An energy-absorbing polyelectrolyte gel matrix composite material

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Abstract

A novel polyacrylic acid gel matrix composite material functionalized by hydrophobic nanoporous silica particulates is developed. When subjected to a high pressure, water molecules can be released from the polyacrylic acid network and forced into the nanopores. Due to the exposure of the large pore surface to the nonwetting liquid, the system free energy increases significantly. As the pressure is removed, the water remains in the confining nanoenvironment, and thus the material is energy absorbing. The energy absorption efficiency is much higher than that of many conventional protective materials.
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1. Introduction

Energy absorption materials (EAM) such as epoxy composites, polymer and metal foams, and Ti–Ni alloys have been widely used for car bumpers, blast-resistant containers, protective layers, among others [1,2]. However, because of the relatively low energy absorption efficiency, the protection systems based on them are often bulky and heavy. Over the years, continuous efforts have been made to search for new energy-absorbing mechanisms.

Based on recent research on pressure induced infiltration [3–6], it has been demonstrated that the ultra-large surfaces of nanoporous materials can be utilized to amplify the well-known capillary effect. By forcing water into hydrophobic nanoporous silica particles, a large amount of external work can be converted to the solid–liquid interfacial tension [7]. While the absolute value of the excess interfacial energy $\Delta\gamma \approx 0.06$ J/m^2 is relatively low, due to the high specific surface area $A \approx 250$ m^2/g, the energy absorption efficiency of this system $E^* = \Delta\gamma \cdot A \approx 15$ J/g is much higher than that of ordinary EAM. For example, the energy absorption efficiencies of polymer foams, metal foams,

and Ti–Ni alloys are around 0.1–1 J/g [8], 1–3 J/g [9], and 0.5 J/g [10], respectively. If nanoporous materials of smaller pores are used, E^* can be further increased by another order of magnitude.

However, since the nanoporous particle–water system contains a liquid phase, it must be sealed appropriately, making it quite incompatible with most of conventional protection devices. In order to minimize the difficulty in implementing this concept in engineering practice, it is desirable to develop a solid-like system consisting of hydrophobic nanoporous particulates dispersed in a gel matrix. Under ambient condition, the system can be placed and handled as a normal EAM; under a high pressure, water molecules become highly mobile in the gel matrix and can be "compressed" into the nanopores, activating the energy absorption process. Such a system can actually be regarded as a composite material, with the gel matrix being functionalized by the nanoporous particulates.

One of the most promising candidates for the gel matrix is superabsorbent. Superabsorbents are polyelectrolytes that can form stable confining networks [11,12]. The commonly used superabsorbents include polyacrylic acid, poly(styrene sulfonate), etc. In this article, we investigate the energy absorption behavior of nanoporous particles in a polyacrylic acid gel.

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2. Experimental

Fig. 1 depicts the microstructure of the specimen. By dispersing 0.5 g of Sigma 100 C_8 reversed phase nanoporous silica particulates in 7 g of distilled water, a liquid energy absorption system was formed. The properties of this system were documented in [5–7]. By adding 0.55 g of VWR 376 polyacrylic acid, the liquid phase was solidified into a gel, and the silica particulates were embedded in it, forming a gel matrix composite material, as shown in Fig. 2. The size of the silica particulates was 25 μm and the standard deviation was 3.5 μm. The average pore size was 7.8 nm and the standard deviation was 2.4 nm. The specific pore volume was 0.55 cm^3/g.
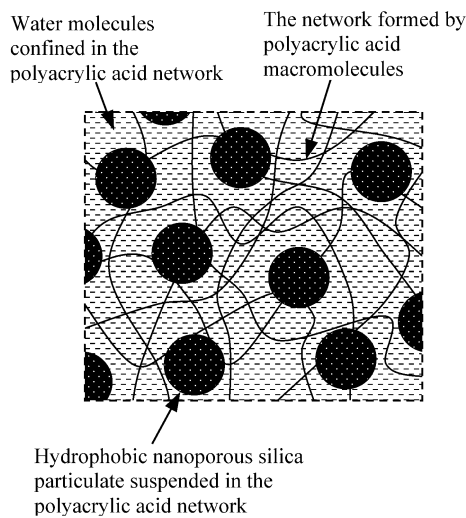

Fig. 1. A schematic diagram of the polyacrylic acid gel matrix composite material functionalized by hydrophobic nanoporous silica particulates.
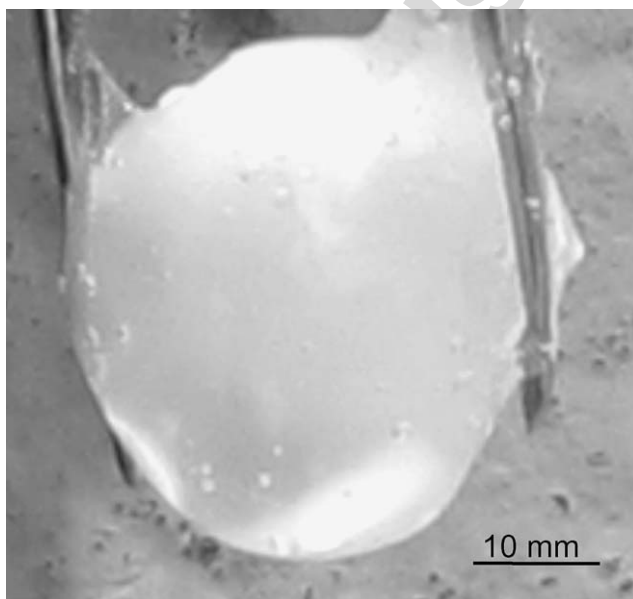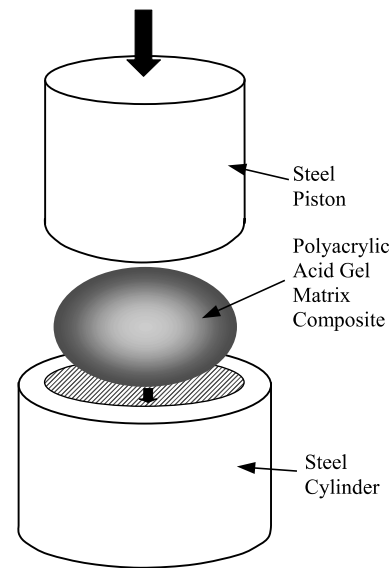

Fig. 2. A photo of the developed material.

Fig. 3. A schematic diagram of the experimental setup.

After removal of remaining water and drying in air for about 10 min, the polyacrylic acid gel functionalized by nanoporous silica particulates with the initial volume of 3.5 cm^3 was placed in an end-capped steel cylinder (see Fig. 3). The inner diameter of the cylinder was $d_0 = 19.05$ mm. By using a type-5569 Instron machine, a steel piston of the same diameter was compressed into the cylinder, applying a uniform pressure on the material. The piston speed was set to 0.5 mm/min. As the pressure reached about 50 MPa, further increase in pressure would not lead to detectable changes in system behavior, and the piston was moved back at the same speed. The pressure was calculated as $p = 4F/(\pi d_0^2)$, with F being the load applied on the piston. The loading–unloading cycle was repeated until the sorption isotherm converged to the steady-state, as shown in Fig. 4. The specific system volume variation was defined as $\Delta V = \left(D \cdot \frac{\pi d_0^2}{4} \right)/m$, where D is the piston displacement and $m = 0.5$ g is the mass of the silica particulates. Altogether three samples were tested. The
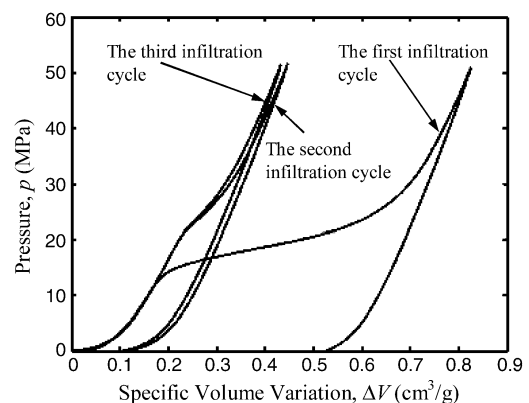

Fig. 4. The sorption isotherm. The curves have been shifted along the horizontal axis.

results of them were quite similar, with the difference in infiltration pressure smaller than 2%.

3. Results and discussion

When dispersed in water, polyacrylic acid macromolecules can crosslink each other through charged groups and form a unified network. The water molecules are confined in the cells of the network. Hence, by adding a small amount of polyacrylic acid, typically 2–6% in weight, in water, the characteristic of fluid would be lost and the system is solidified to a soft matter [11]. When a hydrostatic pressure is applied, if the pressure filed is isotropic, the soft matter would deform and the system free energy would increase as the strain energy is stored. However, the variation in driving force of water diffusion is negligible, and consequently the gel structure is quite stable. If the stress field is not equiaxed, e.g. there exist small voids in the material, the water molecules tend to diffuse from the high-energy region (the polyacrylic acid network) to the low-energy region (the small voids), until the voids are filled. Since this process is energetically favorable, it is governed by kinetics instead of thermodynamics.

In the gel matrix composite material functionalized by nanoporous particulates, the nanopores are hydrophobic. Therefore, the applied pressure must be sufficiently high so that the capillary effect can be overcome. As shown in Fig. 4, initially when the pressure is low, water molecules cannot infiltrate into the nanoporous silica, and, except for the initial concave section caused by the loading system, the sorption isotherm curve increases quite linearly. As the pressure reaches 14.3 MPa, the sorption isotherm becomes highly nonlinear, indicating that the pressure induced infiltration begins. Due to the pore size distribution, the slope of the infiltration plateau is positive. When the pressure reaches 27.2 MPa, most of the pores are saturated and the system compressibility decreases rapidly. The pressure range of the infiltration plateau is quite similar to that of the nanoporous system based on pure water [13], suggesting that this process is dominated by the confined water molecules in nanopores. Note that the width of the infiltration plateau is about 0.5 cm³/g, close to the measured specific pore volume.

The unloading behavior of the polyacrylic acid gel matrix composite material is quite linear, similar to the pure water based nanoporous system [5–7], which is compatible with the previous experimental observation that under ambient condition most of the confined water molecules cannot come out of the nanopores. That is, the increased system free energy associated with the water infiltration cannot be released, resulting in the significant energy absorption. The energy absorption efficiency of the current material, which can be calculated as the area enclosed by the first infiltration cycle of sorption isotherm,

is around 14 J/g, about the same as that of the water based system (15 J/g) [5]. Since most of the porous space remains being filled, from the second loading–unloading cycle the energy absorption capacity of the composite material is largely reduced, i.e. the material is suitable for one-time protection applications.

To summarize, a hydrophobic nanoporous silica particulate functionalized polyacrylic acid gel matrix composite material is developed. Due to the large specific surface area of the nanoporous particulates, the energy absorption efficiency of this material is very high. The pressure induced infiltration is dominated by thermodynamics. This material can be regarded as the solid counterpart of previously investigated water based nanoporous energy absorption systems. It is more compatible with conventional protection devices and therefore is more readily applicable to engineering practice.

Acknowledgements

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