Thermal recoverability of a polyelectrolyte-modified, nanoporous silica-based system

F.B. Surani
Department of Civil Engineering, University of Akron, Akron, Ohio 44325-3905

A. Han and Y. Qiao[a]
Department of Structural Engineering, University of California at San Diego,
La Jolla, California 92093-0085

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The thermal recoverability of a nanoporous silica-based system modified by a cross-linked polyelectrolyte is investigated. At room temperature, as a nominally hydrostatic pressure is applied, the gel matrix can be partially dehydrated. The released water molecules will be forced into the initially energetically unfavorable nanopores and are "locked" there. At an elevated temperature, the infiltration pressure increases slightly, which is contradictory to the experimental data of the unmodified system. More importantly, the defiltration of the confined liquid is significantly promoted, leading to a much higher system recoverability.

I. INTRODUCTION

Developing nanostructured energy-absorbing materials has been an active area of study. The basic concept is quite straightforward: if energy dissipation could take place simultaneously across the large interface between different components, the energy absorption efficiency would be ultrahigh. However, very often, the controllability of the interface behavior of a nanomaterial is poor. For instance, with a relatively high filler content, the fracture mode of a silicate nanolayer-reinforced polyamide 6 composite is cleavage, and the majority of nanolayers are still well bonded with the matrix even after the final failure occurs.[1,2] That is, the large specific interface area cannot be fully used.

To solve this problem, it would be desirable if one of the components is sufficiently "flexible." Based on this concept, nanoporous energy absorption systems (NEAS) have recently received considerable attention.[3–6] As nominally hydrostatic pressure is applied on a system consisting of hydrophobic nanoporous particles immersed in water, pressure-induced infiltration occurs when the capillary effect is overcome. As a result, the large pore surface is exposed to the nonwetting liquid, and a significant amount of mechanical work is converted to the excess solid-liquid interfacial tension, which can be regarded as being dissipated because, in many nanoporous materials, the confined liquid would remain in the initially nonwettable nanopores even after the external pressure is entirely removed. Because of the high specific surface area of the nanoporous material, which typically ranges from 100–2000 m^2/g, the energy absorption efficiency of a NEAS can be much higher than that of conventional protective or damping materials such as polymer foams and Ti-Ni alloys.

Further investigations indicate that the structure of a NEAS can be greatly simplified if a polyelectrolyte is used to "solidify" the liquid phase.[7,8] Under the ambient pressure, a polyelectrolyte-modified system is solid-like. As the applied pressure exceeds the critical value of infiltration pressure, p_{in}, the polyelectrolyte gel matrix can be partially dehydrated and water molecules will be released from the gel network cells and be forced into the nanopores, leading to the superior energy absorption characteristic. Such a system can actually be regarded as a nanocellular composite material, with the handling and placing procedures much simpler and more reliable than that of the liquid systems.

The previous studies in this area were focused on the room-temperature behaviors of the solid-like NEAS. In this study, we investigate the thermal effects on the energy absorption performance of a poly(isobutylene-co-maleic acid) sodium salt (PIMA-Na)-modified, nanoporous silica-based system. The experimental results show that, at an elevated temperature, the infiltration pressure of the PIMA-Na-enhanced NEAS increases, while a more remarkable phenomenon is the significant improvement in system reusability, making the thermal recovery treatment a promising method for the development of reusable protective or damping structures.

II. EXPERIMENTAL

Figure 1 depicts the experimental setup. The testing sample was prepared by first mixing 0.5 g of 100 C_8

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[a] Address all correspondence to this author.
e-mail: yqiao@ucsd.edu

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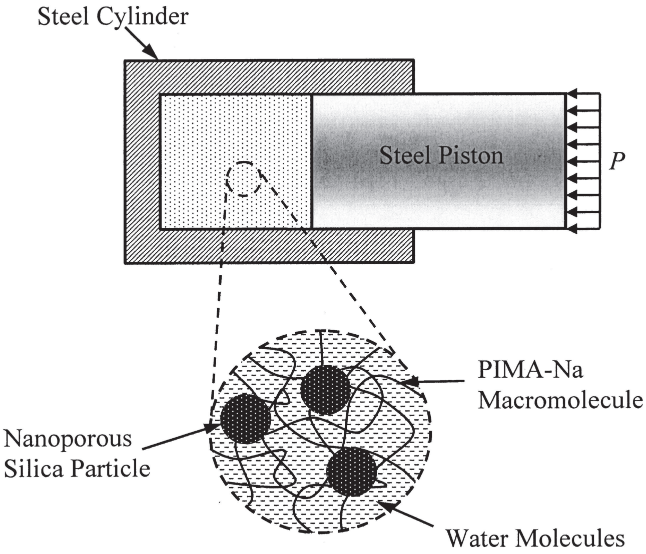

FIG. 1. A schematic diagram of the experimental setup.

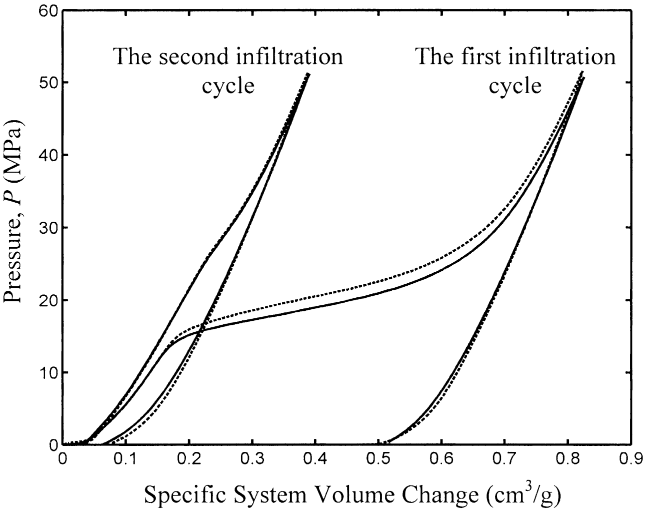

FIG. 2. The sorption isotherm curves at 21 °C. The solid lines and the dashed lines indicate the behaviors of the PIMA-Na-modified system and the water-based system, respectively.

reversed phase end-capped nanoporous silica particles (Fluka, Buchs, Swizterland) in 7 g of distilled water, and then adding 2 wt% of cross-linked PIMA-Na (535141; Aldrich, Milwaukee, WI). According to the Berrett-Joyner-Halenda analysis carried out at Quantachrome Instruments (Boynton Beach, FL), the average pore size of the silica particles was 7.8 nm and the standard deviation was 2.4 nm. The specific pore surface area was 287 m^2/g, and the specific pore volume was 0.55 cm^3/g.

As the PIMA-Na was dispersed in water, the charged functional groups would confine the water molecules inside the cross-linked network cells that had the characteristic length in the broad range of a few nanometers to a few micrometers.[9,10] Consequently, the flowability of the liquid phase was reduced considerably, and the modified NEAS became solid-like. The mixing and the modification procedures were performed in a steel cylinder. By using a type 5569 machine (Instron, Norwood, MA), a nominally hydrostatic pressure was applied on the specimen. A 50KN load cell was used, with the linearity of 0.5% of the full scale, leading to a pressure measurement resolution of approximately 0.8 MPa. The piston moved at a constant rate of 1 mm/min. Once the pressure reached approximately 50 MPa, the piston was moved out at the same speed. A number of specimens were tested at various temperatures in the range of 21 °C–80 °C. The temperature was controlled by a controlled-temperature bath (Z51 317-2; Aldrich). At each temperature, the loading-unloading cycles were repeated four times and the results are shown in Figs. 2–4. The specific volume change is defined as the total volume change normalized by the mass of the nanoporous silica. Because the second, third, and fourth cycles of the sorption isotherm curves were almost identical, only the first two loops are shown.

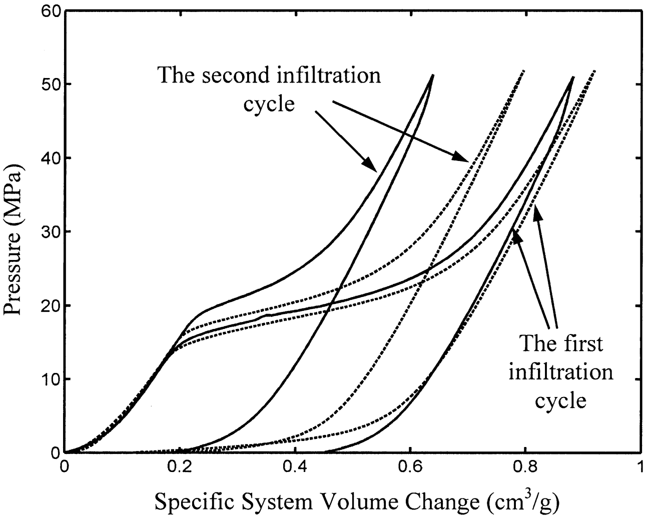

FIG. 3. The sorption isotherm curves at 50 °C. The solid lines and the dashed lines indicate the behaviors of the PIMA-Na-modified system and the water based-system, respectively.

For comparison purposes, a set of pure water-based systems were also tested. The sample preparation and the testing procedure were quite similar to that of the PIMA-Na-modified specimens, except that no PIMA-Na was added. The sorption isotherm curves are given as the dashed lines in Figs. 2–4.

III. RESULTS AND DISCUSSION

At room temperature, as shown in Fig. 2, the energy absorption was achieved successfully in the infiltration experiment. As the pressure was lower than 14 MPa, the system was linearly compressed, with the effective bulk modulus of 1.6 GPa, similar to that of water. As the

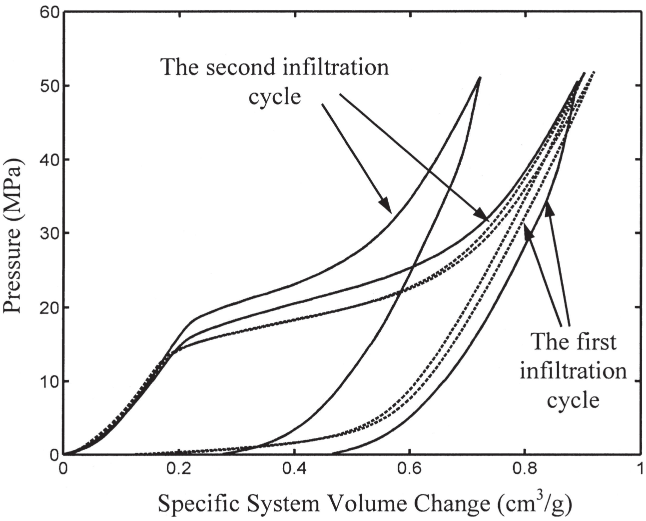

FIG. 4. The sorption isotherm curves at 80 °C. The solid lines and the dashed lines indicate the behaviors of the PIMA-Na-modified system and the water-based system, respectively.

pressure was higher than 14 MPa, the capillary effect of the relatively large nanopores was overcome and the pressure-induced infiltration led to a sudden increase in system compressibility; that is, water molecules were released from the gel matrix and entered the initially energetically unfavorable nanopores. Thus, an infiltration plateau was formed in the sorption isotherm curve. With increasing pressure, more and more smaller pores were involved in the infiltration process, and eventually when most of the pores were filled, the effective system bulk modulus converged to 1.6 GPa again. Note that most of the confined liquid did not come out of the nanopores after the pressure was lowered to 0. Therefore, the sorption isotherm was highly hysteretic and the system was energy absorbing. The energy absorption efficiency can be assessed as the area enclosed by the loading-unloading loop, which was nearly 13 J/g. The mechanisms and processes that govern the phenomenon of “non-outflow” are still under investigation. It may be attributed to the “ink bottle” structures of nanopores,[11] the flow direction effect on the effective solid-liquid interfacial tension,[12] and/or the confinement effect of pore walls and the mass and energy exchanges among liquid, gas, and solid phases.[13]

Because of the “non-outflow,” after the first loading-unloading cycle, the accessible pore volume was largely reduced. For instance, in Fig. 2, the width of the infiltration plateau of the second cycle was only about 8% of that of the first cycle. Compared with the pure water-based system, at room temperature, the infiltration pressure of the PIMA-Na-modified system was slightly lower, most likely because of the strain energy stored in the polyelectrolyte gel matrix, i.e., a certain amount of potential energy would be released as water molecules leave the gel network cells, promoting the pressure-induced infiltration in the silica nanopores.[14]

As temperature, T, increased, through Figs. 3 and 4, it can be seen that the sorption isotherm curves in the second loading-unloading cycles were changed significantly. When $T = 50$ °C, the width of infiltration plateau in the second cycle was about 45% of that of the first one; and when $T = 80$ °C, this ratio increased to 75%. That is, at an elevated temperature, more confined liquid can be released from the nanopores as the pressure is lowered. It was observed in the experiments that the sorption isotherm curves in the following cycles were almost identical to that of the second cycle, suggesting that, after the initial cycle, the infiltration process becomes fully reversible. Hence, thermal recovery treatment can be applied on the solid-like NEAS such that the systems can work repeatedly.

The thermal recovery phenomenon may be related to the gas phase formation inside the nanopores. At a higher temperature, with a constant pressure, the energy barrier of formation of gas phase nuclei is reduced, and it is relatively more energetically favorable for the gas phase to grow.[13] If the gas phase grows across the entire nanopore, at the macroscopic level, the full defiltration takes place. Note that the liquid behaviors in nanopores are dependent on the pore size. At all of the temperatures, the infiltration pressure of the second cycle was much higher than that of the first one, indicating that defiltration in smaller nanopores was easier. This should be attributed to the fact that, in a smaller nanopore, the effect of excess solid-liquid interfacial energy, i.e., the “driving force” of defiltration, was more pronounced. In fact, it can be seen that the sorption isotherm curve in the second cycle is similar with the high-pressure portion of the first loop.

Similar thermal recovery behaviors were also observed for the pure water-based system, which is in agreement with previous experimental data that the motions of confined pressurized liquids are thermally aided.[15] Note that at the same temperature, the recoverability of the pure water-based system was higher than that of the PIMA-Na-modified system. Another interesting phenomenon is the temperature dependence of the infiltration pressure. In the current study, the infiltration pressure, p_{in}, was defined as the pressure at the onset of infiltration at the first loading. In the PIMA-Na-modified system, p_{in} increases with temperature. As $T = 50$ °C and 80 °C, p_{in} rises from 14 to 16 MPa and 17 MPa, respectively. On the other hand, in the pure water-based system, p_{in} decreases with temperature. As $T = 50$ °C and 80 °C, p_{in} is lowered from 17 to 13.5 MPa and 13 MPa, respectively. Thus, while at room temperature infiltration in the pure water-based system requires a higher pressure, as the temperature reaches 80 °C the solid-like system is of a larger p_{in}. Because, according to the analysis of the carbon content of nanoporous silica particles before and after infiltration tests,[8] polyelectrolyte macromolecules cannot enter the nanopores, the change in infiltration pressure should not be related to the solid-liquid interactions in the interior of the nanoporous silica. It is likely that the higher infiltration pressure of the PIMA-Na-modified system is caused by the relatively high mobility of polyelectrolyte macromolecules, such that the nanopores are partly blocked. This also explains why the thermal recoverability of a solid-like system is smaller than that of a pure water-based one, because in a partly blocked nanopore gas phase growth and liquid motions become more difficult. Clearly, this hypothesis needs to be further validated by in situ measurements.

IV. CONCLUDING REMARKS

According to the experimental study on the pressure-induced infiltration of a PIMA-Na-modified nanoporous silica-water system, the defiltration of confined liquid in nanopores is a thermally aided process. Increasing temperatures can largely promote defiltration, leading to a much higher system recoverability, providing a promising way for developing reusable solid-like protective or damping structures. While the infiltration pressure of a pure water-based system decreases as temperature increases, the infiltration pressure of the solid-like NEAS increases with temperature, which may be attributed to the fact that at elevated temperature the nanopores can be partly blocked by the PIMA-Na macromolecules. However, compared with the thermal recovery effect, the variation in infiltration pressure is only secondary.

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