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Original Research

Influences of poly (vinyl alcohol) molecular weight and carbon nanotubes on radiation crosslinking shape memory polymers☆

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ABSTRACT

Polyvinyl alcohol (PVA) of two molecular weights was used to prepare shape memory polymers based on chemical-crosslinking by glutaraldehyde. The chemical-crosslinking was done in the presence of 2-carboxyethyl acrylate oligomers (CEA) and nano-filler [multi-wall carbon nanotubes (MWCNT) and functionalized carbon nanotubes (MWCNT-NH_2)] followed by radiation-induced crosslinking. The analysis of the material revealed an increase in the gel fraction and a significant reduction in swelling of the nanocomposite material that was crosslinked with both glutaraldehyde and ionizing radiation. The radiation crosslinked nanocomposites demonstrated approximately a 90% gelation over a range of 50–300 kGy irradiation doses. The scanning electron microscopy (SEM) analysis showed a homogeneous distribution of nanocomposites in the composite matrix. The thermal properties of radiation crosslinked (PVA/CEA) and (PVA-CEA)-nano-fillers were investigated by a thermogravimetric analysis (TGA). The mechanical properties were examined via dynamic mechanical analysis (DMA) which showed significant variation because of the addition of nanocomposites. This radiation crosslinked materials show good shape memory behavior that may be useful in many applications based on the range of temperatures at which Tan δ appears.

1. Introduction

Shape memory materials are a class of materials that have the ability to change from a temporary to a permanent form of preserves at the request of an external stimulus. Shape memory polymer (SMP) represents a cheap alternative to expensive and effective alloy metal form because it is easy for the production and programming. The discovery of shape memory effect was done by Chang and Read in 1932 [1]. Since the accidental discovery of shape memory in nickel-titanium (Nitinol) by the Naval Ordnance Laboratory in 1968, the research on the shape memory materials has gained worldwide attention for the past half century. In general terms, a shape memory polymer possesses the ability to recover its shape from a deformed state [2]. Thermally induced SMP are the most extensively investigated group of SMP. Lendlein and Kelch [3] found that the shape memory effect could be controlled by a thermomechanical cycle which is the shape fixing process, deformation and shape recovery. SMP is defined as polymer materials with the ability to sense and respond to external stimuli, such as the chemicals, pH, light and temperature. Polymeric materials have different elasticities from hard glass to soft rubber. It has applications for deploying objects in space to manufacturing dynamic molds. The materials shows the shape memory effect if they can be deformed and fixed into a temporary shape and recover their original permanent shape only on exposure to external stimuli like heat, light, etc. [4,5].

Application of radiation technology include the radiation polymerization, radiation crosslinking and controlled degradation of polymers [6]. The radiation crosslinking techniques of polymeric materials have been providing many unique products including heat materials, heat shrinkable materials, curing of coatings and battery separators [7]. PVA has a good radiation crosslinking yield and radiation processed. The physical and chemical properties of PVA depend largely on its method of preparation. An important property of a polymer blend is the miscibility of its components, which affects its mechanical properties, the morphology, permeability and degradation [8].

Multi-wall carbon nanotubes (MWCNT) and functionalized multi-wall carbon nanotubes (F-MWCNT) consist of multiple rolled layers of graphene. MWNTs have the properties such as low density, high chemical, thermal and mechanical strengths and remarkable electrical

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and optical properties. MWCNT create a surface with a roughness at mirco to nanometer level [9–11]. The application of the MWCNT nanocomposites SMP materials are sensors, actively moving materials, high-performance electrochemical energy storage, graphene conducting polymer nanocomposites and supercapacitors [12,13].

The study of (SMP) nanocomposites with carbon nanotubes (MWCNT) has been reported earlier [14–16]. The objective of the study is the preparation and characterization of chemical and radiation crosslinked (PVA/CEA) and (PVA-CEA)-nanocomposites, using PVA of two molecular weights and two types of nanocomposites. In addition, the thermal and mechanical properties and the shape memory behavior of the prepared nanocomposites are studied in this investigation.

2. Material and experimental

2.1. Materials

PVA MW 16,000 (g/mol), PVA MW 146,000 (g/mol) and 2-Carboxyethyl Acrylate oligomers CEA MW170 were purchased from Sigma-Aldrich (St. Louis, USA). Multi-Wall Carbon Nanotubes (MWCNT) and NH_2 Functionality Carbon Nanotubes (MWCNT-NH_2) were procured from Graven Chemical Industries Co. Ancora, Turkey. The surfactant sodium dodecyl sulfate (SDS, C12H25SO4Na) was purchased from Sigma-Aldrich (St. Louis, USA) and used as received.

2.1.1. Synthesis of polymer networks via glutaraldehyde crosslinking

PVA MW 16,000 and PVA MW 146,000 solutions of 10 w/v were prepared by dissolving PVA in water for 8 h at 80 °C. The PVA films were prepared by solution casting. The PVA solutions were mixed with CEA in a 9:1 mol ratio. The PVA solutions were cooled to room temperature, and then its pH was adjusted to 4 with HCl. A certain amount of glutaraldehyde was added and the mixture was stirred for 3 min. The homogeneous mixture was cast onto a glass Petri dish followed by drying in air regulated at 50 °C to remove the solvent traces. The chemical crosslinking for the PVA-CEA film was carried out over 36 h at room temperature. The films obtained were washed with deionized water until pH-neutral, and dried for 48 h at room temperature under vacuum [17]. Two types of additive MWCNT and MWCNT-NH_2 were dispersed into the (PVA:CEA) solution with the aid of sodium dodecyl sulfate (SDS) at concentration 0.5 w $v^{-1\%}$. The rest of the process was similar as previous one.

2.1.2. Radiation crosslinking

The glutaraldehyde crosslinked PVA/CEA films according to the PVA molecular weight of PVA 16,000-MWCNT, PVA 16,000-MWCNT-NH_2, PVA 146,000-MWCNT and PVA 146,000-MWCNT-NH_2 were irradiated with doses of 50, 150, and 300 kGy at room temperature using a ^{60}Co gamma source (Gamma Cell 220; MDS Nordion, Canada). The typical dose rate was 6.9 kGy/h. The source was calibrated using an aqueous ferrous sulfate (Fricke dosimetry) solution according to ASTM Standard Practice E1026, Standard Practice for Using the Fricke Reference-Standard Dosimetry System. The typical dose rate was 6.9 kGy/h; the transit dose was estimated to be 12.07 Gy/s [18].

2.1.3. Gel content measurement

Measuring of the insoluble portion of the films after extraction with distilled water for 48 h at 60 °C was done to estimate the gel content. The reported values of the gel content were averaged over three measurements. The gel fraction was calculated according to Eq. (1).

$$\text{Gel}(\%) = \frac{\text{Mass of residue (g)}}{\text{Original mass (g)}} * 100 \quad (1)$$

The values above 90% indicate good crosslinking yield

2.1.4. Swelling studies

The hydrogel discs were allowed to swell in distilled water at 37 °C up to equilibrium. Swollen specimens removed from water, dried and weighed at different time intervals at room temperature. The reported values of equilibrium water uptake were averaged over three measurements. The swelling degree (%) was determined from Eq. (2),

$$\text{Swelling degree}\ (\%) = \frac{\text{Ws} - \text{Wo}}{\text{Wo}} * 100 \quad (2)$$

where Ws and Wo are the weights of the swollen and the dried hydrogel, respectively. The results were reported as average values.

2.1.5. Thermogravimetric analysis (TGA)

Perkin Elmer TGA7, USA was used for measurement of TGA. The nitrogen gas flow was kept at a constant rate of about 50 ml/min to prevent thermal oxidation processes of polymer samples. The heating rate was 5 °C min^{-1} from ambient up to 600 °C.

2.1.6. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis (DMA) was done by PerkinElmer Inc., USA. Tensile loading was used to determine the storage (*E*'), loss (*E*"), rubbery(Er) moduli and Tan δof the networks. The samples were thermally equilibrated at T_{low} (−50 °C) for 3 min and then heated to T_{high} (280 °C) at a rate of 5 °C min^{-1}. The applied static force was 110 mN, the dynamic force was 110 mN, and the frequency was 1 Hz. T_g was defined to be the peak of tan delta. The samples were measured in triplicate.

2.1.7. Scanning electron microscopy (SEM)

The cross section and the surface topography of the copolymer matrix was studied using JSM 5800 LV from Joel Co., Japan. The maximum magnification of the SEM was 300,000 at a resolution of 3.5 nm. Prior to examination, the samples were dried under sputters coated gold. All the micrographs were taken on a cut edge of the composites as cross-sectional and top view.

3. Results and discussion

3.1. Gel content

The gelation can be defined as "dose for which the smallest amount of gel can be separated from the system" [19]. Fig. 1(A and B) shows the gel content percent of glutaraldehyde crosslinked (PVA/CEA)-MWCNT using PVA of two molecular weights (MW 16,000 and 146,000) as a function of absorbed dose and filler (MWCNT) concentration. Fig. 1(C and D) shows the gel content (%) of the same copolymer composition using MWCNT-NH_2 concentration as a filler instead of MWCNT. The gel content of the prepared matrix is dependent on the irradiation dose, filler concentration and PVA molecular weight. The chemical cross-linking is due to the adjacent side hydroxyl groups have high ability to react with the two aldehyde groups of glutaraldehyde to form the hemiacetal or full acetal with six-membered ring as shown in Scheme 1. The higher cross-link density decreases the number of hydroxyl groups, shortens the chain length between cross-link points, and weakens the formation of hydrogen bonding, so the degree of crystallization decreases [20]. Gel content begins to level near 70% when started with the chemically crosslinked gel of the low molecular weight PVA (MW 16,000).

The effect of the absorbed dose and the MWCNT concentration on the gel fraction approximately reached a maximum of 90%. Using the higher molecular weight PVA (MW 146,000) yields 75% gel fraction at absorbed dose of 300 kGy and MWCNT concentration of 0.5%. The radiation plays the role of crosslinking agent [21]. The higher gel content of the prepared matrix may be due to the crosslinks between the polymer chains as a result of condensation reaction between carbonyl groups of the glutaraldehyde and PVA, OH groups [22]. The variation in the gel content with the irradiation was observed after 50 kGy irradiation. There is a 10% variation in the gelation with the