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Description	

**Interdiffusion of Dangling Chains in Weak Gel and its
Application to Self-Repairing Material**

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Abstract

A weak gel having a lot of dangling chains shows autonomic self-repairing behaviour for a significantly short time at room temperature. Mobility of the dangling chains whose one end is not connected to the network is responsible for the repairing nature via entanglement couplings, whereas the permanent network prohibits the macroscopic flow or deformation. Further, it is clarified by a tear experiment that about 80% of the tear strength is recovered for the sample having longer dangling chains.

Key Words; Polymers; Self-Repairing; Intelligent Material; Sol-Gel Transition

1. Introduction

Self-repairing polymers, as smart, intelligent, and bio-mimetic materials, have been desired intensively for a long time in industries, because it has a great possibility to extend the material life considerably. Although they are not commercially available, the following three methods have been proposed to provide the self-repairing nature; (1) to accelerate molecular interdiffusion by heating or by immersing into solvent; (2) to utilize the metabolic reaction between chain ends generated by molecular scission; and (3) to blend the microcapsules in which healing agent is embedded.

It has been well known that the molecular interdiffusion occurs above the glass transition temperature T_g of polymers, leading to entanglement couplings [1]. Skewis investigated tack strength $\sigma(t)$ as a function of contact time t of two sheets for several pairs of unvulcanized rubbers, such as styrene-butadiene rubber (SBR)/SBR, butyl rubber (IIR)/IIR, and SBR/IIR [2]. He showed that the tack strength increases with the contact time because of the increment of entanglements formed between the sheets, which can be considered as the interfacial healing. Later, Wool demonstrated that $\sigma(t)$ is proportional to $t^{1/4}$, employing the data obtained by Skewis [1]. The same relation was reported by Wool and O'Connor for polybutadiene [3] and by Voyutskii for polyisobutylene [4]. Further, the experimental results were supported by the theoretical approach developed by Wool et al [1,3,5] based on the chain dynamics at interface considering chain-pullout process not chain-scission. Moreover, Forbes and McLeod clarified that the tack strength of a polymer having molecular weight M at a constant contact time, $\sigma(M)$, is given by $\sigma(M) = \sigma_0 + \beta M^{-1/4}$, as far as the fracture occurs via disentanglement [6]. Similar phenomenon is observed in plastics above T_g , which is

known as “crack healing” [1,7-11]. The recovery curve of the critical stress intensity factor K_{IC} was investigated as a function of the applied annealing time t for various glassy polymers having a single crack formed by fracture of a virgin sample. It was found that the magnitude of K_{IC} increases with the annealing time and reaches to the original value of the virgin sample [7-11]. Further, K_{IC} was found to be proportional to $t^{1/4}$, as similar to tack strength [10]. The healing behaviour is accelerated at higher temperature because of the enhanced molecular interdiffusion at interface. Not only a single crack but also mechanically induced damages such as crazes and microvoids are also healed by means of chain interdiffusion above T_g for various polymers including semicrystalline polymers such as polyethylene and polypropylene [1,12]. Moreover, “crack healing” is observed in a specific solvent. This phenomenon is called “solvent healing”, while the former one is called “thermal healing”. At “solvent healing” process, the employed solvent is firstly immersed into a polymer and enhances the chain motion. After healing the crack by molecular diffusion, the solvent is removed. Such type of healing was reported for poly(methyl methacrylate) using methanol and/or ethanol [13,14] and for polycarbonate using carbon tetrachloride [15]. In spite of the abundant experimental data with a great progress on theoretical approach for molecular interdiffusion, this technique has not been applied in industries, because it requires manual intervention. Further, inappropriate temperature control at thermal healing results in the macroscopic flow and thus loses the initial shape.

The metabolic reaction method was proposed by Takeda et al. employing polyphenylene-ether containing copper complex [16]. They demonstrated that the deteriorated polymers by heat, light, and mechanical force, which have radicals at the chain end, are stabilized by a pre-mixed hydrogen donor, such as dibutylamine. Further,

the copper complex leads to the recombination of chain ends by eliminating two protons. Then the deactivated copper complex reacts with oxygen and is activated again. During the process, oxygen is consumed for repairing and water is emitted like a living body. The healing rate increases with increasing the number of chain ends and the amount of plasticizer, because the frequency to meet both chain ends is enhanced. Further, they discussed the repairing system as compared with that of a living body from the view point of the metabolic reaction [16]. Furthermore, they found that a similar technology is applicable for polycarbonate containing sodium carbonate and tri(2,4-di-*t*-butylphenyl)phosphate [17]. This truly bio-mimetic approach is, unfortunately, applicable for specific polymers. Moreover, it takes a long time to recover the mechanical properties because of depressed molecular motion at room temperature.

The microcapsule method was proposed by White et al. employing polyepoxide, one of the most conventional thermosetting resins [18-20]. In this method, microcapsules containing healing agent, e.g., cyclopentadiene, are dispersed in a matrix with a catalyst for the polymerization with healing agent. When a crack is generated in the resin, microcapsules are also ruptured and the healing agent is released into the crack through capillary action. They demonstrated that the mechanical strength is recovered by 75% after 48 hours, although the chemical structure of the repaired material is different from the original one. A similar idea has been proposed at the beginning of 1990's by Dry et al [1,21]. They encapsulated healing agent in hollow fibers and dispersed in a matrix. After failure, the released agent from the fibers seals microcracks in the matrix and rebonds the damaged interface. Recently, Pang and Bond developed this idea and proposed a self-repairing composite [22]. Although the

microcapsule methods do not require any manual intervention, it has not been available yet to the best of our knowledge. The difficulty of the sample preparation, leading to poor cost-performance, and the restriction of the polymer species would be the problem for the industrial application.

In this study, we propose a new idea of material design for self-repairing polymers without any chemical reactions for healing, which is basically applicable to any kind of polymers. Generally, liquid shows repairing nature while solids keep the shape. Therefore, a self-repairing material should exhibit both solid and liquid natures somehow. In fact, the transition from glassy state (solid) to rubbery/liquid state (liquid) is utilized for “crack healing”. We focus on a gel just beyond the sol-gel transition point having the permanent network to keep the material shape (solid). Further, the dangling chains in the gel, defined as the chain segments whose one end is not connected to the network, are responsible for repairing nature, because the dangling chains exhibit segmental interdiffusion like liquid at a local scale.

2. Experimental

2.1. Preparation of prepolymers

Amorphous polyester-diol composed of diethylene glycol and adipic acid (56 KOHmg/g, Nippon Polyurethane Industry, Nippollan 152, purity 99%) was employed as one of the prepolymers, i.e., p-4k, without further purification. Another prepolymer, i.e., p-6k, was prepared by the reaction of p-4k and hexamethylene diisocyanate (Kanto Kagaku) with 100 ppm of dibutyl-tin-dilaurate (Aldrich, purity 95%) as a catalyst, in which the molar ratio of [NCO] to [OH] is 0.5, at 98 °C for 30 min.

2.2. Preparation of network polymers

Polyisocyanate compound containing an isocyanurate ring of hexamethylene diisocyanate (NCO content 21.0%, Nippon Polyurethane Industry, Coronate HX, purity 99%) was employed as a crosslink agent without further purification. Polyurethanes were prepared by the reaction of a prepolymer and the crosslink agent with various molar ratio of [NCO] to [OH] ($[\text{NCO}]/[\text{OH}] = 0.47 - 1.0$). A prepolymer and the polyisocyanate were mixed together at room temperature with 100 ppm of dibutyl-tin-dilaurate. After removal of bubbles in a vacuum oven controlled at 80 °C for 10 min, it was heated up to 150 °C for the reaction and was kept at the temperature for 5 min in a compression-molding machine under a slight pressure. The mixture with 2 mm thickness was sandwiched between a Teflon film and a corona-treated polyethylene terephthalate (PET) film to prepare the sample specimens for tensile and tearing tests. Further, the mixture with 1 mm thickness was sandwiched between Teflon films, and then heated for the reaction to prepare the specimens for the measurements of gel fraction and dynamic mechanical spectra. After removal of the Teflon films, the material was washed by excess amount of acetone in order to eliminate the sol-fraction and then dried at room temperature.

2.3. Rheological Properties

The frequency dependence of the oscillatory shear modulus was measured by a cone-and-plate rheometer (UBM, MR500) at room temperature to determine zero-shear viscosity. Further, the temperature dependence of the oscillatory tensile modulus was

evaluated at 10 Hz by a dynamic mechanical spectrometer (UBM, E4000) at a heating rate of 2 °C/min.

2.4. Evaluation of self-repairing behaviour

The self-repairing behaviour was evaluated qualitatively by a tensile testing using a specimen with 2 mm thickness that has a PET film on the one side. Separated sheet samples cut by a razor blade were butt-jointed at room temperature for 10 min. Then the repaired samples were elongated to 30 mm. Quantitative evaluation of the repairing was also carried out by a tearing test following ISO 6383-1 Trouser tear method. Separated sheet samples with 1 mm thickness, which was cut by a razor blade, were attached at room temperature for 10 min. Then the tearing force was measured as compared with the virgin samples.

3. Results and Discussion

Various network polymers were prepared by urethane reaction between polyester-diol as a prepolymer and trifunctional isocyanate as a crosslink agent. In this study, two types of polyester-diol having different molecular weights, p-4k and p-6k, were employed. The molecular weights of the samples were evaluated by a gel permeation chromatograph, GPC, (Tosoh, HLC-8020) with TSK-GEL® GMHXL, in which chloroform was employed as eluant at 40 °C at a flow rate of 1.0 ml/min. The sample concentration was 1.0 mg/ml. The number- and weight-average molecular weights as a polystyrene standard are as follows: $M_n = 4.2 \times 10^3$ and $M_w = 7.8 \times 10^3$ for p-4k; and $M_n = 6.2 \times 10^3$ and $M_w = 1.3 \times 10^4$ for p-6k. Figure 1 shows the molecular weight dependence of zero-shear viscosity η_0 of the prepolymers evaluated at 25 °C.

The slope is 3.7 as represented by a solid line in the figure, demonstrating that both prepolymers have higher molecular weight than the entanglement molecular weight [23]. Therefore, the dangling chains in polyurethane networks, whose molecular weight is at least higher than that of the prepolymer, show entanglement couplings.

[Figure 1]

The self-repairing behaviour is evaluated employing the gel fraction of crosslinked polyurethane, which is obtained by eliminating sol fraction by excess amount of acetone at room temperature. At the procedure, gel fraction and degree of swelling were measured as shown in Figure 2. It is apparent that polyurethane with low $[\text{NCO}]/[\text{OH}]$ ratio has a small amount of gel and shows high level of swelling. This is reasonable because it has fewer crosslink points. Further, it is found that the molecular weight of the prepolymer slightly affects the gel fraction especially at low level of $[\text{NCO}]/[\text{OH}]$ ratio, which would be attributed to side reaction of isocyanate. If a small amount of isocyanate functionality is consumed for the reaction with water, for example, the gel fraction would be lower than the theoretical one [24]. This is prominent for the prepolymer with high molecular weight, because the amount of isocyanate compound per unit weight is smaller.

[Figure 2]

Figure 3 show the temperature dependence of dynamic tensile moduli, such as storage modulus E' , loss modulus E'' , and loss tangent $\tan \delta$, for PU-0.5-6k, i.e., gel fraction of polyurethane prepared employing p-6k with $[\text{NCO}]/[\text{OH}] = 0.5$ (Figure 3(a)) and PU-1.0-6k, i.e., that with $[\text{NCO}]/[\text{OH}] = 1.0$. The storage modulus decreases with temperature for both samples and keeps a constant value at high temperature, that is

so-called plateau modulus. This is attributed to the existence of a permanent network, prohibiting the macroscopic flow. Because of fewer crosslink points, the storage modulus in the rubbery state for PU-0.5-6k is quite lower than that for PU-1.0-6k. As for the E'' curve around $-50\text{ }^{\circ}\text{C}$, PU-0.5-6k shows a sharp peak as compared with PU-1.0-6k. This result suggests that the network structure of PU-1.0-6k is not homogeneous because of the crowded crosslink points. Furthermore, it should be notified that PU-0.5-6k shows almost a constant value of $\tan \delta$ in the wide range of temperature above T_g . Considering thermorheological simplicity [23], $\tan \delta$ is almost 1.0 in the wide range of frequency above T_g , suggesting that PU-0.5-6k is close to the sol-gel transition point, as demonstrated by Chambon and Winter [25,26]. As pointed out theoretically by de Gennes [27], the gel near the critical point has a lot of dangling chains as well as small amount of the elastically active network chains. The dangling chains show a longer relaxation time that increases exponentially with the length as theoretically and experimentally proved by various researchers [27-31]. Further, the chains have marked mobility like liquid at a local scale and interact with neighbour chain segments by means of entanglement couplings. The pronounced mobility of dangling chains is confirmed by high level of $\tan \delta$ in the wide temperature range above T_g as reported for various gels including polyurethane [30-35]. This nature is applicable to a damping material [33]. On the other hand, a fully crosslinked gel shows low level of $\tan \delta$, suggesting the depressed segmental mobility even above T_g because of the constraint by crosslink points.

[Figure 3]

Figure 4 compares the temperature dependence of $\tan \delta$ for PU-0.5-4k and PU-0.5-6k. It is found that PU-0.5-6k shows slightly sharp E'' peak as compared with PU-0.5-4k. Further, the level of $\tan \delta$ at higher temperature above 50 °C is higher for PU-0.5-6K, indicating that large-scale segmental motion having a long relaxation time is slightly enhanced. The longer dangling chains, which would have a branch structure, are responsible for the difference in dynamic mechanical properties as derived by Dusel et al [24].

[Figure 4]

The self-repairing property is evaluated quantitatively by tensile testing employing repaired samples by the butt-joint technique at the cut surface as illustrated in Figure 5. Since a PET film has high modulus, deformation occurs only at the cut area, i.e., the healed interface. PU-0.5-4k shows the apparent failure from the cut point at the beginning of the tensile testing, indicating that the cut area is not repaired mechanically. In other words, entanglement couplings by the dangling chains are insufficient to heal the applied scar. On the contrary, the cut area is extended greatly in the case of PU-0.5-6k. This result demonstrates that the material exhibits autonomic repair of the mechanical damage for a considerably short time at room temperature, which widens the industrial applications. The difference in the healing efficiency between PU-0.5-4k and PU-0.5-6k would be attributed to the length of dangling chains. Further, it is impossible to perform the tensile testing for butt-jointed PU-1.0-6k (but not presented here). This is plausible because PU-1.0-6k is mostly composed of the elastically active network chains [24].

[Figure 5]

In order to evaluate the healing behaviour quantitatively, healing efficiency, defined as the ratio of tearing strength of a repaired sample to that of the virgin one, is evaluated for various gels prepared from p-6k, i.e., PU-x-6k, by the tearing test. The result, shown in Figure 6, demonstrates that the healing efficiency increases with decreasing [NCO]/[OH] ratio. In other words, the gel fraction of PU prepared from (1) low level of [NCO]/[OH] ratio and (2) high-molecular-weight prepolymer, exhibits self-repairing nature from the view points of mechanical property. In particular, PU-0.47-6k shows almost 80 % as a healing efficiency. This is comparable with the microcapsule method [18], although the present technique does not require any chemical reaction for healing.

[Figure 6]

4. Conclusion

We have developed a new intelligent material showing autonomic self-repairing nature by means of topological interaction associated with dangling chains in the network polymer from a weak gel just beyond the sol-gel transition point. It has been clarified that the repairing occurs quite rapidly like liquid, whereas it never flows macroscopically because of the permanent network. The healing efficient, i.e., the ratio of tear strength of the repaired sample to that of the virgin sample, is found to be 80% for the network polymer obtained from a prepolymer having higher molecular weight. Well developed longer dangling chains would be responsible for the mechanical healing.

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Figure Captions

- Figure 1 Zero shear viscosity at 25 °C for the prepolymers plotted against weigh-average molecular weight.
- Figure 2 Gel fraction (circles) and degree of swelling (diamonds) for polyurethanes with various [NCO]/[OH] ratio; (open symbols) urethanes from p-4k and (closed symbols) those from p-6k.
- Figure 3 Temperature dependence of oscillatory tensile moduli at 10 Hz, such as (closed circles) storage modulus E' , (open circles) loss modulus E'' , and (closed diamonds) $\tan \delta$ for (a) PU-0.5-6k and (b) PU-1.0-6k.
- Figure 4 Temperature dependence of $\tan \delta$ for (open circles) PU-0.5-4k and (closed circles) PU-0.5-6k.
- Figure 5 Self repairing behaviours. (a) experimental procedure, and (b) (top) separated samples prior to butt-joint and (bottom) samples during stretching after butt-joint healing for (left) PU-0.5-4k and (right) PU-0.5-6k.
- Figure 6 Healing efficiency for polyurethane gels with various [NCO]/[OH] ratios.

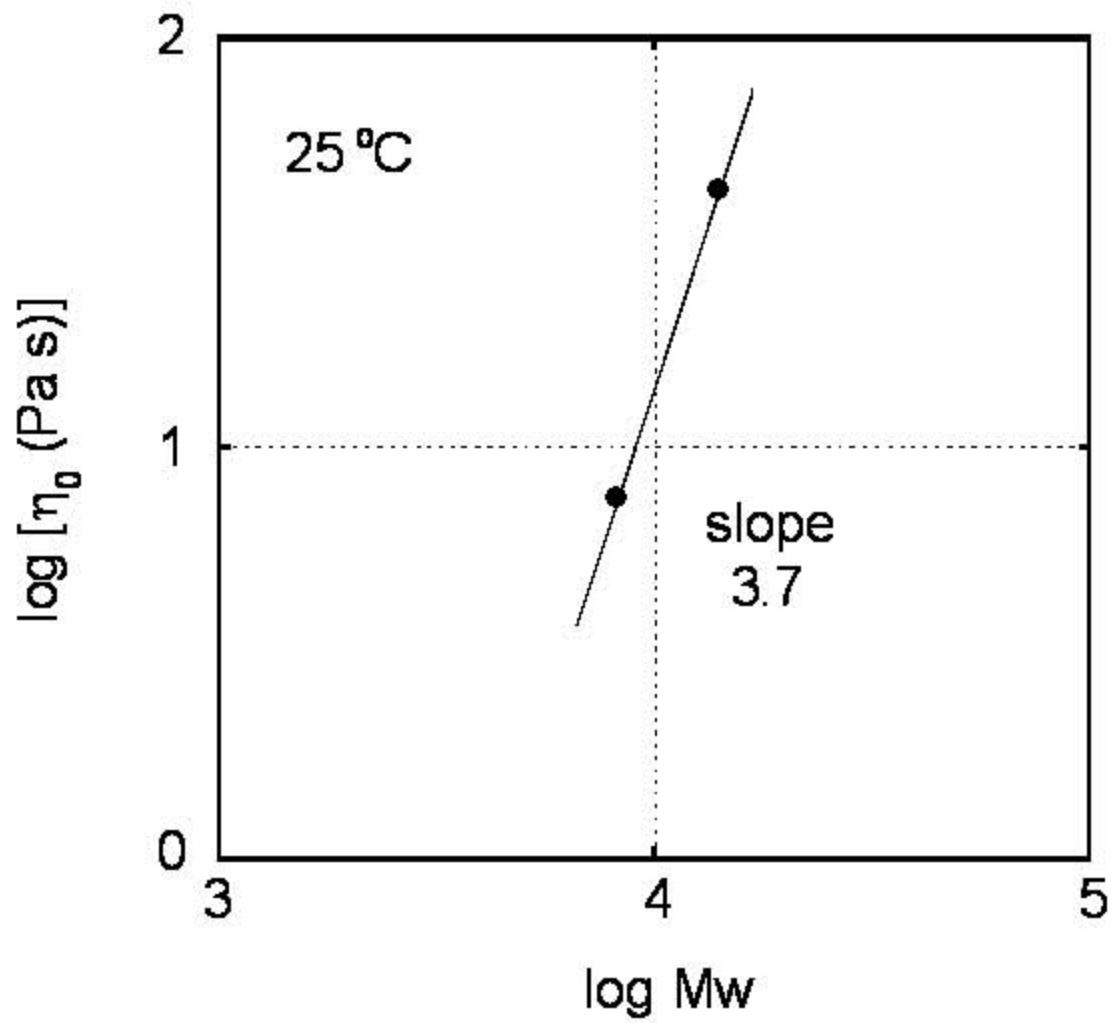


Figure 1

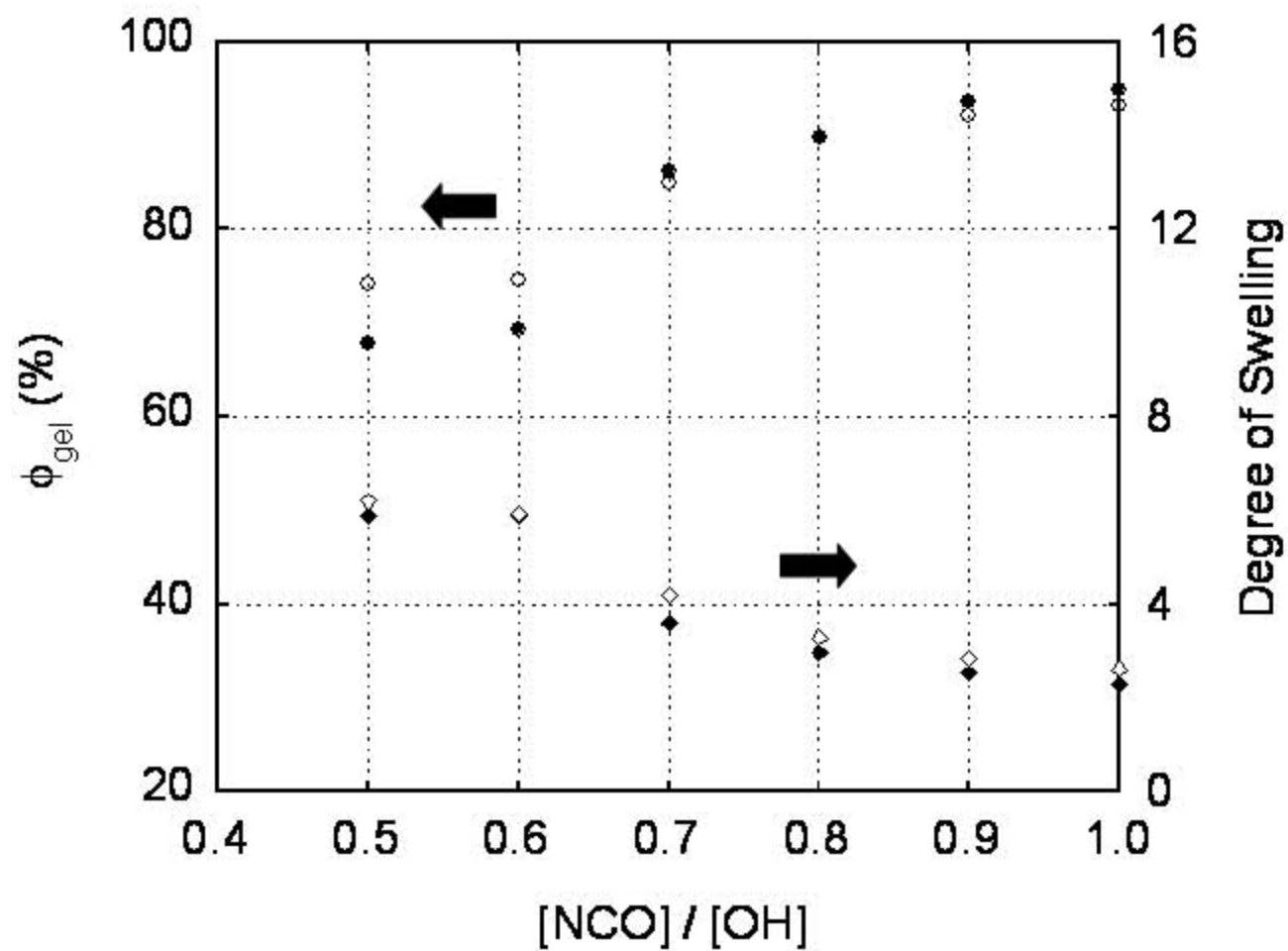


Figure 2

(a)

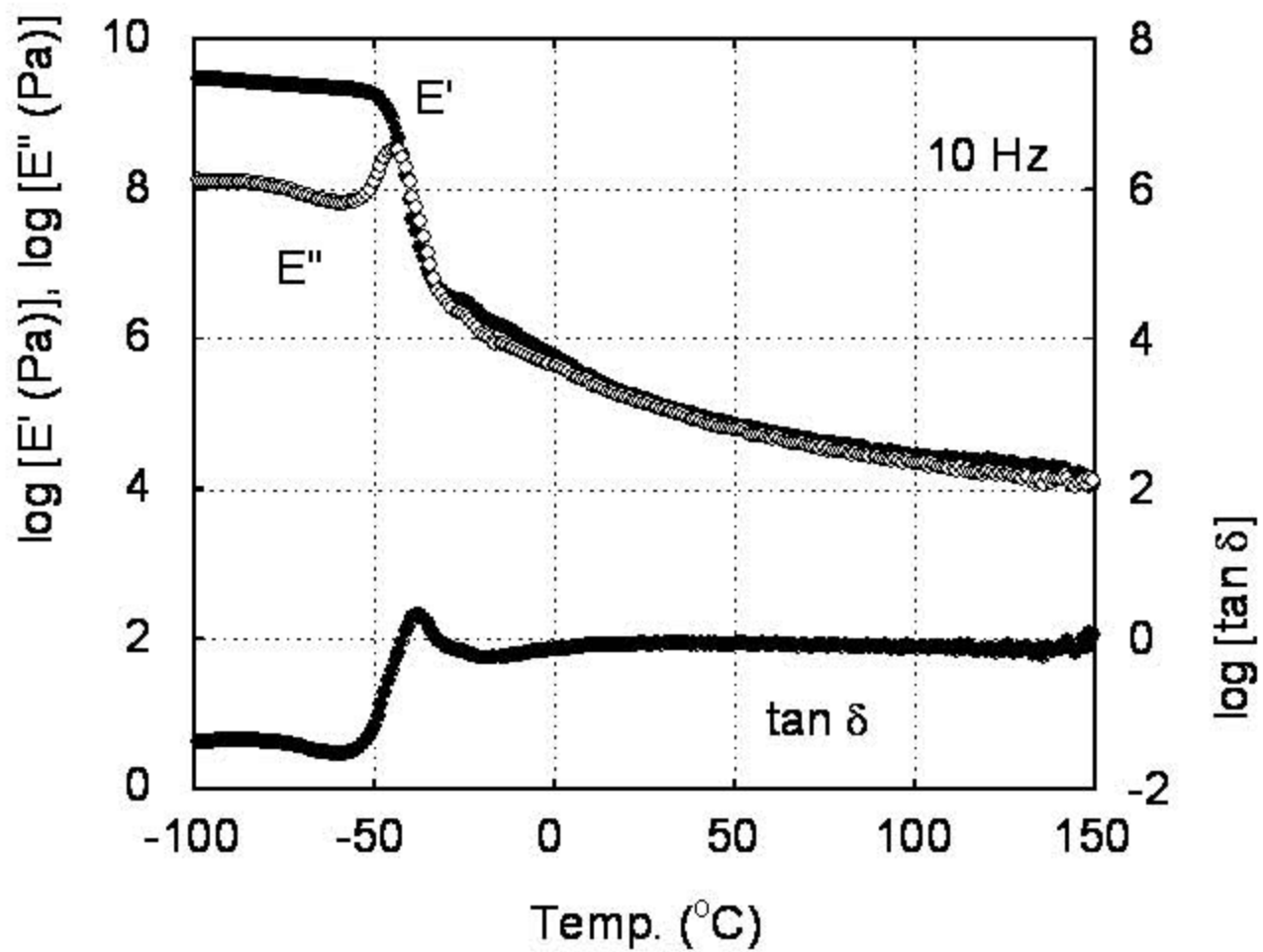


Figure 3

(b)

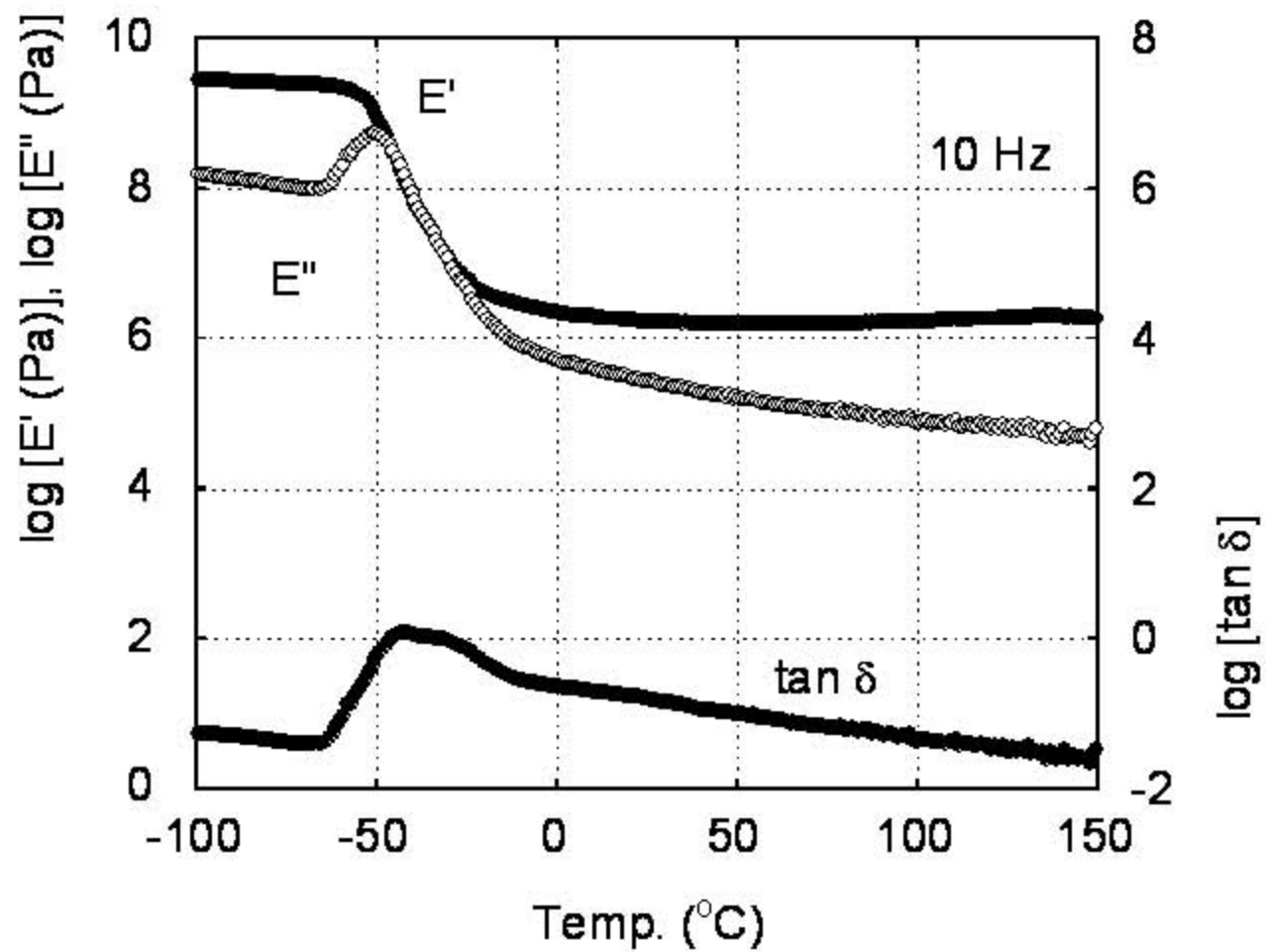


Figure 3

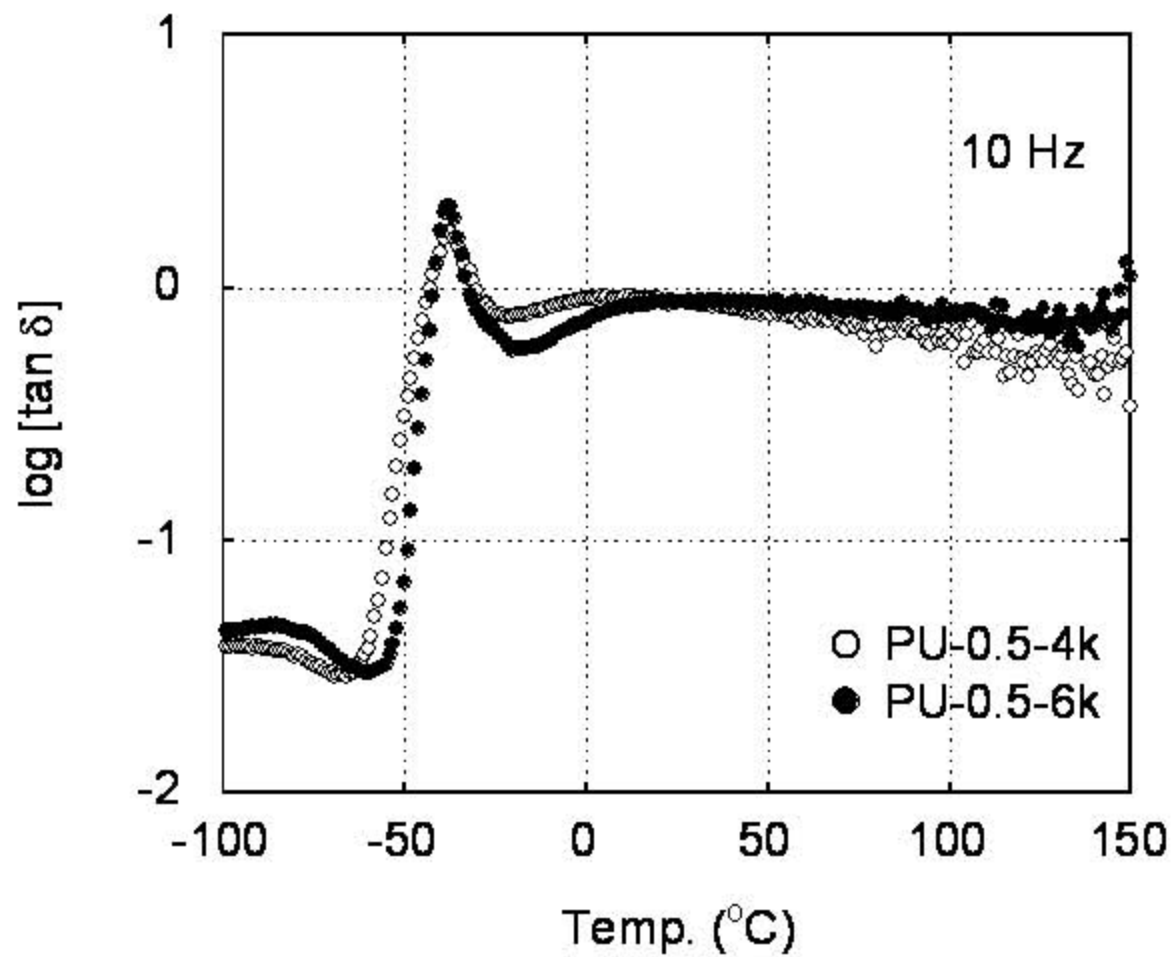
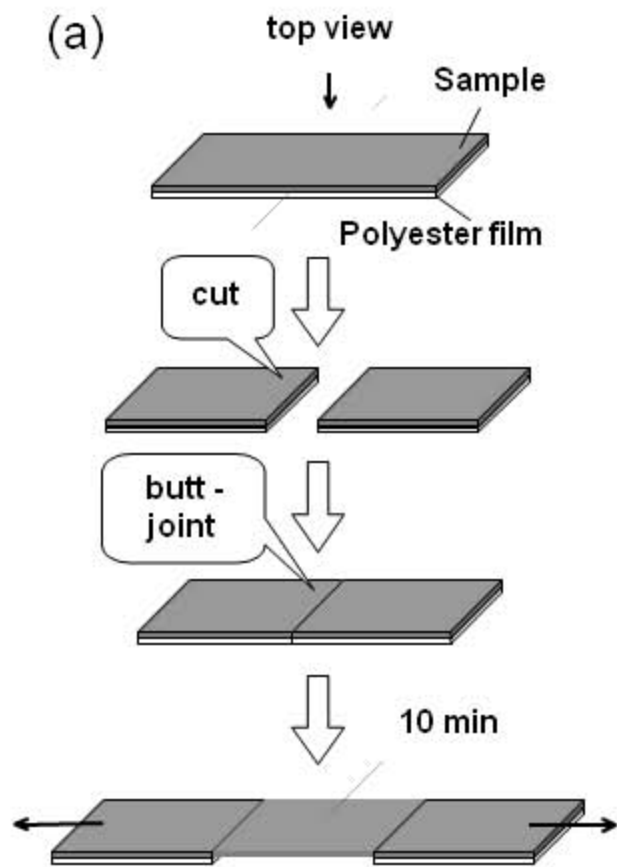


Figure 4



(b) **PU-0.5-4k**



PU-0.5-6k

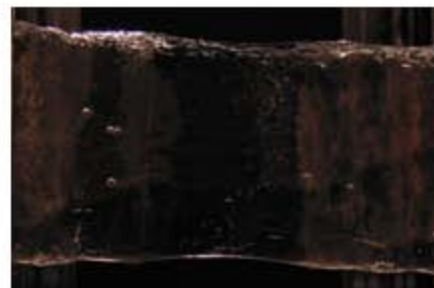


Figure 5

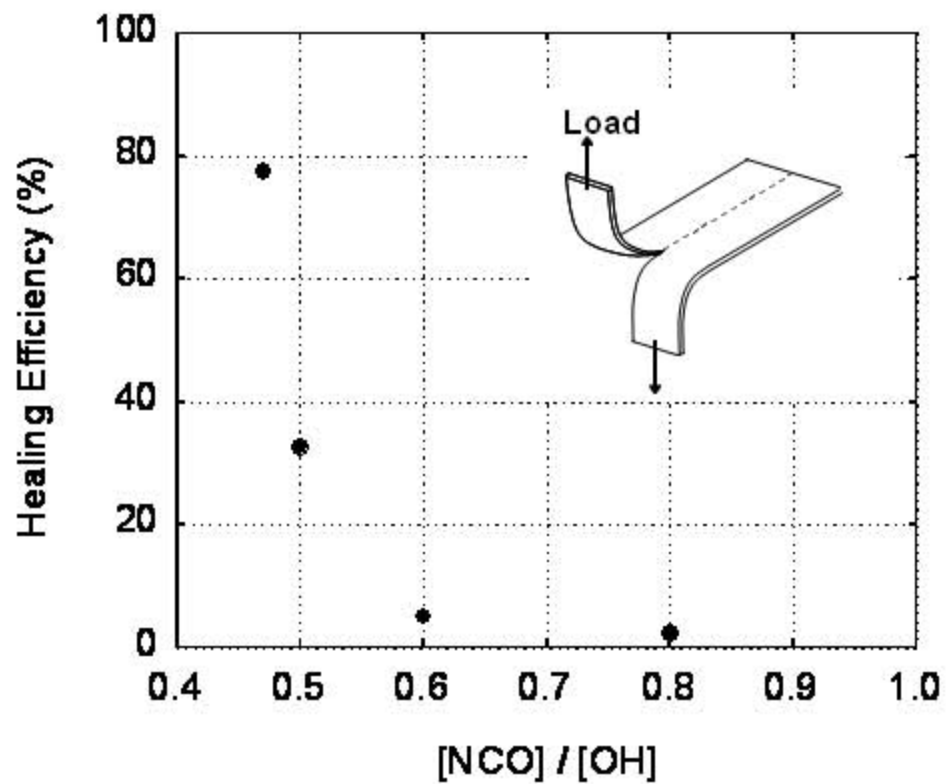
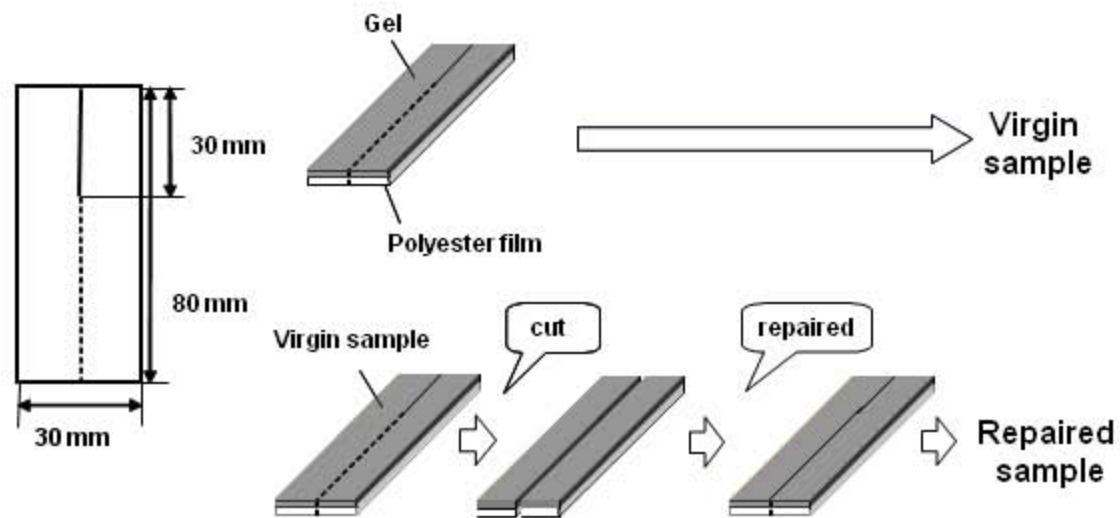


Figure 6