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 an applied cleavage by a razor blade was healed at room temperature without any manual intervention.
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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

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Table 1
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

solvent treatment, for healing. Therefore, various industrial applications will be expected.

2. Experimental

2.1. Materials

The materials studied were polyurethanes with different network structures. Amorphous polyester-diol composed of diethylene glycol and adipic acid (56 KOH mg/g, Nippon Polyurethane Industry, Nippollan 152, purity 99%) and poly-isocyanate 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 up to 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 poly(ethylene terephthalate), PET,
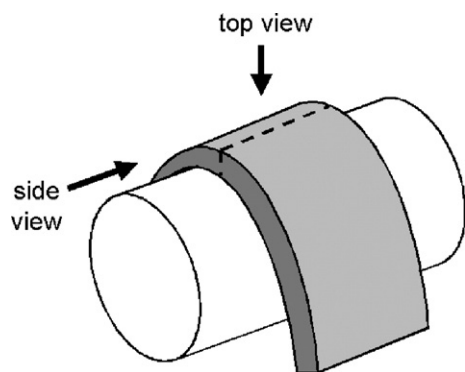
film. After taking off the Teflon sheet, the material was washed by excess amount of acetone in order to eliminate the sol-fraction and then dried at room temperature.
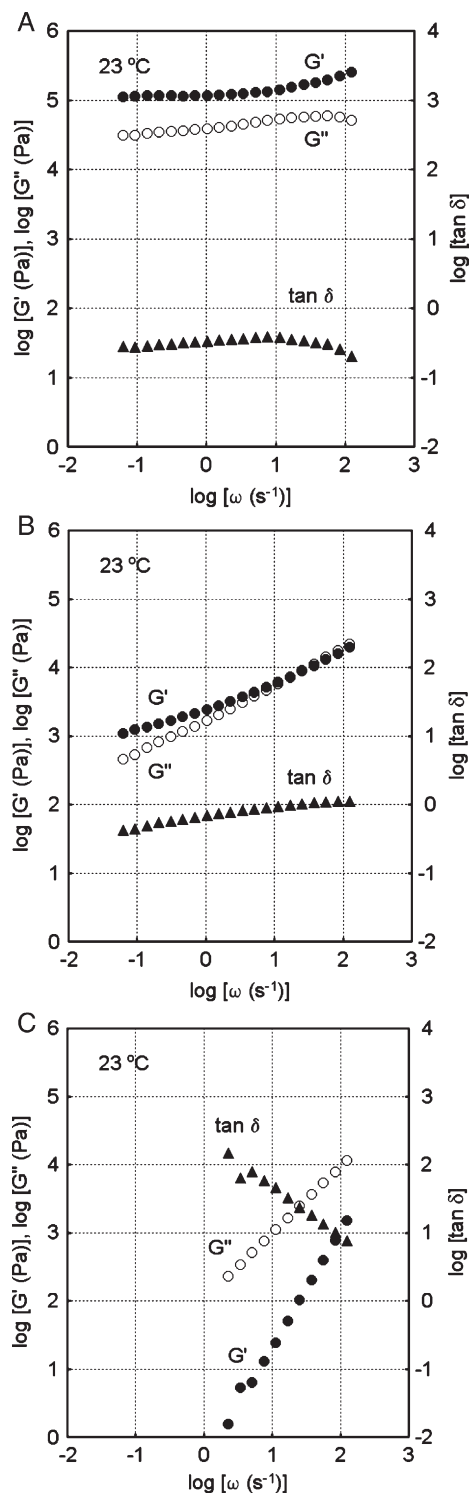

Fig. 2. Angular frequency dependence of shear storage modulus G' (closed circle), loss modulus G'' (open circle), and loss tangent tan δ (closed triangle) at 23 °C for (A) network polymer from PU-1.0, (B) network polymer from PU-0.5, and (C) PU-0.3.

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