doi:10.1246/cl.2010.550

Magnetorheology of Magnetic Poly(vinyl alcohol) Gels with High Mechanical Toughness

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A magnetic-field-sensitive gel that demonstrates both drastic changes in dynamic modulus and high mechanical toughness was obtained. The magnetic gel consists of cross-linked poly(vinyl alcohol) (PVA), iron oxide particles, and water. The storage and loss shear moduli of the magnetic gel remarkably increased by applying a magnetic field, similarly to magnetic carrageenan gels. Compression revealed high mechanical toughness of the magnetic PVA gel and the maximum strain of 0.64 was achieved without inducing permanent strain.

Dispersions of magnetic particles alter its viscoelastic properties in response to magnetic fields. This phenomenon is called the magnetorheological (MR) effect. Similarly, polymer gels containing magnetic fluids or magnetic particles exhibit the MR effect. Many attempts to fabricate MR gels using synthetic polymer,[1] silicone elastomers,[2–5] and rubbers[6] have been tried by many researchers. These papers reported that the relative change in storage modulus was less than threefold with respect to the initial modulus before irradiating magnetic fields.

We have investigated the MR behavior of various polysaccharide hydrogels[7–10] and recently found a new class of magnetic gel that responds to giant and reversible changes in dynamic modulus by a relatively weak magnetic field (500 mT).[11] The storage modulus increased 500-fold due to the magnetic field. However, the mechanical toughness of the magnetic polysaccharide gel was low. The matrix of the magnetic gel is carrageenan that forms a polymer network by hydrogen bonds acting between the polysaccharide chains. Therefore, the magnetic gel lacks mechanical toughness with low yield stress and strain. In this paper, we describe the MR and mechanical properties of a magnetic chemically cross-linked poly(vinyl alcohol) (PVA) gel formed by covalent bonds.

A pregel solution of the magnetic PVA gel was prepared by mixing a 5 wt % aqueous poly(vinyl alcohol) (Degree of polymerization $N \approx 1500$, Wako Chemicals) solution and 40 wt % iron oxide (Fe_3O_4) at room temperature using a mechanical stirrer for 30 min. Glutaraldehyde as a crosslinking agent was added, then hydrochloric acid was added to the solution (pH 2.0). The crosslinking density varied from 0.2 to 5 mol %. The pregel solution was poured in a glass mold and kept at room temperature for 24 h for gelation. The obtained gel was immersed in pure water for over 2 days for washing. Gel which had reached an equilibrium swelling was used for viscoelastic and mechanical measurements. The diameter of iron oxide was 0.6 µm, and the saturation magnetization and coercive force were 3.5×10^4 and 5.1×10^2 A m^{-1}, respectively. The dynamic shear modulus at 1 Hz, 20 °C was measured using a rheometer (MCR301, Anton Paar) under stepwise magnetic fields. The field direction was perpendicular to the strain. The samples were disks of 20 mm diameter and 1.3 mm thickness. The yield point of magnetic gels was measured at room temperature using a compression apparatus (STA-1150, Orientec) with a compression speed of 50 mm min^{-1}. The sample was a disk of 10 mm thick and 35 mm in diameter.

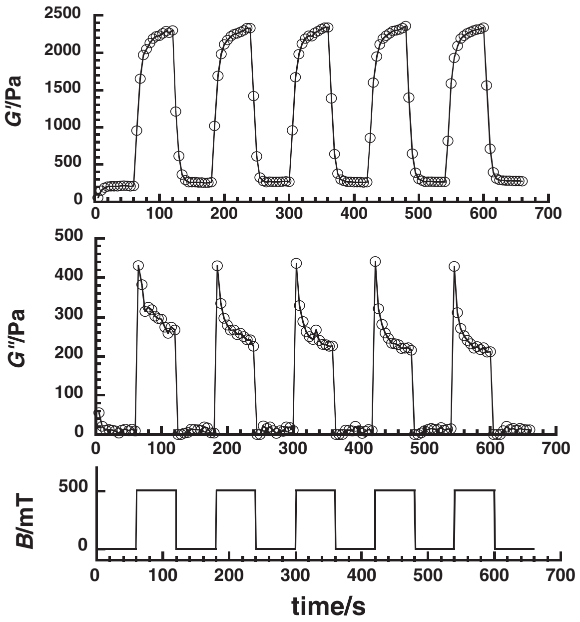

Figure 1. Storage modulus (top) and loss modulus (bottom) of magnetic PVA gels in response to stepwise magnetic fields (at $\gamma \approx 10^{-4}$, $\phi = 0.16$).

Figure 1 shows the storage modulus (G') and loss modulus (G'') at linear viscoelastic regime ($\gamma = 10^{-4}$) of a magnetic PVA gel with 0.3 mol % crosslinking density. A stepwise magnetic field was applied to the magnetic gel. The initial modulus (storage modulus at $B = 0$ mT) was 210 Pa, and the maximum modulus at $B = 500$ mT was 2300 Pa, respectively. The magnetic gel demonstrated large reversible changes in the storage modulus, approximately 10 times the initial modulus. The magnetic gels consisting of synthetic polymer also exhibited significant MR effect, as well as magnetic gels made of polysaccharides. The magnetic gel underwent fast magnetic response and the storage modulus increased more than fourfold in 5 s, from 213 to 954 Pa, as seen in the first pulse. Similar field response was also seen in the loss modulus. The loss modulus increased 50-fold (from 8.6 to 431 Pa) in the magnetic field.

Figure 2 shows the increment in storage modulus $\Delta G'$ and the relative change in the modulus $G'/G'_{B=0}$, as a function of the initial modulus, $G'_{B=0}$. The $G'_{B=0}$ for magnetic carrageenan and PVA gels were changed by varying carrageenan concentration and crosslinking density, respectively. The $\Delta G'$ of magnetic

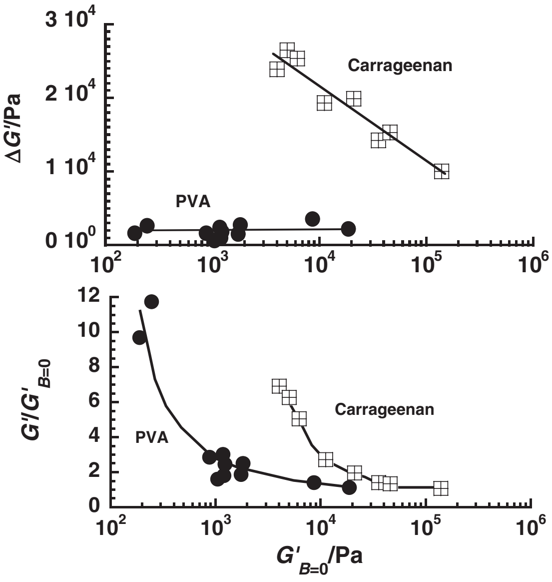

Figure 2. Increment in storage modulus (top) and relative changes in storage modulus (bottom) due to magnetic field ($B = 500\,\mathrm{mT}$) as a function of the initial modulus (at $\gamma \approx 10^{-4}$).

carrageenan gel increased with decreasing initial modulus. On the other hand, the $\Delta G'$ of magnetic PVA gel was independent of the initial modulus. The $\Delta G'$ of magnetic PVA gels was lower than those of magnetic carrageenan gels. The volume fraction of magnetic particle should affect the different behavior of $\Delta G'$ for magnetic PVA and carrageenan gels. Additionally, magnetic particles within PVA gel might be difficult to form chain structure than carrageenan gel. According to the Maxwell stress, the increment in storage modulus can be estimated by $\Delta G' = \mu_0(M\phi)^2$.[8] Here, μ_0, M, and ϕ represent the magnetic permeability in vacuum, magnetization, and volume fraction of magnetic particles, respectively. At 500 mT, the magnetization of iron oxide is saturated to a magnetization of $3.5 \times 10^4\,\mathrm{A\,m^{-1}}$. The volume fraction for magnetic carrageenan gels was constant at 0.32, conversely, the volume fraction of magnetic PVA gels varied from 0.16 to 0.26 depending on the crosslinking density due to swelling. Therefore, the calculated values of $\Delta G'$ for magnetic carrageenan and PVA gels, at maximum, were calculated to be 160 and 100 Pa, respectively. These values are far smaller than those observed. This strongly suggests that the MR behavior observed here originates from the chaining structure of magnetic particles within the gels.

Both magnetic gels showed that the relative change in the storage modulus $G'/G'_{B=0}$ increased with decreasing initial modulus. The maximum values of $G'/G'_{B=0}$ for magnetic carrageenan and PVA gels were 7 and 12, respectively; indicating magnetic PVA gels undergo drastic change in tactile sense. The $G'/G'_{B=0}$ for magnetic carrageenan gels at $G'_{B=0} <$ 4 kPa would be certain to take higher values; however, the carrageenan did not gel.

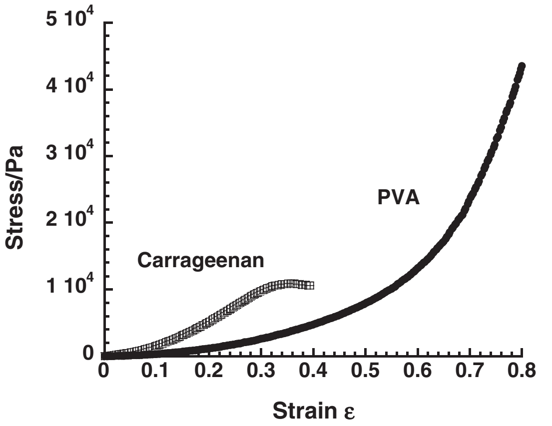

Figure 3. Stress–strain curves of magnetic PVA and carrageenan gels at $B = 0\,\mathrm{mT}$.

Figure 3 shows the stress–strain curves of magnetic PVA and carrageenan gels under no magnetic field. Samples demonstrating the highest value of $G'/G'_{B=0}$ were used in this experiment. A yield point was not seen in the magnetic PVA gel up to a strain of 0.8 without inducing permanent strain. On the other hand, the magnetic carrageenan gel exhibited a yield point at $\varepsilon = 0.35$ with a yield stress of 10.9 kPa. The magnetic carrageenan gel did not recover its original shape after removing the strain. Thus, the magnetic PVA gels possess higher mechanical toughness than magnetic carrageenan gels.

In summary, we synthesized chemically cross-linked magnetic gels and investigated both magnetorheological and mechanical properties. It was revealed that magnetic PVA gels demonstrate giant magnetorheological behavior and high yield point. These features would be useful for damping materials, tactile-sense demonstrators, or smart actuators.

We are grateful to San-Ei Gen F.F.I., Inc. for the offer of samples. This research was partially supported by Panasonic Electric Works Co., Ltd.

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