspension theories can be applied to the sulfur composites.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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