



## Preparation and Characterization of Epoxy Acrylate/Mesoporous Silica Composite Materials

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Mesoporous silica was prepared by sol-gel method. TEOS was the resource of inorganic materials and EO<sub>20</sub>PO<sub>20</sub>EO<sub>20</sub> (P123) as template. The structure of mesoporous silica was tested by SEM and TEM. The diameter of mesoporous silica was 500 nm and the length was about 1 μm. The diameter of pore path was approximate 5 nm. The BET area was 492 m<sup>2</sup>g<sup>-1</sup> and the pore volume was 1.009 cm<sup>3</sup>g<sup>-1</sup> via the experiment of nitrogen adsorption-desorption. Mesoporous silica was uniformly dispersed in epoxy acrylate resin. EA/mesoporous silica begun evident weight loss at 325 °C, 25 °C higher than pure epoxy acrylate resin.

**Key Words:** Mesoporous silica, Pore path, Epoxy acrylate.

### INTRODUCTION

Mesoporous materials were the materials having ordered pore paths, which could be prepared by sol-gel, emulsion and microemulsion method. Kresge *et al.*<sup>1</sup> was firstly reported mesoporous materials. Zhao and Sun<sup>2</sup> utilized block copolymer to prepared mesoporous materials. The diameter was 5 nm to 30 nm and the thickness was 3.1 nm to 6.4 nm. Lin and Wang<sup>3</sup> added mesoporous silica to bromized epoxy resin. The glass transition temperature and the tenacity were increased. Zhang and Lee<sup>4</sup> added different mesoporous materials to PMMA. When the content of mesoporous materials reached to 5 wt %, the thermal stability was the best. Lu and Chun<sup>5</sup> prepared TiO<sub>2</sub>/SiO<sub>2</sub> mesoporous materials and added to epoxy resin. The ability was the best when the content of mesoporous materials arrived 3 wt %.

In this article, mesoporous silica was prepared by sol-gel method P123 template and TEOS as raw materials. And then the mesoporous silica was added to epoxy acrylate resin.

### EXPERIMENTAL

The supplier for the TEOS, HCl and alcohol was Kaifeng Dongda Chemicals Ltd. EO<sub>20</sub>PO<sub>20</sub>EO<sub>20</sub> (P123, Ma = 5800) was supplied by Aldrich Company, U.S.A. In addition, deionized water was used to hydrolyse the inorganic monomer precursors. Epoxy acrylate (EA, trademark DY3100), Darocure 1173 photoinitiator, trimethylpropane triacrylate (TMPTA) and tripropylene glycol diacrylate (TPGDA) were all supplied by Dong Yang Chemical Coating Ltd.

**Preparation:** Firstly, 2 g P123 was added to 65 g deionized water at 40 °C for 2 h. Secondly, 10 mL HCl was added to the mixture for 0.5 h to obtain transparent solution. Then, 4.25 g TEOS was dropwisely added to the solution at 55 °C for 24 h and was left in an oven at 80 °C for 12 h. The mixture was washed by alcohol and deionized water (mole ratio 1:1). Centrifuge was used to receive deposition. The deposition was left in muffle at 550 °C for 5.5 h to remove P123.

Oligomer epoxy acrylate, reactive diluent trimethylpropane triacrylate, tripropylene glycol diacrylate and Darocure 1173 photoinitiator were charged into a three-neck flask. The mixture was vigorously stirred for 1 h. And then the silica was added to the mixture with strong stirring for 1 h. At last, the mixture was poured into mould and was cured by UV lamp for 3 min.

**Characterization:** Chemical reactions were monitored by FT-IR spectroscopy, employing a Thermo-Nicolet Nexus instrument. The structure of hybrid materials was tested X-ray diffraction (XRD, D/MAX-RB, Rigaku Inc., Japan). Scanning electron micrographs were tested using Quanta 400 produced by Oxford Company, England. Transmission electron microscope manufactured by JEOL Company, Japan, was used to detect the microstructure. The pore size distribution was calculated from the adsorption isotherm curves using the Brunauer-Joyner-Halenda (BJH) method<sup>6</sup>.

### RESULTS AND DISCUSSION

The FT-IR spectrum of mesoporous silica was shown in Fig. 1. 3442 cm<sup>-1</sup> was the absorption peak of Si-OH. According

to literatures<sup>7-10</sup>, the absorption peak between  $1000\text{ cm}^{-1}$  and  $1100\text{ cm}^{-1}$  can be assigned to the siloxane bond (Si-O-Si). In Fig. 1, the absorption peak  $1082\text{ cm}^{-1}$  indicated the existence of Si-O-Si. Also,  $802\text{ cm}^{-1}$  was the weak absorption peak of Si-O-Si.

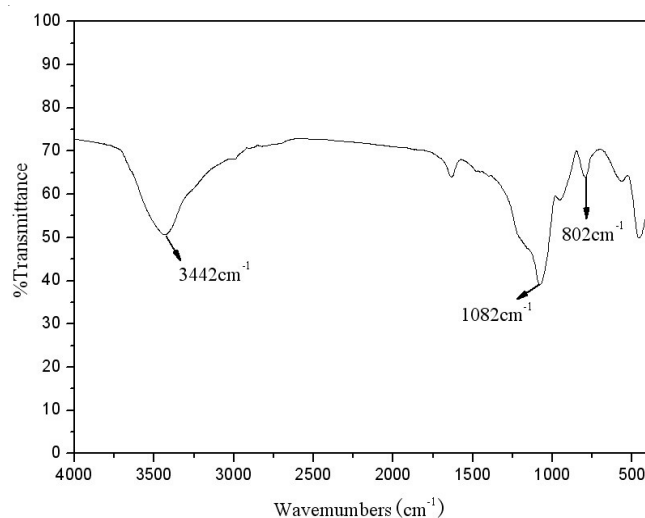


Fig. 1. FT-IR spectrum of mesoporous silica

The X-ray diffraction pattern of mesoporous silica was shown in Fig. 2. A strong diffraction peak near  $2\theta = 0.95^\circ$  appears in the diffraction pattern. There was two weak peaks near  $2\theta = 1.66^\circ$  and  $2\theta = 1.92^\circ$ . According to Bragg equation  $n\lambda = 2d \sin \theta$ , the d-spacing were approximately 9.29 nm, 5.32 nm, 4.60 nm, respectively. So the ratio of  $1/d$  was  $1:\sqrt{3}:\sqrt{4}$ . The result tallied with the structure of hexagonal crystal system. Therefore, the synthesized mesoporous silica belonged to hexagonal crystal system. Using eqn. (1):

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

The indices of crystal face were calculated by eqn. (1). They were (100), (110) and (200).

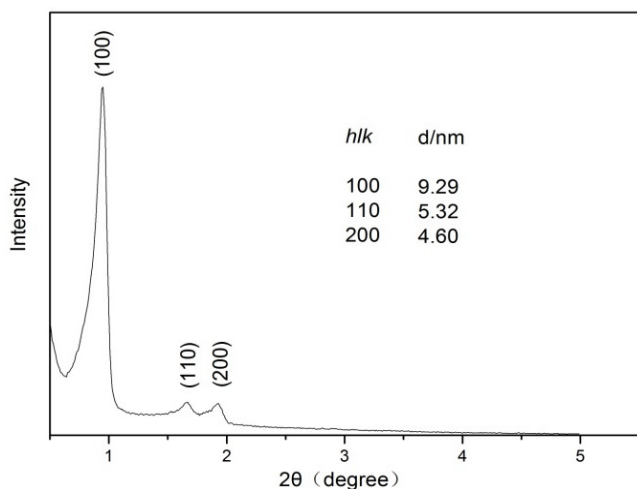


Fig. 2. X-ray diffraction patterns of mesoporous silica

Fig. 3 presented the scanning electron micrographs of mesoporous silica. The mesoporous silica was elliptical and

linear clavate. The diameter of mesoporous silica was 500 nm and the length was about 1  $\mu\text{m}$ . Because of HCl as catalyst, TEOS was hydrolyzed and the silica sol was absorbed above the surface of P123. Besides, P123 was dissolved in water. So the mesoporous silica was linear clavate and P123 could effectively control the length of the mesoporous silica.

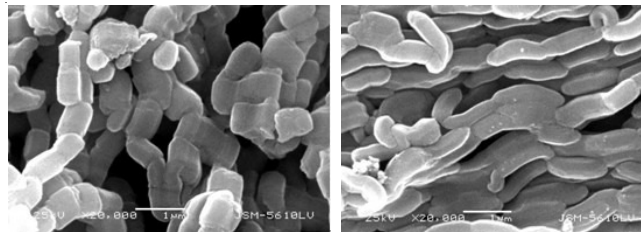


Fig. 3. Scanning electron micrographs of mesoporous silica

The TEM images were shown in Fig. 4. From the images, the production had clear pore paths and the silica was ordered. The two pictures were detected from the side of (100) and (110). It was obvious that some vertical pore paths were intersected with acclinic pore paths. So the mesoporous silica was three-dimensional structure. The diameter of path was approximate 5 nm and the thickness was about 4nm, which was proved by XRD and nitrogen adsorption-desorption.

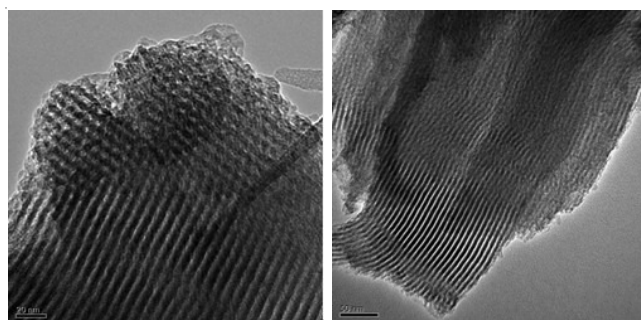


Fig. 4. TEM images of mesoporous silica

The nitrogen adsorption-desorption isotherms of the silica are of type Langmuir(IV) and displayed a clear hysteresis loop in Fig.5, which was characteristic of mesoporous materials with cage-like or disordered pores<sup>11,12</sup>. The BET surface area was calculated by eqn. (2):

$$\frac{P}{V(P_0 - p)} = \frac{1}{V_m \cdot C} + \frac{C-1}{V_m \cdot C} \times \frac{P}{P_0} \quad (2)$$

where, P was partial pressure of nitrogen,  $P_0$  was saturated vapour pressure of nitrogen, V presented the actual adsorptive volume,  $V_m$  was the saturated volume of nitrogen for single floor, C was the adsorption constant of the product. The BET area was  $492\text{ m}^2\text{g}^{-1}$  and the pore volume was  $1.009\text{ cm}^3\text{g}^{-1}$ , measured by BJH method, the diameter was 4.96 nm.

The SEM image was shown in Fig. 6. It was obvious that the mesoporous silica was uniformly dispersed in epoxy acrylate resin. Mesoporous silica was about 5  $\mu\text{m}$  in epoxy acrylate resin. This attributed to the higher surface area and the surface energy compared with common silica.

The TGA curves were shown in Fig. 7. It was evident that epoxy acrylate/mesoporous silica lost weight between  $100^\circ\text{C}$

to 250°C. That may be the evaporation of the remaining reactive diluent, water, alcohol and unreacted TEOS. At the same time, it also may be the dehydration of siloxane bond<sup>13-15</sup>. The turning point for epoxy acrylate was at about 300 °C. However, epoxy acrylate/mesoporous silica begun evident weight loss after 325 °C beside the previous weight loss. Inorganic materials added restricted the movement of the main chain. And mesoporous silica was combined with epoxy acrylate resin perfectly. This increased the energy to break the chain.

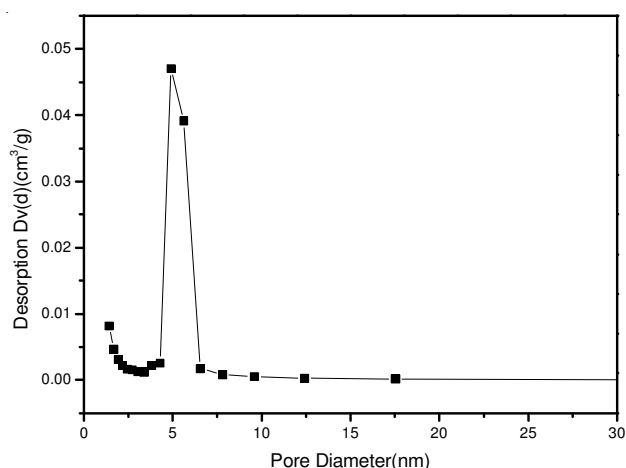
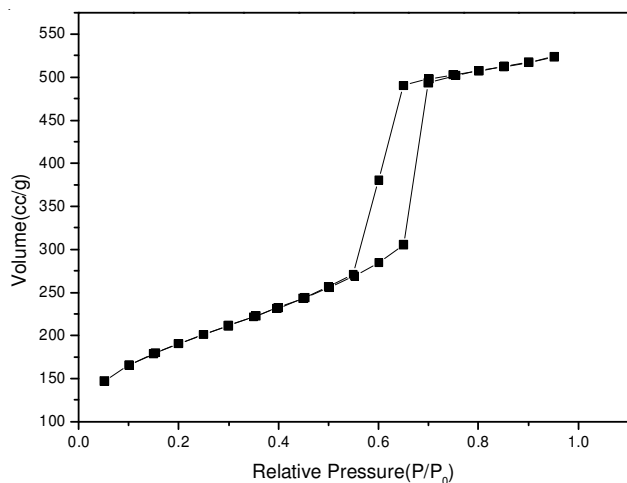


Fig. 5. Nitrogen adsorption-desorption isotherms of mesoporous silica

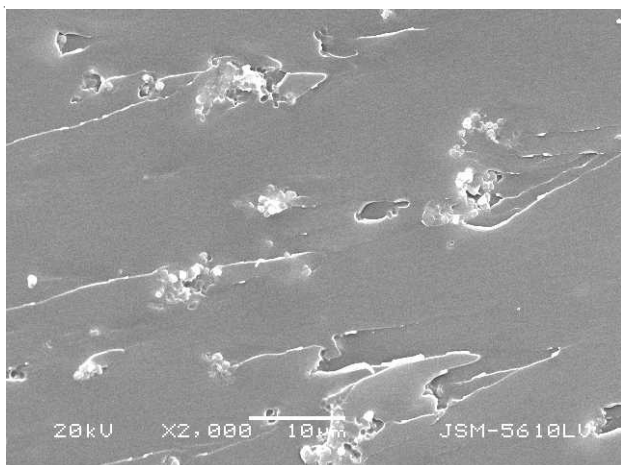


Fig. 6. Scanning electron micrographs of mesoporous silica/epoxy acrylate

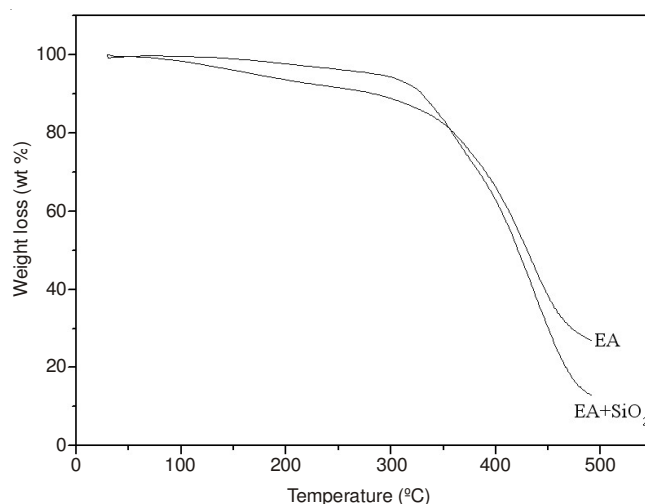


Fig. 7. TGA of mesoporous silica/epoxy acrylate and epoxy acrylate (EA)

## Conclusion

The mesoporous silica was successfully prepared and the diameter of the path was about 5 nm. The BET surface area was  $492 \text{ m}^2\text{g}^{-1}$  and the pore volume was  $1.009 \text{ cm}^3\text{g}^{-1}$ . Mesoporous silica was uniformly dispersed in epoxy acrylate resin. Epoxy acrylate/mesoporous silica began evident weight loss at 325 °C, 25 °C higher than pure epoxy acrylate resin.

## ACKNOWLEDGEMENTS

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