Enhancement of transient thermal stability and flame retardancy of hydrophobic silica xerogel composites via carbon family material doping

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ABSTRACT
In this study, we investigated the influence of the addition of carbon materials on the heat resistance and flame retardancy of silica xerogels. A mixed dispersion prepared by adding 0.1 to 2.5 wt% each of the carbon materials, graphene oxide (GO), poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS), and carbon black (CB) to waterglass (SiO$_2$ 6%) was used as the raw material. By adding acid to this dispersion, a sol-gel reaction was carried out and the hydrogel obtained was hydrophobized with hydrochloric acid and a mixed solution of siloxane/isopropylalcohol. Finally, novel carbon-silica xerogel composites (SX-Carbon-X) were prepared via ambient pressure drying. Similarly, glass-fiber-reinforced silica aerogel composite sheets (GFRSX-Carbon-X) were prepared by impregnating glass fibers with sol. The bulk densities of the samples obtained ranged from 0.204 to 0.217 g/cm$^3$, their thermal conductivities ranged from 0.0187 to 0.0203 W/(m · K). As the amount of carbon material added was increased, the thermal decomposition temperature of the SX-Carbon-X shifted to higher temperatures. In the cone calorimeter test of GFR-SX-Carbon-X, moreover, adding at least 0.5% of the carbon material significantly reduced the combustion time and the peak heat release rate (PHRR), and the flame retardancy improved remarkably.

KEYWORDS
silica xerogel; waterglass; carbon; thermal stability; flame retardancy

1. Introduction
Silica aerogel, a gel with a low-density porous structure composed of silica nanoparticles several tens of nanometers in diameter, was first reported by S. K. Stilke in the 1930s [1]. Highly uniform silica aerogels can be obtained from precursor raw materials such as waterglass and tetra-alkoxysilane. Silica aerogels have a continuous pore structure on a scale of several tens of nanometers that suppresses heat transfer by gas molecules inside the pores, and hence, shows the lowest thermal conductivity (0.012 to 0.020 W/(m · K)) among all solid materials. Silica aerogel is therefore expected to be applied in various fields as a high-performance heat-insulating material [2]. To date, inorganic aerogels composed of inorganic oxides such as silica, alumina and titania, organic aerogels composed of organic polymers such as resorcinol/formaldehyde aerogel (RF aerogel), and many porous materials such as carbon aerogels have been reported [3]. Although silica aerogel is a very attractive material for practical use from the perspective of economic efficiency of raw materials, there are many problems yet to be solved. These include high production costs, low mechanical strength, and lower heat resistance and flame retardancy compared with generic heat-insulating materials.

Assuming that aerogel is used in the medium- to high-temperature range (300°C or above), the challenges include the reduction of thermal conductivity and improvement of heat resistance and flame retardancy. As shown by Equation (1), thermal conductivity is the sum of heat transfer by solids, convection of gases, and heat transfer by radiation:

\[ \lambda = \lambda_s + \lambda_g + \lambda_r \quad (1) \]

\[ \lambda_r = 16\alpha \sigma T^3/(3\beta e(T)) \quad (2) \]

To reduce thermal conductivity, it is necessary to suppress the heat transfer $\lambda_r$ owing to radiation, which increases in proportion to the cube of the temperature in the equation [4]. As shown in Equation (2), the radiation heat transfer $\lambda_r$ is the Boltzmann constant, $n$ is the refractive index, $T$ is the temperature of the material, and $\beta T$ is the Rosseland mean extinction coefficient. Zeng et al. theoretically suggest that heat transfer by infrared rays can be suppressed by adding carbon that absorbs infrared rays to silica aerogel [5]. To date, studies aimed at reducing radiation heat transfer and achieving low thermal conductivity by adding TiO$_2$ [6,7], Y$_2$O$_3$ [8], C [9], and CO$_2$ [10] have been conducted. The current study attempts to improve the thermal stability and flame retardancy of silica aerogels by adding carbon family materials to the raw material dispersion.
Further, it is also important to improve the heat resistance and flame retardancy of silica aerogels. As many silica aerogels reported today are hydrophobized in the medium- to high-temperature range (300 °C or higher), the organic hydrophobic group decomposes thermally and becomes hydrophilic [13,14]. At this instant, the organic functional group generated by thermal decomposition becomes an inflammable gas and, in some cases, the heat-insulating material may start burning and smoking [15]. Assuming that the aerogel is temporarily exposed to a temperature range of 300°C or higher, therefore, it is necessary to improve its transient heat-resistance. As thermal decomposition of the organic functional group cannot be avoided as long as it is subjected to hydrophobic treatment, it is important to delay the thermal decomposition of the hydrophobic group at least slightly. It has been reported that a cryogel obtained by freeze-drying an alcogel prepared from a hybrid material of waterglass and methyltrimethoxysilane (MTMS) has a heat resistance of 550°C [16,17]. Further, heat resistance is improved in a complex made by doping TEOS-based silica aerogel with novolac resin and GO [18,19]. In addition, although heat resistance and flame retardancy are not mentioned, Liu and Komarneni have reported carbon-silica aerogel and aerogel composites derived from tetramethoxysilane (TMOS) [20]. A new approach to improving the heat resistance of silica aerogel prepared from inexpensive waterglass raw material is desirable.

Recently, Gong et al. reported that the higher the molar ratio of the H$_2$O: TEOS, the lower the fire hazard associated with silica aerogel composites [21]. The combustibility of porous silica can be reduced to some extent by using organic fibers with high flame retardancy, such as carbon fiber or aramid fiber. However, organic fibers with high flame retardancy are generally expensive and uneconomical. A technique to improve the flame retardancy by using a generic, inexpensive inorganic fiber such as glass fiber is therefore desirable. If heat resistance and flame retardancy can be imparted to fiber-reinforced silica aerogel via a simple, inexpensive method, the possibility of application development for the medium- to high-temperature range may emerge.

The purpose of this study is to propose a simple, inexpensive method of imparting heat resistance and flame retardancy to waterglass-based glass-fiber-reinforced silica aerogel. Therefore, we examined the effect of adding various carbon materials to silica aerogel. As already reported in reduced graphene oxide (rGO) [22], we hypothesized that thermal decomposition of organic functional groups of silica aerogel can be delayed by utilizing the sublimation heat of a sublimating carbon material at high temperature. Simultaneously, as the carbon material undergoes a combustion reaction with O$_2$ molecules in a high-temperature atmosphere and produces CO$_2$, it is considered to function as a flame retardant by diluting combustible gases. Highly aromatic and sp$^2$ carbon-rich GO, PEDOT:PSS, and CB were therefore selected as candidates for heat-resistant/flame-retardant additives. As it is necessary to disperse the carbon materials uniformly into the raw material, namely waterglass, however, we selected carbon materials that are easily dispersible in water. As GO has excellent electronic properties, its applications in field-effect transistors, sensors, transparent conductive films, etc., are being investigated [23]. PEDOT:PSS is a well-known conductive polymer having excellent electronic properties, optical properties and heat resistance whose applications in antistatic films, transparent conductive films, and hole injection layers of organic light-emitting diodes and organic solar cells are being investigated [24,25]. CB has industrial use as a reinforcing material for rubber tires and a black pigment for paints and printing inks. To the best of the authors’ knowledge, verification of the effect of combining waterglass-based silica aerogel and the above-mentioned carbon material on the heat resistance and flame retardancy of silica aerogel has not been reported to date. In this study, we sought to impart heat resistance and flame retardancy to silica aerogel composite heat-insulating materials by preparing SX-Carbon-X and GFR-SX-Carbon-X using mixed dispersions prepared by adding 0.1 to 2.5 wt% of carbon materials to waterglass (SiO$_2$ 6%) and evaluating the product’s heat resistance and flame retardancy.

2. Experimental procedures

2.1. Preparation of hydrophobic carbon-silica aerogels (SX-Carbon-X)

Figure 1 shows the manufacturing procedure. An aqueous solution of 6% SiO$_2$ obtained by diluting waterglass (SiO$_2$ 28.95%, Na$_2$O 9.41%, molar ratio 3.2) with ultrapure water was used as the starting raw material [14]. For GO, PEDOT:PSS, and CB, a GO aqueous dispersion (4 mg/mL, Sigma Aldrich), AS-Q (Shin-Etsu Polymer), and Aqua Black (19.2 wt%, Tokai Carbon) were used, respectively. These carbon were materials added in advance to the SiO$_2$ in waterglass to make 0.1, 0.5, 1.0 and 2.5 wt% and irradiated with ultrasound waves for 5 min to prepare a mixed dispersion of waterglass and carbon materials. For the preparation of sol, concentrated hydrochloric acid (conc. HCl, Kanto Chemical) was added to waterglass to make 3.6 wt%. Although aging is usually performed to strengthen the silica framework, aging was not performed in order to shorten the process time. Subsequently, hydrogel was pulverized with a spatula and immersed in 6N hydrochloric acid (Kanto Chemical) for 60 min. The gel retrieved from
HCl was immersed in a mixed solution of octamethyltrisiloxane (Shin-Etsu Chemical) and 6.8 wt% isopropanol (IPA) (Kanto Chemical) and hydrophobized by heating at 60°C for 6 h. Drying was carried out for 2 h at 150°C under atmospheric pressure. The time required from preparation of the raw material to production of SX-Carbon-X was only 9.5 h in total.

2.2. Preparation of glass-fiber-reinforced carbon-silica xerogel composite sheets (GFR-SX-Carbon-X)

To prepare glass-fiber-reinforced silica xerogel with a uniform thickness and a structure with silica xerogel finely filling in the fiber, a unique method was devised (Figure 1). First, the sol solution was prepared in excess under the same conditions as above and placed in a resin container. The glass fibers (basis weight 70 g/m², size 120 mm×120 mm, fiber diameter 0.8–1.2 µm, thickness approximately 0.65 mm) were immersed in the sol solution for 1 min, to remove air and impregnate the fibers sufficiently with the sol solution. Subsequently, the workpiece was sandwiched between two PP films, and when the sol thickened, the thickness of the workpiece was regulated by passing it through an SUS biaxial roll (gap setting 1 mm). Subsequently, the workpiece was hydrophobized and dried under the same conditions as described above xerogel, and a sheet-like sample was prepared.

2.3. Characterization

The organic hydrophobic functional group present on the surface of the hydrophobic silica xerogel was examined using Fourier-transform infrared spectroscopy (FT-IR -4700, JASCO). The Raman spectrum was measured using a Raman microscope (NRS-5100; JASCO). The excitation light was measured using a 532 nm diode laser by integrating it twice for an exposure time of 30 s. The nanoporous structures of the SX-Carbon-X and carbon materials were studied by N₂ adsorption-desorption measured at 77K using a MicrotracBel BERSORP-MAX. The pore size distribution and pore parameters of SX-Carbon-X were calculated by the Brunauer-Emmitt-Teller (BET)

Figure 1. Experimental procedure for the preparation of SX-Carbon-X and GFR-SX-Carbon-X.
2.4. Evaluation of thermal conductivity and flame retardancy

The thermal conductivities of the GFR-SX-Carbon-X were measured using a heat flow meter (HFM436/3/1, Erich NETZSCH GmbH). As the prepared specimens were as thin as 1 mm, in order to assure accurate measurement of the heat resistance, a sheet-like specimen was sandwiched between heat-insulating materials of known thermal conductivity (extruded polystyrene form) and the measurement was carried out from the compound law \[26\]. Correlation of this method with the GHP method conducted for the same sample already been confirmed establishing it as a reliable measurement method. In order to evaluate the combustibility of GFR-SX-Carbon-X quantitatively, moreover, the cone calorimeter test (cone calorimeter III C3, TOYOSEIKI) was also conducted (Figure 2).

In the cone calorimeter test, combustion was carried out for 20 min using an electric spark as the ignition source while supplying radiant heat of 50 kW/m\(^2\) to a sample of 10 cm\(^2\). Water contact angle measurements were performed using a contact angle meter (Kyowa Interface Science, PCA-11) to evaluate the degree of hydrophobicity before and after the CCM test.

3. Results and discussions

3.1. Structural analysis

Figure 3(a-d) shows SEM images of bulk silica xerogel. These reveal that, as silica xerogel is formed from silica particles, there is no significant difference in the three-dimensional nanostructure of the xerogel owing to the 2.5% carbon doping. Figure 3(e-h) show TEM images of bulk silica xerogel. In both the samples, the mesh network structure of silica and a pore size distribution of several tens of nanometers were confirmed. Figure 4(a) shows photograph of prepared GFR-SX-Carbon-X (120 mm×120 mm). The sheet has the flexibility to return to its original shape, even if it is bent. Figure 4(b) shows

![Figure 2. Schematic view of a cone calorimeter.](image-url)
a SEM image of GFR-SX. As the space between the glass fibers is finely filled with silica particles from the silica xerogel, it is understood that the silica particles and glass fibers are bonded as planned.

### 3.2. Pore size distribution

As shown in Figure 5(a), the physical adsorption isotherms of all the samples showed a hysteresis loop (Type IV isotherms) corresponding to the characteristics of mesoporous materials. It was observed, moreover, that these isotherms are very similar to the isotherms of silica aerogel obtained via supercritical or atmospheric drying and exhibit a cylindrical pore shape (H1 type).

Figure 5(b) shows the pore size distribution. Although the average pore diameter of SX was 38 nm, the average pore diameter of SX-GO-2.5 was 30 nm and those of SX-PEDOT:PSS-2.5 and SX-CB-2.5 were 10 nm each, which showed that the average pore diameter decreased when SX was doped with 2.5% carbon material. Table 1 presents a list summarizing the pore parameters. The specific surface area of the nanocomposite tended to decrease with increases in the amount of carbon material added. While the specific surface area of SX was 535 m²/g, the specific surface areas of SX-GO-2.5, SX-PEDOT:PSS-2.5, and SX-CB-2.5 were 437 m²/g (△18%), 456 m²/g (△15%), and 429 m²/g (△20%), respectively. The pore volume of silica xerogels ranged from 1 to 2.5 cm³/g. Although this value appears to be relatively small, it is considered that the silica xerogels are greatly compressed during the adsorption process of N₂ gas, and the pore volume is considerably underestimated. In this study, we do not aging hydrogels to synthesize silica xerogels in a short time. Therefore, it is thought that is softer than the aged gel. As carbon material is present inside the pore spaces of the silica xerogel, it is considered that pore characteristics such as the average pore size distribution and specific surface area vary depending on the concentration added.

### 3.3. FT-IR absorbance spectra and raman spectra

Figure 6(a) shows the FT-IR spectra of SX-Carbon-X. In all the samples, absorption corresponding to the C-H bond derived from the hydrophobic group was observed at 2962 cm⁻¹ and 2905 cm⁻¹, and absorption corresponding to the Si-C bond was observed at 1255 cm⁻¹ and 843–757 cm⁻¹. Silica xerogel hydrophobized with octamethyltrisiloxane contains a trimethylsilyl (TMS) group.
and a dimethylsilyl (DMS) group \[12,14\]. The absorption in the vicinity of 757 cm\(^{-1}\) belongs to the Si-C of TMS and the three absorptions at 1255, 843 and 805 cm\(^{-1}\) belong to the Si-C of TMS and DMS. The strong peaks near 1049 and 442 cm\(^{-1}\) belong to absorption of Si-O-Si bond. Further, with the addition of carbon material, the absorption intensity of several peaks increased. The absorption in the vicinity of 1049 and 950 cm\(^{-1}\) is attributed to Si-O-C bond, for example, and the absorptions near 843, 805 and 757 cm\(^{-1}\) are attributed to C-H of the benzene ring. The possibility of carbon material and silicic acid undergoing a dehydration condensation reaction to form the Si-O-C bond is considered.

Figure 6(b) shows Raman spectra of SX-Carbon-X. Silica-derived peaks are observed in the vicinity of 2943 and 2994 cm\(^{-1}\). In the samples doped with 2.5 wt% of GO and CB, scattering peaks of carbon-derived D- and G-bands were confirmed at 1347 and 1603 cm\(^{-1}\). The intensity of the D-band is related to the oxygen and defects present on the surfaces of GO and CB. G-band is related to the number of conjugated double bonds of carbon responsible for the conductivity of the material. In SX-GO-2.5, scattering peaks of the 2D band were detected near 2680 cm\(^{-1}\). In SX-PEDOT:PSS-2.5, SO\(_2\) bending was detected at 437 cm\(^{-1}\), oxyethylene ring deformation was detected at 577 cm\(^{-1}\), symmetric C-S-C deformation was detected at 701 cm\(^{-1}\), oxyethylene ring deformation was detected at 989 cm\(^{-1}\), C\(_\alpha\)-C\(_\beta\) inter-ring stretching was detected at 1255 cm\(^{-1}\), C\(_\alpha\)-C\(_\alpha\) inter-ring stretching was detected at 1365 cm\(^{-1}\), symmetric C\(_\alpha\)-C\(_\beta\) (-O) stretching was detected at 1437 cm\(^{-1}\), asymmetric C\(_\alpha\)-C\(_\beta\) stretching was detected at 1502 cm\(^{-1}\), and asymmetric C\(_\alpha\)-C\(_\beta\) stretching was detected at 1563 cm\(^{-1}\) \[27\].

Figure 5. (a) N\(_2\) adsorption/desorption isotherm and (b) pore size distributions of carbon-silica xerogels. N\(_2\) adsorption/desorption data were calculated using the BJH method.

Table 1. Pore parameters of SX-Carbon-X.

| Sample       | BET surface area (m\(^2\)/g) | Pore volume (cm\(^3\)/g) | Average pore size (nm) |
|--------------|------------------------------|--------------------------|------------------------|
| SX           | 535.16                       | 2.0177                   | 37.87                  |
| SX-GO-0.1    | 495.76                       | 1.2262                   | 18.46                  |
| SX-GO-0.5    | 474.27                       | 1.4859                   | 37.87                  |
| SX-GO-1.0    | 439.50                       | 1.4716                   | 16.29                  |
| SX-GO-2.5    | 437.43                       | 1.9274                   | 29.50                  |
| SX-PEDOT:PSS-0.1 | 540.05                       | 2.1408                   | 67.63                  |
| SX-PEDOT:PSS-0.5 | 516.62                       | 1.6396                   | 37.87                  |
| SX-PEDOT:PSS-1.0 | 397.00                       | 1.0961                   | 9.23                   |
| SX-PEDOT:PSS-2.5 | 455.77                       | 1.2274                   | 10.65                  |
| SX-CB-0.1    | 474.93                       | 2.5358                   | 122.63                 |
| SX-CB-0.5    | 460.57                       | 1.1525                   | 10.65                  |
| SX-CB-1.0    | 437.43                       | 1.1267                   | 10.65                  |
| SX-CB-2.5    | 429.13                       | 1.1202                   | 10.65                  |

Figure 6. (a) FT-IR and (b) Raman spectra of carbon-silica xerogels.
3.4. Transient thermal stability

Figure 7 shows the DSC measurement results. In SX, the exothermic peak accompanying thermal decomposition of the methylsilyl group was observed in the vicinity of 394°C. In hydrophobized silica xerogel, thermal decomposition of the hydrophobic group occurs in this manner. In composite materials with carbon material added, the thermal decomposition peaks shifted uniformly toward higher temperatures, and the respective thermal decomposition peak temperatures were 512°C for SX-PEDOT:PSS-0.1 and 550°C or above for SX-GO-0.1 and SX-CB-0.1. Three factors, endotherm accompanying sublimation of carbon, low thermal conductivity by suppression of the radiant heat of carbon, and adsorption of pyrolysis gas by carbon, are conceivably, the mechanisms of transient thermal resistance phenomenon. Sublimation of amorphous carbon is accompanied by absorption of heat (Equation 3). Carbon is known to cause a combustion reaction in the atmosphere (Equation 4). In other words, if the composite is heated in the atmosphere, sublimation and combustion reactions of carbon may occur. The carbon dioxide released by combustion of the carbon material is expected to act as a self-extinguishing type of flame retardant that performs flame retardation of the xerogel composite heat-insulating material.

\[
C(s) \rightarrow C(g) - 717 \text{ kJ/mol} \quad (3)
\]

\[
C(s) + O_2(g) \rightarrow CO_2(g) + 393.7 \text{ kJ/mol} \quad (4)
\]

To study the mechanism of heat resistance owing to the addition of carbon material, the thermal response behavior of each carbon material was examined. TG-DTA measurements were performed for the bulk materials, GO, PEDOT:PSS, and CB, under a normal atmosphere and a normal atmosphere. Figure 7(b-d) show the results of the TG-DTA measurement. GO shows an exothermic peak caused by a combustion reaction at 450°C or higher under a normal atmosphere. No exothermic peak was observed under an N\textsubscript{2} atmosphere. Up to 450°C, a weight loss of approximately 40% was observed under both N\textsubscript{2} and normal atmospheres. The weight loss of 10% up to approximately 100°C is presumed to be due to the evaporation of moisture, and the remaining 30% could be weight loss owing to sublimation of GO. Even in PEDOT:PSS, behavior similar to that of GO was observed. In CB, under a normal atmosphere, an exothermic peak owing to a combustion reaction was observed from the vicinity of 250°C, and the weight decreased sharply at 400°C or above. Under an N\textsubscript{2} atmosphere, a weight loss of approximately 10% was observed at 400°C.

In order to identify volatile substance emissions from these carbon materials, EGA-MS was performed (Figure 8). In the results for GO, generation of CO\textsubscript{2} was observed in the range of 200°C to 300°C. In PEDOT:PSS, aliphatics and SO\textsubscript{2} were detected at 250°C to 350°C, and aromatics were observed at 350°C to 450°C. In CB, moreover, CO\textsubscript{2} was detected only slightly. In the above results, no clear endothermic peak was detected in the heating process in any of the carbon materials. It is therefore unlikely that the transient heat-resistance factor is endothermic due to sublimation of the carbon material.

Highly possible reason for the improvement in transient heat resistance could be the suppression of radiation heat transfer by the carbon material in silica xerogel, which makes increases in the temperature of silica xerogel difficult [5]. It is also possible, moreover, that the alkyl group formed by thermal decomposition is adsorbed by carbon and emerges slowly. In order to verify this hypothesis, the pore characteristics

Figure 7. (a) DSC curves of carbon-silica xerogels and (b) TG-DTA curves of GO, (c) PEDOT:PSS, and (d) CB under air or N\textsubscript{2} flow.
of the carbon material alone were investigated. The results showed the carbon black exhibiting a relatively large specific surface area of 132.55 m²/g and a pore volume of 0.5826 cm³/g (Table 2). Thus, in addition to suppressing radiation heat transfer, carbon black may contain a mechanism by which decomposed hydrophobic organic groups are adsorbed.

### 3.5. Combustion behavior and thermal conductivity

To examine the combustion behavior of GFR-SX-Carbon-X quantitatively, we conducted the cone calorimeter (CCM) test. The results of the CCM test are shown in Figure 9 and Table 3. Figure 9(a) shows the relationship between the time taken to conduct the CCM test and the peak heat release rate (PHRR). The GFR-SX combusted in 12.7 s and the PHRR of 16.39 kW/m² was recorded at 36 s into the test. The GFR-SX-PEDOT:PSS-0.1 combusted in 15.8 s and the PHRR of 19.92 kW/m² was recorded 28 s after the start of the test. However, GFR-SX-PEDOT:PSS-0.5 did not combust. Furthermore, neither GFR-SX-GO-0.5 nor GFR-SX-CB-0.5 combusted, and the PHRR was as low as 2.5 kW/m². Figure 9(b) shows the relationship between the CCM test time and the total heat release (THR). The THR of GFR-SX was 0.55 MJ/m². Although the samples with 0.1% carbon added showed higher values (0.6 to 0.77 MJ/m²) compared with GFR-SX, the samples with 0.5% carbon added showed extremely low values (0.04–0.12 MJ/m²), demonstrating a flame retarding effect.

The water contact angle of the GFR-SX-Carbon-X before and after the CCM test was examined. As shown in Table 4 and Figure 10, the results showed that before the CCM test, all the samples had a water contact angle of 140° or higher. After the CCM test, however, the GFR-SX and GFR-SX-Carbon-0.1 sheets suffered water absorption and the contact angle fall to zero. Interestingly, GFR-SX-Carbon-0.5 showed a water contact angle of about 90°, even after the CCM test, with hydrophobicity still remaining. GFR-SX-Carbon-0.5 are considered to retain their organic hydrophobic groups.

The bulk densities of GFR-SX-Carbon-X ranged from 0.204 to 0.217 g/cm³. As shown in Table 3, moreover, the thermal conductivities measured using HFM showed extremely low values in the range of 0.0187 to 0.0203 W/(m · K). It is considered that, in a diluted carbon concentration of approximately 0.5%, no heat conduction path is formed in the film thickness direction, because the carbon material is scattered in the silica aerogel, and, hence, the thermal conductivity is low. Table 3 also shows thermal conductivity data from previous studies on a 0.4% graphite-doped silica aerogel composite (SA-G-0.4) [12] and a glass fiber reinforced 0.5% reduced graphene oxide (rGO)-doped silica aerogel composite (GFR-SX-rGO-0.5) [22] for comparison with the present data. As with the present data, very low thermal conductivity of less than 0.02 W/(m · K) is realized in these composites. Although the influence of

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**Table 2. Pore parameters of carbon materials.**

| Sample      | BET surface area (m²/g) | Pore volume (cm³/g) | Average pore size (nm) |
|-------------|-------------------------|---------------------|------------------------|
| GO          | 0.5350                  | 0.1217              | 24.49                  |
| PEDOT:PSS   | 3.6710                  | 0.1230              | 24.49                  |
| CB          | 132.55                  | 0.5826              | 21.30                  |

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**Figure 8.** EGA-MS results for carbon materials.

**Figure 9.** Heat release rate (a) and total heat release (b) from GFR-SX-Carbon-X.
difference in the measuring apparatus and measurement conditions must also be considered, sample SA-G-0.4, especially, has a very low thermal conductivity of 0.017 W/(m · K). Possible reasons for this are that there is no fiber heat conduction path, and that cracking and shrinkage are suppressed because it was carefully fabricated using a supercritical drying apparatus.

Figure 11 shows the relationship between (a) the bulk density and (b) the silica xerogel filling ratio and thermal conductivity. The thermal conductivity of the glass fiber with a bulk density of 0.1 was 0.034 W/(m · K). Interestingly, as the bulk density or silica xerogel filling ratio in composites became larger, the thermal conductivity became lower. It is considered that the packing ratio occupied by silica xerogel between the glass fibers increased and that the thermal conductivity decreased. In other words, this indicates that the air present in the glass fiber is replaced by silica xerogel and that the convection of air is suppressed, resulting in a decrease in thermal conductivity. No clear correlation was found between the microstructure parameters (pore size distribution, pore volume and surface area) and thermal conductivity of the silica xerogels constituting the heat-insulating materials.

4. Summary and conclusions

In this study, we prepared new waterglass-based SX-Carbon and GFR-SX-Carbon materials containing GO, PEDOT:PSS, and CB via a simple method in a short time (9.5 h) and examined the microstructure, thermal conductivity, transient heat resistance and flame retardancy. The bulk densities of the GFR-SX-Carbon-X were 0.204 to 0.217 g/cm³. Despite the addition of conductive carbon materials, moreover, the thermal conductivity was as low as 0.0187 to 0.0203 W/(m · K), indicating their potential for use as high-performance heat-insulating materials. It was observed, moreover, that as the amount of carbon material added increased, the thermal decomposition temperature of the SX-Carbon-X shifted to a higher temperature.

| Sample          | Bulk density (g/cm³) | Silica xerogel filling ratio (wt%) | Thermal conductivity (W/(m · K)) | THR (MJ/m²) | PHRR (kW/m²) | TPHRR (s) | TTI (s) | TTE (s) | BT (s) |
|-----------------|---------------------|-----------------------------------|----------------------------------|-------------|--------------|-----------|--------|--------|-------|
| GF (Glass fiber)| 0.107               | 0                                 | 0.0340                           | -           | -            | -         | -      | -      | -     |
| GFR-SX          | 0.204               | 45.41                             | 0.0203                           | 0.55        | 16.39        | 36.1      | 8.4    | 21.1   | 12.7  |
| GFR-SX-GO-0.1   | 0.208               | 45.52                             | 0.0198                           | 0.77        | 2.50         | 78.1      | -      | -      | -     |
| GFR-SX-GO-0.5   | 0.208               | 44.59                             | 0.0201                           | 0.04        | 1.36         | 68.1      | -      | -      | -     |
| GFR-SX-PEDOT:PSS-0.1 | 0.213       | 45.97                             | 0.0192                           | 0.60        | 19.92        | 28.1      | 10.3   | 26.1   | 15.8  |
| GFR-SX-PEDOT:PSS-0.5 | 0.217       | 45.66                             | 0.0187                           | 0.06        | 1.31         | 30.1      | -      | -      | -     |
| GFR-SX-CB-0.1   | 0.210               | 45.83                             | 0.0195                           | 0.67        | 1.33         | 164       | -      | -      | -     |
| GFR-SX-CB-0.5   | 0.212               | 45.99                             | 0.0193                           | 0.12        | 1.10         | 59.1      | -      | -      | -     |
| Ref 12 (SA-G-0.4) | -                  | -                                 | 0.0170                           | -           | -            | -         | -      | -      | -     |
| Ref 22 (GFR-SX-rGO-0.5) | 0.208      | -                                 | 0.0199                           | -           | -            | -         | -      | -      | -     |

THR; Total heat release, PHRR; Peak of heat release rate, TPHRR; Corresponding time to PHRR, TTI; Time to ignition, TTE; Time to extinguishing, BT; Burning time.

| Sample          | Water contact angle (°) |
|-----------------|------------------------|
| Before CCM test | After CCM test         |
| GF (Glass fiber)| 0                      | -                      |
| GFR-SX          | 145 ± 6                | 0                      |
| GFR-SX-GO-0.1   | 147 ± 4                | 0                      |
| GFR-SX-GO-0.5   | 148 ± 5                | 91 ± 9                 |
| GFR-SX-PEDOT:PSS-0.1 | 146 ± 7          | 0                      |
| GFR-SX-PEDOT:PSS-0.5 | 147 ± 6          | 81 ± 15                |
| GFR-SX-CB-0.1   | 146 ± 6                | 0                      |
| GFR-SX-CB-0.5   | 149 ± 7                | 90 ± 7                 |

Figure 10. Water contact angle measurements for GFR-SX, GFR-SX-GO-0.1, and GFR-SX-GO-0.5 before and after the cone calorie test.
range, and its transient thermal stability was significantly improved. In the CCM test of GFR-SX-Carbon-X, furthermore, it was observed that adding at least 0.5% of each carbon materials significantly reduced the combustion time and the PHRR, and it was also observed that the addition of a small amount of carbon material remarkably improved not only the transient thermal stability but also the flame retardancy. The above results indicate a potential for application of carbon-added glass-fiber-reinforced silica xerogel heat-insulating materials in various fields.

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Disclosure statement
No potential conflict of interest was reported by the authors.

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