

Improvement of recoverability of a nanoporous energy absorption system by using chemical admixture

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(Received 20 September 2004; accepted 1 March 2005; published online 8 April 2005)

In this paper, the behaviors of nanoporous energy absorption systems subjected to cyclic loadings are investigated. The systems consist of hydrophobic mesoporous silica particles immersed in aqueous solutions of sodium chloride (NaCl). In the first loading-unloading loop, increasing NaCl concentration, c , causes only slight increases in infiltration pressure and energy absorption efficiency. In the following loops, however, the system behaviors are strongly dependent on c . As c increases from 0% to 25.9 wt. %, the recoverability is improved by a factor of 3, indicating clearly that the addition of NaCl has a beneficial effect to promoting the outflow in the nanoenvironment. © 2005 American Institute of Physics. [DOI: 10.1063/1.1901830]

In the past two decades, nanoporous processing techniques were established, through which a large number of microporous, mesoporous, and macroporous materials have been developed successfully.¹ According to recent researches, in a system consisting of mesoporous materials, i.e., materials with the pore sizes in the range of 2–80 nm, immersed in a nonwetting liquid, as the pressures increase, once the capillary effect is overcome the liquid can be forced into the nanopores.^{2–5} During this process, the free energy is increased since more surface areas are exposed to the liquid. When the pressure is reduced back to the atmosphere pressure, however, the outflow can be difficult,^{6–8} that is, the interfacial energy cannot be released. Due to the ultrahigh specific area of the nanoporous material, which is often in the range of 100–1000 m²/g, the specific “absorbed” energy of this system can be higher than that of composites or shape memory alloys by orders of magnitude, providing a promising way for the development of advanced protection devices.⁹

Clearly, the liquid behavior in the nanoenvironment is different from that in conventional transport problems of porous media or microchannels, where, although the capillary effect is significant, the analysis can still be carried out in the context of continuum fluid mechanics.¹⁰ In a mesopore, the pore radius is comparable with the molecular size of the liquid, and thus the macroscopic theories cannot be applied. In some previous research, the unique behaviors of the nanoporous systems were related to the variation in contact angle as the flow direction changes,¹¹ the difficulties in the growth of gas phases,⁶ or the saddle point of phase transformation.¹² However, these models reflect only a subset of observed phenomena and lack direct experimental support.

The limited experimental data currently available in open literature are merely proof-of-concept results. Many important parameters, such as the interfacial energy and the equilibrium pressure, or whether these parameters are indeed important, are quite inadequately understood. In view of the above considerations, we are carrying out a study on the energy absorption performance of sodium chloride (NaCl) solution-based systems. It has been well known that, at the macroscopic level, the addition of NaCl in water leads to a

higher surface tension. Since the NaCl solution is neutral, the relationship between the surface tension and the NaCl concentration is quite linear.^{13,14}

The nanoporous material used in the current study was Fluka 100 C₈ reversed phase mesoporous silica of an end-capped structure. The particle size was in the range of 15–35 μ m, and the average pore size was 7.8 nm, with a standard deviation of 2.4 nm. The specific area was 287 m²/g. The surface coverage ranged from 10–12%. The specific pore volume was 0.55 mm³/g. The material was characterized at Quantachrome Instruments in Florida.

The mesoporous silica particles were dispersed in an aqueous solution of NaCl and then sealed in a hydraulic device. By measuring the piston displacement, the volume variation of the energy absorption system was obtained as a function of the pressure. The compressive force was applied by a type-5569 Instron machine in displacement control mode. The crosshead speed was set to 1 mm/min. As the crosshead moved downwards, the force F was measured by an Instron 50KN loadcell and the system pressure P was calculated as F/A , where $A=286.5$ mm² is the cross-sectional area of the container. Once P exceeded 50 MPa, the crosshead was moved back to its initial position at the same speed of 1 mm/min. The loading-unloading cycles were repeated until the P - ΔV curve reached the steady state, where the specific volume change ΔV is defined as the ratio of the volume change, ΔV_0 , to the weight of the mesoporous silica particles, w . A number of energy absorption systems with the NaCl concentrations, c , in the range of 0–25.9 wt. % were studied. At each NaCl concentration, 3–4 samples were tested.

During loading, as the pressure increases, initially the system volume decreases nearly linearly. When P reaches a critical value, the infiltration begins and as a result the slope of the P - ΔV curve decreases considerably, forming a plateau region. In the first loop, the infiltration pressure, p_{in} , which is taken as the pressure at the middle point of the plateau region, varies with c , as it should, since both of the liquid-solid interfacial energy and the gas-liquid interfacial energy are dependent on the NaCl concentration. When $c=0$, $p_{in}=21$ MPa; and when $c=23.1$ wt. %, $p_{in}=26$ MPa. Note that, regardless of the change in c , the specific volume change

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TABLE I. The experimental results of E_1 and P_{out} .

c (wt %)	0.0	4.8	9.1	13.0	16.7	20.0	23.1	25.9
E_1 (J/g)	10.8	10.9	11.2	11.3	11.3	11.4	11.8	12.3
P_{out} (MPa)	2.5	3.8	4.0	4.2	4.4	4.5	5.0	5.3

associated with the plateau is always around $0.5 \text{ cm}^3/\text{g}$, close to the specific pore volume.

During unloading, the pressure decreases rapidly as the crosshead is moved upwards. We define the “outflow” pressure, P_{out} , somewhat arbitrarily as the pressure in the unloading section of the first loop at which the slope decreased by 50%. When $P > P_{out}$, the P - ΔV curve is quite linear, indicating that the outflow of the liquid in the nanopores is difficult. When P is lower than P_{out} , the slope of the P - ΔV curve is lowered, that is, the confined liquid starts to come out. However, until the pressure is reduced back to the atmosphere pressure, there is still a significant portion of liquid confined in the nanoenvironment, resulting in the high-energy absorption efficiency, E_1 , as shown in Table I.

In the second loop, in the system based on pure water [see Fig. 1(a)], initially as the pressure rises, the system is compressed with the bulk modulus quite close to that in the first loop. The system seems slightly stiffer, probably due to the residual liquid in the mesoporous particles. The critical pressure at which the forced infiltration begins, however, is much higher. Another significant difference is that the specific volume change in the plateau region is smaller, as it should, since the residual liquid occupies most of the porous space prior to the onset of the second infiltration. Actually, the plateau region of the second loop resembles the section of the first loop in the same pressure range. When more loading-unloading loops are applied, there is no significant further change in P - ΔV relation.

It is clear that the confined liquid consists of two parts: the reversible and irreversible parts. The reversible part is

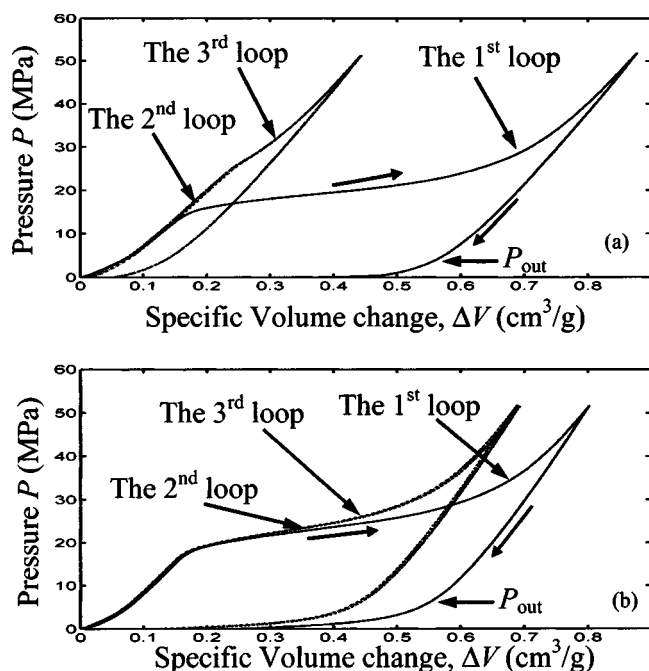


FIG. 1. The energy absorption isotherms under cyclic loading: (a) in pure water and (b) in 23.1 wt. % aqueous solution of NaCl.

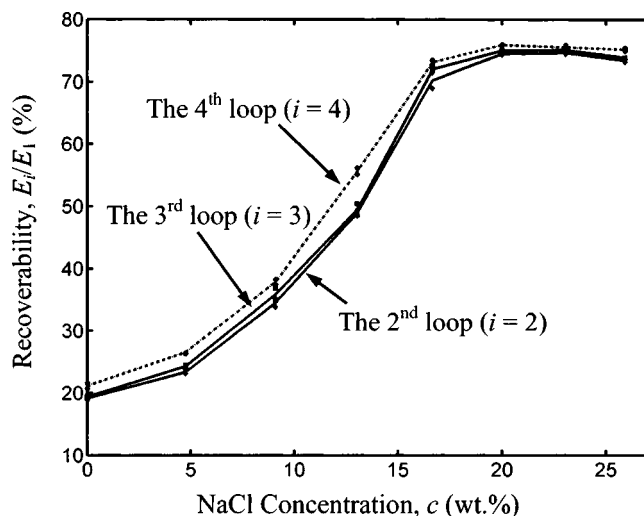


FIG. 2. The system recoverability as a function of the NaCl concentration.

probably related to the liquid in larger pores that can come out once the applied pressure is removed, and the associated porous space can be refilled. The irreversible part, on the other hand, remains in the nanopores even when the pressure is reduced to 0. This phenomenon leads to an 80% decrease in energy absorption efficiency in the pure water-based system. The reason of the nonoutflow is still under investigation. It may be caused by the loss of contact of the liquid body confined in the interior of a particle with the surrounding liquid phase, or the difficulty in gas-phase nucleation.^{6,12}

As the NaCl concentration becomes higher, through Figs. 1 and 2 it can be seen that the fraction of the reversible part increases; that is, the recoverability of the system is improved. The recoverability, E_i/E_1 , where E_i is the specific absorbed energy in the i th loop ($i=2,3,4,\dots$), is sensitive to the NaCl concentration when c is in the range of 5–17 wt. %. When the NaCl concentration is higher than 17 wt. %, the recoverability remains around 75%. Under this condition, the loss of the specific absorbed energy is only about 25%, three times lower than that in a pure water-based system.

The change in recoverability should be attributed to the dependence of P_{out} on c . Table I shows that, as c varies from 0 to 25.9 wt. %, P_{out} increases from 2.5 to 5.3 MPa, and therefore the outflow, while still incomplete, becomes much easier. At the macroscopic scale, since the NaCl solution is neutral and the acid and base terms are quite constant, the interfacial energy is nearly linear to the NaCl concentration.^{13,14} According to the experimental data obtained in the current study, however, for the mesoporous silica particles the c dependences of P_{out} , E_i , and E_i/E_1 are all highly nonlinear, indicating that the conventional interface theories cannot be applied for the nanoenvironment. This phenomenon should be related to the confinement effect of the pore walls.

To summarize, through the experimental study on the energy absorption behaviors of mesoporous silica particles immersed in aqueous solutions of NaCl, it is found that the addition of NaCl can greatly improve the system recoverability, which provides a promising way for developing protection devices that can be repeatedly used. When the NaCl concentration is higher than 17 wt. %, the recoverability is increased to about 75% and no longer sensitive to c . This

phenomenon is attributed to the increase in P_{out} , the reason of which is still not fully understood. The conventional interface zone theories, in which the confinement effects of the nanoenvironment are not taken into consideration, cannot capture the nonlinearity of the system performance.

This work has been supported by the Army Research Office under Grant No. W911NF-04-1-0244, for which we are grateful to Dr. D. M. Stepp. Special thanks are also due to Dr. M. Hu, Dr. M. Jaroniec, and Dr. B. Z. Newby for the useful discussions and valuable suggestions.

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