A selectively-energy-absorbing nanoporous system

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Abstract

By forcing an aqueous solution of *N*-lauroylsarcosine sodium salt and 8-anilino-1-naphthalenesulfonic acid ammonium salt in a hydrophobic nanoporous silica gel, the external work can be largely dissipated due to the amplified capillary effect. The sorption isotherm curve is two-staged, and the height and the width of stage-I infiltration plateau can be adjusted separately by controlling the liquid composition. It provides a scientific basis for developing selective protection and damping liquids.
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1. Introduction

While nanoporous materials have been widely used in catalysis, mixture separation, and purification processes [1,2], their applicability in protection and damping systems have not received the necessary attention. The ultra-large pore surface area of a nanoporous material, which is often in the range of $100–1000$ m^2/g, can greatly amplify the solid–liquid interaction, e.g. the capillary effect. Based on this concept, a novel energy absorption system was recently developed, as depicted in Fig. 1 [3–5]. The liquid is nonwetting to the nanoporous particles, such that initially at the atmosphere pressure the solid and the liquid phases are separate. When an external force, *P*, is applied, the piston can be compressed into the container. The associated pressure is calculated as $p = P/A_0$, with A_0 being the cross-sectional area of the piston. As p reaches a critical value, the capillary effect can be overcome and the pressure induced infiltration takes place. If all the nanopores are of the same size, the effective bulk modulus of the system would decrease to zero as the liquid is forced into the nanopores. In reality, the nanoporous material inevitably exhibits a certain pore size distribution, and therefore the slope of sorption isotherm curve is finite. During the infiltration process, the external work is transformed into the solid–liquid interfacial energy. As the

pressure is lowered, the "outflow" of the confined liquid may not take place [6–8].

The unique structure of the nanoporous system provides a promising way for the development of intelligent energy absorption devices. For a protection application, it is often desirable that the system performance can be optimized for specified pressure windows, for which not only the working pressure but also the energy absorption capacities in different pressure ranges need to be adjusted. According to a previous study, by using ethanol as the promoter, the infiltration pressure of a nanoporous system can be controlled quite precisely in the range of 0–20 MPa [9]. The change in infiltration pressure occurs nearly uniformly across the entire infiltration plateau. In order to obtain different energy absorption properties under different pressure ranges, we have investigated a *N*-lauroylsarcosine sodium salt (sarcosyl) modified system [10]. The sarcosyl molecules acted as promoters carrying water molecules into the nanopores. Since the size of sarcosyl molecules was comparable with the nanopore size, they could enter only the relatively large nanopores, due to the confinement effect of nanopore walls. Consequently, the sorption isotherm curve became two-staged. Compared with the unmodified system, while the liquid–solid interaction is more complicated, the processing procedure and the system cost are nearly the same. However, because in this system sarcosyl was the only admixture, the width of pressure window was coupled with the infiltration pressure. In order to independently control the

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infiltration volume, which dominates the system deformation, and the infiltration pressure, which dominates the energy absorption capacity, in the current study we use an additional promoter, 8-anilino-1-naphthalenesulfonic acid ammonium salt (ANSA), to provide another degree of freedom in system design. Compared with sarcosyl, while ANSA is also wettable to surface treated silica, it has a nonlinear molecular structure and a larger molecular size, and therefore the repelling effect of nanopores is more significant.

2. Experimental

The testing samples were prepared using a Fluka 100 C_8 reversed phase nanoporous silica gel, with the average pore size and the standard deviation of 7.8 nm and 2.4 nm, respectively. The specific pore volume was 0.55 cm^3/g. The pore surface was covered by 10–12% hydrophobic silane groups. The sample consisted of 1 part of silica gel and 5 parts of aqueous solution of promoters. The promoter was either Sigma L9150 sarcosyl or Sigma A3125 ANSA, or a combination of them. The promoter concentration was in the range of 0–6.0 wt.%. The molecular weight of sarcosyl was 293.38, and that of ANSA was 316.37. The system was sealed in a stainless steel container by a reinforced gasket (see Fig. 1). By using a type-5569 Instron machine, the piston was compressed into the container. The crosshead speed was 1.0 mm/s. After the pressure, p, reached about 50 MPa, the crosshead of the Instron machine was moved back at the same speed. The sorption isotherm curves are shown in Figs. 2, 3, and 4.

3. Results and discussion

Without any promoters, the applied pressure must exceed p_{in} = 17 MPa so as to force water molecules into the hydrophobic nanoporous silica, forming an infiltration plateau about 0.5 cm^3/g wide, as demonstrated by the zero promoter concentration curves in Fig. 2. As sarcosyl or ANSA is added, the infiltration pressure, p_{in}, is lowered considerably, since the promoter molecules can wet both pore surfaces and water molecules. The value of p_{in} decreases as the promoter concentration, c, rises. The variation in infiltration pressure is nonuniform across the infiltration plateau. As shown in Fig. 2(a), when the promoter concentration, c, is relatively low, the change in sorption isotherm is quite small. Although the decrease in infiltration pressure in the lower pressure range (i.e. in the larger nanopores) is more pronounced, the sorption isotherm is still continuous. As the ANSA concentration reaches 3.0 wt.%, the infiltration plateau (section "AD") contains two stages: "AB" (stage I) and "CD" (stage II) (also see Fig. 2b). This phenomenon should be attributed to that, in stage II,
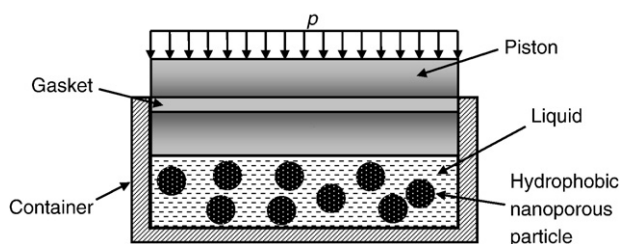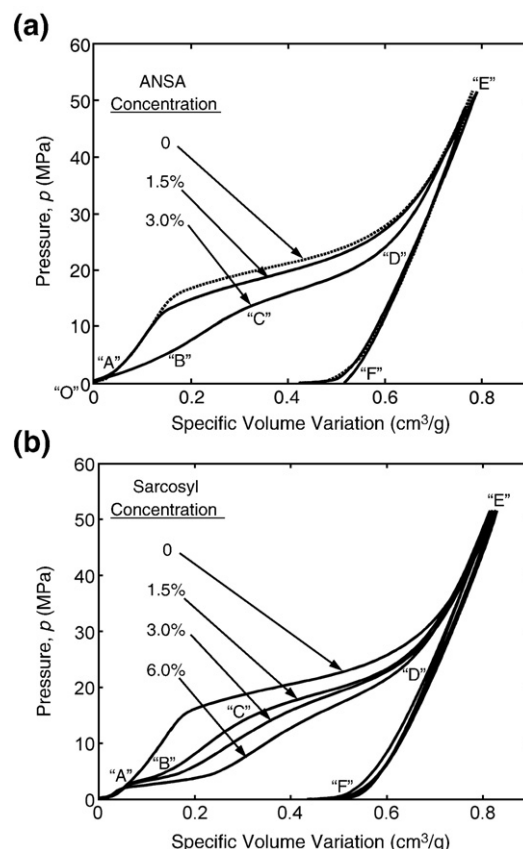

Fig. 2. The sorption isotherm curves of nanoporous systems modified by (a) ANSA and (b) sarcosyl.

since ANSA molecules are too large to enter the relatively small nanopores, their effect on lowering infiltration pressure is suppressed. The width of stage I reflects the specific volume of the relatively large pores that ANSA molecules can enter, which, when c=3.0%, is around 0.1 cm^3/g. The transition zone ("BC") is about 0.1 cm^3/g. The border of stages I and II, which in the current study is taken as the middle point of section "BC", indicates the critical pore size of ANSA infiltration, r_{cr}. If we assume that the pore size distribution is Gaussian, r_{cr}=9.8 nm. The borders of sections of "AB", "BC", and "CD" are set to the points where
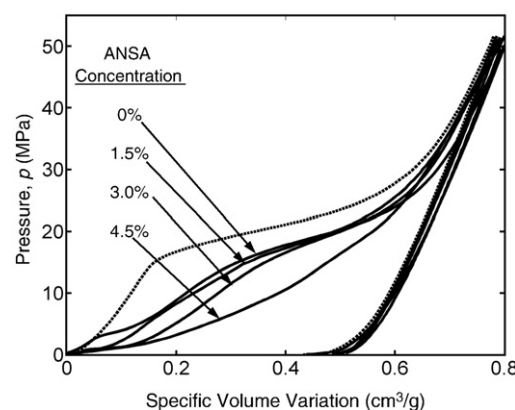

Fig. 3. The sorption isotherm curves of nanoporous systems modified by both of sarcosyl and ANSA. The sarcosyl concentration is 1.5 wt.%. The dashed line indicates the behavior of a pure water based system.

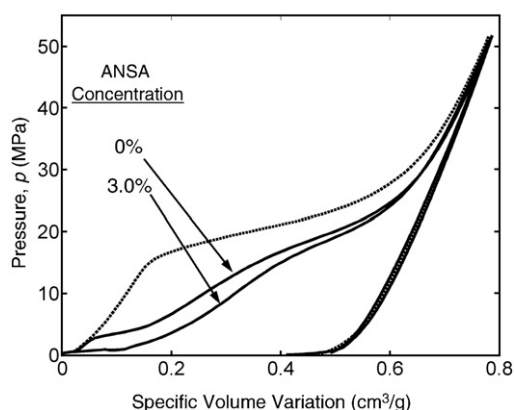Fig. 1. Schematic of the nanoporous energy absorption system.

Fig. 4. The sorption isotherm curves of nanoporous systems modified by both of sarcosyl and ANSA. The sarcosyl concentration is 3.0 wt.%. The dashed line indicates the behavior of a pure water based system.

the slopes of sorption isotherm curve are equal to the average values of slopes of adjacent sections. Note that even though the nanopore surface is not fully covered by surface groups, the side groups prevent the liquid phase from accessing the uncovered areas, unless the pressure is further increased [11]. Upon unloading, the confined liquid remains in the nanopores. Consequently, the unloading paths, "EF", are quite linear.

In the nanoporous systems shown in Fig. 2(a) and (b), since only a single type of promoter is used, the infiltration pressure and the staged infiltration volume are correlated with each other. As the promoter concentration varies, both of p_{in} and r_{cr} are changed. For instance, as ANSA concentration is increased, the stage-I infiltration pressure is lowered and the infiltration volume increases, and vice versa. It is impossible to increase or decrease the stage-I infiltration pressure and volume simultaneously. Figs. 3 and 4 show that, if two promoters are used, by changing their concentrations separately (e.g. by increasing the concentration of one promoter and decreasing that of the other), p_{in} and r_{cr} can be adjusted independently. The influence of the combination of ANSA and sarcosyl does not follow the simple superposition rule. In the systems shown in Fig. 3, the sarcosyl concentration is set to 1.5 wt.% and the ANSA concentration varies from 0% to 4.5 wt.%. Although the critical pore sizes, r_{cr}, for sarcosyl and ANSA are quite different, the sorption isotherm curves are still two-staged; that is, there exists a single effective free volume size limiting the infiltration of promoter molecules.

In Fig. 3, the influence of changing ANSA concentration from 0 to 1.5 wt.% is secondary in most portion of infiltration plateau, except for the beginning section, probably because that sarcosyl has a more significant influence on relatively small nanopores and the effect of ANSA is saturated. As the ANSA concentration rises, the affected area expands from the low pressure range to the high pressure range somewhat uniformly. The stage-I infiltration pressure is quite constant. The most dominant change in the sorption isotherm curve is the increase in the width of the stage-I infiltration plateau, i.e. the infiltration pressure and the infiltration volume are adjusted separately. As the ANSA concentration reaches 4.5 wt.%, the stage-I infiltration

plateau becomes sufficiently wide such that the stage-II infiltration vanishes. An interesting phenomenon is, unlike in the single-promoter system, the saturation effect of the addition of ANSA cannot be observed in the multiple-promoter system, which, again, should be attributed to the interactions among promoter molecules in the nanopores. Similar results can also be observed in the systems shown in Fig. 4, where the sarcosyl concentration is set at 3.0 wt.%. Compared with Fig. 3, the effect of increasing sarcosyl concentration from 1.5 wt.% to 3.0 wt.% is less pronounced, while as the ANSA concentration rises the stage-I infiltration plateau width increases faster. That is, as sarcosyl and ANSA are used at the same time, the effect of addition of sarcosyl is suppressed while that of ANSA is promoted, particularly in the low pressure range.

4. Concluding remarks

Due to the interactions among promoter molecules, the behaviors of a nanoporous system modified by two promoters do not follow the simple rule of superposition. Addition of either ANSA or sarcosyl can lower the infiltration pressure in relatively large nanopores, while has little influence on relatively small nanopores, leading to the formation of two-staged sorption isotherm curves. The infiltration pressure and the infiltration volume can be adjusted quite independently as the concentrations of ANSA and sarcosyl are changed.

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