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Thermally healable/heat-resistant properties of thermosets bearing dynamic and thermally stable bonds formed by the Diels-Alder and thiol-maleimide "click" reactions

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ABSTRACT

The thiol-maleimide "click" reaction of 4,4′-bismaleimidodiphenylmethane (BMI) and furfuryl mercaptan generated 4,4′-bis(2-furfurylthiosuccinimido)diphenylmethane (BFSI). Mixtures of BFSI, BMI, and a tetrathiol (S4P) at a (furan + thiol)/maleimide ratio of 1/1 were prepolymerized at 100 or 200 °C and molded at 100–120 or 200–230 °C to produce cured products (BFSI-BMI-S4Ps or hBFSI-BMI-S4Ps). The FT-IR analysis revealed that the thiol-maleimide and DA reactions occurred for BFSI-BMI-S4Ps, while the structure of DA adducts was not retained for hBFSI-BMI-S4Ps. The BFSI-BMI-S4Ps were thermally healable, and the healing efficiency increased with the increase in the S4P/BFSI ratio unexpectedly. Although the hBFSI-BMI-S4Ps were not healed, they exhibited better thermo-mechanical properties than BFSI-BMI-S4Ps.

1. Introduction

Self-healing polymers have become an exciting research field, and much effort has been devoted to the development of polymers with excellent healing performance [1–7]. Although thermosetting polymers are widely used in building materials, aircrafts, coatings, electronics, and so on because of their high strength and thermal and environmental stability, crosslinked polymers are generally brittle and susceptible to cracking. Furthermore, their material failure often causes serious damage to products and safety problems. Therefore, healing of thermosetting polymers is of particular interest [7, 8]. The formation of reversible dynamic crosslinkages by the Diels-Alder (DA) reaction between furan and maleimide groups is one of the most extensively investigated in the study of self-healing polymers. Previous studies on healable thermosets have mainly focused on modifying epoxy [8–20] and polyurethane [21–25] resins by performing the DA reaction between furan and maleimide groups. For example, Palmese et al. reported that the crack surface of a furan-functionalized epoxy-amine network can be healed by the injection of a solution of 4,4′-bismaleimidodiphenylmethane (BMI) in *N,N*-dimethylformamide (DMF) as a healing agent [8]. Simon et al. reported that scratches on the surface of a cured product of diglycidyl ether of bisphenol A (DGEBPA) and a diamine crosslinker (DA adduct of 1,8-bismaleimidooctane and furfuryl amine) can be healed by the retro-DA (rDA) reaction at 140 °C and subsequent DA reaction at 50 °C [12]. Wang et al. reported healable polyurethane/urea networks by the crosslinking reaction of BMI and a furan-functionalized polyesterurethane [22]. Although these bismaleimides are exclusively used as DA crosslinkers to achieve a high healing efficiency, it is concerned that the heat resistance and mechanical performance are seriously deteriorated because of the rapid lowering of the crosslinking density caused by the rDA reaction at a temperature higher than 100 °C. Therefore, the introduction of both furan-maleimide DA crosslinkages and thermally stable crosslinkages is considered effective for the improvement of the heat resistance of DA-adduct-based self-healing thermosets. However, healing and thermo-mechanical properties of the thermosets dually crosslinked by the dynamic DA linkages and thermally stable covalent bonds have not been sufficiently clarified in the past studies.

The combination of BMI with 4,4′-diaminodiphenylmethane (DDM) [26] or 2,2′-diallylbisphenol A (DABPA) [27] is the most well-known high-performance thermosetting bismaleimide resin system. Its curing mechanism involves the Michael addition for BMI/DDM [28] and ene reaction/addition copolymerization for BMI/DABPA [28–30]. Recently, we had reported that the cured products of BMI and polythiol compounds by the thiol-maleimide "click" reaction exhibit excellent thermal and mechanical properties [31]. However, the BMI/polythiol thermosets were not healable materials because of the absence of dynamic DA crosslinkages. In this study, thermally cured products of BMI, a pentaerythritol-based tetrathiol (S4P) and 4,4′-bis(2-furfurylthiosuccinimido)diphenylmethane (BFSI), which was prepared by the

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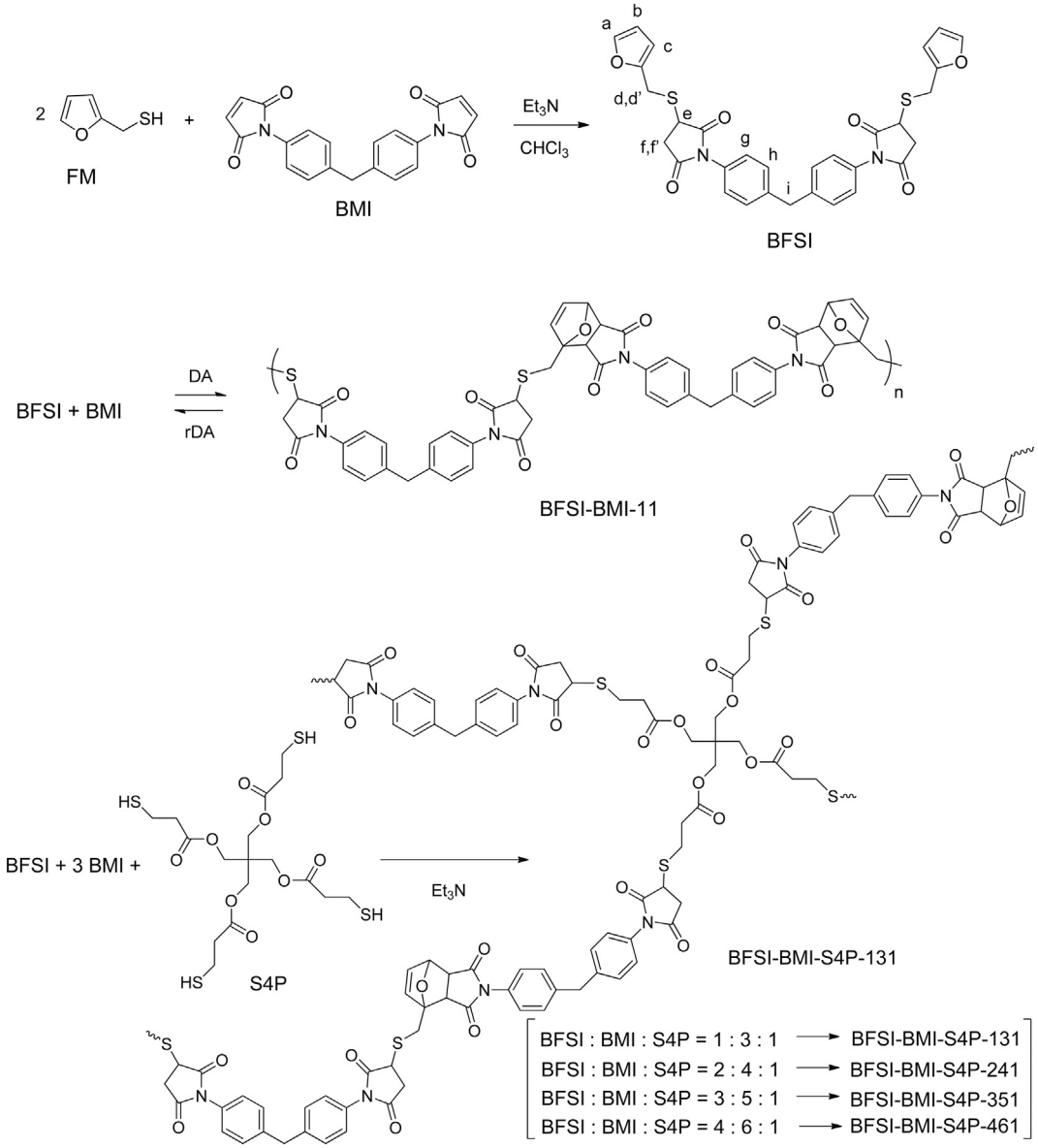

Scheme 1. Synthesis of BFSI, BFSI-BMI-11, and BFSI-BMI-S4Ps.

thiol-maleimide "click" reaction of BMI and furfuryl mercaptan (FM) at a molar ratio of 1/2, were prepared and their self-healing and thermo-mechanical properties were investigated (Scheme 1). Our attention is focused on the influence of the fraction of the dynamic furan-maleimide DA linkages and thermally stable thiol-maleimide sulfide bonds on the self-healing and thermo-mechanical properties. In addition, we investigated the influence of the curing temperature on these properties.

2. Experimental

2.1. Materials

FM and BMI were purchased from Tokyo Chemical Industry (Tokyo, Japan). Triethylamine was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Pentaerythritol-based tetrathiol (S4P, pentaerythritol tetrakis(3-mercaptopropionate)) was purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA). All the commercially available reagents were used without further purification.

2.2. Synthesis of BFSI

Triethylamine (4.04 g, 40.0 mmol) and FM (22.83 g, 0.200 mol) were added to a solution of BMI (35.8 g, 0.100 mol) in chloroform (350 mL). After the solution was stirred at room temperature for 3 h, the reaction mixture was washed with water, dried over sodium sulfate, and concentrated in vacuo to give BFSI as a brown viscous liquid. BFSI: Yield 90%; FT-IR (ν_{max}, cm^{-1}) 3005, 2914, 2891, 1778, 1705, 1512, 1381, 1170, 1150, 1070, 1011, 935, 887, 816, 743, 669, 600; ^{1}H NMR ($CDCl_3$, δ, ppm) 7.40 (dd, 2H, H-a, J_{ab} = 1.9 Hz, J_{ac} = 0.9 Hz), 7.29 (d, 4H, H-h, J_{hg} = 8.5 Hz), 7.22 (d, 4H, H-g, J_{gh} = 8.5 Hz), 6.33 (dd, 2H, H-b J_{bc} = 3.2 Hz, J_{ba} = 1.9 Hz), 6.31 (dd, 2H, H-c, J_{cb} = 3.2 Hz, J_{ca} = 0.9 Hz), 4.35 (d, 2H, H-d, $J_{dd'}$ = 14.9 Hz) 4.05 (s, 2H, H-i), 3.88 (d, 2H, H-d', $J_{d'd}$ = 14.9 Hz), 3.82 (dd, 2H, H-e, J_{ef} = 9.2 Hz, $J_{ef'}$ = 4.0 Hz), 3.21 (dd, 2H, H-f, $J_{ff'}$ = 19.2 Hz, J_{fe} = 9.2 Hz), and 2.57 (dd, 2H, H-f', $J_{f'f}$ = 19.2 Hz, $J_{f'e}$ = 4.0 Hz).

2.3. DA polymerization of BFSI and BMI

BFSI (5.87 g, 10.0 mmol) was added to a solution of BMI (3.58 g,