INTRINSIC SELF-HEALING OF POLYMER SOLID WHILE KEEPING INTEGRITY AND LOAD-BEARING CAPABILITY

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ABSTRACT

Generally, intrinsic self-healing polymers based on reversible covalent bonds scission and reconnection would lose their load bearing capability as a result of molecular cleavage during healing process. This shortcoming also results in creep deformation of the products. To solve the problem, we introduce a novel healing mechanism by using dynamically reversible C-ON bonds. Upon heating to a certain homolysis temperature, C-ON bonds in alkoxyamines moieties frequently cleave but immediately recombine. When alkoxyamines are incorporated into polymer chains, C-ON covalent bonds fission and recombination synchronously take place with very high frequency, and the equilibrium tends to the combination side. Cracked parts can thus be restored through chemical exchange reaction of alkoxyamine moieties. More importantly, because a large amount of C-ON bonds remain connection, the possible material deformation in the course of crack remending could be avoided.

Here, crosslinked polystyrenes and epoxy with alkoxyamine moieties are synthesized as model polymers to prove feasibility of the above considerations. It is shown that the polymers can repeatedly self-heal cracks without deformation induced by chain scission, and provides the polymer with mechanical stability at elevated temperature as well. Moreover, the healing can be conducted within a wide temperature range when different alkoxyamines moieties are used.

Molecular structures of alkoxyamines moieties, as well as thermodynamic behavior of C-ON bonds scission and recombination, etc., are studied in detail to optimize self-healing behavior of the polymers. Full reversibility can be acquired when only one type of C-ON bond is included in the polymers. Accordingly, synthesis routes, molecular structures, thermally reversible characteristics, self-healing performance and self-healing mechanism, thermal stability and thermal-mechanical properties, etc, have been studied in detail.

1. INTRODUCTION

To remend damaged polymer intrinsically, thermally reversible covalent bonds, typically like Diels-Alder (DA) bonds, were introduced to polymer chains [1]. Cracks in polymers can be repeatedly restored via fission and reconnection processes of reversible covalent bonds upon heating. However, the polymers should inevitably lose their functions as a result of molecular cleavage during healing processes. Here we show the feasibility of using dynamically reversible C-ON bond as the healing chemistry, which combines the aforesaid covalent bond breakage and re-connection into one step. The possible material deformation in the course of crack remending would thus be avoided.

2. MATERIALS

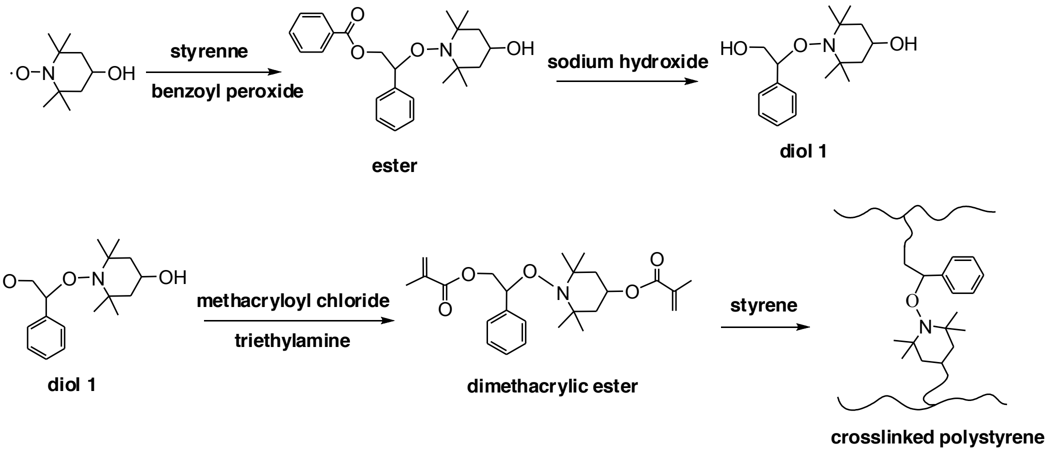
4-Hydroxy-2,2,6,6-tetramethylpiperidinyloxy (4-OH-TEMPO, 98%) and methacryloyl chloride (98%) were purchased from Aldrich and used as received. Styrene (99%) was obtained from Alfa Aesar and purified by distillation under reduced pressure in the presence of calcium hydride. Linear PS (GPPS 685D) was provided by Dow Chemical. All the other reagents and solvents were commercial products and used without further purification.

3. METHODS

Starting from 4-OH-TEMPO, a diol containing alkoxyamine unit was obtained. Then, two alkoxyamine-based monomers, which were functionalized with bi-C=C (dimethylacrylic ester) and bi-epoxy group (diEPO), were prepared from this diol respectively. Their molecular structures were confirmed by FTIR, NMR and MS. Crosslinked polystyrenes were prepared through bulk polymerization of styrene and dimethylacrylic ester (Scheme 1). Epoxy was prepared via curing the mixture of diEPO and Epo828 using diethylenetriamine (DETA) as hardener. Healing efficiency of the materials was evaluated by double cleavage drilled compression (DCDC) tests [2], using a SANS CMT 6000 universal tester. Healing efficiency was calculated from the ratio of the fracture toughness of the healed specimen over that of the virgin specimen. To conduct the calculation, for a measured critical stress of the virgin specimen at a certain crack length, the corresponding critical stress of the healed specimen at the same crack length was estimated by interpolation from the fitted crack length dependence of the measured critical stress of the healed specimen.

4. RESULTS

The resultant crosslinked PS possesses similar mechanical properties as conventional crosslinked PS with ethyleneglycol dimethacrylate (EGDMA) as crosslinking agent. When the molar feeding ratio of styrene over cross-linker is fixed at 10/1, for example, flexural strength and modulus of the former are 99.4 MPa and 5.0 GPa, while those of the latter are 93.0 MPa and 5.2 GPa. Thermal reversibility of C-ON bonds for all the polymers was carefully studied by temperature dependent ESR spectroscopy. The data show that with a rise in temperature homolytic C-ON bonds in the system increased until a homolysis-recombination equilibrium is reached (Figure 1). Crosslinking density and chain flexibility are main factors that influence reversibility of C-ON bonds. Lower crosslinking density and flexible chains give better reversibility of C-ON bonds, and thus offer higher healing performance. Dynamic mechanical behavior of the polymers during repeated heating and cooling cycles were studied by DMA. The results show that the alkoxylamines-based polymers exhibit reversibly dynamic equilibriums after several heating-cooling cycles. Even at higher temperatures, the C-ON bonds at crosslinking points can still help to maintain shape and integrity of materials. Thermal stabilities of the polymers were investigated by TGA. The initial weight loss temperatures of these alkoxyamines-based polymers are lower than the counterparts excluding alkoxyamines, owing to the fact that the radicals generated from alkoxyamine moieties induce decomposition of materials.



Scheme 1: Synthesis route of alkoxyamine-based crosslinked polystryrene.

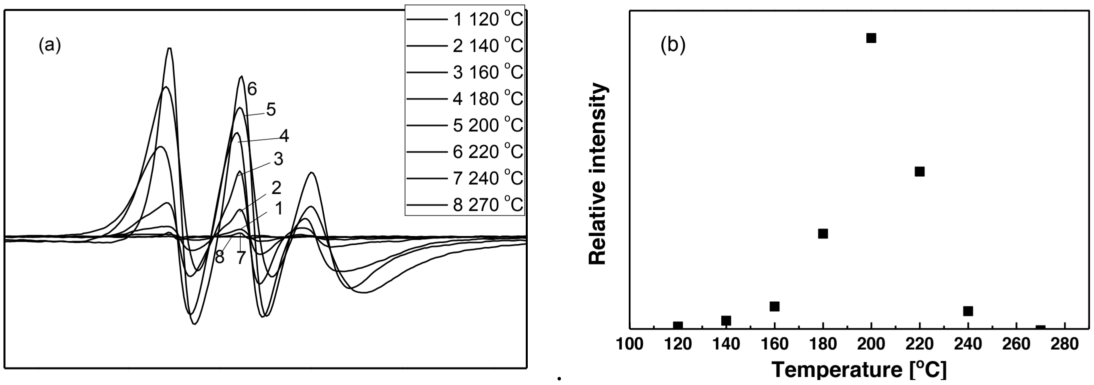


Figure 1: (a) ESR spectra of PS with the molar feeding ratio of styrene over cross-linker 7.5/1 measured at various temperatures. (b) Relative ESR signal intensities calculated from integral area of the normalized absorption lines.

Healing efficiency was defined as the ratio of strength property of the healed specimen over that of the virgin one. Different methods were employed depending on the polymers' mechanical characteristics: DCDC test for the hard and brittle crosslinked polystyrene, while Izod impact test for the tough epoxy. The experimental results show that all the polymers are characterized by repeatable self-healing ability, with healing efficiency ranging from 50% to 75% (Table 1 and 2). In general, the higher concentration of alkoxylamines in the polymers and the greater reversibility of C-ON bonds, the higher healing efficiency.

Table 1: Healing efficiencies of polystyrene with the molar feeding ratio of styrene over cross-linker 7.5/1, healed at 130 °C for 2.5 h.

	virgin	Healing 1	healing 2	healing 3	healing 4	healing 5
K_c [MPa $m^{1/2}$]	0.54	0.41	0.40	0.37	0.39	0.35
η [%]	--------	75.9	74.1	68.5	72.2	64.8

Table 2: Healing efficiencies of polystyrene with the molar feeding ratio of styrene over cross-linker 5/1 healed at (**a,** 130 °C, **b,** 145 °C) for 2.5 h and 10/1 healed at 130 °C for 2.5 h.

	5/1			10/1	
	virgin	healed **a**	healed **b**	virgin	healed
K_c [MPa $m^{1/2}$]	0.57	0.15	0.40	0.46	0.15
η [%]	--------	26.4	70.1	--------	32.6

5. CONCLUSIONS

In this work, alkoxyamine moieties are introduced into crosslinked polystryrene, polyurethane and epoxy, respectively, providing the polymers with self-healing ability. Under ceratin homolysis temperature, alkoxyamines undergo a reversible radical reaction and there exists a fast dynamic equilibrium between dissociation and association. By taking advantage of this behavior, possible material deformation in the course of crack remending would thus be avoided even when the healing is carried out above its glass transition temperature.

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