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Novel porous bioabsorbable phosphate glass matrix nanocomposites incorporating trisilanolphenyl polyhedral oligomeric silsesquioxane prepared by extrusion

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ABSTRACT

Phosphate glass matrix nanocomposites containing trisilanolphenyl polyhedral oligomeric silsesquioxane (POSS) were investigated for the first time to accelerate efforts to develop novel hybrid phosphate glass/POSS composites with enhanced benefits. Tin fluorophosphate glass (Pglass) having ultra-low glass transition temperature (T_g) was utilized as the matrix material in extrusion at relatively low processing temperature (i.e., 270 ± 10 °C) compared to that of typical borosilicate and sodalime glasses. The resulting nanocomposites materials were highly porous due to evaporation of condensed water produced *in situ* from polysiloxane condensation reaction between the Pglass and POSS during the extrusion process. As the amount of POSS was increased in the Pglass matrix material, the glass transition temperature was significantly changed by the bulky POSS molecules. The novel porous nanocomposites should find a number of uses in applications at elevated temperatures where conventional organic polymer foam materials are not useable.

1. Introduction

While novel bioabsorbable phosphate glass-polymer composites [1] and porous scaffolds [2,3] with enhanced benefits have been reported in the literature, to our knowledge, the work described in this article is the first reported study that demonstrated feasibility of making porous glass matrix nanocomposites using extrusion processing (traditionally used for organic polymer processing) that takes advantage of the relative low-cost and high efficiency in distributing the nanofiller materials in the glass matrix materials [4]. The improved nanofiller dispersion of the trisilanolphenyl polyhedral oligomeric silsesquioxane (TSP-POSS) used here translates to an increase in interfacial surface area of the nanocomposite and improved nano-reinforcement and biomedical function [5]. Other researchers have reported borosilicate glass matrix composites [6] and porous glass foam materials with uses in membrane, catalyst and biotechnology applications with improved properties [7].

In the current study, TSP-POSS was incorporated for the first time into a phosphate glass (Pglass) matrix to yield functional micro(nano)structured porosity without using foaming agents such as calcium carbonate to generate the gas phase during the processing [8]. It is worthy to note that phosphate glass was selected for this study because it is the lowest glass transition temperature Pglass (*ca.* ~100 °C) with optimal combination of water resistance and desirable rheological characteristics, as well as, complete and congruent biodegradation and biocompatibility as previously reported [1,9].

2. Experimental

2.1. Materials

The Pglass was synthesized with a molar composition of $50SnF_2 + 20SnO + 30P_2O_5$ by heating, in a furnace maintained at 430 °C, a mixture of the stoichiometric amounts of the initial raw materials in an appropriate high-temperature crucible for 30 min [9].

Fig. 1 shows the chemical structures of Pglass and TSP-POSS. Pure Pglass and two different amounts of TSP-POSS (~10 wt%) were used and manually mixed using a mortar and pestle. Trisilanol phenyl POSS (TSP-POSS, $C_{42}H_{38}O_{12}Si_7$, Hybrid Plastics) was used. Analytical grade reagents, Tin(II) oxide (SnO), tin(II) fluoride (SnF_2), ammonium dihydrogen phosphate ($(NH_4)H_2PO_4$) were purchased from Sigma-Aldrich and used as received.

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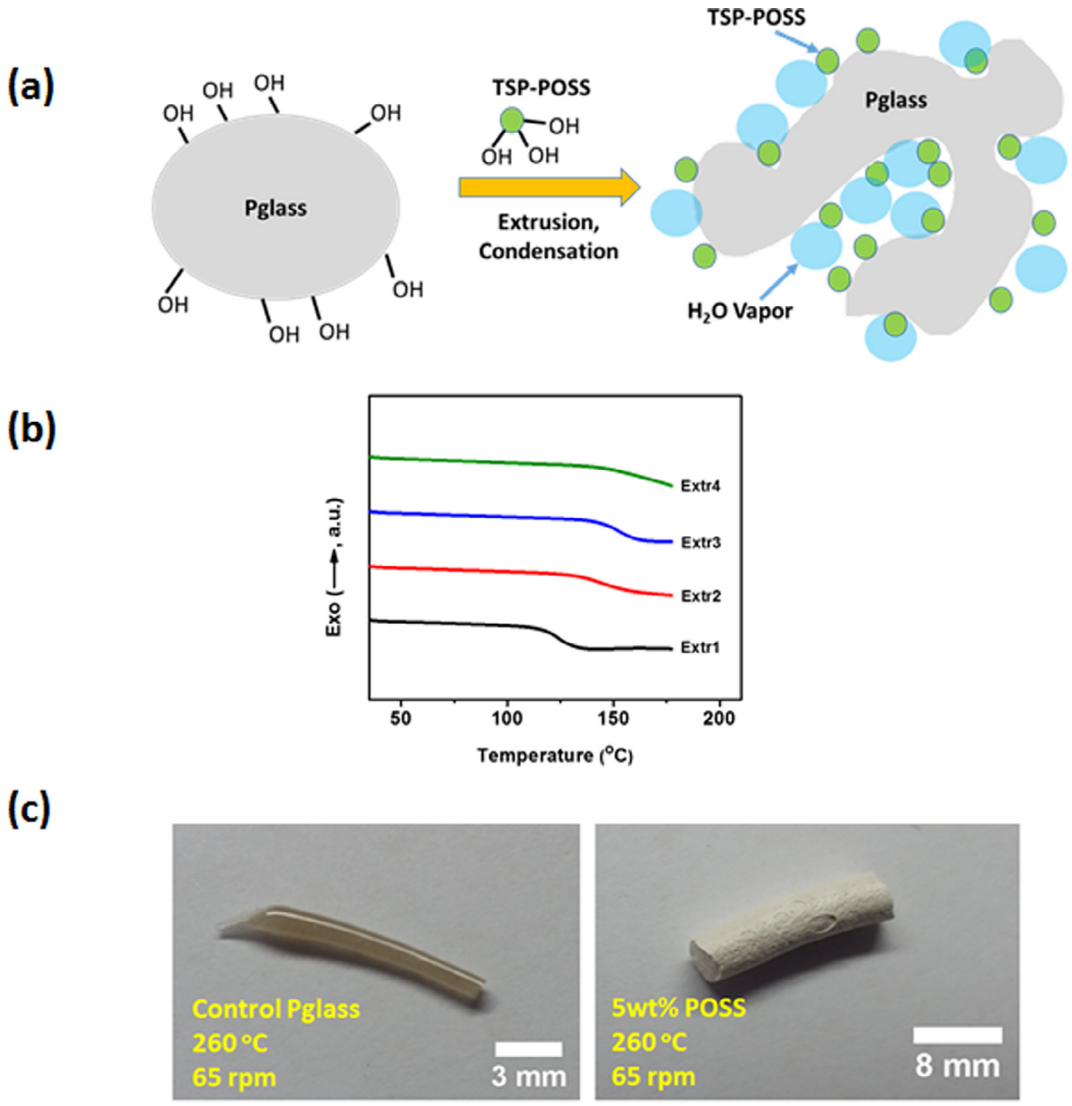

Fig. 1. (a) The expected macroscopic structure, (b) DSC thermograms, and (c) pictures of Pglass/TSP-POSS nanocomposites prepared by extrusion.

2.2. Extrusion processing

The desired amount of Pglass powder and POSS powder was mixed manually and continuously introduced into the feed-throat of a MiniLab® twin-screw extruder and conveyed by the extruder screws through the extruder slit die of 1 mm diameter to yield the glass matrix nanocomposite containing POSS as presented in details in Supplementary information.

2.3. Measurements

T_g was characterized by standard differential thermal analysis (PerkinElmer Pyris Diamond® DSC) under dry nitrogen atmosphere from 30 °C to 180 °C, 10 °C/min rate. Standard SEM-EDX analysis was used to investigate the morphology and elemental compositions of the samples. Standard ^{31}P NMR, solid-state NMR, and solid-state CP/MAS ^{29}Si NMR spectroscopy were used to characterize the chemical structure and dynamics of the samples as presented in details in the Supplementary information. The porosity of samples was estimated by comparing measured density to theoretical density of the samples.

3. Results and discussion

Fig. 1(a) illustrates how the TSP-POSS was dispersed in Pglass matrix via mechanical mixing and hydrogen bonding in the extrusion process, allowing condensation reaction between TSP-POSS and Pglass and between two of each material, that produced water vapor inside of the Pglass matrix, transforming into homogeneous porosity in the nanocomposites. As the amount of POSS was increased in the Pglass matrix materials, the T_g increased until it finally disappeared as shown in Table 1. This observation suggests that either the glass changed to a glass-ceramic or the T_g value of nanocomposites probably occurred at higher temperature, where thermal degradation prevented its determination. The obtained results suggest that mobility of the Pglass chains is restricted by the addition of the relatively bulky POSS molecules, leading to a decrease of mobility of the Pglass chains that was signaled by the observed increased T_g [10]. The extruded pure Pglass and nanocomposites materials are shown in Fig. 1(c).

The molecular structure and miscibility of the nanocomposites and its constituents were analyzed via solid-state NMR studies. ^{29}Si CPMAS NMR was conducted to obtain the local structural information between the Pglass and pure POSS as shown in Fig. 2(a). This