Calcium Sulfate Hemihydrate Whisker Reinforced Polyvinyl Alcohol with Improved Shape Memory Effect

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Experimental

Raw materials:

Polyvinyl alcohol (PVA) is 98.5%-99% hydrolysed with an average polymerization degree of 1700 (Kermel Chemical,Tianjin, China). Calcium sulfate whisker (HHW) is synthesized by ourselves [1]. Deionized water is used in all experiments.

Synthesis of PVA/HHW composite:

PVA/HHW composite was prepared by solvent casting method. Specially, solution (10 wt% PVA) was prepared by dissolving PVA in 98^{o}C water for 3 h. Certain amount of HHW was added to 10 ml 98 ^{o}C water and treated with ultrasound for 3 min. Then the HHW solution was gradually dropped into PVA solution, and stirred at 98 ^{o}C for 2h. The homogeneous PVA/HHW solution was poured into a Teflon plate (80 mm x 80 mm x 1 mm) and kept for 4 h at 90 oC to cast the film. All films were sealed and kept in a desiccator. The film was cut into desired shapes and sizes, and then kept 3h at 60 oC before characterization.

Characterization:

The X-ray diffraction pattern of the composites (10 mm x 10 mm x 0.5 mm) was carried out on a diffractometer (XRD, Rigaku D-MAX-2500/PC, Japan) using Cu Kα1 radiation (λ=1.54178 Å), with a scanning rate of 5 omin-1 and scanning 2θ range of 5 to 80o. DSC characterizations were carried on a Netzsch instrument (DSC204F1) in the temperature range 10-140 ^{o}C with a heating rate of 10 ^{o}C min^{-1}.FT-IR spectra were carried out on TENSOR 27 instrument (Bruker, USA) using KBr method in the range of 400-4000 cm^{-1}.Termo-gravimetric analysis were carried out on a TG-DTA 6200 LAB SYS analyzer under Nitrogen, at a flow rate of 200 ml min^{-1} with a heating rate of 10 ^{o}C min^{-1}.ATR-FTIR spectra were carried out on a Vertex 70 instrument (Bruker, Germany). Mechanical properties of samples (40 mm x 4 mm x 0.5 mm) were measured on an ASG-J electronic universal testing machine (Shimadzu, Japan) at room temperature with a crosshead speed of 20 mm min^{-1}. Dynamic mechanical analyses of samples (40 mm x 4 mm x 0.5 mm) were carried out on a TA Q800 Dynamic Mechanical Analysis (DMA) instrument (TA Instrument Inc.) in the tensile mode (frequency 10 Hz, heating rate 3 ^{o}C min^{-1}, range of temperature -20 ^{o}C-90 ^{o}C). Swelling measurements of samples (40 mm x 4 mm x 0.5 mm) were carried out by immersing samples in 37^{o}C water, the weight of the samples were measured at specific times after removing excess water on the surface. The swelling ratio was defined as swollen mass dividing initial mass.

Shape memory behaviour:

The shape effect was evaluated in a quantitative manner using bending test which first described by Lendlein [2]. The samples (40 mm x 4 mm x 0.5 mm) were bent to an angle at 90 ^{o}C, then

cooled down to room temperature, the samples maintain the temporary shape (ϑ_0) under external force. At last, the sample with temporary shape was immersed in 37 °C water, and the shape recovery process and the change of the angle (ϑ_1) with time were recorded. Shape recovery ratio was defined as $(\vartheta_0-\vartheta_1)/\vartheta_0$.

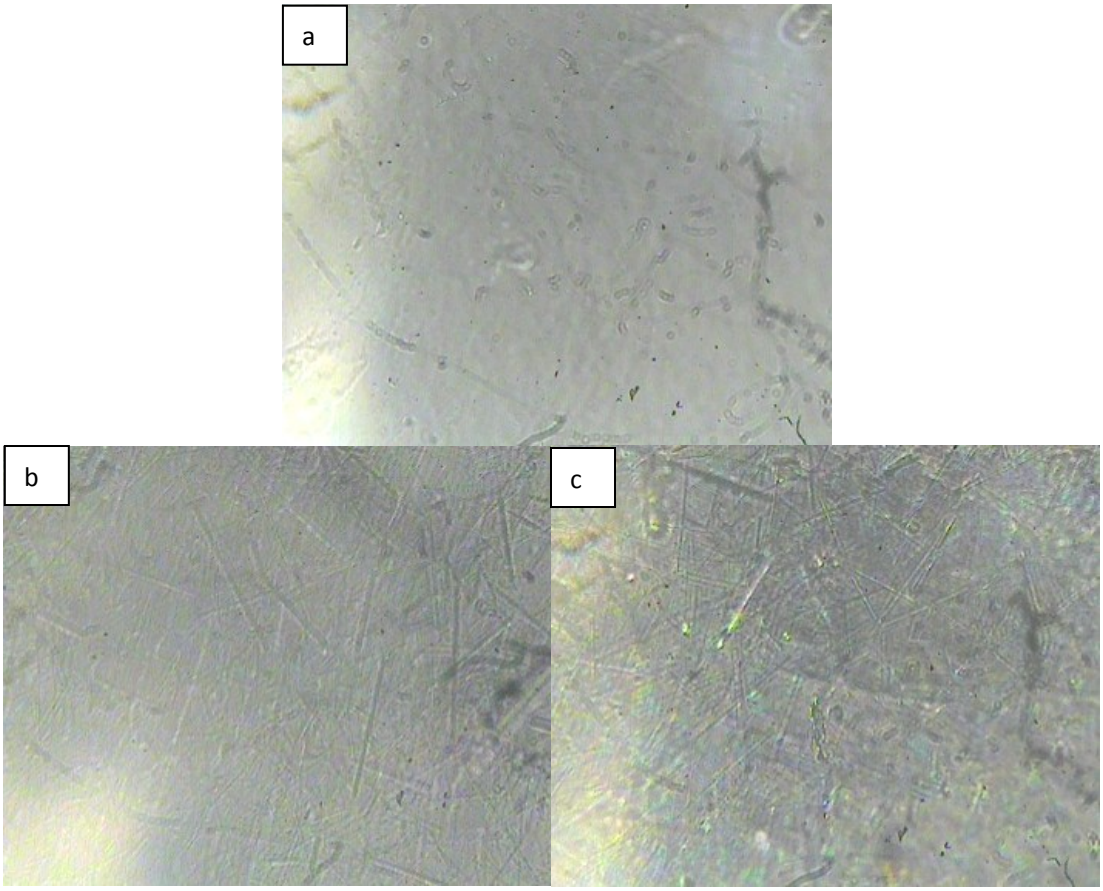

Figure s1 Optical microscope images of PVA/HHW composite with different HHW loading. (a) pure PVA, (b) 5 wt% HHW loading, (c) 7 wt% HHW loading.

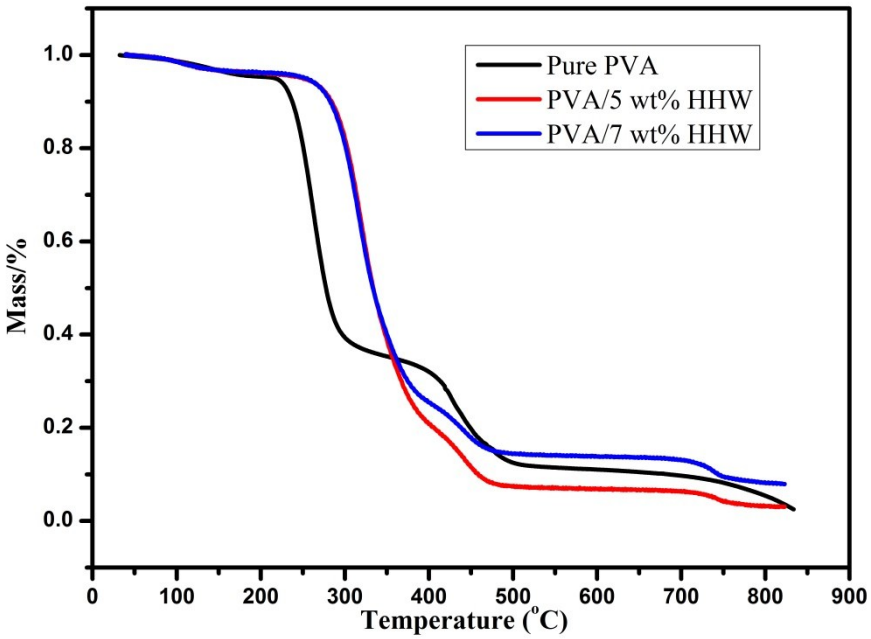

Figure s2 TGA curves of pure PVA, PVA/HHW with 5 wt% and 7 wt% HHW loading.

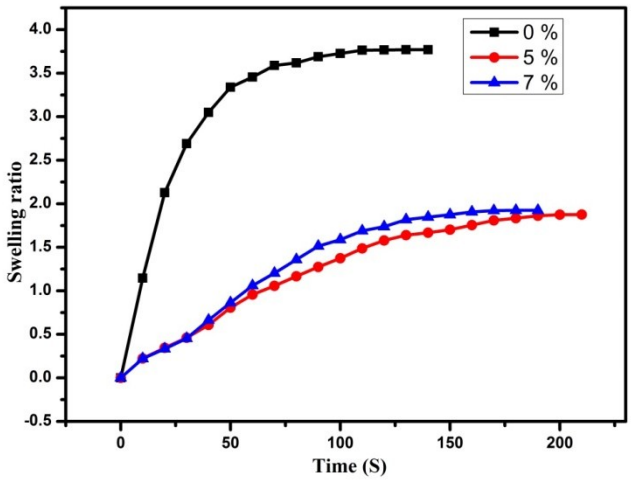

Figure s3 Swelling behaviors of pure PVA, PVA/HHW with 5 wt% and 7 wt% HHW loding.

1 Wenpeng Zhao, Chuanhui Gao, Fangrong Guo, Yumin Wu, Res. Chem. Intermed. 2016, 42, 2953.
2 A. Lendlein and S. Kelch, Angew. Chem., Int. Ed., 2002, 41, 2034.