

Engineering Mechanically Stiff and Elastomeric Nanocomposites by Covalently Crosslinking Poly(glycerol sebacate) and Silicate Nanoplatelets

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INTRODUCTION: Poly(glycerol sebacate) (PGS) has been proposed to engineering soft tissues due to its elastomeric properties, biocompatibility, linear degradation rate and non-toxic byproducts.[1] However, one of the problems with PGS is low mechanical stiffness, that limits its application to soft tissues engineering.[2] Here we report the synthesis and characterizations of highly elastomeric and mechanically stiff nanocomposites by covalently reinforcing PGS network with synthetic silicate nanoplatelets. Synthetic silicates are plate-like polyions composed of simple or complex salts of silicic acids and are recently shown to induce osteogenic differentiation of stem cells without using any growth factors.[3] We hypothesize that by tailoring the crosslinking density, it is possible to engineer scaffolds with customized mechanical stiffness, hydration properties and degradation characteristics. The addition of silicate nanoplatelets also enhances the bioactivity of polymeric scaffolds. The unique combination of high mechanical stiffness, elastomeric nature and bioactive character may be processed to design scaffolds for musculoskeletal tissue engineering.

EXPERIMENTAL: PGS prepolymer was synthesized by polycondensation of glycerol (Sigma-Aldrich, USA) and sebacic acid (Sigma-Aldrich, USA) in 50:50 ratio at 130 °C under Argon for 2 hours according to previously published protocol (Fig 1a).[1,2] The nanocomposite was prepared by mixing the solution of 50% PGS in chloroform with 0, 2.5, 5 and 7.5% silicate nanoplatelets in ethanol. The final composition of silicates in PGS was 0, 5, 10 and 15 wt%. The mixture was probe sonicated for 30 minutes and then dried under vacuum for 24 hours. The dried mixture was subjected to thermal curing at 130 °C (under vacuum) for 40 hours. The effects of silicates on sol-gel content, hydration properties, contact angle measurements, thermal properties, mechanical stiffness, degradation rate and *in vitro* properties were determined.

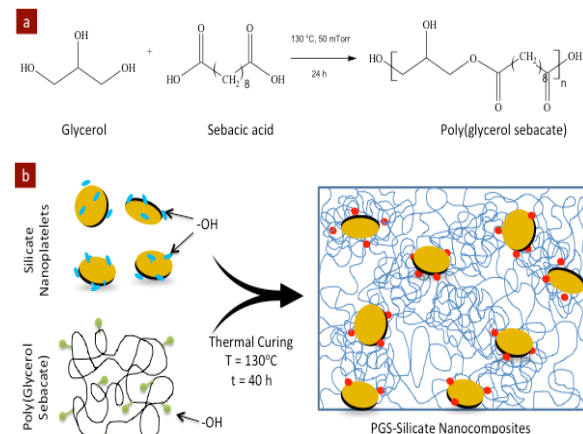


Figure 1. Synthesis of PGS-Silicate nanocomposites involved (a) polycondensation of glycerol and sebacic acid. (b) PGS-silicate nanocomposites were prepared by thermal crosslinking process.

RESULTS: Fully crosslinked nanocomposites were obtained by subjecting the PGS pre-polymer/silicate solution to thermal curing process at 130 °C for 48 h. The hydroxyl groups (-OH) present on PGS backbone reacted with (-OH) present on silicate nanoparticles to form covalently crosslinked networks (Fig. 1b). The addition of silicate improved the hydrophilicity of nanocomposite as evidenced by the decrease in contact angle of water (Fig. 2a). The addition of silicate nanoplatelets significantly enhanced the mechanical strength of the polymeric networks. The compressive strength and the energy absorbed during the cycle increased with increasing silicate concentration (Fig. 2b). In addition, it was observed that PGS-silicate nanocomposites were able to maintain elastomeric properties. All the PGS-silicate nanocomposites were able to recover back to their original shape when subjected to cyclic loading (Fig. 2c). Furthermore, the degradation studies showed that the addition of silicates significantly reduced the degradation rate of nanocomposites by more than 50%. Preliminary *in vitro* studies showed enhanced hMSCs adhesion and proliferation on PGS-silicate compared to PGS.

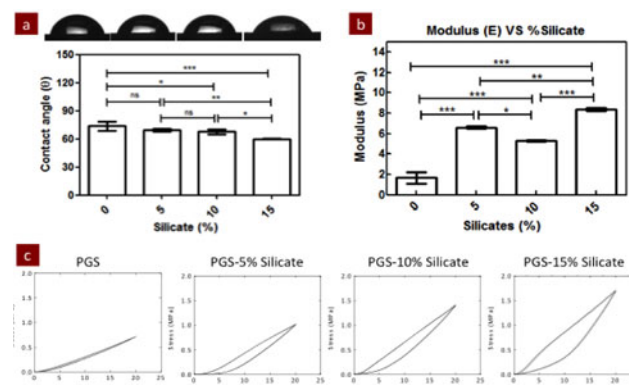


Figure 2. The addition of silicate to PGS influenced (a) surface characteristic and (b) mechanical strength. More than 3-fold increase in compressive modulus was observed due to the addition of 5% silicates. (c) Both PGS and PGS-Silicate nanocomposites showed high elastomeric behavior

CONCLUSION: The addition of silicate nanoplatelets to poly(glycerol sebacate) created the tough, elastomeric, and bioactive PGS-silicate nanocomposites. Overall, the mechanical strength, modulus, stability, and hydrophilicity of the nanocomposites increased with increasing %silicate, while the elastic characteristics of the polymer were still preserved. These properties could be tuned by altering the compositions, allowing the development of scaffolds for engineering various tissues.

REFERENCES: (1) Wang, Y. et al., *Nature biotechnology* **2002**, *20*, 602-606, (2) Patel, A. et al. *Biomaterials* **2013**, *34*, 3970-3983. (3) Gaharwar, A. K. et al., *Advanced Materials* **2013**, *24*, 3329-3336.