Fabrication, Thermal and Sound Absorption Properties of Porous Polyimide Reinforcing by SiO$_2$ Nanoparticles

Yalin Zhao$^1$, Mingxin Geng$^1$, Jiangang Ma$^1$ and Longgui Peng$^{2,*}$

$^1$ State Grid Shaanxi Electric Power Research Institute, Xi’an 710100, China
$^2$ College of Materials Science and Engineering, Xi’an University of Science and Technology, Xi’an 710054, China.
*Corresponding author email: penglonggui@163.com

Abstract. Special requirements of the service environment put forward higher requirements for the comprehensive performances of porous sound-absorbing materials. In this study, the polyimide/nano-SiO$_2$ composite foams were prepared based via the sol-gel and foaming methods. The effect of different addition of SiO$_2$ nanoparticles on the pore structure, sound absorption properties as well as the thermal properties of polyimide/SiO$_2$ nanocomposite foams are studied. Results indicate that: the addition of the nano-SiO$_2$ particles not only could improve the thermal stability of the composites, but also increase the sound absorption performances. Particularly, the samples with 2% addition of SiO$_2$ nanoparticles shows the optimal thermal and sound absorption performance. Therefore, adding the SiO$_2$ nanoparticles into the polyimide foams is an efficient way to improve its thermal and sound absorption performance, which would give insights into designing sound-absorbing materials with excellent comprehensive performance to curb the noise pollution.

1. Introduction
Noise pollution has become a critical issue that cannot be ignored in this rapidly developing society, since noise would not only harm people’s hearing system, resulting in tiredness and deafness, but also accelerate the aging of buildings and mechanical structures as well as the accuracy and service life of equipment and meters[1-5]. In order to solve this problem, the fundamental approach is to reduce noise intensity by controlling source, but this method is bound to limit the performance and industrial applications of acoustic devices[6, 7]. Another indirect way is to introduce sound absorbing materials/structures, which would greatly reduce the sound intensity by the sound dissipation effect. Compared with the resonance sound absorption materials[8], porous materials show more efficient absorption ability due to two effects[9-12]: the sound wave reflecting loss on the surface of the material and the dissipation due to the viscosity and heat conduction effect. Foams with open-cell structure generally have sound absorption properties, which have been studied with experimental investigations and simulation methods. However, for some particular applications, especially high temperature environment such as power stations, higher thermal resistance for sound absorbing materials is required. Polyimide(PI)[13-15], which has been proved to have excellent thermal, electrical and sound absorption properties, is believed to be potential candidates for high-performance sound-absorbing materials applied in high-temperature environments. However, the most conspicuous disadvantage for PI is that its strength is not high enough and would be easily fragile when in use. It has been proved that introducing the nanofillers into the polymer matrix to enhance the interfacial intensity is the efficient way to improve the comprehensive performances of composites with reinforcing effect. Thus, in this paper, the nano-Silica(n-SiO$_2$) is chosen as the strengthening phase to
prepare the PI/n-SiO$_2$ porous composite. Cross-linking point could be formed between the PI macromolecular chain and the SiO$_2$ nano particles, making the composite simultaneously have excellent properties of polyimide and nanoparticles. Particularly, the effect of n-SiO$_2$ addition on thermal properties and sound absorption performances of PI/n-SiO$_2$ porous composites would be investigated systematically, which would provide a reference and contributes to designing high-performance sound-absorbing materials with comprehensive properties.

2. Materials and Experiments

2.1 Preparation of n-SiO$_2$ Particles
The ethyl orthosilicate, absolute ethanol, and deionized water were formulated into a solution with the volume ratio of 1:2:2, and then stirred vigorously at 70°C for 1.5 hours for reacting. The catalyst is then added, following by 1 hour stirring to obtain a transparent white liquid. The liquid was then poured into a beaker and put in a fume hood, and the wet gel is obtained after days. The wet gel was dried in an oven at 70°C for a few hours. After being powdered, it is calcined in a medium temperature tubular resistance furnace at 600°C for 1.5 hours, and then naturally cooled to room temperature, which finally obtained the n-SiO$_2$ particles.

2.2 Preparation of Porous PI/n-SiO$_2$ Composites
The porous PI/n-SiO$_2$ composite was prepared by the foaming method: The certain amount of BTDA was dissolved in methanol, and the diacid diester was obtained after heating reflow process. Then an equimolar amount of ODA was added, and a reddish-brown liquid with a certain viscosity will be obtained. After siting for 2 hours, the liquid was poured on the PTFE cloth and then put into a precision blast drying oven at 70°C and dried for 6~8 hours. Then the product was dried and pulverized to obtain the precursor powder. The n-SiO$_2$ powder and precursor powder were mixed in a certain proportion, and put into the mold for foaming. Finally, the PI/n-SiO$_2$ composite foams could be obtained.

3. Results and Discussions

3.1 Cell Structure of Porous PI/n-SiO$_2$ Composites
The size of the cell structure, whether it is open or closed, have a certain impact on the sound absorption performance of PI/n-SiO$_2$ composites. Therefore, the structure of the cells in the samples were analyzed by the Polarizing microscope (CK330-D, Shanghai Caikang Optical Instrument Co., Ltd.), and the snapshots for samples with different additions of n-SiO$_2$ are shown in Figure 1. The ratio of closed cells in polyimide foams $\delta$ is defined as the fraction of closed cell pore volume in the total void volume:

$$\delta = \frac{V_{\text{closed}}}{V_{\text{total}}} \times 100\% = \frac{V_{\text{closed}}}{(V_{\text{closed}} + V_{\text{open}})} \times 100\%$$  \hspace{1cm} (1)

Where $V_{\text{open}}$ is the volume of open cell pores in the foam, $V_{\text{closed}}$ is the volume of closed cell pores in the foam; $V_{\text{total}}$ is the total volume of foam pores. Different n-SiO$_2$ additions have a certain effect on the cell structure of the composites, and the cell structure in Figure 1(c) shows relative regular shape and size distributions, which would resulted in improved sound absorption performances.
Figure 1. Microscope Structure of the porous PI/Nano-SiO$_2$ with different additions of n-SiO$_2$. (a) Pure PI; (b) 1% nano-SiO$_2$; (b) 2% nano-SiO$_2$; (b) 4% nano-SiO$_2$

Furthermore, the density of PI/n-SiO$_2$ composite samples can be easily calculated by the ratio of the mass of the foam to its volume as shown in Table 1. With increasing content of the n-SiO$_2$, the density of the composite foams increases first and reaches the maximum value at 2% n-SiO$_2$ addition, and the density is basically unchanged increased content of the n-SiO$_2$.

| n-SiO2 addition (%) | Sample weight (g) | Volume (cm$^3$) | Density (g/cm$^3$) |
|---------------------|-------------------|-----------------|-------------------|
| 0                   | 22.8427           | 142.6           | 0.160             |
| 1                   | 23.8432           | 121.2           | 0.197             |
| 2                   | 27.2175           | 80.8            | 0.337             |
| 4                   | 26.9888           | 81.5            | 0.331             |

3.2 Thermo Properties
It has been proved that PI nanocomposites have excellent heat resistance, dimensional stability and mechanical properties[16], thus, thermo properties of the prepared PI/n-SiO$_2$ composite foam samples was examined via the Differential Scanning Calorimetry (DSC) and Thermogravimetric (TG) analysis.
Figure 2. DSC curves of PI/nano-SiO2 composite foams

From the DSC profiles in Figure 2, the $T_g$ of the composites with SiO2 additions (1%, 2%, and 4%) are 277.76°C, 285.72°C, and 283.35°C, respectively, which are all above 270°C and higher than the $T_g$ of the pure PI. With the increase values of SiO2 content, the $T_g$ of the composites increased slightly and reaches the maximum value with 2% SiO2 addition, and the $T_g$ will decrease again with 4% SiO2 addition. The reason for this nonlinear relationship between $T_g$ and the added amount of n-SiO2, could be attributed to the microstructure the nanocomposites: the particle dispersion is fairly uniform with 2% n-SiO2 addition, leading to the better overall heat resistance; with large added amount of n-SiO2 (4%), the uniform distribution cell structures would be destructed due to the agglomeration during the foaming, which might affect the $T_g$ of the composites.

Figure 3. TGA curves characteristic data of PI/n-SiO2 composite foams with different contents of n-SiO2

As shown in Figure 3(a), the TGA curves of PI/n-SiO2 composite foams of the four samples almost overlap before 400°C, indicating that the initial decomposition temperature of the four samples is almost the same, and the slight weight loss in the early stage is mainly attributed to the moisture in the system or the added methanol caused by solvent volatilization. With increasing temperature from 400°C, composite foam with 4% n-SiO2 addition has the best stability, followed by composite foams with 1% and 2% n-SiO2 addition, and pure PI has the worst stability. When the temperature reaches
about 550°C, all samples decompose rapidly, the decomposition rate decreases with increasing added amount of the n-SiO₂, indicating the improved overall thermal stability of the composites with large n-SiO₂ additions. The addition of n-SiO₂ particles which has good thermal stability could hinder the movement of the polyimide molecular chain, and improve the thermal stability of the composites. In general, the 5% thermal weight loss temperature (T5) of all samples are all above 520°C, which shows good thermal stability of all composite foams. In addition, the heat resistance grade (TI) is measured and calculated by the secant method based on values of the 5% and 30% thermal weight loss temperature T5 and T30 in Figure 3(b) and 3(c):

$$TI = 0.49 \times [T5 + 0.60 \times (T30 - T5)]$$  \hspace{1cm} (2)

It can be clearly seen from Figure 3(d) that the heat resistance grade of pure PI is the lowest, and the TI gradually increases with increasing content of n-SiO₂, indicating the improved thermal stability with large amount of n-SiO₂ addition.

### 3.3 Sound Absorption Properties

![Figure 4. Sound absorption coefficients of composite foams with different n-SiO₂ additions.](image)

The cylindrical samples with different n-SiO₂ additions were prepared with a diameter of 30 mm, and the vertical incident sound absorption coefficients were measured via the standing wave tube method referring to the GB J88-85 standard. As shown in Figure 4(a), the sound absorption performances with different amounts of n-SiO₂ addition all shows frequency-dependent features, and the frequency correlation shows different changes with different amounts of addition. As shown in Figure 4(b), The overall sound absorption coefficient of foams with 2% n-SiO₂ addition is higher comparing with the average sound absorption coefficient of other samples, which should attributed to the cell structures as shown in Figure 1. The sample with 2% n-SiO₂ addition formed structure with small and uniform pore, which would significantly influence propagation and loss process of the sound wave in porous foams.

### 4. Conclusion

In this study, the PI/n-SiO₂ composite foams were successfully prepared, and the structure, thermal and sound absorption performance of these nanocomposite foams were systematically investigated. Based on the obtained results, the following conclusions can be drawn:

1. The cell structure of the composite foam material has a great influence on the sound absorption coefficient of the foams. PI/n-SiO₂ composite foam with 2% n-SiO₂ addition has small and uniform cells, resulting in the highest sound absorption coefficient.

2. The TGA and DSC results indicate that the thermal stability of PI/n-SiO₂ composite foams is improved comparing with the pure PI, and the thermal stability is improved with increasing with large amount of SiO₂ nanoparticles addition.
5. Acknowledgement
This work is financially supported by State Grid Shaanxi Electric Power Company Science & Technology Project (grant number: 5226KY19005J).

6. Reference
[1] Tie T S, Mo K H, Putra A, Loo S C, Alengaram U G and Ling T C 2020 J Build Eng 30 101219
[2] Bhingare N H, Prakash S and Jatti V S 2019 Polym Test 80 106142
[3] Kalauni K and Pawar S J 2019 J Porous Mat 26 1795
[4] Cao L T, Fu Q X, Si Y, Ding B and Yu J Y 2018 Compos Commun 10 25
[5] Tang X N and Yan X 2017 Compos Part A-Apppl S 101 360
[6] Liu L Y, Qiu Y, Hao Z Y and Zheng X 2020 Appl Acoust 168 107420
[7] Shi C, Jia Z Y, Xie R and Li H Y 2020 Mech Sys Signal Pr 144 106878
[8] Gao N S and Lu K 2020 Appl Acoust 169 107500.
[9] Soltani P, Taban E, Faridan M, Samaei S E and Amininasab S 2020 Appl Acoust 157 106999.
[10] Ao Q B, Wang J Z, Ma J and Tang H P 2019 Rare Metal Mat Eng 48 3241
[11] Wang J Z, Ao Q B, Ma J, Kang X T, Wu C, Tang H P and Song W D 2019 Appl Acoust 145 431
[12] Ao Q B, Wang J Z, Tang H P, Zhi H, Ma J and Bao T F 2015 Rare Metal Mat Eng 44 2646
[13] Wang C B, Cong B, Zhao J Y, Zhao X G, Wang D M, Zhou H W and Chen C H 2020 RSC Adv 10 13517
[14] Jiang B, Cao F H, Wang H S, Yi D Q, Jiang Y, Shen F H, Wang B and Liu H Q 2019 Mat Sci Eng A-Struct 740 157
[15] Liu Y, Xu X Z, Mo S, Zhai L, He M H and Fan L 2019 Chem J Chinese U 40 187
[16] Liang M F, Yang A N, Zhu Y and Sun S H 2020 Nano 15 2050041.