PREPARATION AND PROPERTIES OF EPOXY FOAM MATERIALS FOR DEEP IN-SITU CONDITION-PRESERVED CORING DEVICE

by

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To maintain the in-situ temperature of rock cores, a specialized coring device equipped with temperature-preserved module is essential. The thermal insulation material with low thermal conductivity and high compressive strength is a critical component. In this study, an innovative foaming agent was utilized to fabricate an epoxy resin-based insulation material. Nanosilica particles were synthesized via the sol-gel method, followed by the preparation of porous SiO_2 microspheres using the polymer-induced colloid aggregation method. The porous SiO_2 microspheres were combined with the chemical blowing agent to create a composite blowing agent. Using high strength epoxy resin as the matrix, the study examined the effects of the foaming process and blowing agent content on the properties of the resulting epoxy foam materials.

Key words: *thermal insulation materials, epoxy foam materials, silica particles, composite blowing agents*

Introduction

The depths of oil, coal, and natural gas extraction continue to increase annually. However, theories that adequately support deep resource exploration and extraction remain underdeveloped. To address this gap, Gao *et al*. [1] and Xie [2] proposed establishing a new theory of deep rock mechanics, focusing on the extraction of cores that retain in-situ deep conditions. The deep environment is marked by high geothermal temperatures [3], which critically influence the physical properties of rocks, including permeability [4].

To maintain the in-situ temperature of deep cores, Xie *et al.* [5] proposed a coring system that combines active and passive thermal insulation. Passive thermal insulation system refers to the development of high strength passive insulation materials to serve as insulation layers [6, 7]. Epoxy resin, characterized by high strength, low thermal conductivity, and strong temperature resistance, can be used as the matrix for insulation materials [8-10]. To further reduce its thermal conductivity, a composite blowing agent can be prepared by combining nano-

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materials and blowing agents, which can reduce the particle size of the blowing agent and enhance its mono-dispersity in the epoxy resin, while providing nucleation sites for bubbles and increasing the system's viscosity, ensuring that the small bubbles formed by individual blowing agent particles are fixed in the epoxy resin matrix [11]. Some scholars have explored these aspects. Guo *et al*. [12] developed an azodicarbonamide/montmorillonite composite blowing agent, successfully producing microcellular plastics with a smaller average cell diameter. Soriano *et al*. [13] created an azodicarbonamide-ZnO/SiO_2 composite blowing agent, successfully low density polyethylene/ethylene vinyl acetate. Therefore, this study produced a composite blowing agent by loading the chemical blowing agent OBSH on silica particles and examined how the foaming process and composite blowing agent concentration affected the properties of the epoxy foam materials.

Preparation of epoxy foam materials

Preparation of composite blowing agent

Monodisperse silica particles were prepared using the sol-gel method, with TEOS as the precursor and a mixed solution of ethanol and water as the solvent, under alkaline conditions provided by ammonia water [14]. Then, silica particles were assembled into porous silica particles with larger pore volumes. In the acidic colloidal silica solution, urea and formaldehyde were added for a polymerization reaction through polymer-induced colloid aggregation, where the produced polymer adheres to the surface of the silica colloids and further induces their aggregation. Calcination in a muffle furnace was performed to remove the urea-formaldehyde polymer, resulting in porous silica microspheres. The silica particles were modified with KH550, resulting in NH_2-SiO_2 particles. The porous NH_2-SiO_2 particles were added to an OBSH/DMF solution (1.8 mol/L) and stirred at 40 °C for 12 hours. After stirring, the mixture was filtered, washed with methanol, and vacuum-dried to obtain the composite blowing agent.

Preparation of epoxy foam materials

The epoxy resin prepolymer E51 and an appropriate amount of composite blowing agent were placed in a beaker and stirred in an oil bath at 75 °C for 30 minutes. The curing agent *m*-PDA was then added. The mixture was stirred and then poured into molds and heated in ovens under different heating conditions. The specific preparation process is shown in tab. 1.

Table 1. Preparation process of epoxy insulation materials

Experimental group	Blowing agent ratio	Foaming process
1	3.5 wt.%	Stir for 30 minutes, heat at 65 °C/12 hours
2	3.5 wt.%	Stir for 30 minutes, heat at 120 °C/2 hours
3	3.5 wt.%	Stir for 30 minutes, heat at 125 °C/2 hours
4	3.5 wt.%	Stir for 30 minutes, heat at 140 °C/2 hours
5	3.5 wt.%	Stir for 30 minutes, heat at 150 °C/2 hours
6	3.5 wt.%	Stir for 20 minutes, heat at 125 °C/2 hours
7	5.0 wt.%	Stir for 30 minutes, heat at 125 °C/2 hours

Results and discussion

Performance study of composite blowing agent

The TEM images of the particles are shown in the fig. 1(a). The silica particles are spherical, with an average particle size of 168 nm. The TEM images of the porous silica particles, as shown in the fig. 1(b), indicate that under the bridging effect of the urea-formaldehyde resin, the silica particles have orderly aggregated to form porous silica particles with a hollow structure (thicker at the periphery, thinner at the center). Therefore, as shown in the SEM images of composite agent in fig. 1(c), the porous and hollow structures of the porous silica particles can effectively load the blowing agent OBSH.

The thermogravimetric infrared absorption spectra curves of the composite blowing agent and other samples are shown in figs. 1(d) and 1(e). The final residual mass of the composite blowing agent is 89.43%, suggesting that the loaded OBSH accounts for 10.70 wt.%. As shown in the infrared absorption spectrum of compound chemical blowing agent, the strong absorption band around 1066 cm^{-1} is attributed to the antisymmetric stretching vibration of the Si-O-Si bond. Bands of the OBSH appear at 1578 cm^{-1}, 1485 cm^{-1} (stretching vibration of the aromatic C=C), 3225 cm^{-1} and 3292 cm^{-1} (stretching vibration of -NH_2) and 796 cm^{-1} (out-of-plane vibration of aromatic C–H). The results indicate that the porous silica particles successfully loaded OBSH.

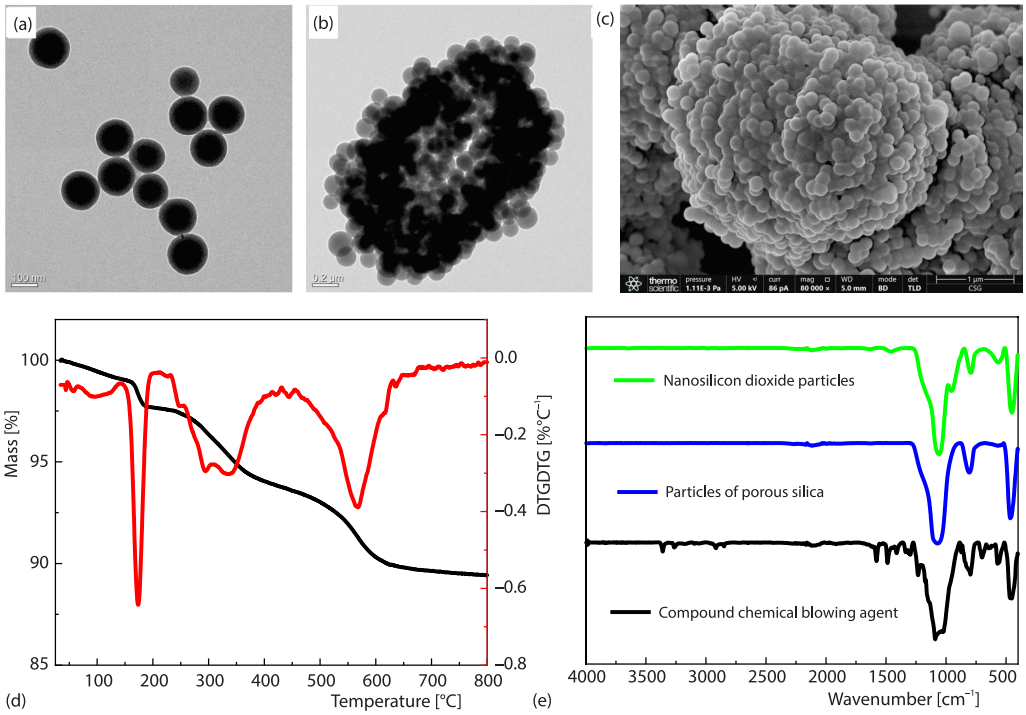

Figure 1. Characterization results of compound blowing agent;
(a) TEM images of monodisperse silica particles, (b) TEM images of porous silica particles,
(c) SEM images of composite foam agent, (d) TG curves of composite foam agent, and
(e) infrared absorption spectra curves of the composite blowing agent

Performance study of epoxy insulation materials

The SEM images, fig. 2(a), show that experimental groups 2-7 successfully produced epoxy foam insulation materials. The pore density [15]:

$$N_f = \left(\frac{n}{A}\right)^{3/2}\left(\frac{\rho_m}{\rho_f}\right)$$

where n is the number of foam cells, A – the area of the SEM image, ρ_m – the density of the epoxy resin, and ρ_f – the density of the epoxy resin foam. According the N_f formula and the SEM images of groups 2-7 shown in figs. 2(b)-2(g), the calculation results of N_f are summarized in tab. 2.

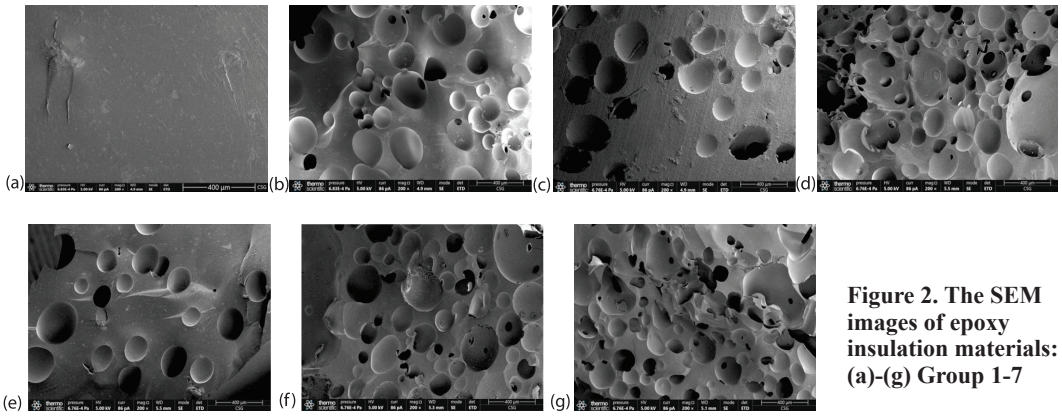

Figure 2. The SEM images of epoxy insulation materials: (a)-(g) Group 1-7

Table 2. Pore information and compressive strength of epoxy foam material

Experimental group	Average particle size [μm]	N_f [cells per cm³]	Compressive modulus [GPa]	Compressive strength [MPa]
1	–	0	2.25	149.97
2	196	78000	0.79	38.20
3	262	44000	0.71	30.20
4	132	168000	0.47	17.94
5	216	28000	1.06	73.07
6	198	128000	0.34	15.22
7	164	168000	0.51	24.45

As OSBH decomposes under heat, the epoxy resin cures, and its viscosity increases. These two processes occur simultaneously. The density of epoxy insulation material is shown in fig. 3(a). The densities of experimental groups 1-5 indicate that different curing processes have a significant impact on the density of the epoxy insulation materials. Under the conditions of experimental Group 1, due to the high initial decomposition temperature of OSBH, the epoxy resin showed no foaming after curing for 12 hours at 65 °C. Comparing experimental Groups 3-5 shows that the density of the epoxy foam material first decreases and then increases. This indicates that as the temperature increases from 125-140 °C, the decomposition rate of OSBH and the curing rate of the epoxy resin both increases, but the OSBH decomposition rate increases more rapidly. As the temperature further increases to 150° C, the curing rate of the epoxy resin accelerates significantly, rapidly increasing viscosity, making it difficult for the nitrogen gas produced by OSBH decomposition form more or larger pore structures in the highly viscous matrix. Group 6 a lower density than group 3, for it had a shorter pre-curing time for the epoxy

resin, and resulting in a longer gelation time. This allowed the gas produced by OSBH decomposition during the foaming stage to form more pore structures. Group 7 used a larger amount of OSBH than Group 3, resulting in more gas produced during thermal decomposition, more pore structures formed, and a lower density.

As shown in fig. 3(b), the thermal conductivity trend of the epoxy foam material is positively correlated with its density. For epoxy resin, typically, the lower the density, the more porous the structure, the fewer solid heat transfer media, and thus the lower the thermal conductivity. It is evident that although the experimental groups 2 and 3 have similar densities, experimental Group 2 exhibits smaller average pore size and higher pore density, resulting in lower thermal conductivity of the foam material. As shown in figs. 3(d) and 3(e), For experimental Group 1-7, the thermal decomposition temperatures are fairly consistent, with an initial decomposition temperature of approximately 296 °C, a peak decomposition temperature near 377 °C, and a final decomposition temperature around 604 °C.

The stress-strain curve of the epoxy foam material is shown in fig. 3(c), and its compressive strength and modulus are listed in tab. 2. Under the conditions of experimental Group 1, the epoxy resin did not significantly foam, resulting in the highest compressive modulus. Additionally, the epoxy foam material obtained from experimental Group 5 had the highest compressive modulus among all foam materials due to its higher density and lower foaming ratio. Experimental Groups 6 and 7, with lower density (0.45 g/cm^3, 0.55 g/cm^3) and thermal conductivity (0.098 W/mK, 0.104 W/mK), had compressive modulus of 0.34 GPa and 0.51 MPa, and compressive strengths of 15.22 MPa and 24.45 MPa, respectively. Although the density and thermal conductivity of experimental Groups 6 and 7 are similar, the pore diameter in Group 7 is smaller, and the pore density is higher, resulting in significantly higher compressive strength and modulus compared to Group 6. Overall, Group 7 is more suitable as an insulation material.

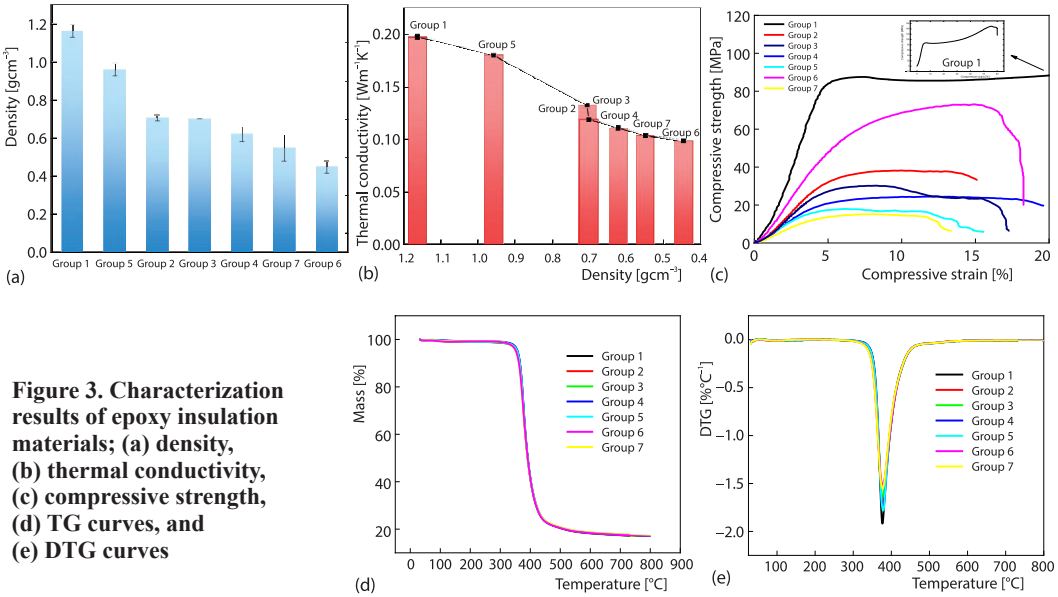

Figure 3. Characterization results of epoxy insulation materials; (a) density, (b) thermal conductivity, (c) compressive strength, (d) TG curves, and (e) DTG curves

Conclusion

This study presents the innovative development of epoxy foam as a passive insulation material specifically designed for deep in-situ condition-preserved coring devices. The OBSH-

SiO_2 composite blowing agent was synthesized via solution impregnation, achieving a 10.70% OBSH loading. In experimental Group 7, the epoxy insulation material exhibited optimal performance, with a thermal conductivity of 0.104 W/mK, compressive strength of 24.45 MPa, and thermal decomposition temperature of 296 °C.

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Nomenclature

N_f – pore density, [cells per cm^2]
ρ_m – the density of the epoxy resin, [gcm^{-3}]
n – the number of foam cells
ρ_f – the density of the epoxy resin foam, [gcm^{-3}]

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