Repairing behavior of weal gels having dangling chains

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Abstract
In this paper, it is demonstrated that an applied cleavage by a razor blade is healed at room temperature without any manual intervention for a weak gel having a lot of dangling chains. Because the healing occurs by interdiffusion of dangling chains, the relation between the ambient temperature and the glass transition temperature decides the time required for healing. Therefore, a soft rubbery material whose glass transition temperature is lower than room temperature shows rapid healing. In this study, however, it is revealed that a weak gel whose tensile modulus is 100 MPa at room temperature, i.e., a leather-like material, shows autonomic healing even at room temperature in a relatively short time. Because the material has permanent network structure, it will not show macroscopic flow even after exposure to high temperature.

1. Introduction

Self-healing property has been desired for various applications of artificial materials [1-4]. Up to now, several approaches have been proposed for such kinds of smart intelligent polymers: microcapsule and hollow fiber methods in which repairing agent is encapsulated [1,5], reversible chemical reaction methods [6,7], and intermolecular bondings such as hydrogen bond [8-10], ionic interaction [11,12], and $\pi-\pi$ stacking [13]. Moreover, it has been known for a long time that "crack healing" takes place for plastics when a damaged material is annealed beyond the glass transition temperature (T_g). Wool and O'Connor [14] and Kim and Wool [15] theoretically predicted the recovery process as a function of healing time based on the concept of the reptation model proposed by de Gennes [16].

Meanwhile, our research group has reported that a weak gel just beyond the sol-gel transition critical point exhibits self-repairing behavior without any chemical reaction [17-19]. This material does not show macroscopic flow even at high temperature because of the permanent network. The healing occurs by the interdiffusion of dangling chains. At the temperature lower than T_g, it occurs immediately without any manual intervention. However, it is difficult to apply the material in industries because of the low modulus. This is reasonable because an amorphous polymer network having low crosslink density shows low modulus.

In this study, various weak polyurethane gels having different T_g's are prepared to investigate the healing behavior. For the purpose, two types of polyester diol are employed. Furthermore, a cellulose derivative is added to increase T_g. Since cellulose derivative has hydroxyl group the reaction with polyurethane is expected.

2. Experimental

2.1. Sample preparation

Two types of polyester diol (Nippon Polyurethane Industry) were employed; One is composed of adipic acid and diethylene glycol (AA) and the other contains isophthalic acid (IPA). The molecular weight of both materials is 2,000. The cellulose derivative used was cellulose acetate butyrate (CAB) commerciallized from Eastman. The butyryl and hydroxyl contents are 52 and 1.8 wt%, respectively. The weight-average molecular weight is 78,000 as a polystyrene standard. The details of CAB were expalined in other articles [20,21].

The crosslinking was performed by the polyisocyanate compound containing an isocyanurate ring of hexamethylene diisocyanate (NCO content 21 %), commerciallized from Nippon Polyurethane Industry.

The polyester diol and polyisocyanate compound were mixed with various [NCO]/[OH] ratios, denoted R. The contribution of hydroxyl group in CAB to the urethane reaction is ignored to calculate R. Furthermore, 40 wt% of CAB was added prior to the urethane reaction carried out at 100 °C with dibutyl-tin-dilaurate (100 ppm) as a catalyst.

2.2. Measuremements

Temperature dependence of oscillatory tensile modulus was evaluated at 10 Hz at temperatures between -100 and 150 °C by a dynamic mechanical spectrometer (UBM, E-4000) at a heating of 2 °C /min.

The sample was cut by a knife at room temperature. After leaving the sample at various temperatures, the repairing behavior was evaluated.

3. Results and discussion

3.1. Effect of species of polyester diol

The polyurethanes without CAB are prepared using both polyester diols. As already demonstrated in our previous paper [17], a weak polyurethane gel (R=0.6) prepared from AA (polyetster diol composed of adipic acid and diethylene glycol) shows immediate healing without any manual operation. Another polyurethane weak gel prepared from IPA (polyester diol composed of isophthalic acid) also shows autonomic healing at room temperature as shown in Figure 1. The gel, however, needs a long time to be healed (still shorter than one hour) as compared to the former gel, which is attributed to the difference in T_g´s; -30 °C for the former gel and 18 °C for the latter one. Although the latter gel shows relatively high T_g, the storage modulus is significantly sensitive to the ambient temperature, especially around room temperature.
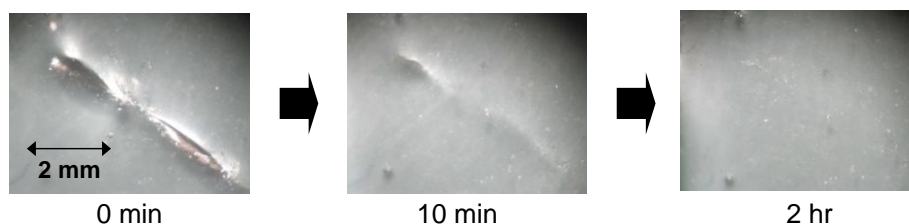

2 mm		
0 min	10 min	2 hr

Figure 1 Healing behavior at room temperature for a polyurethane weak gel (R=0.6) composed of IPA as a polyester diol

3.2. Blends with CAB

In order to rise T_g of the material, CAB is added. Figure 3 shows the temperature dependence of the dynamic tensile modulus for the sample composed of 60 wt% of polyurethane (IPA, R=0.6) and 40 wt% of CAB. The figure shows that there is a broad peak of loss modulus *tan δ* ascribed to the glass-to-rubber transition. Considering that the peak temperature of pure CAB is around 128 °C, both polymer chains are almost dissolved each other. The chemical reaction between CAB and isocyanate, which generates the copolymer of polyurethane-CAB, will enhance the miscibility. Furthermore, the infra-red spectroscopy measurements are carried out using the gel fraction of the blend. It is found that most CAB is detected in the gel fraction. The result directly demonstrates that the urethane reaction occurs between isocyanate and CAB.

The storage modulus of this sample is still sensitive to the ambient temperature. However, it behaves like a leather at room temperature (100 MPa at 23 °C).
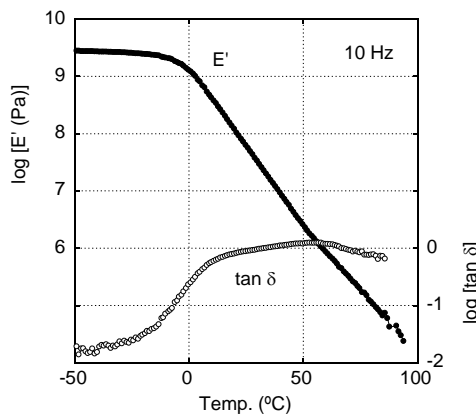

Figure 2 Dynamic mechanical properties of polyurethane (R=0.6, IPA)/CAB (60/40) blends at 10 Hz.

Figure 3 shows the self-repairing behaviors of the blend sample, i.e., polyurethane (R=0.6, IPA)/CAB (60/40) blend. Since the sample does not have isocyanate function, further reaction does not occur during annealing.

It is clarified that self-repairing occurs even at room temperature for two fours to some degree, which is further improved at high temperatures. At 60 °C, the applied scar is almost healed for two hours. Moreover, it is repaired completely at 80 °C for two hours.

In contrast, the samples having a large amount of crosslink points, i.e., R≧0.8, do not show healing even at 100 °C. The experimental results indicate that only weak gels having a lot of dangling chains show self-repairing by intermolecular diffusion of dangling chains.
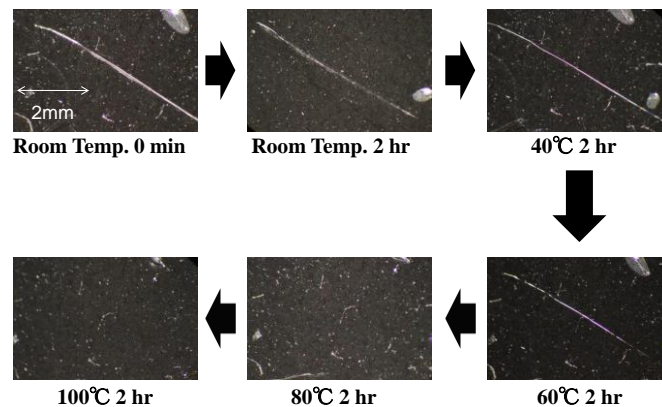

Figure 3 Self-repairing behaviors of Polyurethane([NCO]/[OH]=0.6, IPA)/CAB (6/4)

4. Conclusion

It has been known that a weak gel having a lot of dangling chains can be prepared by controlling the amount of a crosslinking agent. In this study, we demonstrate that the weak gel shows autonomic self-healing without any manual operation and chemical reaction. The healing time is dependent upon T_g, because the healing occurs by the interdiffusion of dangling chains. The weak gel whose T_g is beyond the room temperature also shows the self-healing behavior, although it takes a longer time. It is concluded that the self-healing leather-like material can be prepared using the interdiffusion of dangling chains. Since a lot of skin products covering metals and ceramics show a similar modulus, it can be used in various applications.

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