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Thermal sensitive shape recovery and mass transfer properties of polyurethane/modified MWNT composite membranes synthesized via *in situ* solution pre-polymerization

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ABSTRACT

Polyurethane/multiwalled carbon nanotube (MWNT) composite membranes with thermal sensitive shape memory and mass transfer properties were synthesized via *in situ* pre-polymerization from concentration pretreated MWNT in DMF (*N*,*N*-dimethylformamide). Composite membranes were made from these polyurethane/MWNT solutions by casting them into Teflon plates. SEM photographs demonstrated that the MWNT distributed relatively homogenously in polyurethane matrix at low content and preferred to align in the membrane 2-dimension plane. The shape recovery and mass transfer properties of the prepared membranes were studied. Thermo-mechanical cyclic tensile testing results suggested that the shape recovery ratio increased prominently at below 2.0 wt% of MWNT because of the MWNTs high interaction with the hard segments; however at 3.0 wt% MWNT content, the shape recovery ratios decreased which can be ascribed to the relatively inhomogeneous distribution of MWNT and the decrease phase separation of the polyurethane at this high MWNT content. The water vapor permeability (WVP) studies showed that at below the soft segment melting transition temperature, at 0.25 wt% MWNT content, the WVP of the composite membrane decreased because the nano-sized MWNT acting as nucleating agent, thus, enhanced soft segment ordered crystal structure. In contrast, with increasing MWNT content, the WVP increased because in one aspect, MWNT constrained the forming of ordered soft segment phase structure; in another aspect, the straight MWNT with large aspect ratios offered a relatively straight "free" pathway for water molecule diffusion on the surface of MWNT or inside MWNT to pass through. At temperature above the soft segment phase melting transition temperature, the WVP increased markedly with increasing MWNT content. This could also be attributed to the pathway effect of MWNT by forming a channel through which water molecules could diffuse rapidly.

1. Introduction

Thermal sensitive polyurethanes are segmented block copolymers with phase separation between the constituent segments, namely hard segment phase and soft segment phase. Upon heating above the soft segment phase thermal transition temperature (T_{trans}), large elastic deformation can be performed and the deformation can be fixed by subsequently cooling the polymers to below T_{trans}. Once reheated over the temperature of the switch transition temperature, the polymers recover to their original shape as a result of releasing internal stress stored in physically crosslinked hard segments. The switch temperature may be a glass transition temperature or a melting transition temperature of soft segment phase, or it also may be a combination of glass transition temperature of soft segment phase and hard segment phase [1,2]. In addition, the shape recovery force can also be afforded by chemically covalent bonds network in polyurethane [3].

Within the past several decades, the thermal sensitive shape memory polyurethanes have found broad applications in areas such as smart textiles and apparels [4,5], biomedical materials [6–8], actuators, high-performance water vapor permeability (WVP) materials [9,10], filtration media and damping materials [11–15]. For use in different circumstances, different forms of polyurethanes such as solution, emulsion, bulk and foam have been developed.

Carbon nanotubes are attracting considerable attention due to their exceptional mechanical, superior thermal, chemical and electrical properties [16–20]. They are excellent nanofillers of poly-

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mer matrix to prepare nanocomposites with advanced properties [21–27]. The present paper is intending to study the thermal sensitive shape memory behavior and mass transfer properties of the polyurethane/carbon nanotube composite membrane. Dispersion of carbon nanotubes in polymer matrix has always been a challenge to the chemist due to their nanosize dimension. Efforts have been made to improve carbon nanotube dispersion in polymer matrix, which include the use of micro-scale twin-screw extruder, surfactants and the oxidation or chemical functionalization of the carbon nanotube surface. Thostenson and Chou [28] utilized a micro-scale twin-screw extruder to obtain the high shear mixing necessary to disentangle multiwalled carbon nanotube (MWNT) and disperse them uniformly in a polystyrene thermoplastic matrix. Hou et al. [29] prepared polyacrylonitrile nanofibers containing a high concentration of MWNT. They ascribed the high stability of the polyacrylonitrile–MWNT–DMF (*N*,*N*-dimethylformamide) to the high interaction between the molecules of solvent (DMF) and the carboxylic groups attached to MWNT surface. For conventional elastic polyurethane/carbon nanotube systems, Kwon and Kim [30] and Jung et al. [24] improved the compatibility of MWNT with elastic polyurethane matrix by treating MWNT with 60% nitric acid after purification. Chen and Tao [31] described a simple compounding technique for the fabrication of polyurethane nanocomposites with aligned single-walled carbon nanotubes by dispersing single-walled carbon nanotubes in polyurethane solution with tetrahydrofuran as solvent. They reported that the solvent–polymer interactions served as the driving force for the macroscopic alignment of the carbon nanotubes. There was also one report on the shape memory polyurethane/carbon nanotube system. The study conducted by Ni et al. [32] introduced a shape memory polyurethane/carbon nanotube composite which was prepared by distributing the carbon nanotubes in shape memory polyurethane solution using an ultrasonic process. The shape memory polyurethane used was MS4510 produced by Mitsubishi Heavy Industries Ltd. The influence of carbon nanotubes on the shape memory effect was studied.

For smart polyurethanes use in the fields of textiles, biomedical and many other industrial areas, not only good shape memory effect but also high mass permeability is required. Therefore, it is necessary to study the influence of to the polyurethane membrane mass transfer properties. In dense polymer membranes, permeability occurs in molecular mechanism, viz. sorption–diffusion–desorption. Mass transport through the breathable dense polyurethane membranes strongly depends on microstructure of polyurethane. Due to the MWNT change the microstructure of the shape memory polyurethane, it will influence the mass transfer properties of smart polyurethane as well. Jeong, Chen and Mondal have studied the water vapor permeability of polyurethane membrane. Jeong et al. [33,34] modified the polyurethane structure by employing hydrophilic segment such as dimethylpropionic acid (DMPA), diol terminated poly (ethylene oxide) to enhance the sensitivity of the thermoresponsive WVP. Chen et al. [35] improved the water swollen ratio by increasing hydrophilic segment molecular weight and decreasing density of the chemical cross bonding. Mondal and co-workers [9,36–39] also found that the mass transfer properties were not only influenced by amorphous region, but also by the interaction between the polymer chains.

On the basis of the previous contributions, in this work, the author incorporated MWNT into shape memory polyurethanes by *in situ* solution polymerization in DMF. The shape memory properties of the prepared polyurethane/MWNT membranes were studied. The influence of the MWNT on WVP was investigated. The underlying mechanism governing these property changes are explored in this paper.

2. Experimental

2.1. Materials

MWNT with purity >95%, outside diameter ~20 nm, inside diameter 5–10 nm and ~50 μm in length, were supplied by Chengdu Organic Chemicals Co., Ltd, Chinese Academy of Sciences. The shape memory polyurethane/MWNT composites were synthesized via *in situ* solution polymerization with polycaprolactone diol-4000 (PCL) (Solvay Interox Ltd.) as soft segment while isophorone disocyanate (IPDI) (Aldrich Chemical Company) and chain extender, 1,4-butanediol (BDO) (Acros Organics) as hard segment. The solvent used was *N*,*N*-dimethylformamide, analytical reagent (Ajax Finechem (NZ) Ltd.).

2.2. Treatment of MWNT

Fig. 1 shows the schematic for the treatment of MWNT. The MWNT were modified by a mixture of 70% nitric acid and 98% sulfuric acid [30,40] (1.0:2.5, v/v). The acid and MWNT mixture was heated at 140 °C for 10 min with mechanical stirring. Then an ultrasonicator with a power of 100 W and nominal frequency 50 kHz was used to distribute the MWNT in acid solution for 1 h. The treated MWNT were collected by a glass filter (pore size = 500 nm) after washed with sufficient distilled water repeatedly. The collected MWNT were dried in a vacuum oven to remove the residual moisture. Then dried MWNT were stored in a desiccator containing phosphorous pentoxide prior to use.

2.3. In situ solution polymerization

The preparation process of the polyurethane/MWNT composites is also presented in Fig. 1. All the glass vessels were cleaned and heated in a muffle to remove any organic and moisture residue. All the chemicals were de-moisturized in a vacuum oven before use. A calculated amount of modified MWNT was pre-distributed in IPDI solution of DMF in a four-necked flask. The pre-polymer was prepared by terminating PCL with excessive IPDI on both ends at 80 °C for 2 h. Pure nitrogen was purged in the reactor in order to prevent the influence of atmospheric moisture. The pre-polymer was subsequently chain extended with BDO for 1 h while keeping temperature below 90 °C.

2.4. Thermal sensitive membrane preparation

Membranes were made from diluted (concentration 5%, w/v) solution of polyurethane/MWNT by casting a calculated amount of solution into Teflon coated steel plates. In order to make pinhole free membranes, the solution was first degassed at 50 Pa for 30 min. Then solvent was evaporated at 60 °C for 12 h and residual solvent was removed at 80 °C for another 12 h in a vacuum oven. The obtained membrane thickness was about 100 μm.

2.5. Characterization

2.5.1. Scanning electron microscopy (SEM) analysis

The membrane cross section images and in-plane images of the polyurethane/MWNT membrane were taken by using a JEOL JSM-6335F field-emission scanning electron microscope. The operating voltage was 5 kV. To prepare the cross section of the membrane, the membrane was first embedded in an epoxy resin 1 day before the test. In this study, the membrane cross section was obtained by cutting the membrane embedded in epoxy using a freezing microtome (Frigocut 2800E, Leica Inc.) instead of by using the widely applied method, freeze-fracture in liquid nitrogen [41,42]. This was