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# Facile preparation of sulfur polymer cement via low-temperature curing

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Sulfur has been considered as one of the promising construction materials because of its excellent mechanical and chemical properties, and ease of abundant production. However, there are some challenges for revealing high performance of sulfur materials due to their rigidity and shrinkage. While polymerized sulfur has been suggested as an alternative, the conventional process to synthesize sulfur polymer (SP) is unfavorable for practical applications due to the explosive reaction. Here, we report a facile route to prepare a SP without exothermic reaction through a post-curing process of the as-prepared SP. The reaction between sulfur and dicyclopentadiene (DCPD) was carried out within 10 min at 140 °C to form a precursor of the SP, followed by solidification at room temperature. The as-prepared SP was again heated to 120 °C for curing process. The cured SP cement (SPC) exhibited the decreased viscosity and increased bending strength compared to conventionally prepared SPC regardless of the reaction time.

Key words: Sulfur polymer, Cement, Viscosity, Bending strength.

## Introduction

Recycling sulfur, which is by-product produced from the petroleum refining process, is of great interest due to its abundant production and the limitations to use pure sulfur [1-3]. Residual sulfur has been recycled as road pavement and building materials due to its excellent mechanical strength and chemical resistance compared to conventional asphalt and concretes [4-6]. However, the use of sulfur has been limited by drawbacks such as rigidity and dimension instability derived from its intrinsic structure [7]. Sulfur has been used as the form polymerized with olefin modifiers, such as styrene, propylene sulfide, and dicyclopentadiene (DCPD) to impart a structural flexibility in its molecular unit. When the sulfur is heated above its melting temperature (119 °C), the sulfur eight-ring ( $S_8$ ) with crown structure are opened and form biradicals from the both chain ends. The reactive biradicals could covalently bond to the olefin modifiers, resulting in the

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stable, linearized sulfur-rich molecules [8-11]. The polymerized sulfur provide improved mechanical flexibility and dimensional stability over pure sulfur. Moreover, the sulfur polymer (SP) maintain the intrinsic chemical resistance and excellent hydrophobicity of pure sulfur, in spite of a change in chemical structure of sulfur [12-14]. Especially, among the modifiers, the DCPD has been widely investigated to modify the sulfur due to the high yield and efficiency of polymerization. However, the polymerization between the radicals of sulfur and DCPD leads to an extremely exothermic reaction [15, 16]. The explosive reaction restricts the use of sulfur as polymerized form due the reaction instability. For example, although the SP gained improved mechanical reliabilities by polymerization, applying this material in practical fields of construction, which requires the mass production, has been limited by the dangerousness of the reaction. To solve these problems, Kim et al. reported the use of DCPD with high fraction of oligomer for modification of sulfur. The oligomeric DCPD reduced and delayed the explosive reaction between sulfur and DCPD molecules. However, the exotherm remained with the increased content of modifier and reaction temperature [17]. Yu et al. reported that the exothermic reaction between sulfur and DCPD was effectively suppressed by

addition of pyridine in spite of the increased content of DCPD by 30 wt%. However, the existence of residual pyridine in the completely polymerized SP cause the offensive smell, resulting in critical harmfulness to human body. In order to effectively exploit the attractive properties of SP, it would be challenging to find approach for leading the reliable condition by suppressing the exothermic reaction of sulfur and DCPD.

In this work, we report a facile method to prepare a SP with stable reaction conditions by curing of the SP. The SP, which was synthesized in minimum reaction time to form a precursor, was solidified and cured at the given temperature for curing. The cured SP provided decreased viscosity with similar bending strength compared to the conventionally prepared SP.

## **Experimental**

Sulfur (99.9%) and silica powder was purchased from Samchun Chemical, South Korea. DCPD with an

oligomer of more than 80% was purchased from Kolon Industries, South Korea. SP was prepared according to our previous procedure [18]. Briefly, 100 g of molten sulfur was mixed with 3 g of dicyclopentadiene (DCPD) under vigorous stirring at 140 °C. The reaction time was varied from 10 to 300 min. For curing of SP, the SP synthesized during 10 min was solidified at room temperature, followed by curing in an incubator at 120 °C.

SPC was prepared by mixing SP with silica powder as filler through conventional melt mixing process. Before mixing, the silica powder was pre-heated at 100 °C to remove the moisture. The pieces of SP were put into the homemade mixer and heated at 120 °C to achieve the melting state. The pre-heated silica powder was added to the molten SP and further mixed for 5 min by a shear force. Finally, the SPC sample was fabricated by pouring the SP/silica mixture into the mold with the given size and cooled down.

The spectroscopic data was characterized using fourier transform-infrared spectroscopy (FT-IR, Perkin-



Fig. 1. (a) FT-IR spectra of sulfur and SP, (b) DSC traces and (c) melting temperatures of sulfur, cured sulfur, SP, and cured SP.



**Fig. 2.** (a) Photographs of sulfur, SP, and cured SP with an increase of curing time. SEM images of (b,c) sulfur, (d,e) cured sulfur, (f,g) SP, and (h,i) cured SP, respectively.

Elmer FTIR system Spectrum-GX). The thermal properties were analyzed using differential scanning calorimetry (DSC, ULVAC Sinku-Riko DSC9400). The morphology and the microstructures was characterized using a field emission-scanning electron microscope (FE-SEM, Inspect F). The viscosity was measured in a chamber jacketed with a heater at 120 °C using a viscometer (Brookfield DV2+). The bending strength was evaluated using a universal testing machine (UTM, INSTRON 4465).

## **Results and Discussion**

The chemical structure of the synthesized SP was analyzed by FT-IR. As shown in Fig. 1(a), the peaks assigned to the S-C bands at 1,200 and 2,950 cm<sup>-1</sup> were observed, demonstrating that the reaction between sulfur and DCPD was completed. After the chemical modification, a change in characteristic transition temperatures were observed as shown in Fig. 1(b). The DSC traces exhibited that the  $\alpha$  to  $\beta$  phase transition temperature of the sulfur was decreased from 96 to 119 °C by the ring opening reaction of sulfur. The melting temperature of the as-synthesized SP was also decreased up to approximately 116 °C, as shown in Fig. 1(c). However, the cured SP exhibited a slightly increased melting temperature of approximately 118 °C, which could be explained by the rearrangement of SP molecules [19].

The morphologies of the SP were characterized as a function of curing time as shown in Fig. 2. The SP exhibited a typical yellowish colored pristine sulfur. With an increase of curing time, the SP exhibited a prominent color change to brown, which is generally observed in the SP with high DCPD content [20]. The pristine sulfur showed large size of alpha crystal ( $S_{\alpha}$ ) with an orthorhombic structure. After polymerization, SP in the fractured side exhibited dense morphology without any characteristics of orthorhombic or monoclinic crystals, and the micropores with a wide distribution of diameter were formed. By curing of SP, the microstructures became denser and hardened, and the size of pores was reduced.

Based on the time to form a precursor of SP, the continuous polymerization and curing were examined to compare the viscosity and bending strength. The cured SP was fabricated via polymerization for a minimum time of 10 min at 140 °C to form the precursor, followed by solidification and curing at 120 °C as shown in Fig. 3(a). For comparison, the conventional SP was fabricated at 140 °C for given times. In the conventional pavement applications, it is needed to use the materials with low viscosity to possess facile workability. In our experiments, the viscosities of as-polymerized SP and cured SP were measured at 120 °C, which is the temperature to the materials enable to mix with other fillers as shown in



**Fig. 3.** (a) Temperature plots for preparation of SP via curing and polymerization, (b) Viscosity of SP and cured SP at 120 °C, (c) Bending strength of SP and cured SP.

Fig. 3(b). The cured SP prepared below 150 min exhibited slightly lower viscosity compared to that of the as-polymerized SP. With an increase of reaction time above approximately 150 min, the viscosity of the as-polymerized SP rapidly increased by 70 cP for 190 min. Meanwhile, the viscosity of the cured SP exhibited a linearly increasing trend with the reaction time, resulting in 60 cP for 310 min due to the increased interaction of the SP molecules.

The bending strength of the conventional and cured SP were evaluated as a function of reaction time as shown in Fig. 3(c). Above 60 min, the SP exhibited slightly increased bending strength, and the value was reached up to approximately 0.25 MPa after reaction of 300 min. Similarly, the cured SP exhibited an increase in bending strength with increasing reaction time, in spite of a mild thermal treatment compared to conventional polymerization of SP.

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**Fig. 4.** Bending strength of SP/silica and cured SPC as a function of reaction time. The curing of SPC was performed 5 hrs using the each as-polymerized SP at the given times.

The bending strength of the cured SPC was evaluated as shown in Fig. 4. The SPC was prepared through meltmixing to inhibit surface subsidence, which occurs by a phase transition of sulfur during natural cooling. In this experiment, curing of the SP was performed for 300 min after polymerization during the given time (10, 20, 30, 60, and 120 min, respectively). The conventional SPC exhibited negligible bending strength values at insufficient polymerization time below 30 min. However, the bending strength of these samples was remarkably increased above 0.6 MPa through curing of 5 hrs. At 60 and 120 min of polymerization, the conventional SPC exhibited the bending strength of approximately 0.54 and 0.66 MPa, respectively. After curing of these samples, the bending strength was slightly increased by approximately 0.68 MPa. It is ascribed that the SP was prepared with sufficient polymerization degree to reveal mechanical reliability after 60 min. Consequently, considering the absence of strength of the SP prepared within 30 min, the low temperature curing is useful to apply these materials in actual construction field because the facile process reduces efficiently the reaction temperature. For example, it is possible to use extremely short reaction time of 10 min, followed by curing at low temperature to avoid the highly exothermic reaction, which directly linked to reliable production of SP as well as safety for working.

#### Conclusions

In conclusion, we demonstrated a straightforward strategy to prepare a SP by a two-step method including polymerization and curing. The SP was cured at low temperature, enabling stable reaction of the polymer without exothermic reaction between sulfur and DCPD. The cured SP showed similar bending strength compared to the conventionally prepared SP as well as decreased viscosity, which provides workability for the operator. Moreover, the SPC prepared at various reaction times revealed a restoration of bending strength by curing of the SP. The fabrication process can serve as a universal procedure to control the stable polymerization of sulfur.

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