Thermal stability change of insoluble sulfur by heat treatment and its mechanism study

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Abstract

Insoluble sulfur (IS) used as a vulcanizing reagent of rubber is prepared by thermal ring-opening polymerization of sulfur ($S_8$). Enhancing its thermal stability and content ratio (yield) is important for industrial production of IS. The post-heating process at a high temperature of 70°C or 90°C of the mixture of IS and $S_8$ enhanced the thermal stability of IS and reduced the yield of IS. While the process at 30°C enhanced its thermal stability and maintained its yield. Since the thermal stability of IS is considered to be closely related to the chain length of polymer sulfur, a method for determining the chain length of IS was investigated by quantifying the amount of electron spin of radicals from sulfur estimated from electron spin resonance (ESR) measurement. We confirmed that the long-period post-heating process at 30°C induced high thermal stability without reducing the yield of IS due to growth of the sulfur polymer chains.

**Keywords** Insoluble sulfur, polymer sulfur, rubber vulcanizing agent, ESR, thermal stability, chain length
Introduction

Vulcanization is a key process in rubber manufacturing, such as tire production. 1 Insoluble sulfur (IS) is used as a vulcanization reagent. 2 IS which has long linear sulfur chain and is insoluble in carbon disulfide that is a good solvent for sulfur ($S_8$) is known as an allotrope of sulfur. 3, 4 Rubber and IS are mixed and kneaded each other under high temperature condition (80-120°C) 5 for vulcanization. In the vulcanization process, some amount of the IS is decomposed into $S_8$. IS is known to have a radical at the end of their polymeric sulfur chains, 6 and gradually returns to $S_8$ in the temperature range over 50°C as a result of chain cleavage by the radicals. 7 The produced $S_8$ is soluble into the rubber and migrate to the rubber surface. This phenomenon is called “blooming”, and is a serious problem that prevents good adhesion between the vulcanized rubber and tire cords. 8 There is a need in the tire production process to enhance thermal stability of IS.

Several methods have been implemented for producing IS, including a method of quenching melted sulfur. 9,10 Any effective methods have not been developed that can convert all the amount of sulfur used as a raw material into IS. Extraction process of unreacted $S_8$ with carbon disulfide is essential for commercial production of thermally stabilized IS. The ratio of the weight of the produced IS to the weight of $S_8$ as the raw material is defined as the content ratio (i.e., yield). The enhancement of the content ratio of IS is also one of the significant viewpoints for its industrial productivity.

Previously, we confirmed that several post-heat treatment processes (at 70 °C or 90 °C) of the mixture of IS and $S_8$ enhanced the thermal stability of IS and reduced the content ratio of IS. 11 We also reported that more thermally stabilized IS shows endothermic peak at higher temperature in the differential scanning calorimetry (DSC) chart. 11 Jiménez-Mateos et al. explained that the endothermic peak is due to polymer sulfur (IS) melting and polymer sulfur
chain breakage. 12 The melting point of polymers is generally associated with the molecular weight, i.e., a polymer with higher melting point has higher molecular weight. For example, Takahashi et al. reported that increasing the molecular weight of polyimide, which is a high heat-resistant polymer, elevates the melting point and the heat resistance of the polymer. 13 Taking the results into account, it is considered that chain length (molecular weight) of IS (polymer sulfur) is closely related with its thermal stability. However, IS is insoluble in normally used solvents, 14 and the conventional molecular weight measurement techniques, gel permeation chromatography, osmometric measurement, or light-scattering method, are not available. Tobolsky and Eisenberg estimated the chain length of polymer sulfur from the relationship between temperature and viscosity of the molten sulfur. 15 Olkhov and Jurkowski reported that they measured temperature-cycled deformation of an IS pellet as a function of temperature and time by thermomechanical analysis technique and estimated the chain length of polymer sulfur. 16 Gardner and Fraenkel calculated the chain length of polymer sulfur in molten sulfur from the ESR results. 17 These reported techniques is unsuitable for continuously estimating variation of the chain length of IS in solid state.

In this present work, we confirmed variation of the thermal stability and the content ratio of the IS during post-heating process at low temperature (30°C). We also measured the amount of radicals from sulfur, hereinafter, referred to as "sulfur radicals", in solid IS by the ESR technique and estimated average the chain length of IS by end group determination. By combining both results, we indicated the variation mechanism of the thermal stability and the content ratio of IS by the post-heating process.

Experimental
Sample preparation

Sulfur (S₈, Showa Shell Sekiyu K. K., Japan) was used in the experiments described below. Sulfur (400 mg) was added into a Pyrex glass tube (5 mm in outer diameter). The glass tube was pre-heated in the home-made furnace (as shown in Fig. S1 (Supporting Information)) from room temperature to 120°C. After the sulfur melted in the glass tube, the temperature of the furnace was elevated gradually from 120°C to 260°C for 30 minutes and maintained at 260°C (the temperature of main-heating process) for 5 minutes. Then the glass tube was quenched into a water bath at 40°C for 15 minutes. After the quench process, the glass tube was immersed into another water bath (at 65°C) for 90 minutes. The post-heating process at 30°C, 70°C, and 90°C for various periods was performed with the glass tubes in a convection oven (DRM 320 DD, ADVANTEC, Japan). The resulted sulfur in the tube is referred to as Sₓ (temperature of post-heating process, post-heating period).

Measurement of content ratio of IS in the heat-treated sulfur

The glass tube was cut to collect Sₓ. Sulfur (S₈) in the collected Sₓ was extracted with carbon disulfide (ca. 50 mL) (25 °C, 1 hour). The solubility of S₈ in carbon disulfide is reported as 24.2g of S / 100 g solvent (22°C). Thus, S₈ in the collected Sₓ was completely removed by this extraction process. The content ratio (X) of insoluble sulfur (IS) was calculated according to Eq. (1).

\[ X(\%) = \frac{W_a}{W_b} \times 100 \]  

(1)
where, \( W_a \) is the weight (in milligrams) remaining after extraction with carbon disulfide; \( W_b \) is the weight (in milligrams) of \( S_x \) before the extraction process.

The IS obtained by extracting \( S_x \) (temperature of post-heating process, post-heating period) with carbon disulfide is referred to as \( S_{ins} \) (temperature of post-heating process, post-heating period).

**Measurement of the thermal stability of IS**

Insoluble sulfur (IS) undergoes a thermal transition by heating and gradually changes to stable soluble sulfur (\( S_8 \)). The percentage remaining when IS is heated at a given temperature and time is defined as thermal stability. \(^{19}\) JIS K 6222-1 procedure (conventional method) is used for evaluating thermal stability of IS. \(^{20}\) The detail of this procedure is as following. A sample (IS, at least 10 grams) is precisely weighed and heated in liquid paraffin at 105 °C for 15 minutes, then washed with carbon disulfide. The residual ratio (in %) of the sample is calculated from the residual weight of the washed sample and indicates the thermal stability of the sample. Due to the limitations of sample weight in our experimental conditions the procedure was unavailable. Previously, we reported that thermal stability of IS can be evaluated by using DSC technique with very small amount of samples (in few milligrams). \(^{11}\) An IS sample which is pre-determined its thermal stability with the conventional method, JIS K 6222-1, was set in a DSC instrument and recorded its thermal behavior. A clear relationship between the peak temperature of the endothermic peak in the DSC chart and the pre-determined thermal stability of IS was observed as shown in Fig. S2 (Supporting Information). We used this relationship to determine thermal stability of all of samples in this investigation.
**DSC measurements of IS**

DSC curves were recorded with a DSC7200 (Hitachi High-Tech Science, Japan). The sample was put in an aluminum sample pan and sealed with a crimper. The sample was heated from 60°C to 140°C with a heating rate of 3°C/min in nitrogen atmosphere (ca. 50 mL/min). The DSC system was calibrated with indium (m.p.= 429.6 K; ΔH=28.54 J/g).

**XRD measurements of IS**

SmartLab (RIGAKU, Japan) was used for X-ray diffraction (XRD) analysis of IS with Cu Kα radiation, λ = 0.154059 nm, tube voltage of 45 kV, tube current of 200 mA, and scanning speed at 10 deg/min.

**ESR measurement of IS and determination of electron spin amount**

The sample was prepared by adding sulfur (50 mg) in a Suprasil quartz glass tube (5mm in outer diameter) and performing a series of heat treatments in air under the same condition as those for the thermal stability experiments. The ESR spectra were measured on an X-band spectrometer (JES-RE1X, JEOL, Japan) at room temperature. The typical measurement conditions were as follows, central magnetic field: 335 mT, sweep width: 30 mT, modulation depth: 0.34 mT, microwave power: 1 mW, where it is confirmed that ESR signals of the sulfur sample and the Mn²⁺/MgO standard sample are not saturated. The absolute value of the amount of spin for the “sulfur radicals” was determined by ESR measurements together with an internal standard (i.e. secondary standard) sample of MgO doped with Mn³⁺ (Mn²⁺/MgO). Under the present spectrometer settings, three of six peaks due to the Mn²⁺/MgO sample were observed with a single of “sulfur radicals”, corresponding to the electronic transitions at \( m_l = -3/2 \) and
±1/2 in hyperfine structure of $^{55}$Mn$^{2+}$ due to the $I = 5/2$ nuclear spin. Each of the three peaks was doubly integrated and their average was compared with the “sulfur radicals”. The spin number of the Mn$^{2+}$ signal in the Mn$^{2+}$/MgO was calibrated to be $2 \times 10^{13}$ spins/peak by using a primary standard sample, a solution of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, Aldrich, sublimation purification, purity 98.5%) / benzene ($1 \times 10^4$ mol/L). Unexpected inclination of the baseline was visible in the observed spectra. Before the double integration, then, the baseline of the singly integrated spectra was reproduced by an interpolating cubic spline technique including more than 15 knots, and the calculated baseline was subtracted from the observation to correct the spectral line shape. Finally, the spin number of the “sulfur radicals” $E$ (spins/g) in the sample was calculated using Eq. (2).

$$E \text{ (spins/g)} = \frac{W_c}{W_d \times W_{Mn}} \times (1000/50), \quad (2)$$

where, $W_c$ is the value of doubly integrated ESR signal for “sulfur radicals”; $W_d$ is the average value of doubly integrated three peaks of Mn$^{2+}$/MgO; $W_{Mn}$ is the electron spin number of Mn$^{2+}$/MgO ($= 2 \times 10^{13}$ spins/peak).

**Results and Discussion**

**Structure and thermal properties of IS**

Fig. 1 shows the XRD patterns of S$_{ins}$ (30°C, 0 h) and insoluble sulfur (IS) (commercially available product). The main peaks in the figures are assigned with reference to the previous
Fig. 1(a) and (b) indicate that the structure of $S_{ins}$ (30°C, 0 h) is very similar with that of IS (commercially available product). IS (commercially available product) has been confirmed not to contain $S_8$. Therefore, $S_8$ is not included in $S_{ins}$ (30°C, 0 h) due to the extraction with carbon disulfide.

The thermal properties of $S_{ins}$ (30°C, 0 h) were checked by DSC measurements. Fig. 2 shows the DSC charts of $S_{ins}$ (30°C, 0 h), IS (commercially available product), and sulfur ($S_8$). As shown in Fig. 2 (c), $S_8$ has an endothermic peak attributed to the transition from orthorhombic sulfur $\alpha$-$S_8$ to monoclinic sulfur $\beta$-$S_8$ appears around 105°C, and an endothermic peak attributed to melting appears around 120°C. It is reported that the DSC chart of IS (commercially available product) has an endothermic peak at 117-125°C due to its melting, and an exothermic peak at 127-134°C due to the reformation of sulfur. As shown in Fig. 2(a), $S_{ins}$ (30°C, 0 h) had an endothermic peak at 113.5°C and an exothermic peak at 117.6°C. The results also support that $S_{ins}$ (30°C, 0 h) is IS, i.e., polymer sulfur.

Estimation of chain length of IS from quantitative measurement of “sulfur radicals” with ESR

IS has linear polymer-like structure, connecting many sulfur atoms each other. However, there are few investigations on estimation of chain length of IS. Although the measurement of the chain length of molten sulfur has been reported, no method for continuously following the change in the chain length in the solid state has been reported. We estimated chain length of solid-state IS by using quantitative measurement of “sulfur radicals” with ESR technique as follows. We assumed that radicals exist at the both terminals of all polymeric sulfur chains in IS, thus there are two radicals in one sulfur chain. It is possible to calculate the average chain length
of polymeric sulfur by dividing the number of sulfur atoms present in the sample by the amount of electron spin with the measurement result of ESR. From the hypothesis, the average sulfur chain length ($L$) of IS is represented by the following the formula.

$$L = \left( \frac{X}{100} / \frac{32.07 \times N_A}{E \times 1/2} \right),$$

(3)

where, $X$ is the content ratio (in %) of IS contained in $S_x$; $N_A$ is Avogadro's number; $E$ (in spins per gram) is the amount of electron spin of IS obtained by the Eq. (2). The amount of electron spin was halved because it was assumed that the radicals exist at both terminals of one polymeric sulfur chain. The preparation procedure was performed twice under the same conditions and the average chain length was calculated. For example, the chain length of $S_{\text{ins}}$ (30°C, 0 h) was $1.599 \times 10^6$ and $2.226 \times 10^6$, respectively. The average number of the sample was $1.913 \times 10^6$. This value is almost consistent with the value reported by Gardner and Fraenkel, the average sulfur chain length $(1.5 \pm 0.7) \times 10^6$ at 171°C calculated from the electron spin amount of molten sulfur. We used the method to estimate the average chain length of IS in the other samples.

**Effects of post-heating process on thermal stability and content ratio of IS**

It has been reported that IS gradually returns to sulfur ($S_x$) in the temperature range of 50°C or higher due to the reaction of radicals at the end of the sulfur chain. Our studies also
suggested that post-heating processes (applied temperature and period) for Sx affect thermal stability and content ratio of IS. Fig. 3 illustrates the results of post-heating process for Sx. The hatched square in the figure indicates required quality of IS for commercial use. The required content ratio of IS was estimated from the references to the reported ratio of Sµ (insoluble sulfur) in molten sulfur. 7 23

As shown in Fig. 3, post-heating process at 70°C for 16 h or 90°C for 1.5 h enhanced the thermal stability and reduced the content ratio of IS. While, the post-heating process at 30°C for longer post-heating process period improved the thermal stability of IS without reduction of its content ratio.

It has been reported that the cleavage of polymer sulfur chains provides some amount of shorter polymer sulfur chains and S8. 21 According to the reaction mechanism, variation in the thermal stability and the content ratio of IS with the post-heating process are estimated as follows.

Eq. (4) indicates the reaction between the radicals on the terminals of the IS chains. It is the chain lengthening reaction of the polymeric sulfur chain. Generally, such chain lengthening reaction enhances the thermal stability of polymer materials. 13

\[
\cdot S - S_{x1} - S\cdot + \cdot S - S_{x2} - S\cdot \rightarrow \cdot S - S_{x1} - S - S - S_{x2} - S\cdot
\] (4)

Eq. (5) is the chain cleavage reaction of polymeric sulfur chain and formation of S8 bi-radical. The chain scission reaction generates shorter linear polymer sulfur with bi-radicals and S8.
bi-radical. The $S_8$ bi-radical forms the eight-membered ring sulfur (soluble in carbon disulfide) by intramolecular recombination as indicated in Eq. (6). The occurrences of the reactions (Eqs. (5)) and (6)) reduce the thermal stability and the content ratio of IS.

\[
\cdot S - S_y - S\cdot \rightarrow \cdot S - S_6 - S\cdot + \cdot S - S_{y-8} - S\cdot \tag{5}
\]

\[
\cdot S - S_6 - S\cdot \rightarrow S_8 \tag{6}
\]

To confirm the effect of lower post-heating process (at 30°C) on IS and the mechanism of enhanced the thermal stability and the content ratio of IS, variation of the amount of spin in the $S_x$ (30°C, various period) was measured with ESR technique. Fig. 4 shows the ESR results of $S_x$ (30°C, 0 h), $S_x$ (30°C, 20 days), and $S_x$ (30°C, 40 days). The depression of the ESR signal intensity was observed with lengthened post-heating period. Variation of average sulfur chain length estimated from the amount of spins in the samples are illustrated in Fig. 5. Longer post-heating period at 30°C provided longer polymeric sulfur chains in the IS samples. It suggests that the reaction, Eq. (4), chain progress reaction mainly proceeds in the post-heated process at 30°C. The post-heating processes at 70°C or 90°C provided shorter sulfur chain in the IS samples. It suggests that the chain cleavage reaction and the formation of $S_8$ bi-radical mainly proceed in the post-heating process at higher temperature as indicated in Eqs. (5) and (6).

Effects of post-heat treatments on the thermal stability and the content ratio of IS are induced by two reactions, chain cleavage and chain progress reactions. At high temperatures
(above 70°C), main chain scission occurs preferentially to produce cyclic sulfur ($S_8$). However, under mild condition of 30°C, the chain scission is suppressed, so that chain length is extended by intermolecular recombination reaction between radicals. The post-heating process at lower temperature, 30°C for a long time (20-40 days) is suitable to preparation of IS with high thermal stability and inhibition of formation of $S_8$. Application of the post-heating process at lower temperature to industrial production of IS needs searching the conditions that are more efficient in a shorter time. We are going to progress this investigation for searching highly efficient conditions that enhance the content ratio and the thermal stability of IS.

Conclusions

We estimated the mechanism of the decrease in the content ratio of insoluble sulfur (IS) and the increase in thermal stability, by post-heating process of IS, and confirmed the reaction mechanism by calculating the sulfur chain length from the ESR measurement results. At first, we investigated the method of calculating the chain length of sulfur polymer by measuring ESR of solid IS and quantifying the amount of electron spin of the radicals from sulfur. We improved thermal stability without decreasing the content ratio of IS by post-heating process the mixture of IS and sulfur ($S_8$) for a long period at low temperature (30°C). Subsequently, we described the estimated the mechanism of variation in the thermal stability and the content ratio of IS with post-heating process of IS. To confirm this mechanism, we investigated the change in the average sulfur chain length of IS by measuring ESR over time with post-heating process of IS.
Post-heating process at a low temperature of 30°C is suitable to preparation of IS with high thermal stability and inhibited formation of sulfur ($S_8$).

**Supporting Information**

Fig. S1 (Supporting Information) shows Illustration of the home-made furnace for this investigation. Fig. S2 (Supporting Information) shows Relationship between endothermic peak temperature in DSC curve and thermal stability of insoluble sulfur (IS). This material is available free of charge on the Web at [http://www.jsac.or.jp/analsci/](http://www.jsac.or.jp/analsci/).
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**Figure Captions**

Fig. 1 X-ray diffraction patterns of (a) \(S_{\text{ins}}(30^\circ \text{C}, 0 \text{ h})\) and (b) insoluble sulfur (commercial product). Cu K\(\alpha\) as the source (wavelength \(\lambda = 0.154059 \text{ nm}\)).

Fig. 2 DSC curves of (a) \(S_{\text{ins}}(30^\circ \text{C}, 0 \text{ h})\), (b) insoluble sulfur (commercial product) and (c) sulfur (\(S_8\)). Heating rate was at 3\(^\circ\)C/min.

Fig. 3 Variation of thermal stability and content ratio of insoluble sulfur with post-heating process. Post-heating condition was at 30\(^\circ\)C for 9 days, 23 days, and 37 days, 70\(^\circ\)C for 16 hours, and 90\(^\circ\)C for 1.5 hours. The hatched square in the figure indicates required quality of insoluble sulfur for commercial use.

Fig. 4 ESR signals were observed at room temperature for \(S_x(30^\circ \text{C}, t)\), \(t = 0, 20, \text{ and } 40 \text{ days}\).

Fig. 5 Variation in chain length of insoluble sulfur with post-heating process period at 30\(^\circ\)C, 70\(^\circ\)C and 90\(^\circ\)C. The numbers (%) in the figure are the thermal stability of insoluble sulfur prepared under the same conditions.
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