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Improved mechanical properties of solution-cast silicone film reinforced with electrospun polyurethane nanofiber containing carbon nanotubes

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ABSTRACT

In this study, we describe the enhancing ability of electrospun polyurethane (PU) nanofibers containing carbon nanotubes (CNTs) as nanofillers for silicone film in improving the physico-mechanical properties of the composite material. We prepared the samples combining two simple techniques: solution casting and electrospinning. Neat PU nanofibers alone are good reinforcing materials but the presence of CNTs inside the PU nanofibers has drastically improved the mechanical properties of the silicone composite film. The silicone film increased its tensile strength by 226% and its tensile modulus by more than 14-fold when CNT/PU nanofibers were incorporated.

1. Introduction

The development of polymer nanocomposites has gained great scientific and technological interest in recent years [1]. Combining nanofillers and polymers leads to substantial improvements in the mechanical, thermal, electrical, biological, antibacterial and antifouling properties of polymer nanocomposites [2–4]. A large number of publications have been on incorporating nanoparticles in polymeric matrix in order to improve the overall properties and make a new material [5–7]. However, only limited studies have been carried out on the use of fibers as fillers to make a new composite material [8]. Many in the industry and academia use microfibers as filler material, thereby creating a microcomposite. Comparing a microfiber and a nanofiber, the latter has several orders of magnitude lower in size, thus making it ideal as nanofiller because of its availability of very high surface area for interfacial interaction. The best method for the production of nanofibers is by electrospinning. Owing to the very small dimension of nanoparticles, electrospinning of nanofibers presents itself as a facile method to decorate or incorporate nanoparticles on polymeric nanofibers to add functionality [9–13]. Carbon nanotubes (CNTs) are one of the best nanofillers in nanofibers to improve the mechanical, electrical and thermal properties of the composite material. Here, we utilized an electrospinning technique to produce polyurethane (PU) nanofibers containing well-dispersed CNTs. Based from previous studies and from our group's experience, the incorporation of CNTs in PU nanofibers has considerably improved the composite nanofiber's mechanical and thermal properties compared to its neat PU nanofiber counterpart. Polyurethane is one of the most versatile polymers for many different applications because of its good biocompatibility and favorable mechanical properties [14].

The objective of the present study was to explore the effect of electrospun CNT/PU nanofibers as nanofillers on the mechanical performance of a solution-casted silicone film matrix. Silicone is known to have stable and inactive properties in living bodies [15] and has high flexibility, however, silicone suffers from low tensile strength. Among many applications, silicone film is commonly used as polymeric cover of nonvascular stents, which is employed in

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order to inhibit the overgrowth of malignant tissues that could cause blockage of passageway such as in the case of esophageal cancer. The low tensile strength of silicone film gives high tendency for silicone film cover to be damaged during crimping of stent in catheter, or during stent delivery, or from the forces acting on the stent inside the body after deployment. The continuous growth of tumor could also eventually break the stent cover resulting in re-obstruction of the channel. Thus, there is a need to improve the mechanical properties of the silicone cover to increase the patency of stent.

2. Materials and methods

2.1. Materials

The polymers in this study consisted of silicone (Nusil Silicone Technology), and high molecular weight thermoplastic polyurethane (Lubrizol Advanced Materials, Inc.). N,N dimethylformamide (DMF) and methyl ethyl ketone (MEK) were purchased from Showa Chemical Co., Ltd., Japan and Junsei, Japan, respectively. Xylene was received from M.I. Tech, Korea. Triton X-100 was received from OCI Company. All reagents were used without any further purification. We used multi-walled CNTs with an average diameter of 11 nm and purity >95%, which were synthesized by chemical vapor deposition (CVD) and were provided by Nanosolutions, Inc. from Jeonju City, South Korea.

2.2. Preparation of solutions

Three different solutions were prepared in this study, namely: neat PU, neat silicone, and CNT/PU solutions. For neat PU solution, PU pellets were dried in a dry oven at 80 °C for at least 3 h. Neat PU solution (10 wt%) was prepared by dissolving pre-dried PU pellets in a mixed solvent of DMF/MEK (50/50, %, w/w), magnetically stirred for 12–15 h. Neat silicone solution was prepared by dissolving 30 wt% silicone mixture, which we received from M.I. Tech, Korea in xylene solvent by magnetic stirring. To prepare CNT/PU solution with 0.1 wt% CNT, 10 mg of CNTs was first dispersed in 20 g DMF containing 50 mg Triton X-100 (i.e., 5:1 ratio of Triton X to MWNT) by bath sonication (40 Hz, Mujigae, Korea) for 3 h. This CNT/DMF/Triton X solution was poured to a neat PU solution and the mixture was magnetically stirred for at least 2 h.

2.3. Fabrication of samples

Neat silicone solution was solution-casted using a bar coating machine (IPAE, Korea). The prepared solution was poured onto a flat solid substrate with a mold made of adhesive tapes. The dimensions of the mold was 20 cm × 7 cm ($L \times W$). The thickness of the tape was about 500 μm. The bar coating speed was maintained at 5 mm/s. The casted film was dried for a total of 48 h at 60 °C for the first 24 h, and at 80 °C for the next 24 h. The obtained film was peeled off from the flat solid substrate manually and was subjected to characterization. Electrospinning was utilized to fabricate neat PU and CNT/PU nanofibers. Electrospinning was carried out at 11 kV, a feed rate of 1 ml/h, and humidity of 30%. The distance between spinneret and collector was maintained at 15 cm. The spinneret was oriented perpendicularly to the flat collector. After electrospinning, both neat PU and CNT/PU nanofibrous mats were dried at 80 °C for 48 h to remove residual solvents. To fabricate the nanofiber-reinforced composite film, silicone solution was first poured and lathered on a flat solid substrate mold. Immediately after, the prepared neat PU or CNT/PU nanofibrous mat was then slowly placed over the still wet silicone film. Additional silicone solution was poured over the nanofibrous mat, and was lathered gently covering the entire mat. The composite material was then dried at 60 °C for the first 24 h, and at 80 °C for the next 24 h.

2.4. Characterization and measurements

Tensile tests were performed using an Instron bench-type tensile test machine (LR5K Plus) with a load limit of 100 N according to ASTM D882-10. The crosshead speed was 5 mm/min. At least 5 dog-bone-shaped specimens for each sample were tested, the average of which was used as the tensile property of the sample. The surface and cross-section morphology and structure of the fabricated nanofibers, films, and composite material were investigated by field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan) and transmission electron microscopy (TEM, H-7650, Hitachi, Japan). The samples for FESEM were coated with platinum using a Pt coater (K575x, Emitech) and examined at an accelerating voltage of 15 kV. The TEM samples for nanofibers were prepared by electrospinning directly on a copper grid mesh coated with carbon and formvar for 15 s. The distribution of fiber sizes was determined using an image processing software (ImageJ, NIH, USA), checking the diameters of at least 100 fibers and the average was calculated. Water contact angle measurements were carried out using GBX, Digidrop (France) water contact angle meter. Deionized water with a drop diameter of 6 μm was automatically dropped onto the mat. Raman spectra of the neat and CNT/PU composites were recorded using a Raman confocal spectroscopy (Nanofinder 30, Japan) with a He—Ne light source at 632.8-nm with a spectral resolution of 1 cm^{-1}. The FTIR spectra of the samples were measured using a Paragon 1000 Spectrometer (PerkinElmer, USA) in the range of 400–4000 cm^{-1} with a signal resolution of 1 cm^{-1} and a minimum of 16 scans.

3. Results and discussion

3.1. Morphology

Fig. 1 shows the morphology of the electrospun nanofibrous mats and the fiber/film composites. The neat PU (Fig. 1a) and CNT/PU (Fig. 1b) mats showed average nanofiber diameters of 210 ± 120 nm and 340 ± 210 nm, respectively. Compared to fibers obtained from conventional melt spinning technique, which are about 30 μm in diameter, the fibers obtained here from electrospinning are about one order of magnitude smaller diameter, i.e., about 10 times larger specific surface area [8]. The increased diameter of CNT/PU nanofibers was attributed to the increased CNT/PU solution conductivity and viscosity as also reported in other studies [16–18]. The neat PU nanofibers showed smooth surfaces (Fig. 2a), while the CNT/PU nanofibers also showed generally smooth fibers but with some protrusions on the side due to the presence of CNTs. The CNTs in the PU nanofiber were found to be well-embedded and many were oriented along the axis of the nanofiber (see Fig. 2b). Both neat PU and CNT/PU nanofibrous mats possess high surface area-to-volume ratio, so that when they were incorporated into the solution-cast silicone film, it provides high surface area for adhesion, which could improve the overall mechanical properties of the composite. In Fig. 1c and d, the SEM images show that the nanofibers were successfully embedded in the silicone matrix for both fiber-reinforced film composites. The EDS spectra in Fig. 3 further indicate the successful incorporation of nanofibers into the silicone film matrix, showing the presence of Si peaks for both composites.

3.2. Mechanical properties

Fig. 4 shows typical stress–strain curves of the neat and composite samples. Table 1 also shows the different mechanical properties