Adhesion Properties of Physically Crosslinked Hydrogels of Poly(Sodium Acrylate)

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The poly(sodium acrylate) gel physically cross-linked by aluminum ions were prepared at different temperatures. The gelation processes of the gels were examined using a dynamic viscoelastic measurement. The adhesion of the gels were also measured with the use of a simple tack-evaluation technique using a point contact. As a result, adhesion, stiffness, and time for the completion of the gelation strongly depended on the gelation temperature. The results were discussed in terms of the physical and chemical properties of gel surface formed at gelation.

Key words: adhesion, point contact, hydrogel, gelation, viscoelasticity

1. INTRODUCTION

Poly(sodium acrylate) (PSA) gel, which is physically cross-linked through a chelation mechanism by metal ions, has been widely used in the medical fields, for example, as anti-inflammatory analgesic cataplasms. The fundamental properties of PSA gels have been reported, especially with respect to the swelling behavior [1-3]. Among the properties, controlling the adhesion between polymer gel surfaces is of great importance in many applications. Recently we developed a new technique for measuring the surface adhesion of soft materials [4,5], in which the adhesion force, F_A, of a point contact of soft materials and the total energy, E_A, required to completely separate the contact can be easily and reproducibly obtained using the springs of phosphor-bronze thin plates with strain gauges (four active gauges). In this technique, two swollen hydrogels that were adhered on cylindrical glass sticks were placed in a crossed-cylinder geometry, thus, forming a point contact (a "point-contact method"). With the use of this simple tack-evaluation technique by a point-contact method, we have studied the fundamental adhesion properties of PSA hydrogels in air at room temperature. As a result, F_A and E_A increased with increasing the experimental conditions, such as the normal force, W, the waiting period, t_W, and the separation velocity, v, and

obeyed power laws when the respective parameter is not too small. The experimental results were qualitatively understood on the basis of the balance between the interfacial adhesion (surface physical and chemical properties) and the bulk elasticity; F_A and E_A were determined not only by the interfacial adhesion but also by the bulk elastic properties.

In order to understand further the adhesion properties of PSA gels, two different experiments were conducted in this paper. One was on the adhesion properties of the gels prepared at different temperatures, which were evaluated by the simple tack-evaluation technique. The other was on the mechanical properties, which were evaluated by the bulk viscoelastic measurements. The effects of the gelation temperature on the adhesion properties are discussed here.

2. EXPERIMENTAL

2.1 Sample preparation

PSA gels were made of poly(sodium acrylate) and aluminum ions [1]; the pregel solution was obtained by mixing PSA aqueous solution (for the main constituent, Wako Pure Chemical Industries) with aluminum hydroxide $Al(OH)_3$ (for the cross-linker, Kyowa Chemical Industry) of 3wt% of PSA solution under an acidic condition. The pregel solution was mixed with a
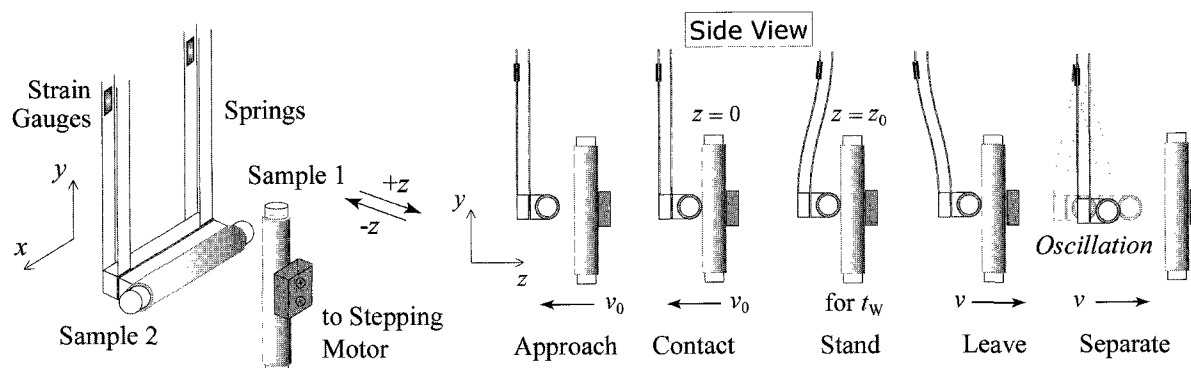

Fig. 1 Schematics of the side view of experimental setup and the method of measurement with 4 active strain gauges. After the position-controlled stage stopped and stood for t_W, it moved along the +z-direction (opposite to the approach) to completely separate the samples.

spatula and sealed using Parafilm to prevent evaporation. The gel was shaped into a thin plate, which was prepared with the use of two flat plates (made of a glass slide and a polystyrene plate) and a 1-mm-thick spacer. A non-woven textile with a 0.6-mm thickness was attached with Scotch tape onto the slide. The mixed solution was mounted onto the non-woven textile on the glass slide and sandwiched by the polystyrene plate, which was separated from the glass slide with the spacer. The solution on a set of flat plates was left in the respective temperature controlled water bath between 20 and 50°C. After gelation, the polystyrene plate was carefully removed from the gel by hand, thus forming a clamped thin plate gel on the upper surface of the non-woven textile.

2.2 Measurements of the adhesion properties and the viscoelastic properties

The lower surface of the textile was adhered onto a glass stick with an 8-mm outer diameter. The top surface of gel has a curvature of a 5.6-mm radius. The contact area is formed by placing two glass sticks with the gels in a crossed-cylinder geometry. One of the sticks (Sample 1) was fixed to the position-controlled stage by the stepping motor and moved with velocity, v (in the range between 0.2 and 10 mm/s). The other stick (Sample 2) was fixed to the springs (a phosphor-bronze thin plate) with strain gauges (Kyowa Electronic Instruments, KFG-2-120-C1-16 L1M2R). By moving Sample 1 with a constant advancing velocity, v_0 along the $-z$-direction, Sample 1 could approach and contact Sample 2. After the position-controlled stage stopped (at the appropriate position, z_0, from the initial contact position) and stood for t_w, it moved at a constant velocity, v, along the $+z$-direction (opposite to the approach) to completely separate Sample 1 from Sample 2. The strain gauge responded with a linear change in electrical resistance, which was calibrated using a set of well-known loads. We used four active gauges to maintain the accuracy of the measurements.

The dynamic shear viscoelasticity were measured using a rheometer (UBM Co.,Ltd.; MR300) equipped with a parallel plate geometry at a frequency range between 0.05 and 3Hz.

3. RESULTS AND DISCUSSION

3.1 Adhesion curve

A typical example of the relationship between the adhesion force, F, and the time, t, is shown in Fig. 2. This adhesion curve consists of three processes;

(1) the advancing contact of Sample 2 with a constant velocity, v_0 (from $t=1.68$ to 2.33sec),

(2) the standing at a constant position for a waiting period, t_w (from $t=2.33$ to 64.15sec), and

(3) the receding separation with a constant velocity, v (from $t=64.15$sec).

After reaching the maximum at $t=64.77$sec, F rapidly decreased, and Sample 1 completely separated from Sample 2 at $t=64.9$sec. In this figure, F_A and E_A are defined as the maximum tension force during the connection and the separation energy throughout the separation process, and W is the normal force (equal to $-F$). After complete separation, the gel oscillated for a while and attenuated in a few to several tens of seconds.

The adhesion curve is expected to depend strongly on the experimental conditions at a fixed temperature, such as W, t_W, and v. In the present experiments, as is mentioned in section 1, it was interesting to observe that the v-dependences of F_A and E_A in all adhesion curves was simply approximated by the respective power law, indicating a single mechanism of the separation when the respective parameter is not too small. In the following experiments, W was fixed to 30gf, t_W to 60sec, and v to 1.5mm/sec. These values were large enough to confirm the power law relationship.

3.2 Effects of the gelation temperatures on F_A and E_A.

In Fig. 3, F_A and E_A are plotted as functions of gelation temperature, T_{gel}, which were calculated from the adhesion curves. Although there is a scattering to
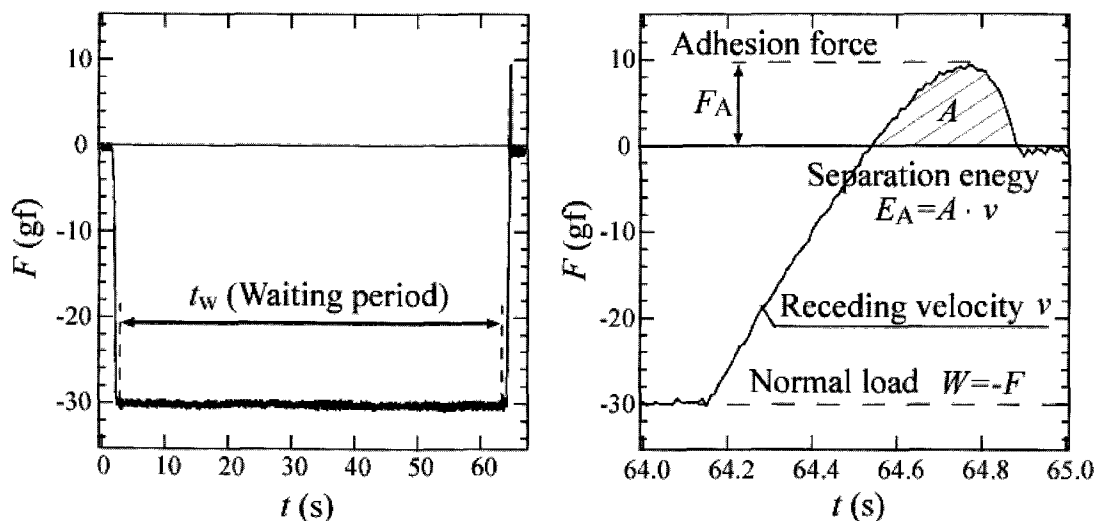

Fig. 2 Adhesion curve (adhesion force, F, vs. time, t,) (a) and the definition of F_A and E_A (b). A denotes the hatched area by vertical lines in this F-t plot. F_A and E_A are defined as the maximum F and the product of A and v (the separation energy), respectively.
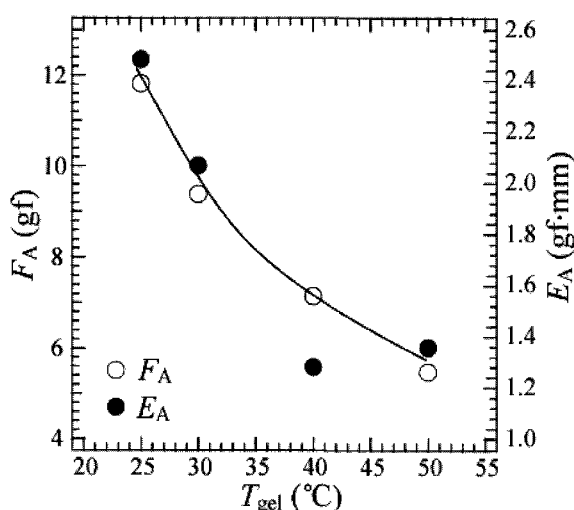
Fig. 3   Effects of the gelation temperature, T_{gel} on the absolute values of F_A and E_A.

some extent in the data points (depending on the sample as well as the measurement position), F_A and E_A decreased when T_{gel} increased.

It should be noted that T_{gel} changed drastically the adhesion properties of PSA gels; both F_A and E_A of the gel prepared at 50°C was less than one second of those of the gel prepared at 25°C. Although the absolute values of F_A and E_A depended on the samples prepared at different times, we obtained reproducibly the adhesion curves against T_{gel}, which are reliable for the present qualitative discussion. The most difficulties in the experiments were in the sample preparation rather than the measurement itself. The experiments should be conducted quickly to prevent from dehydration, which will be discussed in section 3.4.

3.3 Viscoelastic properties

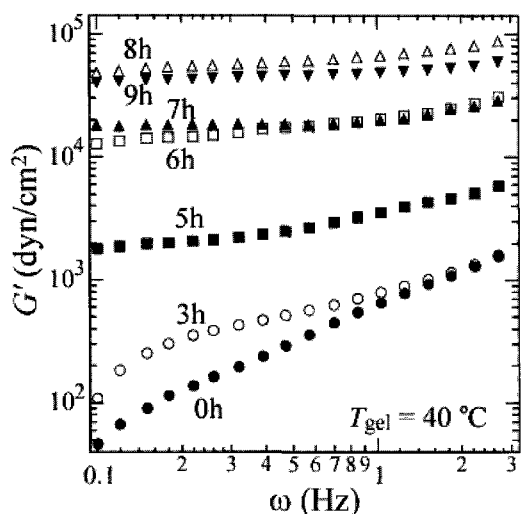In order to investigate the bulk stiffness and the gelation process, the measurements of the dynamic shear

viscoelasticity were conducted. In the cases of gels after gelation, the storage modulus G' was larger than the loss modulus, G'', showing that the elastic characteristic has a principal role in the gel structure. As is shown in Fig. 4, the storage modulus G' increased with time and became independent of the frequency after the gelation, in agreement with the existence of a network structure. The increase of G' with time suggests an increase of the number of cross-linking; Al ions were expected to be complexed with the carboxyl groups on PSA. It increased rapidly below 5h and slowly above 6h. We can roughly determine the time to complete the gelation, which is shown in Fig. 5. The gelation time were highly correlated with T_{gel}; it decreased rapidly with increasing T_{gel} below 30°C, and it tended to saturate above 40°C. The averaged G' values are also plotted in Fig. 5, which also depended apparently on the gelation temperature. Although the error bar is relatively large (depending on the sample), G' tended to increase with increasing the gelation temperature.

3.4 Effects of T_{gel} on the adhesion properties

From the present results using the point-contact method for soft materials, there appeared several interesting features in the adhesion properties of PSA-gels. Among them, the observation of strong dependence of F_A and E_A on T_{gel} seemed highly specific to the cross-linked polymeric soft materials.

According to our recent study [5], the adhesion properties of hydrogels were qualitatively understood on the basis of the balance between the interfacial adhesion (surface physical and chemical properties) and the bulk elastic properties; F_A and E_A were determined not only by the interfacial adhesion but also by the bulk elastic properties. As for the effects of T_{gel} on the adhesion properties, the material parameters should be examined on the basis of the present results.

First of all, the deformation by a contact along the normal direction to the surface should be considered. The change in G' should result in the change in the apparent contact area, S, which should affect F_A and E_A. The decrement of F_A and E_A with increasing T_{gel} should
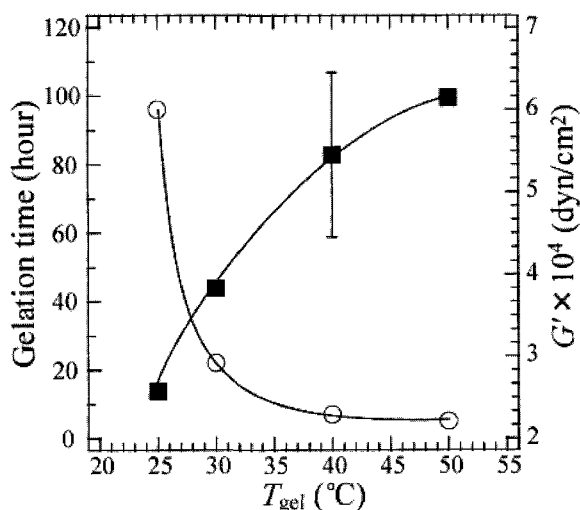

Fig. 4   Time evolution of shear storage modulus, G', which were measured using a rheometer with a parallel plate geometry.

Fig. 5   Gelation time against gelation temperature T_{gel}. The shear storage modulus, G', of gel after complete gelation is also plotted.

be partly attributed to the decrement of S, since the contact number of the microdomains in the mesoscopic level should decrease with decreasing S. In general, the determination of S for an adhesion test provides critical information, especially for proper interpretation of the bulk and interfacial contributions to adhesion. Although the direct in-situ measurements of S were in principle difficult in the present experimental situations, we can qualitatively estimate the effects of S on F_A and E_A, if the deformation along the normal direction to the surface can be experimentally measured [5]. This is an important subject for future investigations.

Secondly, the deformation by a contact in the microdomains in the nanoscopic level should be examined. As for the effects of T_{gel} on F_A and E_A, we can infer what were the origins of adhesive interactions at the molecular scale. It is reasonable to suppose that the surface of hydrogels consists of a large number of asperities [1,6,7], which originates in the micro-domains introduced at gelation [8]. Therefore, the true contact area, S_T could be expected to be different from S. In the nanoscopic level, each asperity consisted of polymer chains; S_T was made of a large number of small regions that formed asperities, where the molecular-to-molecular contacts in polymer chains [9,10] took place. Therefore, the deformation of the asperities might increase S_T (the number of interactions in the molecular scale), and S_T, which might be affected by the gelation temperature could determine F_A and E_A. One can say that the fluctuation of the polymer in the pregel solution could be quenched into the gel network at the onset of the gelation in totally different manners at different gelation temperatures.

The present results could be understood on the basis of the balance between the apparent contact (the number of asperities) due to the change in the stiffness (G') and the asperity contact (the true contact area) due to the microdomains. The physical and chemical properties of the gel surface resulted from the competition between the phase separation and the cross-linking of network polymer at gelation. Therefore, T_{gel} has an important role to determine the adhesion properties of gels in general.

Finally, we can briefly mention the effects of the water content in the gel after gelation, which is defined as the ratio of the water weight in the gel to the total weight of the as-prepared gel. As a result it was 0.73 ± 0.15 and did not have a correlation with gelation temperatures. However, the water content in the top surface should be affected to some extent in the present measurements in air, even if the experiments were conducted quickly. This extrinsic factor should be taken into account in a future experiment.

4. CONCLUSION

The PSA hydrogels physically cross-linked by aluminum ions were prepared at different temperatures. The adhesion properties of swollen PSA hydrogels were evaluated by a point-contact method in air at room temperature. As a result, F_A and E_A decreased with increasing the gelation temperature.

The measurements of the dynamic shear viscoelasticity were also conducted. With increasing the gelation temperature, the stiffness increased and the gelation time decreased. From these experiments, the experimental results were qualitatively understood on the basis of the network structure; F_A and E_A were determined not only by the interfacial adhesion and the bulk elastic properties, but also by the network structure formed at gelation.

The present observations, we believe, are of crucial importance when designing the adhesion force and separation energy of swollen hydrogels in general. In order to understand the network structure formed at gelation, experiments on not only the microscopic but also nanoscopic studies of polymer gel surfaces are important subjects for future investigations.

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