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Self-Repairing Property of Polymer Network with Dangling Chains

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Abstract

A new type of self-repairing polymer was proposed by utilizing strong topological interaction of dangling chains in the network polymer that was obtained by eliminating sol-fraction in a weak gel just beyond sol-gel transition point. It was confirmed that applied cleavage by a razor blade was healed at room temperature without any manual intervention.

Key words: polymers; viscoelasticity; self-repairing; sol-gel transition; bio-mimetic

1. Introduction

Healing or repairing a mechanical-induced damage of artificial materials, as one of the bio-mimetic properties, has been desired for various applications. Up to now, several approaches have been proposed to establish the material design for such kinds of smart intelligent polymers.

White et al. reported autonomic healing for an epoxy-resin without manual intervention by blending the microcapsules in which repair-chemical-agent was filled. The agent was released, when broken, from them into the matrix polymer with a catalyst [1-3]. Dry also proposed the idea employing the hollow fibers containing repair-chemicals [4,5], leading to the development of a self-repairing epoxy-composite by Pang and Bond [6]. Further, Takeda et al. demonstrated that recombination of the main chain occurs after chain scission for the composite of polyphenylene-ether with (1) hydrogen donor to stabilize the radical at the chain ends and (2) Cu(II) to combine chain ends by eliminating two protons [7]. They also pointed out that polycarbonate has a great potential for self-repairing when blended with sodium carbonate and so on [7,8].

Besides the healing associated with chemical reaction, molecular interdiffusion is also responsible for self-repairing of polymeric materials. It has been known for a long time that "crack healing" takes place for plastics when a damaged material is annealed above the glass transition temperature. After pioneering works by Jud and Kaush [9] and Wool and O'Connor [10], "crack healing" by molecular diffusion has received great attention for various polymers. Wool and O'Connor [10] and Kim and Wool [11] theoretically predicted the recovery process as a function of healing time based on the concept of "reptation model" proposed by de Gennes [12,13]. In this model, a polymer chain is considered to move back-and-forward like a snake (reptation) within a tube-like region composed of intermolecular interaction with neighbor chains, *i.e.*, entanglement couplings. Further, it has been known that "crack healing" is also observed in a specific solvent. This phenomenon is called "solvent healing", while the former one is called "thermal healing". In this healing process, the solvent is firstly immersed into a polymer until healing and then removed, which was reported for poly(methyl methacrylate) using methanol and/or ethanol [14-16] and for polycarbonate using carbon tetrachloride [17].

In this paper, we propose a new method for the design of a self-repairing polymer, which is essentially attributed to the molecular interdiffusion. The material design is, however, quite different and is based upon the strong topological interaction, *i.e.*, entanglement couplings, of dangling chains in a network polymer close to a critical point. The material presented in this study does not require any manual intervention, such as annealing procedure and/or solvent treatment, for healing. Therefore, various industrial applications will be expected.

2. Experimental

2.1. Materials

The materials studied were polyurethanes with different network structure. Amorphous polyester-diol composed of diethylene glycol and adipic acid (56 KOHmg/g, Nippon Polyurethane Industry, Nippollan 152, purity 99%) and polyisocyanate compound containing an isocyanurate ring of hexamethylene diisocyanate (NCO content 21.0%, Nippon Polyurethane Industry, Coronate HX, purity 99%) were employed to prepare the polyurethanes without further purification. Both materials were supplied by Nippon Polyurethane Industry in Japan.

2.2. Preparation of network polymers

As listed in Table 1, three types of polyurethanes were prepared with various reaction ratios, *i.e.*, molar ratio of [NCO] to [OH]. Since the polyisocyanate is a trifunctional material, a polyurethane with higher reaction ratio has more crosslink points.

The polyester-diol and the polyisocyanate were mixed together at room temperature with 100 ppm of dibutyl-tin-dilaurate (Aldrich) as a catalyst for urethane reaction. Then the mixture was put into a vacuum oven at 80 °C for 10 min to remove bubbles. Further, the mixture was heated upto 50 °C for the reaction and was kept at the temperature for 5 min in a compression-molding machine under slight pressure. The sample with 2 mm thickness was sandwiched by a Teflon film and a corona-treated polyethylene terephthalate (PET) film. After taking off the Teflon sheet, 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 oscillatory shear modulus was measured as a function of the angular frequency employing a strain-controlled parallel-plate rheometer (UBM, MR-500) at room temperature. Furthermore, the temperature dependence of the oscillatory tensile modulus was also 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 behavior

The self-repairing behavior was evaluated for the sample cleaved by a razor blade. The length of the cleavage was 20 mm and the depth was about 2 mm, which was confirmed by a stereomicroscope (Leica, S6E). The cleaved condition was checked by rolling, *i.e.*, curling, the sample sheet onto a column with 12 mm in diameter to apply a slight force onto the cleavage, as illustrated in Figure 1. After taking a picture, the sheet was unrolled immediately and kept without external force at room temperature for 10 min. Then the repairing behavior was checked again by rolling the sheet onto the column.

[Figure 1]

3. Results and Discussion

3. 1. Characterization of polyurethanes

The gel fraction - defined as the weight ratio of dried network polymer to that of the polyurethane before washing by acetone - was evaluated for all polyurethanes. It is found that PU-0.3 has no gel, whereas both PU-1.0 and PU-0.5 have the following gel fractions; 91% for PU-1.0 and 65 % for PU-0.5. Therefore, two types of network polymers were employed in this study.

Figure 2 shows the angular frequency dependence of shear storage modulus *G'*, loss modulus *G"*, and loss tangent *tan* δ at room temperature for the network polymers obtained from PU-1.0 and PU-0.5. Further, as a comparison, the shear moduli for PU-0.3

were also plotted in Figure 2(c). As seen in Figure 2(c), both moduli decrease with *G”>G’*, and *tan δ* increases with decreasing the angular frequency; these are the typical behaviors for flow region of polymer melts without permanent network. On the contrary, the network polymer from PU-1.0, as depicted in Figure 2(a), shows a plateau in the wide frequency region ascribed to a permanent network, which is similar to the rheological properties for a conventional vulcanized rubber. As for the network polymer from PU-0.5, both moduli show similar values, *i.e.*, constant *tan δ*, especially in the higher frequency region, and decrease with decreasing the angular frequency; these are the characteristics for the material at the critical point of sol-gel transition as demonstrated by Chambon and Winter [18,19]. Further, in the lower frequency region, storage modulus shows higher values, with a less frequency-dependent fashion, than loss modulus, suggesting the existence of a plateau. Although the level of the plateau modulus is lower than that for the network from PU-1.0, the material will never flow macroscopically because of the permanent network.

[Figure 2]

It is well known that a gel close to the critical point has a lot of dangling chains, defined as inactive chains to elasticity whose one end is not connected to the network. The relaxation peak of dangling chains appears above the glass transition temperature because it has a prolonged relaxation time as pointed out by de Gennes [12]. Figure 3 shows the temperature dependence of tensile storage modulus *E’*, loss modulus *E”*, and loss tangent *tan δ* at 10 Hz for the network polymers. The network polymer from PU-0.5 (Figure 3(b)) shows high level of *tan δ* in the wide range above the glass transition temperature, whereas that from PU-1.0 (Figure 3(a)) shows lower values in the high temperature region. Similar dynamic mechanical properties in Figure 3(a) have been reported for various vulcanized rubbers. The results in Figure 3 demonstrate that the network from PU-0.5 has a lot of dangling chains.

[Figure 3]

3. 2. Self-repairing behavior

Figure 4(a) is the top and side views of cleavage on the network polymer from PU-1.0. As shown in the pictures at the right-hand side, the appearance of the cleavage on the surface was not changed. Further, it is also confirmed that it remains even after 24 hours, indicating that the cleavage is never repaired for the sample. The network polymer from PU-0.5 does, however, exhibit repairing as shown in Figure 4(b). The pictures demonstrate that the network polymer with a lot of dangling chains shows liquid-like behavior, *i.e.*, self-repairing property. Further, it is quite useful from the viewpoint of industrial application because the healing time is less than 10 min, which is quite different from “thermal healing” of a glassy polymer.

[Figure 4]

The self-repairing behavior in this study would be attributed to topological interaction, *i.e.*, entanglement couplings, between dangling chains. It is plausible because it has been reported recently that a weak gel plays a significant role on melt elasticity due to entanglement couplings in a blend with a linear polymer [20-24]. Although the self-repairing mechanism shown in the study is somewhat similar to that for “thermal healing” due to molecular interdiffusion of whole chains, it should be noted that healing of the network polymer with dangling chains occurs in a very short time without any manual intervention, such as annealing procedure and/or solvent treatment.

We are preparing further investigation on self-repairing property of the network polymer with dangling chains from the view point of mechanical response. Moreover, the effect of molecular structure of a network polymer, such as the length of dangling chains as well as the chemical structure of a network, will be studied in detail.

4. Conclusion

The self-repairing property of a network polymer having dangling chains has been studied employing gel-fraction of crosslinked polyurethane. It was found that the network polymer obtained from a weak gel just beyond the critical point exhibits autonomic self-repairing. This would be attributed to the topological interaction of dangling chains in the network polymer. Further, it has been clarified that the repairing occurs quite rapidly like liquid, whereas it never flows macroscopically because of the permanent network.

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Figure Captions

Figure 1 Schematic illustration of the sample sheet when taking a picture.

Figure 2 Angular frequency dependence of shear storage modulus *G'* (open circle), loss modulus *G"* (closed circle), and loss tangent *tan* δ (closed triangle) at 23 °C for (a) the network polymer from PU-1.0, (b) the network polymer from PU-0.5, and (c) PU-0.3.

Figure 3 Temperature dependence of tensile storage modulus *E'* (open circle), loss modulus *E"* (closed circle), and loss tangent *tan* δ (closed triangle) at 10 Hz for the network polymers from (a) PU-1.0 and (b) PU-0.5.

Figure 4 Self-repairing behavior of top and side views for the network polymers from (a) PU-1.0 and (b) PU-0.5.

Table I Recipe of polyurethanes

Sample	Polyurethane		Reaction ratio
	Polyester-diol (wt%)	Polyisocyanate (wt%)	
PU-0.3	94.3	5.7	0.3
PU-0.5	90.9	9.1	0.5
PU-1.0	83.1	16.9	1.0

Figure 1

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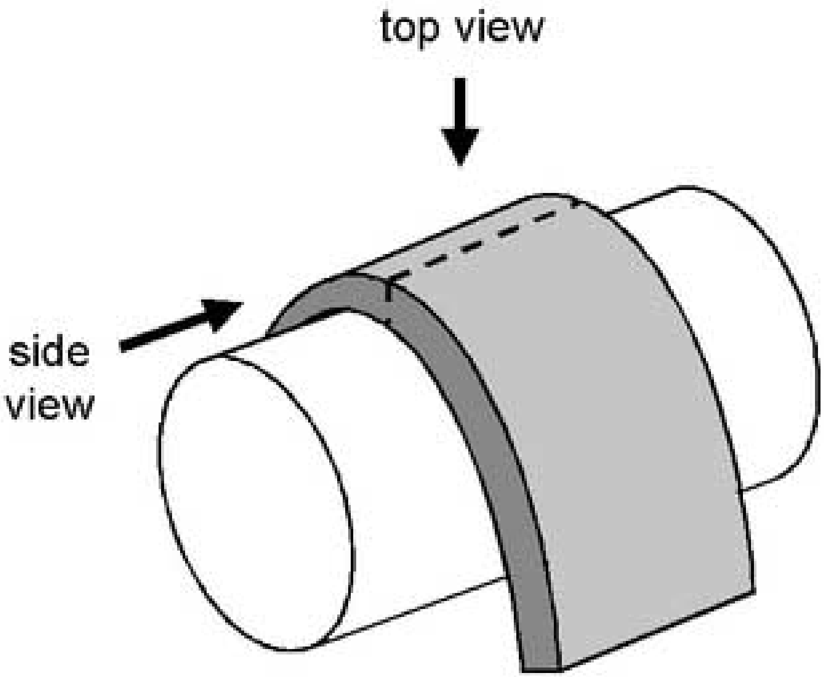

Figure 2(a)

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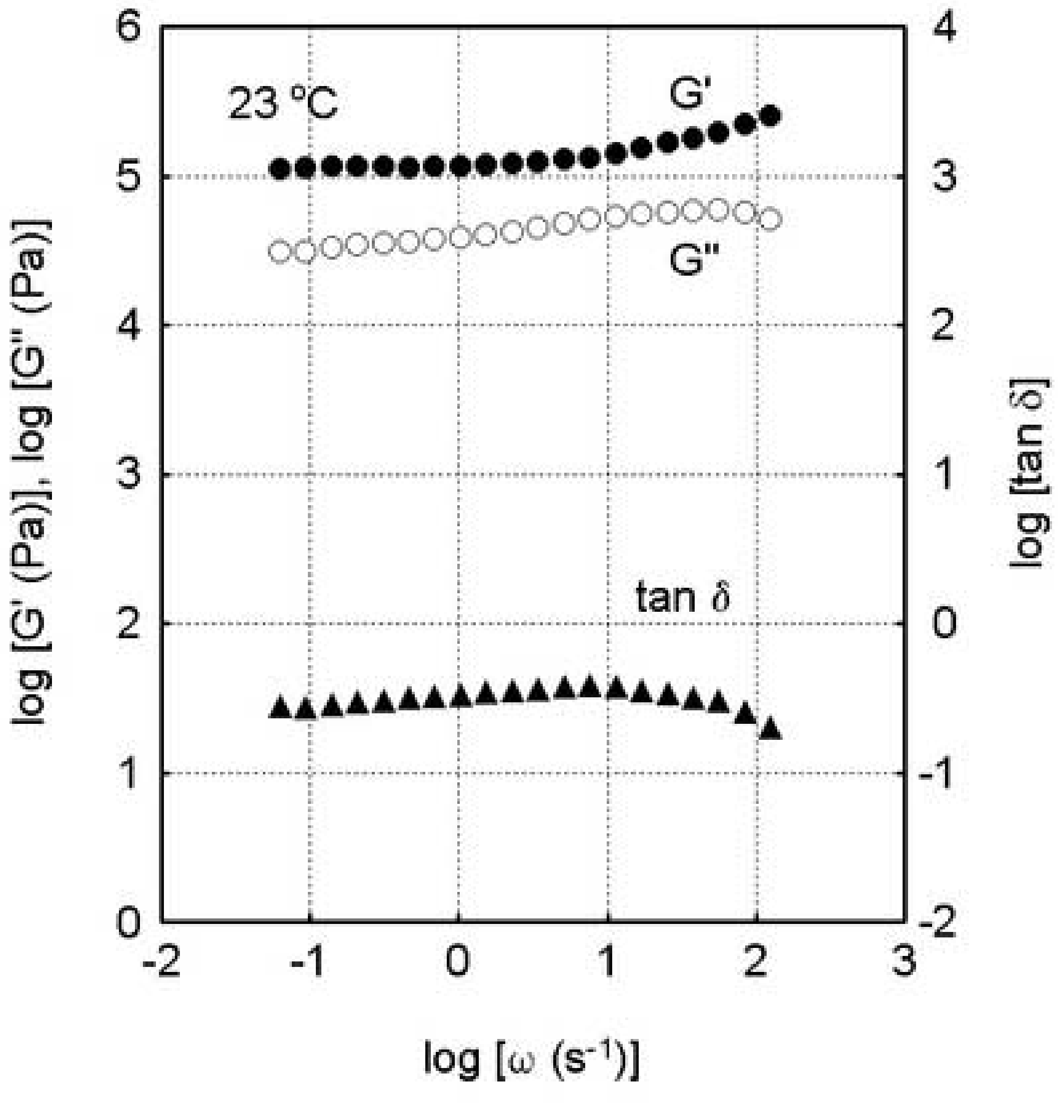

Figure 2(b)

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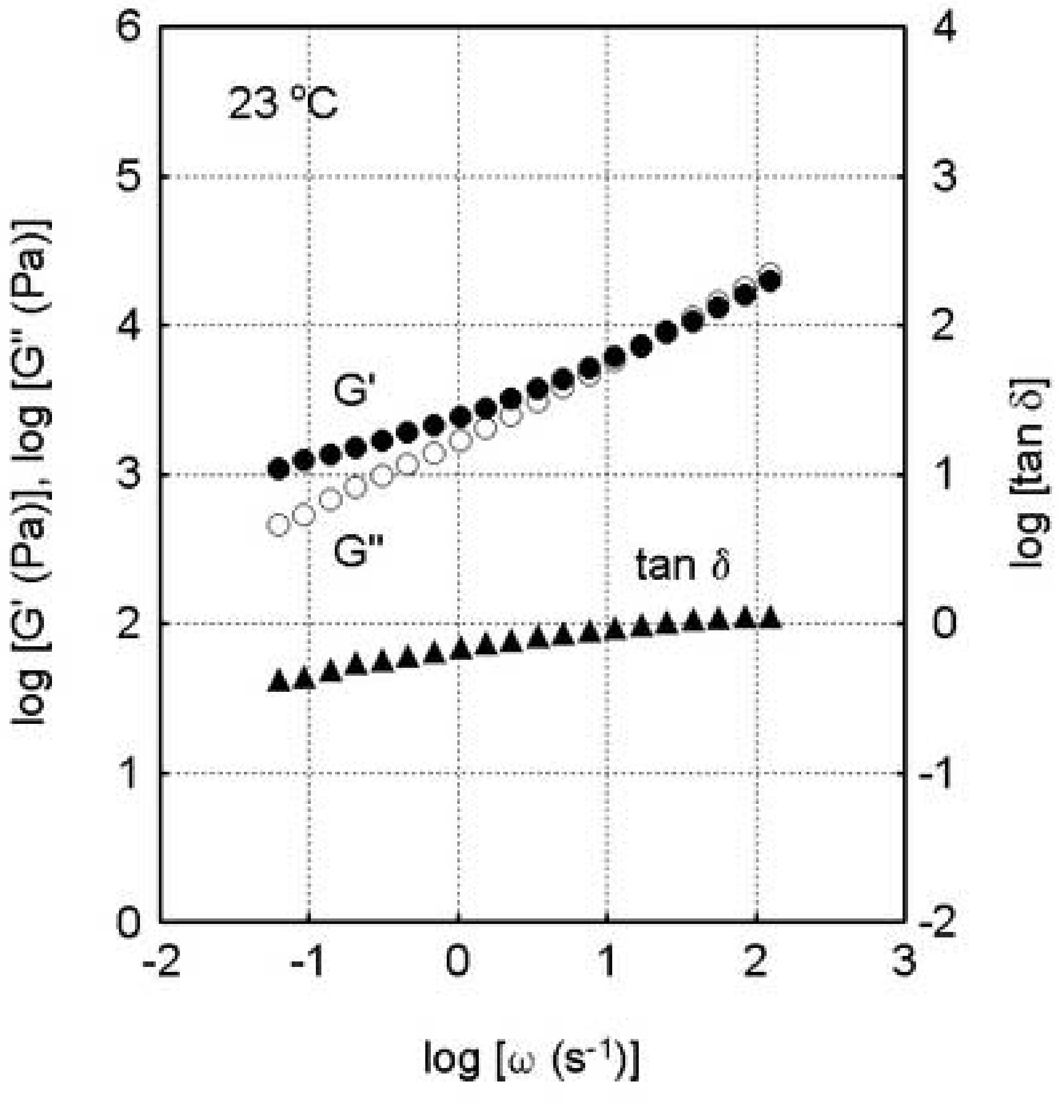

Figure 2(c)

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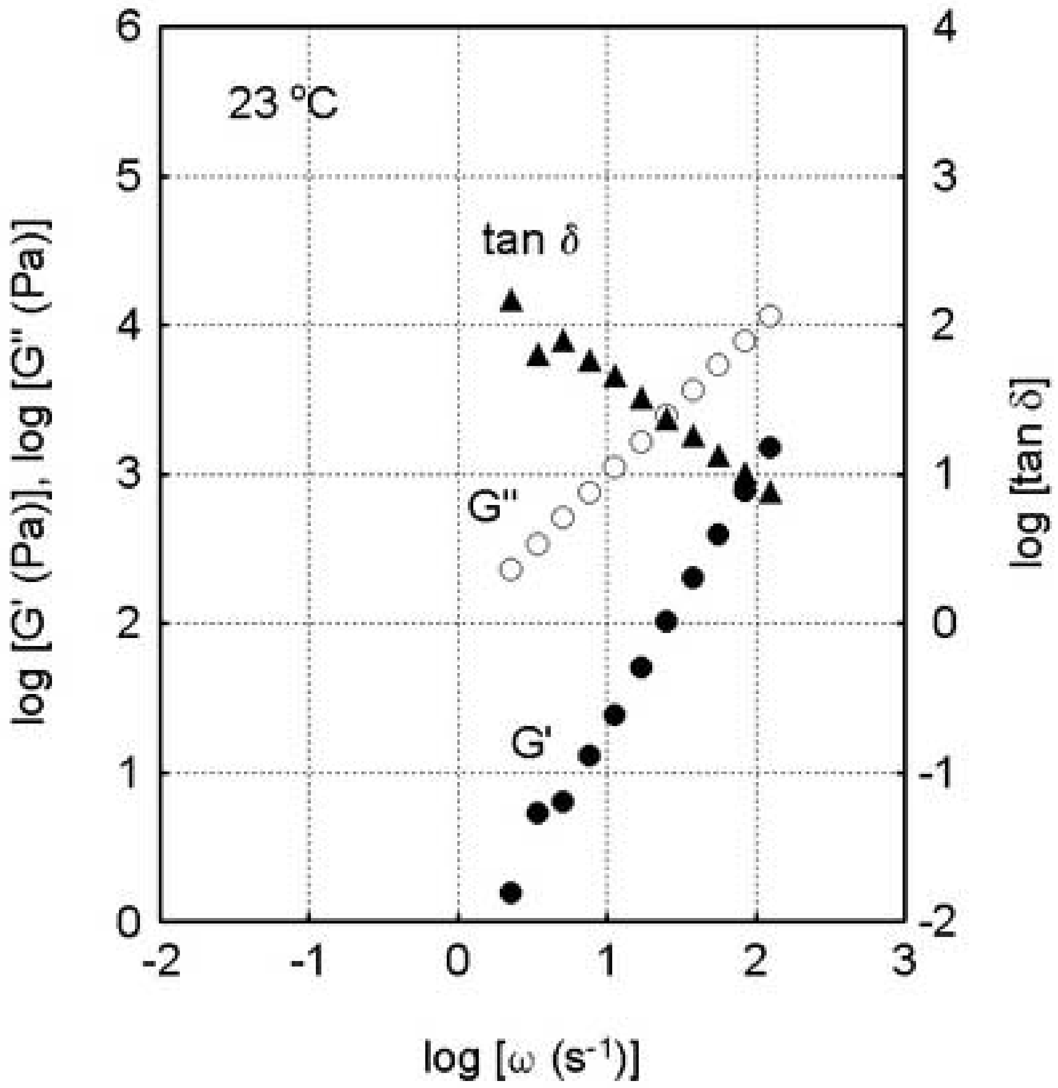

Figure 3(a)

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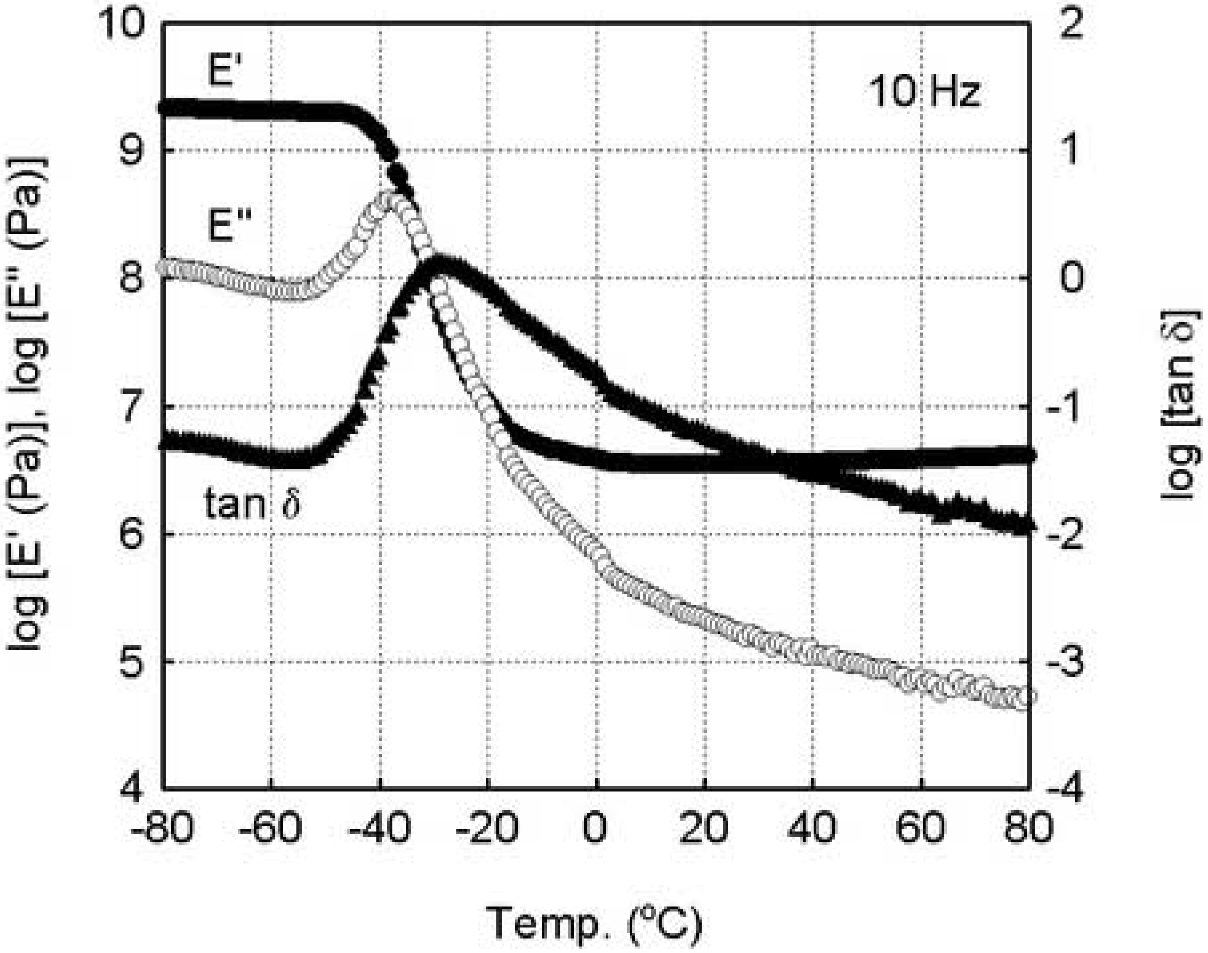

Figure 3(b)

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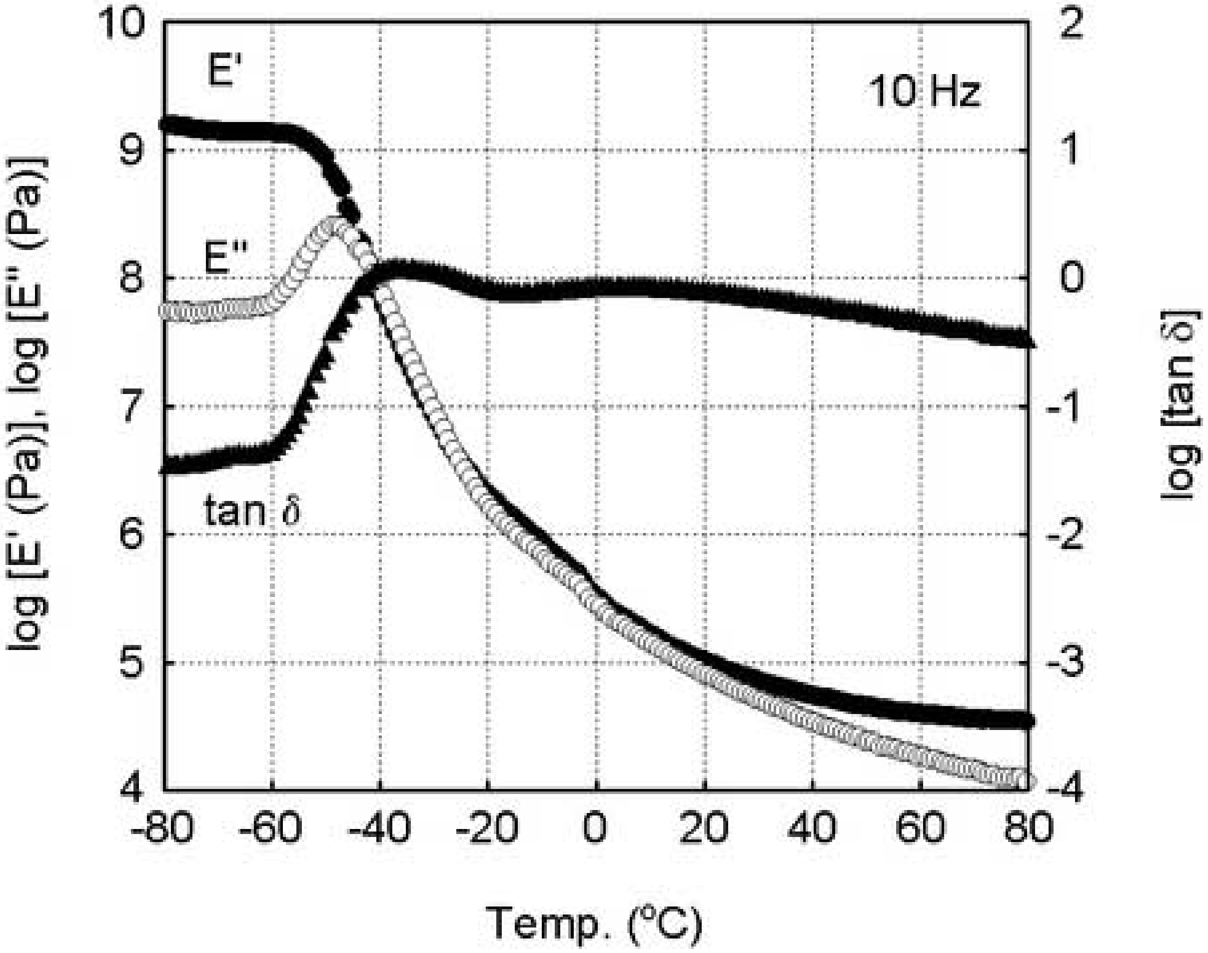

Figure 4(a)

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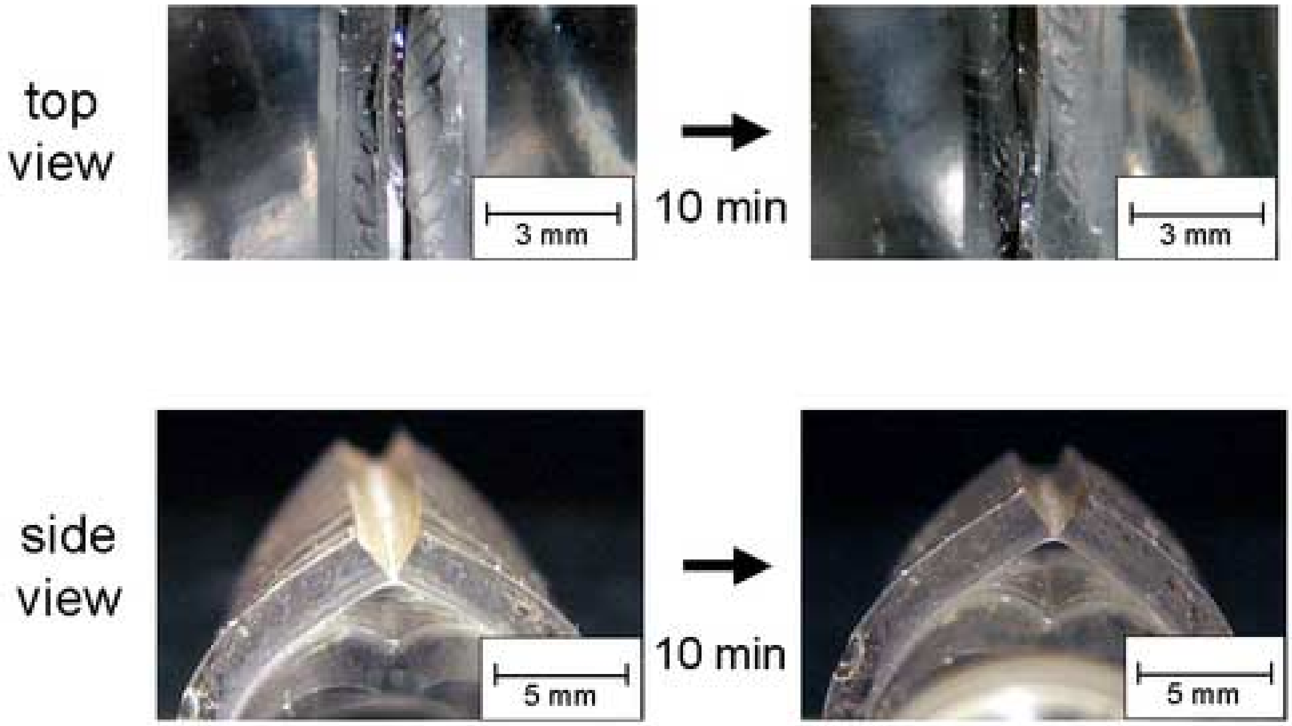

Figure 4(b)

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