

DOI: 10.1002/adem.200600177

Damping Properties of Nanoporous Carbon-Cyclohexane Mixtures**

By Venkata K. Punyamurtula, Aijie Han and Yu Qiao*

Using liquids in mounting stages, packaging layers, helmets and healthcare pads, etc. has been a common engineering practice.^[1] Usually, a “liquid damper” contains a sealing layer and a liquid core, which can nearly perfectly fit with the target to be protected. As a result, the contact area is maximized and thus the contact pressure is lowered. Damages associated with interface mismatches that commonly exist in solid systems, especially in systems of changing configurations, are also largely reduced. Additionally, the internal friction caused by liquid motions can considerably change the load and deformation distribution profiles. For instance, shear thickening liquids exhibit attractive mechanical characteristics when subjected to high-strain-rate shear loadings, and therefore can be used in protection layers, soldier armors, among others.^[2] A major problem of most of the liquid systems is that the compressibility of the liquids is poor, and the loading-unloading processes are reversible. Consequently, under a compressive loading, the energy absorption of the liquid phase is negligible. While this is not an issue for quasi-static loadings, for dynamics loadings the transmitted high-stress waves can cause serious damages, e.g. blast-lung problems.^[3,4]

In order to improve the energy dissipation capacities of liquids, the technique of nanoporous-admixture functionalization has been recently developed.^[5–9] By immersing a lyophobic nanoporous material in a liquid, as the pressure is increased so that the capillary effect is overcome, the liquid can be compressed into the nanopores, accompanied by the large increase in liquid-solid contact area. Since the specific area of a nanoporous material is typically millions of times larger than in bulk materials, the associated specific free energy increase can be as high as 10–100 J/g; that is, as the energy converted from the quasi-hydrostatic pressure to the solid-liquid interfacial tension can be regarded as being dissipated,

the energy absorption efficiency of the nanoporous liquid is ultrahigh. However, the previous studies were mainly focused on nanoporous silicas and zeolite-like materials, which are relatively cost inefficient, especially for large-scale structures such as damping foundations. It would be desirable if more available materials, such as nanoporous carbons, can be used for energy absorption applications. Moreover, in the previously developed systems, the system recoverability was usually quite poor; i.e. after the first loading-unloading cycle, since most of the confined liquid could not defiltrate from the nanopores, the energy absorption capacity became much smaller at the second loading. While a few techniques, such as thermal treatment and recovery agent addition have been developed,^[10,11] the system performance under cyclic loadings was still far from satisfactory.

Results and Discussion

In the current study, we investigated two J. B. Baker nanoporous carbons: E-343 and E-345 using the experimental setup depicted in Figure 1. The results are shown in Figures 2 and 3, according to which the pressure induced infiltration occurs smoothly as the pressure is increased. During the loading process, in the pressure range of 0 to 24 MPa, the capillary effect of nanopores cannot be overcome and therefore the system response reflects the linear compression of the liquid phase and the empty nanoporous carbon particles. As the pressure reaches 24 MPa, the liquid phase starts to infiltrate into the relatively large nanopores, and as the pressure continues to increase, enters smaller nanopores, leading to the formation of the infiltration plateau. Note that the liquid phase may undergo a phase transformation as the pressure is higher than 20–40 MPa,^[12,13] while the associated volume variation is much smaller than that caused by the pressure induced infiltration, and therefore will be ignored in the following discussion.

The pressure induced infiltration continues throughout the rest of the loading process. Even when the pressure is 155 MPa, close to the capacity of the testing machine, the infiltration is still not completed, which is reflected by the difference in the loading path and the unloading path in the

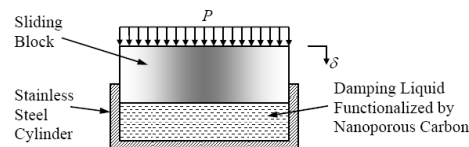


Fig. 1. The experimental setup.

[*] V. K. Punyamurtula, Dr. A. Han, Dr. Y. Qiao
Department of Structural Engineering
University of California at San Diego
9500 Gilman Drive (MC 0085), La Jolla, CA 92093-0085,
USA
Email: yqiao@ucsd.edu

[**] This work was supported by The Army Research Office under Grant No. W911NF-05-1-0288, for which the authors are grateful to Dr. David M. Stepp.

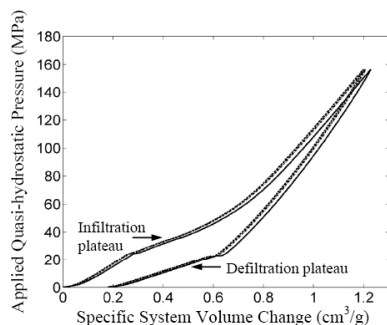


Fig. 2. Typical sorption isotherm curves of the damping liquid functionalized by type-E343 nanoporous carbon. The solid line indicates the first loading-unloading cycle; the dashed line indicates the second loading-unloading cycle; and the dotted line indicates the third loading-unloading cycle.

high-pressure range. This result is in agreement with the fact that the pore size of the nanoporous carbon distributes in a broad range across 2–3 orders of magnitude, and therefore the infiltration would be completed only when the pressure is higher than 2 GPa, 100 times larger than the pressure at the onset of the infiltration. However, for the energy absorption application, the high-pressure behavior of the system is of little interest since the energy dissipation mechanism must be activated at the harmless pressure level. The infiltration volume in the pressure range lower than 60 MPa, which can be measured by the width of the infiltration plateau of the sorption isotherm curve, is about $0.4 \text{ cm}^3/\text{g}$. Here the value of 60 MPa is taken somewhat arbitrarily as the upper limit of energy absorption, since many composite materials would fail at this level.

As the pressure is lowered, the sorption isotherm curve is irreversible. In the high-pressure range, the sorption isotherm curve is quite linear, with the effective stiffness larger than that in both the low-pressure and the high-pressure sections of the loading process, which should be attributed to that the confined liquid in the nanopores does not defiltrate immediately as the unloading begins, and the compressibility of nanoporous carbon particles filled by cyclohexane is smaller than that of empty ones. The defiltration starts to take place as the pressure is decreased to 22 MPa, beginning with the relatively small nanopores where the defiltration “driven

force”, i.e. the excess solid-liquid interfacial tension, is large. As a result, the slope of the sorption isotherm curve largely decreases, forming the defiltration plateau. The slope of the defiltration plateau is quite similar with that of the infiltration plateau, as it should be, since the nanopore size distribution is the same in the loading and the unloading procedures. The defiltration continues until the applied pressure is entirely removed.

The significant hysteresis of the sorption isotherm curves results in a large energy absorption efficiency. In a single loading-unloading cycle, in the pressure range of 0 to 60 MPa, the dissipated energy, which is calculated as the area enclosed by the sorption isotherm loop, is about 10 J/g , much higher than that of conventional damping materials such as polymer foams. The difficulties in defiltration are caused by the energy barrier for formation and expansion of gas molecular clusters, which is related to the pore-wall confinement effect, the energy exchange among solid/liquid/gas phases, and the mass exchange between liquid/gas phases.^[14] The blocking effect of gas molecules in the smallest nanopores, together with their attraction/repelling effect, may also play a critical role.^[15]

As the first loading-unloading cycle is finished, the second loading is applied within 15 sec. It can be seen that in the systems based on both types of nanoporous carbons, the repeatability of the sorption isotherm curve is quite high. In the type E343 carbon based system, the infiltration and defiltration pressures at the second loading is nearly the same as that in the first loading, while the widths of infiltration and defiltration plateaus, which reflect the accessible nanopore volume, are slightly smaller. The sorption isotherm curves in the third and all the following loading cycles are almost identical to the second one, indicating that the system behavior quickly converges. In the type E345 carbon based system, from the second cycle the system behavior is almost perfectly repeatable; that is, from the first loading the energy absorption process in all the nanopores is reversible. Therefore, both systems can dissipate energy continuously under cyclic loadings, attractive for damping applications. The slight difference between the two systems may be caused by the impurities, which can either block the largest nanopores or cause local damages of nanoporous structures.

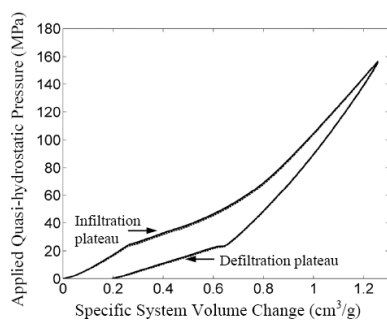


Fig. 3. Typical sorption isotherm curves of the damping liquid functionalized by type-E345 nanoporous carbon. The solid line indicates the first loading-unloading cycle, and the dashed line indicates the second loading-unloading cycle.

Conclusions

The damping behaviors of nanoporous carbon functionalized cyclohexane are investigated experimentally. Compared with ordinary liquids, the compressibility of the functionalized liquids is much higher, leading to a high energy absorption efficiency of about 10 J/g . In the pressure range of 20 to 60 MPa, the specific infiltration volume is around $0.4 \text{ cm}^3/\text{g}$. Another attractive property of the system is the superior recoverability; that is, the system can return to its initial configuration as the pressure is fully removed, and therefore can work continuously under cyclic loadings.

Experimental

Both of the two nanoporous carbons were steam activated and acid washed, with the specific surface area of about 800 m²/g. The nanopore size distribute in a broad range from about 0.5 nm to a few hundreds nm. The main difference between them was the purity. Type E-343 carbon contained about 5% impurities, including graphite and quartz grains. Type E-345 carbon was of a high purity close to 100%. The as-received materials were in powder form, with the grain size around 100 μm. Both carbons were hydrophilic, and therefore the energy absorption system could not be water based, since the liquid phase must be nonwetting to the nanopore surface. While a few surface treatment techniques have been developed to adjust the degree of hydrophobicity of carbon materials,^[16,17] the distribution uniformity and the reliability of the surface functional groups, particularly in the pressurized liquid environments, are still relatively poor. Thus, a nonpolar liquid, EMD CX2290 cyclohexane, was employed. The molecular formula of cyclohexane is C₆H₁₂. It is nonwetting to carbon materials, and its molecular size is much smaller than the nanopore size.

The experimental setup is depicted in Figure 1. In a stainless steel cylinder, 0.4 g of nanoporous sample and 7 g of cyclohexane were mixed together, forming the nanoporous carbon functionalized damping liquid, which was sealed by a stainless steel sliding block. Immediately prior to the experiment, the nanoporous carbon had been dried in vacuum at 150 °C for 6 hrs. By using a type 5569 Instron machine, a quasi-hydrostatic compressive pressure, P , was applied on the liquid phase through the sliding block. The friction force between the sliding block and the cylinder was less than 0.5% of the full scale of the loadcell, close to the measurement resolution. As the pressure increased, the liquid phase was compressed, and the system volume change could be calculated as $\Delta V = \delta \cdot A_0$, with δ and A_0 being the displacement and the cross-sectional area of the sliding block, respectively. As P exceeded 155 MPa, the applied load was gradually decreased to zero, and thus the sliding block moved back. The loading-unloading procedure was repeated for 4-5 times so that the system behavior converged to the steady-state. The time interval between each loading was less than 15 sec. The measured sorption isotherm curves are shown in Figure 2 and Figure 3, where the specific system volume change is defined as ΔV normalized by the mass of the nanoporous carbon. Since from the 2nd loading the variations in infiltration-defiltration loops were negligible, only the first 2-3 cycles are shown.

Received: July 04, 2006

Final version: August 17, 2006

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