

Water dynamics of double-network polymers in a primarily hierarchical structure

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Double-network polymers (DN-polymers) are xerogels prepared by the complete freeze-drying of double-network hydrogels, which are composed of poly(2-acrylamido-2-methylpropanesulphonic acid sodium salt) and polyacrylamide. DN-polymers with a multi-level hierarchical architecture exhibit unique mechanical properties depending on the moisture at room temperature. They possess maximum Young's modulus and tensile stress values at 30% relative humidity (RH). At $RH > 70\%$, the Young's modulus of the DN-polymers drops to 1/1000th of that observed for its dry counterpart, and transform from a glassy to a rubbery state. To understand the mechanism of the mechanical properties, water dynamics of DN-polymers were investigated through quasielastic neutron scattering experiments. At $RH < 30\%$, the water dynamics exhibited a local motion, whereas at $RH > 30\%$, the water molecules demonstrated a jump-diffusive motion. When RH was $\sim 35\%$, a few mobile water molecules were observed; thus, at the RH of approximately 30%, a boundary was formed, which correlated with the macroscopic mechanical properties of the DN-polymers.

KEYWORDS: DN-polymers, mechanical properties, hierarchy, Humidity, water, dynamics, QENS

1. Introduction

Double-network polymers (DN-polymers) [1] are xerogels prepared by complete freeze-drying of double-network hydrogels (DN-hydrogels) [2] using poly(2-acrylamido-2-methylpropanesulphonic acid sodium salt) and polyacrylamide. The DN-polymers possess a fractal-like architecture [3] with a primary hierarchical network structure having small pores (diameter: 1.7–10 nm). Tensile experiments indicated that the Young's modulus value was almost constant at relative humidity (RH) levels below 70%, whereas the quantity of water was approximately 18 wt% at 70% RH. When $RH > 70\%$, the Young's modulus decreased to 1/1000th of that of its dried counterpart, and the DN polymers transformed from a glassy to a rubbery state [1]. Notably, the maximum values of both Young's modulus and maximum tensile stress were observed at 30 %RH.

Generally, water acts as a plasticizer in terms of the mechanical properties of materials. In the case of the DN-polymers, the mechanical properties do not change even at 18 wt% of water at 70% RH. In addition, the mechanical properties of the DN-polymers containing a small amount of water (~ 5 wt% at 30% RH) are superior to



those under dry conditions. These properties are exceptional compared to those of other commercial materials.

In this study, we determined the water dynamics within the DN-polymers by the quasielastic neutron scattering (QENS) technique [4] using a backscattering spectrometer (BL02, J-PARC MLF). The spectroscopy provides dynamical information of water molecules on a length scale access within the first-level network structure of the DN-polymers.

2. Materials and Measurements

Sheet-shaped water-swollen DN-hydrogels [2] were prepared from 2-acrylamido-2-methylpropanesulphonic acid sodium salt (NaAMPS) (Sigma-Aldrich Co.), recrystallized acrylamide (AAM), and recrystallized *N,N'*-methylenebisacrylamide. Then, the sheet-shaped DN-hydrogels were lyophilized using liquid nitrogen, yielding sheet-shaped freeze-dried DN-polymers. The details are available in literature [2].

The QENS measurements were performed using a time-of-flight near-backscattering spectrometer BL02 (DNA) [5] at the Materials and Life Science Experimental Facility (MLF) in the Japan Proton Accelerator Research Complex (J-PARC), Japan. The injected proton beam power incident on the neutron target was ~ 300 kW. The energy resolution was $3.6 \mu\text{eV}$ using the Si 111 analyzer. The Q range was $0.125\text{--}1.54 \text{ \AA}^{-1}$. The QENS measurements were performed at 298 K using pulse-shaping chopper phase settings, whose energy transfer (E) range was $-20 < E [\mu\text{eV}] < 50$. Although the exposure time for each humidity condition was ~ 6 h, data were collected after equilibrium condition of each humidity condition. The data of latter approximately 3 h were analyzed. The instrumental resolution was measured at 50 K of the DN-polymers itself. Slab-shaped DN-polymers of 0.4 mm^t thickness were set into a humidity cell and connected to a humidity apparatus that was installed to BL02. The humidity was regulated—from dry to moist condition—in *situ* by controlling the absolute pressure remotely using electromagnetic valves.

3. Results

To investigate the water dynamics, we controlled the humidity using H_2O . The most effective method is to prepare deuterated DN-polymers. While purchasing deuterated AAM is easy, preparing deuterated NaAMPS is not easy. In this study we selected hydrogenated DN-polymers and water humidity.

Figure 1 shows the raw data of $S(Q, E)$ at $Q = 1 [\text{ \AA}^{-1}]$ with respect to the RH at room temperature. With increasing RH, the integral intensity under $-20 < E [\mu\text{eV}] < 50$ at $Q \sim 1 \text{ \AA}^{-1}$ increased (Fig. 1b). The difference in the integral intensity of 0% RH corresponded to the increase of incoherent scattering of H_2O within of the DN-polymers.

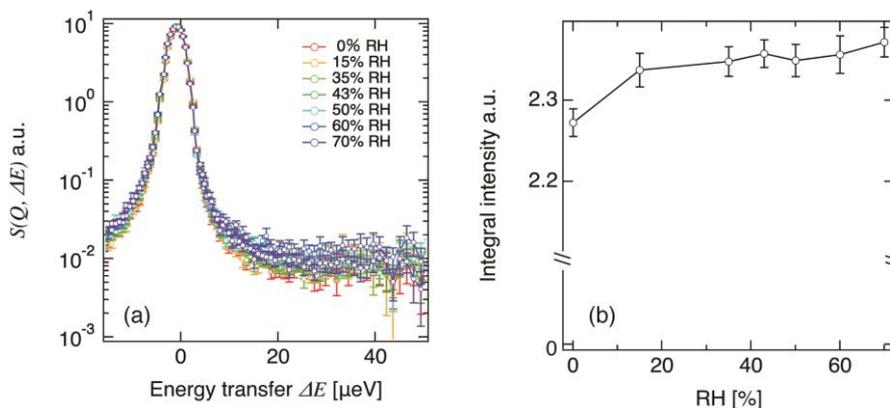


Fig. 1. QENS profiles of the DN-polymers at $Q = 1 \text{ \AA}^{-1}$ with respect to the humidity (a). Humidity dependence on the integral intensity under the E range of $-20 < E [\mu\text{eV}] < 50$ at $Q = 1 \text{ \AA}^{-1}$ (b).

4. Discussion

To investigate the water dynamics within DN-polymers, we subtracted the QENS profile under dry conditions from that under moist conditions. The subtracted $S(Q, E)$ can only represent water dynamics within DN-polymers. Because the Young's modulus of the DN-polymers at $\text{RH} < 70\%$ is almost constant [1], as a first-order approximation, the dynamic contribution of DN-polymers is regarded to be the same at $\text{RH} < 70\%$.

Figures 2 (a–c) show $S(Q, E)$ at RH of 15%, 35%, and 70% at room temperature. The following fitting model for water dynamics was adopted:

$$S(Q, E) = R(Q, E) \otimes (\delta(Q, E) + L(\Gamma, E)) + B_g, \quad (1)$$

where $R(Q, E)$, $\delta(Q, E)$, $L(\Gamma, E)$, and B_g represent the resolution function, delta function, Lorentz function, and constant background, respectively. Furthermore, $\delta(E)$ and $L(\Gamma, E)$ represent the immobile water and mobile water, respectively, which can be obtained by the resolution and the Q - E window of BL02 spectrometer. The fitting was performed using the least squares method on Igor Pro (WaveMetrics). Figure 2 (d) shows a stacked bar chart of area of $\delta(Q, E)$ and $L(\Gamma, E)$ from the fitting result with respect to RH. Furthermore, water was mostly immobile, that is, approximately 90% below 70% RH. The fitted results indicate that when RH is approximately 30%, the number of mobile water molecules was relatively low, and the mobility of water within the DN-polymers changes was approximately between $30 < \text{RH} [\%] < 45$. With increasing RH, the total amount of adsorbed water increased, and at high RH, the number of mobile water also increased. This is in good agreement with the adsorption isotherm of water (Fig.2a [1]) and the mechanical properties against humidity. The DN-polymers are rigid but brittle at $\text{RH} < 30\%$, and the DN-polymers become stretchable at $\text{RH} > 50\%$ (Fig.1[1]).

To determine the mobile water dynamics, Γ as a function of Q^2 at 15% RH and 60% RH is shown in Fig. 2e and 2f. The results indicate that the mobility of water at below 30% RH is different from that at above 45% RH. Below 30% RH, the mobile water molecules exhibit local motion within the first hierarchical structure of the DN-polymers (Fig. 10 in the literature [3]), and those above 45% RH exhibit a jump-diffusion process

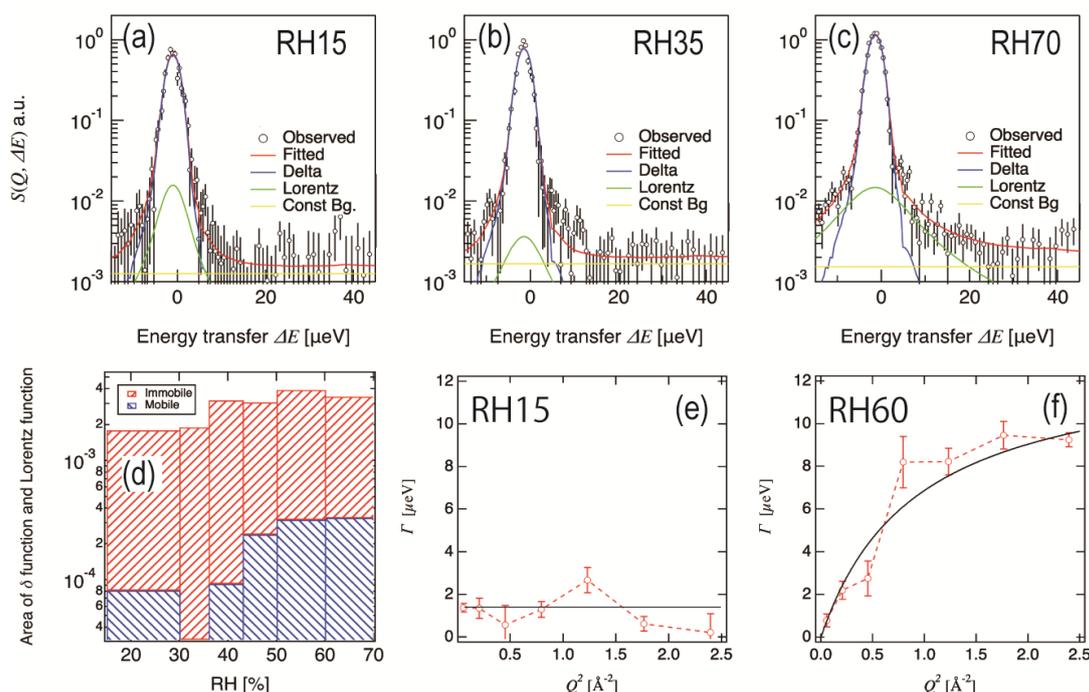


Fig. 2. QENS profiles of water within the DN-polymers at $Q \sim 1 \text{ \AA}^{-1}$ at (a) 15% RH, (b) 35% RH, and (c) 70% RH. Humidity dependence on the contribution of water molecules; (d) Stacked bar chart of area of δ function as an immobile component and area of Lorentz function as a mobile component at $Q \sim 1 \text{ \AA}^{-1}$. HWHM of mobile water Γ as a function of Q^2 (e) at 15% RH and (f) 60% RH.

[4]. The fitted parameter of diffusion constant was $2.2 \times 10^{10} \text{ \AA}^2/\text{s}$ and the relaxation time was $4.99 \times 10^{-11} \text{ s}$. These parameters were approximately one order of magnitude smaller and longer than those of the bulk water [6], and the dynamics of the adsorbed water was restricted. The jump distance L , which is estimated by $D = L^2/6\tau$ [4], was $\sim 0.25 \text{ nm}$. The adsorption isotherm of water in our previous report (Fig. 2a [1]) clarified the water adsorbed in the nanometer scale pore, which could be the length scale, which is large enough for the jump distance.

The DN-polymers are composed of hydrophilic polymers. Hydrophilic polymer can adsorb water molecules. However, the association of PNaAMPS and PAAm interacts favorably with each other while in water [7]. When $\text{RH} > 45\%$, the water molecules exhibit jump-diffusion. As mentioned above, the obtained diffusion constant and mean residence time was smaller and longer than those of bulk water. The water exhibiting the jump-diffusion could interact with the polymer network, however the interaction would be weaker than that of the immobile water. Under $\text{RH} < 30\%$, slow dynamics could be observed due to the weak interaction between water molecules and hydrophilic polymer chains.

On the basis of the QENS data and structural information [3], we present an interpretation of the process of introducing water to the DN-polymers. From dried state, approximately 4.5% of water molecules are attached to the polymer chain [1] at the sites locally below $\text{RH} < 30\%$ [4]. The interaction between water molecules might not sufficient to bridge water molecules network by hydrogen bonding. At approximately 30% RH, the water molecules might bind with each other within the first level of the hierarchical network of DN-polymers [3]. Furthermore, an increasing number of water molecules exhibit jump-diffusion motion. The water molecules easily move sites and exchange with immobile/mobile water molecules. The mechanism enhancing mechanical properties of water at approximately 30% RH remains unclear. Therefore, a further study

needs to be done to determine the polymer dynamics with respect to humidity changes using heavy water and the results are expected to establish the role of water in enhancing enhance mechanical properties.

5. Conclusion

In this study, the water dynamics within the DN-polymers, which possess robust mechanical properties against moisture, were investigated by the QENS technique at room temperature using H₂O gas. It was found that more than approximately 90% of the water molecules were immobile, indicating that they were attached to the polymer chains; this result is in good agreement with the water resistance of the Young's modulus of DN-polymers. The remaining water molecules (less than 10%) exhibited no Q -dependence at RH < 30 %, indicating that the water molecules exhibited a local motion (non-diffusive motion) behavior. On the contrary, when RH > 45%, they exhibited a jump-diffusive motion. When RH was ~35%, only a few mobile water molecules were found; thus, the RH of approximately 30% shows a boundary, which would correlate with the macroscopic properties of DN-polymers.

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