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Original Research Paper

Free-standing, roll-able, and transparent silicone polymer film prepared by using nanoparticles as cross-linking agents

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ABSTRACT

A free-standing, roll-able, and transparent silicone-based polymer film with a tensile modulus of ca. 7.8 MPa and strain at the break point of 0.76% was successfully prepared by reaction between a reactive silicone oligomer with methyl- and methoxy-side groups and hydrophilic SiO_2 nanoparticles. First, SiO_2 nanoparticles were grafted with silicone chains by a controlled wet chemical sol–gel-type reaction with the reactive oligomers. The solvent of the resulting solution was evaporated to form a viscous suspension, casted into a film, and finally heat-treated at 100 °C and 150 °C. A hydrolysis and condensation reaction among silicone-grafted SiO_2 nanoparticles and free silicone oligomers in the final heat treatment resulted to produce free-standing, roll-able, and transparent silicone-based polymer film. The fact that the silicone film cannot be synthesized without the presence of SiO_2 nanoparticles suggests that these nanoparticles act as cross-linking agents of silicone components providing the improved mechanical properties to the composite film. The rate-controlled mixing and heating of the SiO_2 aqueous/alcohol suspension and the silicone oligomer/alcohol solution was found to be the key step in the synthesis of the free-standing transparent film. While rapid addition/mixing resulted in a fragile and opaque film, a transparent material was achieved when those solutions were slowly mixed. The effect of the synthesis process on the macroscopic and microscopic properties of the prepared films is discussed along with their formation mechanism.

1. Introduction

Owing to the recent requirements of electronic devices to be lighter, smaller, and more flexible, free-standing and transparent polymer films have become indispensable components that are widely used in printing circuit boards, touch sensors, thin film solar cells, and displays for electronic papers and organic electroluminescence appliances [1–4]. In order to successfully apply these transparent and flexible polymeric films in electronic devices, these materials are required to show high tensile strength, Young's modulus, flexibility (i.e. resistance against fragile during rolling the material), and resistance characteristics against heat, weather, light, and chemicals. In addition, the processability of the transparent films into a roll-to-roll process will also be a promising character of the film to raise the productivity of the final devices. Various transparent and flexible polymeric materials, including polyethylene terephthalate, polyethylene naphthalate, polyethersulfone, polyimide, and poly(cyclic-olefins) have been developed and successfully embedded into final devices so far [5–8]. With the aim to improve the physical properties (such as tensile strength, Young's modulus, and resistance against heat) of these polymeric films, a nanocomposite concept involving dispersion of surface-modified nanoscale fillers on polymeric materials has been studied by numerous researchers [9–12]. However, owing to the nature of C–C bond structures, the improvement in the strength and resistance against heat, weather, light, and chemicals characteristics seems to be limited. For instance, fabrication of polymeric film which can resist under a condition of ca. 300 °C, which is a necessary temperature to fabricate circuits on a board, for long duration will be challenging.

Silicone-based polymers, mainly composed from Si–O backbone structures showing a higher chemical energy compared to C–C bonds, could also be good candidates to fabricate transparent and flexile films with improved resistance against heat, weather, and lights. In spite of the high potential of silicone-based polymers, there are various problems to process these materials into free-standing, transparent, and flexible films to be used in electronic devices. For example, silicone elastomers such as polydimethylsiloxane (PDMS) and modified-PDMS are widely applied in the field of microfabrication [13–15] but their elastic properties

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(e.g., high elongation and low Young's modulus) are sometimes not favorable for thin-film devices. For example, the high elongation and low Young's modulus of the film will damage the structure of printed circuits on the film. On the other hand, silicone-based polymers fabricated by sol–gel and/or chemical vapor deposition processes are typically applied as hard coating materials on a substrate [16–18]. As a result of highly-dense cross-linking reactions among the reagents, the as-fabricated polymers typically result in hard but inflexible films which easily fragile by bending the materials. With the aim to tune these mechanical properties of the silicone-based polymer films, the combination with other polymer/organic materials has been conducted [19,20], although the increased organic composition led to increasing levels of C–C-based segments with the corresponding reduction in the resistance against heat, weather, light, and chemicals. Therefore, the achievement of silicone-based polymer films which possesses all of the properties such as high transparency, roll-able characteristics, Young's modulus, tensile strength, and resistance against heat, weather and lights is indeed quite challenging, and its success would pave the way for new transparent film materials.

Based on these backgrounds, in this article, we report a new processing route for the conversion of silicone-based oligomers into a free-standable film structure which possesses high transparent and flexible (i.e. roll-able characteristics without forming cracks) properties with improved Young's modulus while maintaining the tensile strength and the resistance against heat of the silicone. The approach involves utilization of metal oxide nanoparticles as cross-linking agents during the polymerization of reactive silicone oligomers with methyl- and methoxy-side groups. Since the oxide nanoparticles have sufficient metal–OH bonds on their surface to react with alkoxides and since they are non-combustible, they can directly cross-link the silicone components while maintaining/improving the resistance against heat. By controlling the cross-linking reaction between the silicone oligomers and the nanoparticles, a less elastic although roll-able film could be fabricated. The effects of the nanoparticle cross-linkers on the properties of fabricated silicone polymer film will be analyzed by using silica nanoparticles.

2. Experimental section

2.1. Materials

Silicone oligomers with methyl side-group and reactive methoxy group (X-40-9225, alkoxide content: 24 wt%, residual SiO_2 component after combustion: 67 wt%, viscosity: 100 mm^2/s at 25 °C) was supplied by Shin-Etsu Chemical Co., Ltd. SiO_2 (SNOWTEX OS, ca. 10 nm, 20 wt%, pH 2–4) aqueous suspension was donated by Nissan Chemical Industries, Ltd. Isopropyl alcohol (super dehydrated, 99%), 2-methoxyethanol (99%), and hydrochloric acid (35–37%) were purchased from Wako Pure Chemical Industry Ltd., Japan. n-Hexadecane (>98%) was purchased from Tokyo Chemical Industry Co., Ltd. The mould releasing film (MRF38, silicone treated on PET) was supplied by Mitsubishi Plastics, Inc. All materials were used without further purification.

2.2. Synthesis of free-standing, transparent, and roll-able silicone films

The synthesis process can be divided into three steps. First, 10 g of a 20 wt% aqueous SiO_2 sol was carefully diluted with 10 g of isopropyl alcohol and 5.0 g of 2-methoxyethanol. The pH of the resulting solution was subsequently adjusted to ca. 2.0 by using a hydrochloric acid solution. The temperature of the solution was increased up to 80 °C by gentle stirring, and a mixture of 10 g of isopropyl alcohol and 10 g of silicone oligomers was carefully dropped in under controlled additive rates (0.15–2.5 g/min). After stirring the solution for 1.5 h (dropping time included), 15 g of isopropyl alcohol was added and further stirred for 1.0 h at 100 °C (Step 1). Next, the solvents of the reaction system were evaporated (ca. 92 wt% of the solvents were evaporated) by using a vacuum rotary evaporator at 60 °C (Step 2). Finally, the obtained viscous transparent paste was cast on a mould releasing film using doctor blades (300 μm gap) and heat-treated for at 100 °C (1.0 h) and 150 °C (1.0 h, Step 3). Following the heat treatment, a free-standing and roll-able film was collected by simply peeling it off from the mould releasing film. At least two replica samples were prepared and characterized for each synthesis condition to ensure the reproductivity of the films.

2.3. Characterization

The transparency of the as-prepared films was determined by using a UV–vis spectrometer (Hitachi, U-2010). The advancing/receding contact angle measurements of water and n-hexadecane on the prepared film were analyzed by using video microscope system (Scaler, VS-60S). For transparency and contact angle measurements, 10 different areas from two individual films per each condition were evaluated. The mechanical properties of the prepared films were determined by a tensile tester (Orientec, RTC-1250) as follows. The silicone composite films were cut into 10 mm $\times$ 100 mm size pieces and loaded onto the testing machine. The testing area of the sample was controlled to be 10 mm (in width) $\times$ 50 mm (in length) and the length of the testing area were used as a reference to calculate the strain value. 20 pieces of samples from at least two individual films were used to characterize the mechanical properties. The microstructure of the film was analyzed by FE-SEM (JEOL, JSM6335-FS). A small scratch was made on the edge of the film, and self fracture was induced by dipping the film into liquid nitrogen. The microstructure of the fractured area of the film was subsequently observed.

In order to discuss the formation mechanism of the composite films, the particle size of the cross-linking nanoparticles in the synthesis solution and the changes in the surface structure while processing the film were also characterized. A dynamic light scattering (DLS) analysis (Malvern, HPP5001) and a TEM observation (JEOL, JEM-1400) was performed to characterize the particle size of cross-linking nanoparticles in the synthesis solution at the end of the steps 1 and 2 (which were described above). With regard to the surface structure, an excess of toluene was added to the synthesis solution at the end of steps 1 and 2. The flocculated cross-linking nanoparticles were then collected by centrifugation. This process was repeated several times with the aim to wash the nanoparticles. The cake obtained after the final centrifugation step was dried under vacuum at 40 °C and further characterized by TG–DTA and FTIR in a RIGAKU Thermo Plus EVO and a Nicolet Nexus 470 apparatus, respectively.

3. Results and discussions

The structure of the silicone polymer films prepared from reactive silicone oligomers with and without SiO_2 nanoparticles are shown in Figs. 1 and 2. It can be clearly seen that the silicone polymer was fragile and could not be fabricated into a free-standing film when the oligomers were polymerized without SiO_2 nanoparticles. On the other hand, polymerization with SiO_2 nanoparticles resulted in a free-standing film. The addition rate of the silicone oligomer solution into the SiO_2 nanoparticle suspension during the synthesis step 1 (described above) was found to be critical for controlling the properties of the prepared composite films. While a high addition rate (2.5 g/min) led to an opaque film, the