

Pressure Induced Liquid Infiltration In A Functionalized Poly(acrylic acid-co-acrylamide) Potassium Salt Gel Matrix Material

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Developing high-performance energy absorbing materials is essential to the design of protective and damping structures, such as car bumpers, body armors, mounting stages, etc. For the past decade, intensive studies have been conducted on nanocomposites [1-5]. Recently, the energy absorption characteristics of liquid suspensions of nanoporous particles (LSNP) have received considerable attention [6-10]. By immersing hydrophobic nanoporous particles in water, the liquid phase can enter the nanopores when a high pressure is applied. Once the pressure induced infiltration occurs, most of the nanopore surface can be exposed to the liquid, leading to a significant increase in system free energy, $\Delta\gamma \cdot A$, where $\Delta\gamma$ is the excess solid-liquid interface tension and A is the specific area of the nanoporous material, often in the range of $10^2 - 10^3 \text{ m}^2/\text{g}$. Typically, $\Delta\gamma$ is at the level of $10 - 10^2 \text{ mJ/m}^2$, and thus the energy absorption efficiency of the nanoporous solid-liquid system can be as high as $10 - 100 \text{ J/g}$, orders-of-magnitude larger than that of many conventional protective materials such as polymer foams, Ti-Ni alloys, etc. However, the LSNP must be sealed appropriately throughout the operation procedure; otherwise the energy absorption capacity would be lost. This would considerably increase the complexity in fabrication and maintenance, especially when the working pressure is relatively high.

In this article, we report the development of a solid material consisting of a gel matrix functionalized by hydrophobic nanoporous silica particles. The nanoporous silica has been discussed elsewhere [7]. The average pore size was 7.8 nm , with the standard deviation of 2.4 nm . The particle size ranged from 15 nm to 35 nm . The pore walls were covered by a layer of hydrophobic silane groups, making the nanopores energetically

unfavorable for water molecules. After immersing 0.5 g of the silica particles in 7 g of distilled water, the gel matrix was formed by adding $1-2 \text{ wt.}\%$ of Aldrich type-432776 crosslinked poly (acrylic acid-co-acrylamide) potassium salt (PAAK). The chemical formula of PAAK is $(\text{CH}_2\text{CHCOOR})_x(\text{CH}_2\text{CHCONH}_2)_y$, with R being either K^+ or H^+ ions and x and y the numbers of repeat units. The as-received PAAK was in powder form with the particle size of $200-1000 \text{ nm}$. When the PAAK powders were mixed with water, the macromolecules would form unified networks [11, 12]. Due to the polar nature of functional groups, the networks would attract surrounding water molecules and confine their motions. As a result, the water phase was no longer able to flow under shear loadings; that is, the liquid was “solidified.”

The gel formation process took about 2 minutes. The nanoporous silica functionalized sample was then placed in a steel cylinder, and compressed by an Instron type-5569 machine through a steel sliding block. As the sliding block moved downward, the sample was subjected to a uniform pressure, p . As p increased to about 50 MPa , the load was reduced gradually and the sliding block was moved back. The speed of the sliding block was maintained at 0.5 mm/min during the experiment. The typical sorption isotherm curves are shown in Fig. 1. The specific volume change is defined as $A_0 d/m$, where d is the displacement of the sliding block and $m = 0.5 \text{ g}$ is the mass of the nanoporous silica particles.

Since a neat PAAK gel is isotropic and homogeneous, it is quite stable under hydrostatic pressures [11, 12]. Once being functionalized by the nanoporous particles, however, the system becomes heterogeneous. As the gel is subjected to compressive stresses, because silica is much stiffer than the gel matrix, the pressure in the gel is much higher than that in the nanopores. Hence, the water molecules can be “squeezed” out of the gel network and infiltrate into the nanoporous particles. Initially, when the pressure is lower than 17 MPa , the water molecules remain in the matrix and the nanopores are empty. Consequently, the system response resembles that of a neat gel, and the pressure increases quite linearly with the system volume change. As the pressure reaches 17 MPa , with the aid of the pressure field, water molecules start to diffuse from the gel network to the relatively large nanopores. With the increase of pressure, more and more smaller nanopores are involved in the pressure induced infiltration, resulting in the infiltration plateau. Eventually, when the pressure reaches 28 MPa , the porous space is nearly filled and the pressure induced infiltration ends. The post-infiltration system behavior is somewhat similar with before the infiltration, except that the system compressibility is

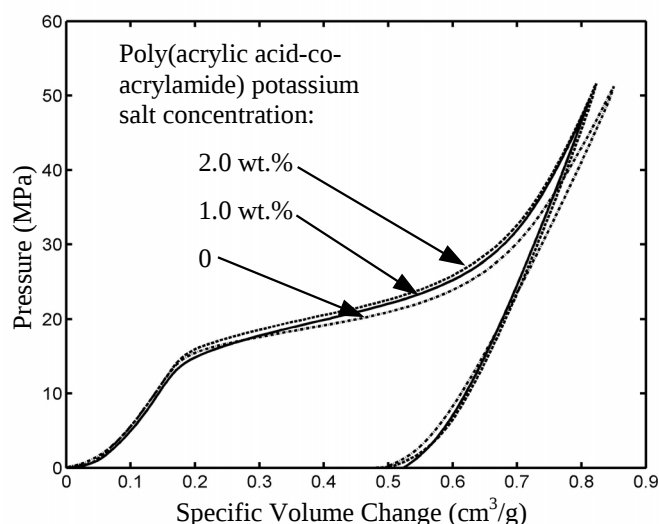


Fig. 3. The sorption isotherm curves of the first loading-unloading cycle

slightly higher, probably because that the effective stiffness of filled silica particles is larger than that of empty ones.

As the pressure is lowered, most of the confined water molecules do not come out of the nanopores, even though the pore walls are non-wettable, the mechanism of which is still under investigation [7]. It may be caused by the lack of a driving force of defiltration, or related to kinetics [13]. Therefore, the unloading section of the sorption isotherm curve is very different from the loading part, leading to the pronounced hysteresis. The area enclosed by the hysteretic loop indicates the energy absorption efficiency, which is about 11 J/g. Note that the infiltration pressure and the width of infiltration plateau are quite insensitive to the PAAK concentration, suggesting that the capillary effect of nanopores is the dominant factor.

Acknowledgements

This study was supported by The Army Research Office under Grant No. W911NF-05-1-0288, for which we are grateful to Dr. David M. Stepp.

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Preparation And Characterization Of High-Purity PZT Powders And Ceramics Made By Modified Spray-Drying Techniques

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The spray drying technique has been of particular interest for decades because of the potential in mass production of high-quality PZT powders. Although fine and very homogeneous

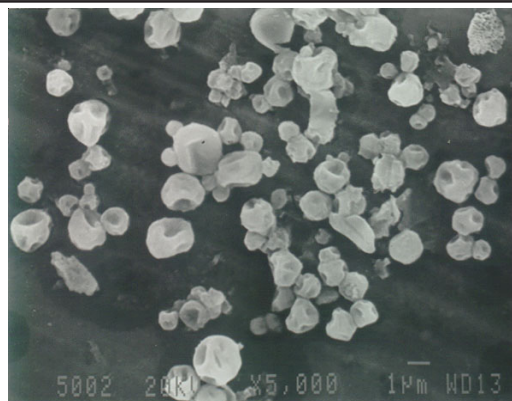


Fig. 3a. Scanning electron micrographs as-sprayed

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Pressure Induced Liquid Infiltration In A Functionalized Poly(acrylic Acid-co acrylamide) Potassium Salt Gel Matrix Material

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Keywords Nanoporous Polyelectrolyte Energy absorption Silica

A nanoporous silica functionalized, energy absorbing material is developed based on crosslinked poly(acrylic acid-co-acrylamide) potassium salt (PAAK) gel. When subjected to a sufficiently high pressure, water molecules can be released from the gel matrix and forced into the nanoporous particles. Since the large nanopore surface can significantly amplify the capillary effect, the energy absorption efficiency is very high, making this material attractive for protection and damping applications. The sorption isotherm curves are quite independent of the PAAK concentration, suggesting that the capillary effect of nanopores is the dominant factor.

Introduction

Developing high-performance energy absorbing materials, particularly materials of high energy absorption capacities per unit mass, is essential to the design of protective and damping structures, such as car bumpers, body armors, blast-resistant containers, mounting stages, etc. For the past decade, intensive studies have been conducted on nanocomposites [1, 2, 3]. The basic idea is quite straightforward: in a composite material reinforced by nanoparticles, nanolayers, and/or nanofibers, when an external loading is applied, if the nanofillers can debond from the matrix, a large amount of energy would be dissipated at the ultra-large nanofiller-matrix interface, and thus the mechanical work is absorbed and the target is protected. However, there exists an intrinsic difficulty that the filler-matrix interaction is difficult to control. For instance, very often with the addition of the nanofillers, the material becomes less ductile and would fail via catastrophic cracking [e.g. 4, 5]. Therefore, only a small fraction of nanofillers are involved in the energy absorption process; that is, the large nanofill-matrix interface cannot be utilized.

One way to fully take advantage of the large surface/interface area of a nanostructured material, as to maximize the energy absorption efficiency, is to introduce in a liquid phase. Recently, the energy absorption characteristics of liquid suspensions of nanoporous particles (LSNP) have received considerable attention [6-10]. By immersing hydrophobic nanoporous particles in water, the liquid phase can enter the nanopores when a high pressure is applied so that the capillary effect is overcome. Once the pressure induced infiltration occurs, since the liquid is quite “flexible” even at the nanometer scale, most of the nanopore surface can be exposed to it, leading to a significant increase

in system free energy, $\Delta\gamma \cdot A$, where $\Delta\gamma$ is the excess solid-liquid interface tension and A is the specific area of the nanoporous material, often in the range of $10^2 - 10^3 \text{ m}^2/\text{g}$. Typically, $\Delta\gamma$ is at the level of $10 - 10^2 \text{ mJ/m}^2$, and thus the energy absorption efficiency of the nanoporous solid-liquid system can be as high as $10 - 100 \text{ J/g}$, orders-of-magnitude larger than that of many conventional protective materials such as polymer foams, Ti-Ni alloys, etc.

While the use of the liquid phase in LSNP assures the “perfect match” of components at solid-liquid interfaces, it also becomes a disadvantage due to the somewhat sophisticated system structure. The LSNP must be sealed appropriately throughout the operation procedure; otherwise the energy absorption capacity would be lost. This would considerably increase the complexity in fabrication and maintenance, especially when the working pressure is relatively high.

In this article, we report the development of a solid material based on crosslinked poly(acrylic acid-co-acrylamide) potassium salt gel and functionalized by nanoporous silica. When the pressure is low, the liquid (water) molecules are confined in the gel matrix; when the pressure is high, the liquid can be released from the matrix and infiltrates into the nanoporous particles, resulting in the energy absorbing behaviors. The nanopores provide additional free space so that the liquid-matrix phase separation, which is otherwise impossible, can take place under nominally hydrostatic loadings. This material has great potential to receive broad applications in engineering practice.

Experimental

Figure 1 depicts the energy absorbing material. It consists of a gel matrix functionalized by hydrophobic nanoporous silica particles. The nanoporous silica had been used in the liquid systems and discussed elsewhere [7]. The average pore size, $2r$, was 7.8 nm, with the standard deviation of 2.4 nm. The particle size, D , ranged from 15 μm to 35 μm . The pore walls were covered by a layer of hydrophobic silane groups, with the surface coverage of 10-12%, making the nanopores energetically unfavorable for water molecules. After immersing 0.5 g of the silica particles in 7 g of distilled water, the gel matrix was formed by adding 1-2 wt.% of Aldrich type-432776 crosslinked poly(acrylic acid-co-acrylamide) potassium salt (PAAK). The chemical formula of PAAK is $(\text{CH}_2\text{CHCOOR})_x(\text{CH}_2\text{CHCONH}_2)_y$, with R being either K^+ or H^+ ions and x and y the numbers of repeat units. The as-received PAAK was in powder form with the particle size of 200-1000 μm . When the PAAK powders were mixed with water, the macromolecules would form unified networks [11]. Due to the polar nature of functional groups, the networks would attract surrounding water molecules and confine their motions. As a result, the water phase was no longer able to flow under shear loadings; that is, the liquid was “solidified”. This property of PAAK has been well known in the superabsorbent industry [12].

The gel formation process took about 2 minutes. The nanoporous silica functionalized sample was then placed in a steel container, and compressed by an Instron type-5569 machine through a steel sliding block, as shown in Fig. 2. As the sliding block moved downward, the sample was subjected to a uniform pressure, p , which can be calculated as

P/A_0 , with P being the load applied on the sliding block and A_0 the cross-sectional area. As pressure p increased to about 50 MPa, the load was reduced gradually and the sliding block was moved back. The speed of the sliding block was maintained at 0.5 mm/min during the experiment. The loading-unloading process was repeated for 4 times, and the typical sorption isotherm curves for the first two cycles are shown in Figs. 3 and 4, respectively. The specific volume change is defined as $A_0 d/m$, where d is the displacement of the sliding block and $m = 0.5$ g is the mass the nanoporous silica particles.

Results and Discussion

Since a neat PAAK gel is isotropic and homogeneous, it is quite stable under hydrostatic pressures [11, 12]. Once being functionalized by the nanoporous particles, however, the system becomes heterogeneous. The average distance among the silica particles, L , was about 80 μm . As the gel is subjected to compressive stresses, because silica is much stiffer than the gel matrix, the pressure in the gel is much higher than that in the nanopores. Hence, the water molecules can be “squeezed” out of the gel network and infiltrate into the nanoporous particles, which is shown clearly in Fig. 3. Initially, when the pressure is lower than 17 MPa, the water molecules remain in the matrix and the nanopores are empty. Consequently, the system response resembles that of a neat gel, and the pressure increases quite linearly with the system volume change. As the pressure reaches 17 MPa, with the aid of the pressure field, water molecules starts to diffuse from the gel network to the relatively large nanopores. With the increase of pressure, more and more smaller nanopores are involved in the pressure induced infiltration, resulting in the infiltration plateau. Eventually, when the pressure reaches 28 MPa, the porous space is nearly filled and the pressure induced infiltration ends. The post-infiltration system behavior is somewhat similar with before the infiltration, except that the system compressibility is slightly higher, probably because that the effective stiffness of filled silica particles is larger than that of empty ones.

As the pressure is lowered, most of the confined water molecules do not come out of the nanopores, even though the pore walls are non-wettable, the mechanism of which is still under investigation [7]. It may be caused by the lack of driving force of defiltration, or related to kinetics [13]. Consequently, the unloading section of the sorption isotherm curve is very different from the loading part, leading to the pronounced hysteresis. The area enclosed by the hysteretic loop indicates the energy absorption efficiency, which is about 11 J/g. Since the nanopores remain being filled after the first loading-unloading cycle, the energy absorption capacity is largely reduced in the second cycle (see Fig. 4), and therefore the developed material is suitable for one-time protection and damping applications. The width of the infiltration plateau, which reflects the volume of the nanopores involved in the pressure induced infiltration, in the second cycles is less than 10% of that of the first one, while the infiltration pressure is much higher, suggesting that the nanopores active in the second cycle are those of relatively small sizes; that is, defiltration in smaller nanopores is easier. The variation in sorption isotherm curves in the following cycles is negligible, indicating that the silica particles and the gel networks are stable.

Note that the sorption isotherms are quite insensitive to the PAAK concentration, c . As c increases from 0 to 2 wt.%, according to Fig. 3, the infiltration pressure increases by less than 8%, and the width of the infiltration plateau decreases by only about 3%. That is, with the addition of PAAK, the pressure induced infiltration becomes slightly more difficult, but this effect is secondary compared with the significant change in sample appearance. When $c = 0$, the sample is actually a liquid; when $c = 1$ wt.%, the sample is solid-like but water can be released easily from the surface, i.e. the confinement effect of the gel network is relatively weak; when $c = 2$ wt.%, the sample is “dry” and further increase in PAAK concentration would not cause any detectable variations. Since the infiltration pressure is somewhat independent of c , it must be dominated by the capillary effect. As p reaches the infiltration pressure, the water molecules outside the nanoporous silica particles should be free to diffuse; otherwise significant additional work must be done to overcome the energy barrier caused by the gel matrix.

Through Fig. 4, it can be seen that the variations in infiltration pressure and width of infiltration plateau in the second loading-unloading cycle are not correlated with c , probably due to the systematic errors in measurements of displacement and sample mass. Because in the first loading-unloading cycle the involved pore volume is large, these errors do not affect the repeatability of the testing data. In the second cycle, as the width of infiltration plateau becomes order-of-magnitude smaller, the errors cannot be ignored. Nevertheless, Fig. 4 shows that there is no measurable difference in sorption isotherm curves for the second cycle, which supports the previous discussion that the pressure to overcome the confinement effect of matrix is lower than that required to overcome the capillary effect of nanopores.

Conclusion

To summarize, a solid energy absorbing material is developed based on the previously reported liquid infiltration behaviors of nanoporous materials. By functionalizing a poly(acrylic acid-co-acrylamide) potassium salt gel with hydrophobic nanoporous silica particles, while at a relatively low pressure the water molecules are confined by the polyelectrolyte network, at a relatively high pressure they can be released from the matrix and forced into the nanopores. Associated with the capillary effect, the system free energy increases significantly. As the pressure is reduced, most of the water molecules in the nanopores do not come out, and thus the excess solid-liquid interface tension is absorbed. The infiltration pressure and the accessible pore volume are somewhat independent of the polyelectrolyte concentration. This material can be handled quite conveniently, similar with ordinary solids. The energy absorption efficiency is 11 J/g. It is envisioned that, as the material is functionalized by nanoporous materials of smaller pores, larger pore volume fractions, and/or higher degrees of hydrophobicity, the energy absorption efficiency can be further improved.

Acknowledgements

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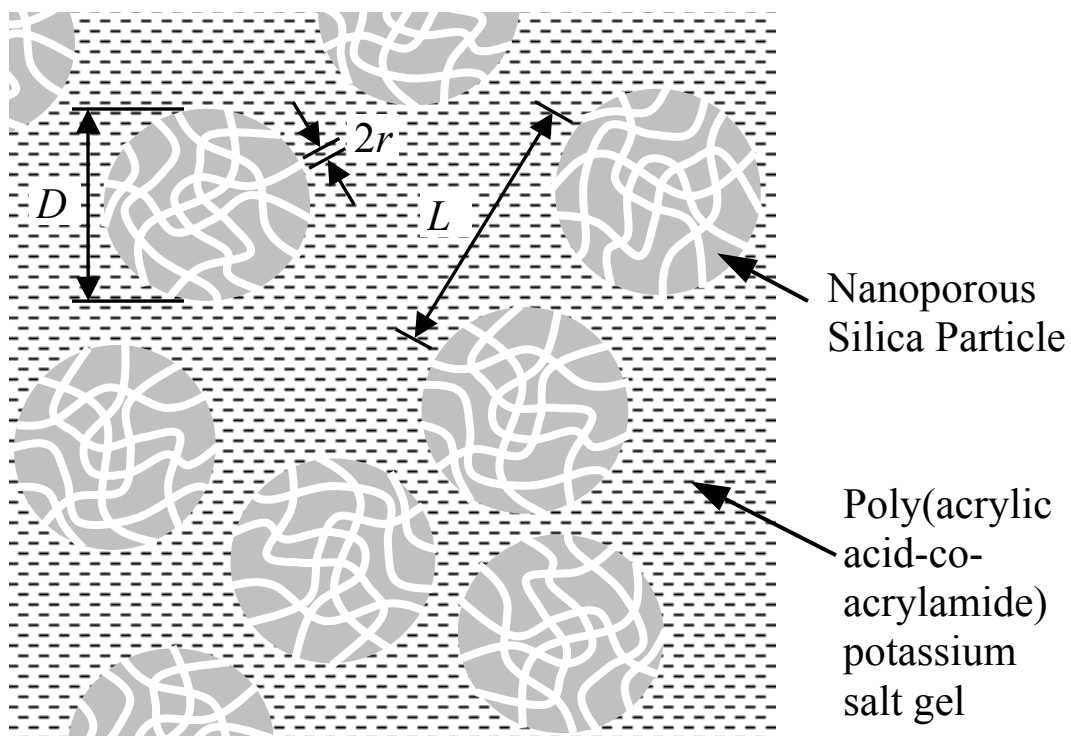


Fig. 1. A schematic diagram of the nanoporous silica functionalized material. The nanopore size, $2r$, is 7.8 nm and the silica particle size, D , is 15-35 μm .

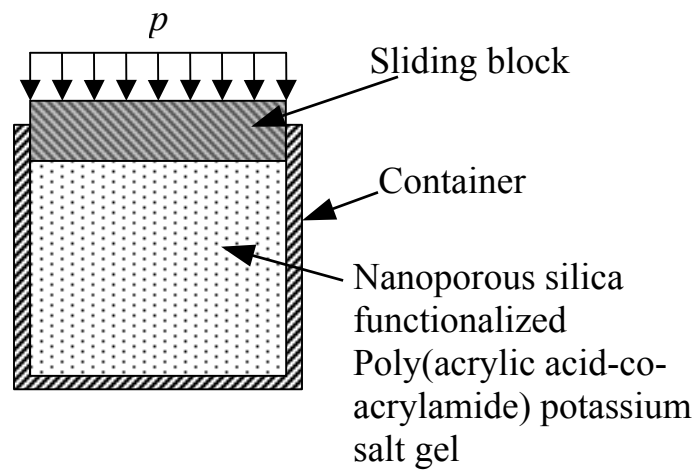


Fig. 2. A schematic diagram of the energy absorption system.

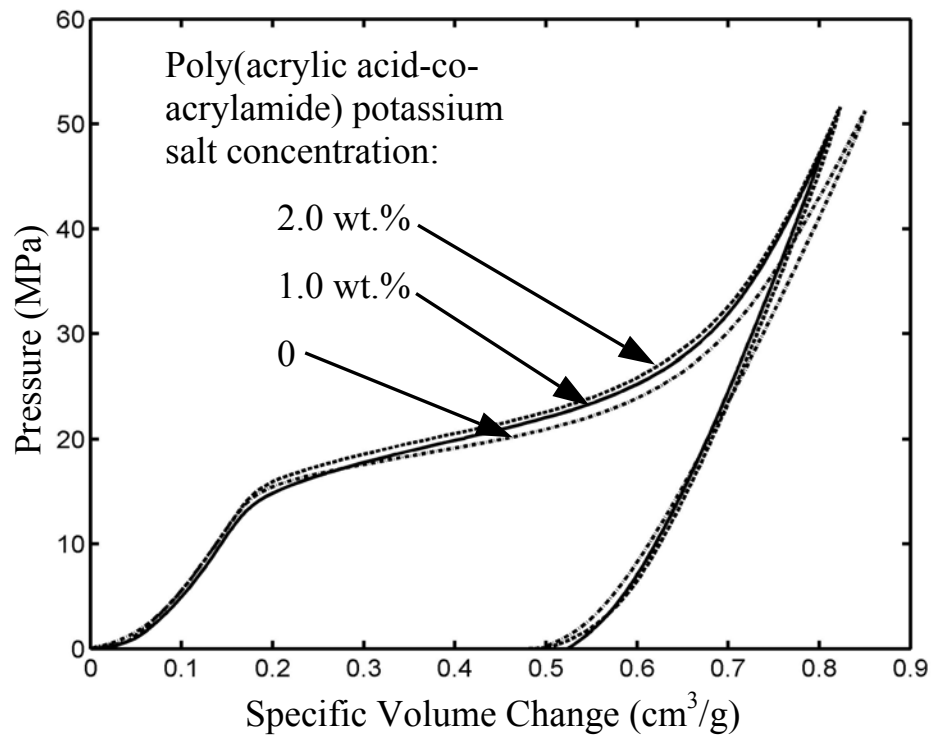


Fig. 3. The sorption isotherm curves of the first loading-unloading cycle.

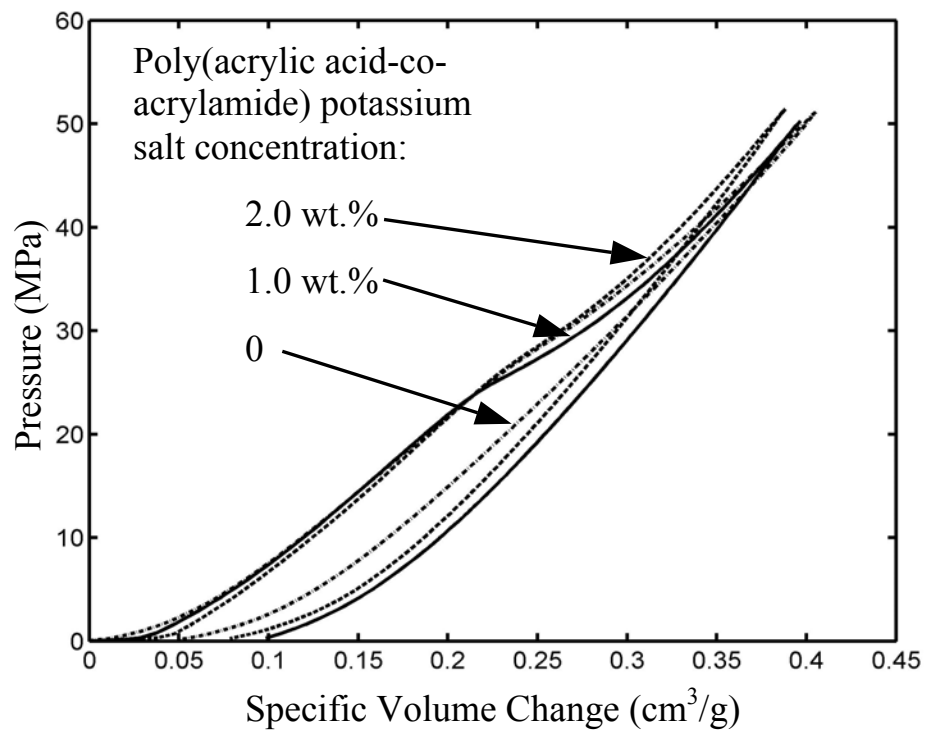


Fig. 4. The sorption isotherm curves of the second loading-unloading cycle.