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Full Length Article

Recyclable thermosetting thermal pad using silicone-based polyurethane crosslinked by Diels-Alder adduct

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ABSTRACT

The recyclable silicone-based thermoset was successfully synthesized by making use of a Diels-Alder (DA) adduct as a cross-linker. The incorporation of the furan-tethered diol **1** into the polymer backbones realized the crosslinking of polymers via the DA reaction. The thermosetting polymer was dissolved in DMF after the retro DA reaction which was monitored by ^{1}H NMR spectroscopy. Due to the retro DA reaction, polymer showed the mendable behavior when it was scratched followed by being heated. This polymer was mixed with alumina powders to fabricate the thermal pad. The thermal resistance of this pad was measured to be 0.48 K/W by a thermal transient test. The thermosetting composite was recycled via the retro DA reaction. The thermal resistance of the recycled one was similar to that of the original one.

1. Introduction

The accumulation of thermal energy generated by the heat sources such as light emitting diodes and chips deteriorates the functions of the electronics shortening their life expectancy [1,2]. To address this, several types of thermally conductive materials have been placed between heat sources and heat spreaders [3]. Even though thermal grease showed the good thermal conductivity, the flow of the grease led to the leak of the grease during the operation. To overcome this, the polymers filled with ceramics [4,5] and carbon fillers [6–8] have been developed to produce the composite pads featuring heat dissipation. As the micron-sized gap between the heat source and the heat sink has been the cause of the heat accumulation, the thermal interface materials should fill the air gap between them to dissipate the heat efficiently [9]. Taking this into account, the soft polymer composite would be beneficial to assemble the two components without air gap. Silicone-based thermal pads have been prevalent for dissipating the accumulated heat because they were conformable and displayed moderate thermal conductivity. PDMS184 was synthesized by mixing the vinyl terminated polydimethylsiloxane (PDMS) oligomer and the curing agent followed by being cured at high temperature [10]. Unlike other composites, the PDMS184-based composites were soft due to the flexibility and stretchability of the PDMS backbone [11,12]. Although the PDMS184-based composites were applied for various products such as thermal pads [13,14], and conductive films [15–17], they were difficult to recycle owing to the high crosslink density which led to the thermoset. Before the pads were applied for the assembly process, they sometimes needed to be punched to fit to the shape corresponding to the designs of the components. In this punching process, the remainder of the pads was discarded as wastes. In order to reuse the polymers, several types of recyclable thermosets have been investigated [18–20]. Here we reported the new PDMS-based thermal pad which was recyclable thermoset. The thermally reversible cross-linker of a Diels-Alder (DA) adduct has been employed to achieve this property of the thermal pad [21,22]. The DA adduct was formed by reacting the diene and dienophile via a [4 + 2] cycloaddition which was reversible [23–25]. The combination of a furan group as a diene and a maleimide as a dienophile was prevalent due to the mild conditions of forward and retro DA reactions [26]. We have utilized the hydroxyl terminated PMDS as a soft polyol to synthesize the furan-tethered silicone based polyurethane (SPU) [27,28]. The SPU/ceramic filler composite was crosslinked by a bismaleimide derivative to form the free-standing thermal pad (SPU-C). For the strong interaction between the polymer and filler, carboxylic acid groups were incorporated into the backbone of SPU. The pad was recyclable due to the reversibility of the DA adduct which served as the cross-linker. The thermal resis-

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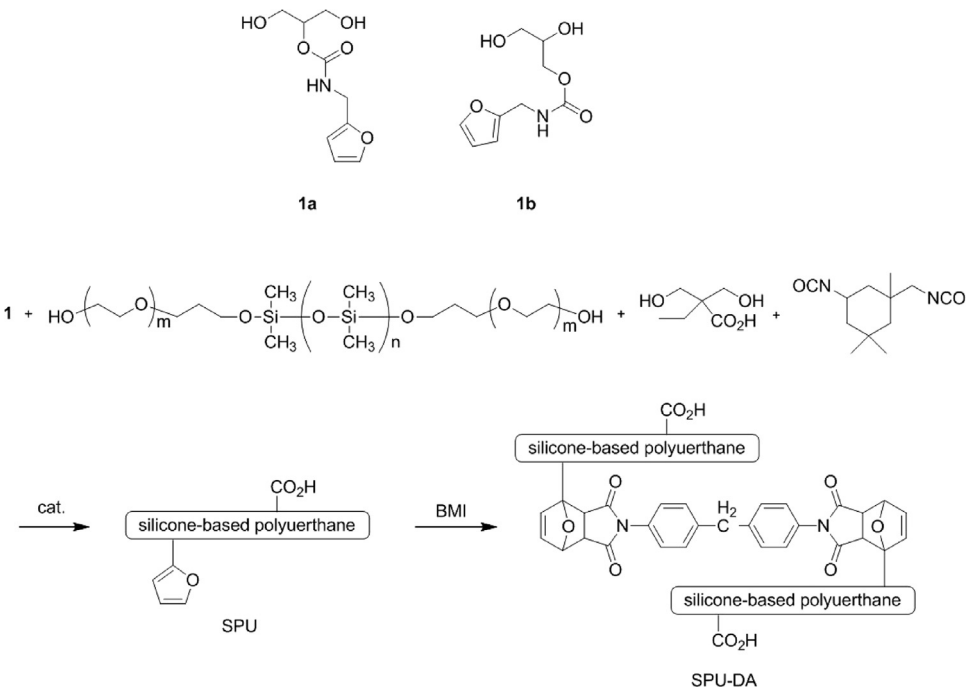

Scheme 1. The synthesis of SPU and SPU-DA.

tance of the SPU-C film was measured utilizing a thermal transient test. Interestingly, there was little change in thermal resistance after the recycling of the thermal pad.

2. Experimental procedures

2.1. Materials

Hydroxyl terminate PDMS (silicone diol, Mw ~ 1000 g/mol) was purchased from Gelest, Inc. USA. Isophorone diisocyanate (IPDI), and furfurylamine were purchased from Tokyo Chemical Industry, Japan. Dimethylol butanoic acid (DMBA), dibutyltin dilaurate and 1,1′-(methylenedi-4,1-phenylene)bismaleimide (BMI) were purchased from Sigma-Aldrich, USA. Alumina was purchased from Denka Company Limited, Japan. All chemicals were used as received without purification.

2.2. Preparation of SPU solution

The furan-tethered diol **1** (the mixture of **1a** and **1b**) was prepared following the previous method [25]. The furan diol **1** (0.67 g, 3.11 mmol) and silicone diol (8.75 g, 8.75 mmol) was mixed. To this mixture were added DMF (12.5 g), DMBA (0.1 g, 0.67 mmol), IPDI (2.78 g, 12.51 mmol) and dibutyltin dilaurate (1 drop). This solution was heated at 80 °C for 2 h to afford the SPU solution which was used for the next steps without further purification. The FTIR and ^{1}H NMR spectra of SPU were shown in Fig. S1 and Fig. S2, respectively.

2.3. Synthesis of SPU-DA

The as-prepared SPU solution (25.0 g) was mixed with BMI (0.55 g) and stirred at 50 °C. After 20 min, the mixture was bar-coated on the silicone-coated PET film (release liner) and kept in the oven (50 °C) overnight to afford the SPU-DA film.

2.4. Synthesis of SPU-C

The SPU was mixed with alumina fillers in the ratio 4:6 polymer to filler by weight. The mixture was homogenized through the ball milling process for 80 min. These composite was mixed stoichiometrically with BMI, bar-coated on the release liner and dried at 50 °C overnight to afford the SPU-C as the thermal pad.

2.5. Thermal transient tests

Thermal performances of the thermal pads were measured by thermal transient tester equipped with T3ster Master software (T3ster, Mentor Graphics, USA). Transient cooling curve of test structure including heat source and thermal pad was transformed to structure function curve showing thermal capacitance and resistance. Thermal resistance of thermal pad was obtained by subtracting that of heat source from the structure function curve.

2.6. Instrumentation

The proton NMR spectra were measured at 400 MHz on an NMR spectrometer equipped with Bruker Top Spin 3.2 software (AscendTM 400, Bruker, Germany). The optical transmittance of the film was measured using a UV–vis spectrophotometer equipped with Color Data Software CM-S100 w (V-560, Jasco, Japan). Surface profiles were measured by a laser confocal microscope (VK–9710 K, Keyence, Japan).

3. Results and discussion

The synthesis of the polyurethane tethered with the furan group was materialized by making use of the furan diol **1**. The mixture of the diol **1** and the hydroxyl terminated PDMS was allowed to react with diisocyanate at the NCO:OH ratio of 1:1 to form the soft polyurethane (Scheme 1). For fabricating the thermal pad, the soft polymer needed to accompany the ceramic filler which featured a high thermal conductivity [29]. Here, the alumina with 3–5 um in size was employed as the filler. In order to improve the dispersion of

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