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LETTER

Spectroscopic evaluation, thermal, and thermomechanical characterization of poly(glycerol-sebacate) with variations in curing temperatures and durations

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Novel materials possessing physical, mechanical, and chemical properties similar to those found in vivo provide a potential platform in building artificial microenvironments for tissue engineering and therapeutic applications. Poly(glycerol-sebacate) (PGS) [1], a tough elastomer that is synthesized through the polycondensation of glycerol and sebacic acid, shows promise in the field of biomimetic materials. PGS is both biocompatible and biodegradable, with tunable mechanical properties within the range of common soft tissue. Studies have found that PGS is superior, in terms of mechanical properties, biodegradation characteristics, as well as cell response and morphology to poly(L-lactic–glycolic acid) (PLGA) [1, 2], a commonly used polymer in biointerface studies. Characterization studies on PGS have looked at its mechanical characteristics [3], thermal analysis via differential scanning calorimetry (DSC) [1, 4], molecular bonding schemes via Fourier transform infrared (FTIR) spectroscopy [1, 4], in vitro as well as in vivo degradation characteristics [1, 2], biocompatibility [1, 5, 6], swelling behavior [2, 3], and shape-memory effect [4]. However, a controlled wide-range study of these properties as a function of curing parameters has yet to be reported, limiting the standardization of property "tunability".

The present study aims to expand on this body of knowledge by examining the effect of cure schedule on both its physical and mechanical properties. The optimization and standardization of the pre-polymer and polymeric curing parameters will allow researchers to "tune" the biomimetic properties of PGS for a given application. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), DSC, dynamic mechanical analysis (DMA), and equilibrium tensile testing were used to characterize various PGS samples. We report here that PGS is a semi-crystalline elastomer that is fully amorphous above 35 °C with the largest melting transition temperature being approximately −25 to 35 °C for the pre-polymer. We also show that the degree of crosslinking in this material is dependent on cure temperature and duration of cure, and that this parameter can be inferred from changes in ATR-FTIR spectral data and material elasticity. A relationship between a specific ATR-FTIR spectral peak and material equilibrium modulus has also been derived. However, the investigation also encountered unexpected data where PGS exhibits a glass transition temperature (T_g) that does not change, and a heightened damping capacity at T_g with increasing degrees of crosslinking. We were also interested in finding the optimum pre-polymer synthesis and cure times. These reasons provided the impetus for us to conduct further characterization on PGS.

The PGS pre-polymer synthesis was adapted from established methods [1]. Briefly, equimolar (1:1) amounts of anhydrous glycerol (Sigma–Aldrich) and sebacic acid (Sigma–Aldrich) were mixed in an airtight glass jar that was partially immersed in a heated silicone bath. The mixture was gradually heated to 120 °C under nitrogen gas flow and stirred with a rotor at 50 rpm for 24 h. The gas flow was then stopped and vacuum (at −20 kPa) was applied for 48 h. Polycondensation results in a highly viscous pre-polymer. PGS samples were obtained by curing the pre-polymer in a vacuum oven (at −20 kPa) at set

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Table 1 Cure temperatures and durations of PGS specimens used in the study

Temperature (°C)	Duration (h)
120	24 (axial tensile, ATR-FTIR)
130	24 (DSC, DMA, axial tensile, ATR-FTIR)
150	24 (axial tensile, ATR-FTIR)
140	24 (DSC, DMA, axial tensile, ATR-FTIR)
165	2, 4, 10, 24, 48 (DSC, DMA, ATR-FTIR)

Notations within the brackets indicate the type of test each sample case was subjected to

cure times and temperatures, as indicated in Table 1. Others hypothesized that curing of PGS is achieved via a trans-esterification reaction where glycerol is removed from the polymer [7]. Covalent crosslinks are formed which lock the glycerol-sebacate chains into a random three-dimensional network of coils, transforming the viscous pre-polymer into a solid elastomer.

The main difference between this method and that referenced above is the level of vacuum of pressure used and how it was applied. For example, previous work [1, 3] applied low vacuum (approximately 6.67 kPa), after the initial 24-h period of inert gas flow, which was achieved gradually over a 5-h period, whereas in this work high vacuum pressure (−20 kPa) was applied instantly after the inert gas flow stage. This may account for variations in our material's mechanical properties compared to those established in literature [3, 4].

The ATR-FTIR spectra for PGS cured at 165 °C at different durations are plotted in Fig. 1. The spectrum is typical for a carboxylic acid with a –COOH functional group. There is a broad O–H stretch between 3300 and 2500 cm^{-1}. The intense stretch at 1740 cm^{-1} is for the double bond, C=O, and that at 940 cm^{-1} is for the O–H stretch. The ATR-FTIR spectra of the PGS pre-polymer and samples cured at 165 °C and varying cure durations is also shown in Fig. 1. Generally, PGS exhibits peaks for the alkane group (–CH_2) at 2930 and 2855 cm^{-1}, and intense stretches at 1740 and 1164 cm^{-1}, attributed to the formation of ester bonds (C=O and C–O, respectively). This is observed for the pre-polymer and all cure duration samples. The main changes in the PGS spectra when cure time is increased is (i) the significant reduction in the carboxylic acid O–H bend at 1418 cm^{-1} (Fig. 1 inset A) signifying that as the cure time proceeds acids further react with alcohols in the mixture to form the ester bonds, and (ii) the O–H stretch at approximately 3300 cm^{-1}(Fig. 1 inset B), signifying that the hydroxyls are consumed to form the ester based crosslinks. These appear to be the most prominent indicators of the extent of cure in the material.

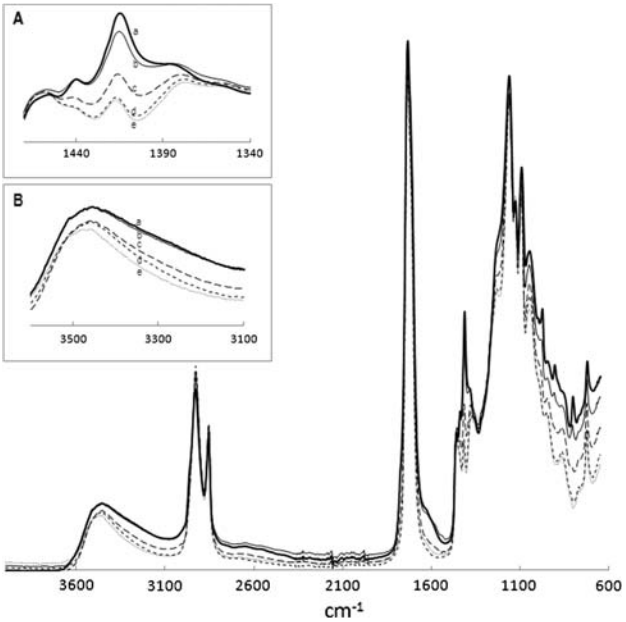

Fig. 1 ATR-FTIR absorbance spectra for PGS (*a*) pre-polymer, and samples cured at 165 °C for (*b*) 2 h, (*c*) 4 h, (*d*) 10 h, and (*e*) 24 h; there are no distinguishable changes in peak intensity for the alkane group (2930 and 2855 cm^{-1}) and ester bond peaks (1740 and 1164 cm^{-1}) between the PGS samples. Changes are observed for the carboxylic acid bend at 1418 cm^{-1}(inset *A*), and the hydroxyl stretch between 3600 and 3100 cm^{-1}(inset *B*), which signifies further formation of ester bonds as curing proceeds with time

A DSC analysis was conducted to quantify the extent of cure using heats of reaction or changes in T_g. Neither was observed here. However, it was useful in detecting the presence of crystallinity in the material. DSC measured both a crystallization temperature (T_c) during cooling and a melting temperature (T_m) during heating. Figure 2 plots the results for the pre-polymer, and samples cured at different temperatures and cure times. The T_g, which is observed as a slightly discernable step in the curves between −30 and −40 °C, does not appear to shift for all the cases. A broad melting transition is exhibited, initiating approximately at −15 °C and extending to 35 °C. The trend noted for the endothermic melting transition of PGS, as cure temperature and duration are increased, is a narrowing of the transition region, reduction in peak magnitude, and a general shift of the peaks towards lower temperatures. The relative differences in a sample's degree of crystallinity can be quantified by measuring the relative differences between areas under the melting peaks, as given in Table 2. A tenfold decrease in energy for the sample cured at 165 °C compared to those cured at 130 and 140 °C, indicates that the relative percentage crystallinity in the material drops significantly when this curing temperature and cure time is applied.

The presence of exothermic peaks at approximately −20 °C and endothermic peaks at ~5 °C indicate that the PGS samples are semi-crystalline. The degree of crystallization decreases significantly with the extent of cure. At

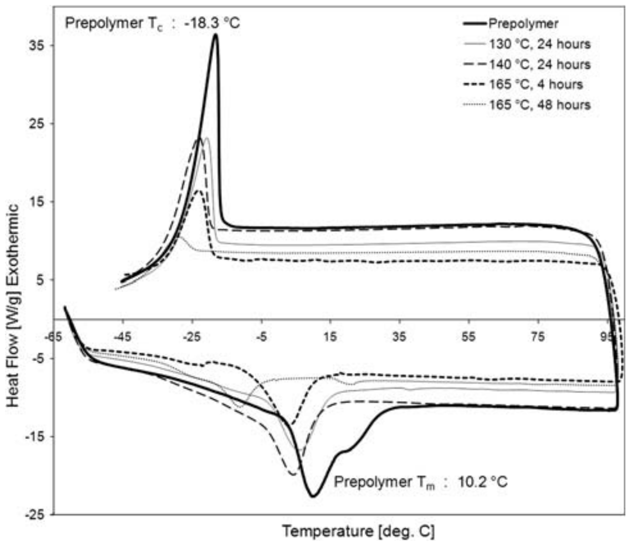

Fig. 2 DSC curves for PGS pre-polymer and samples cured at different temperatures and durations. The recrystallization peak height at approximately −20 °C decreases with curing temperature and time. Although the curves signify the material is fully amorphous at room temperature, the recrystallization occurrence signifies that it is a semi-crystalline material. The slightly discernible steps between −30 and −40 °C signifies the material's glass transition temperature. This is observed to remain fairly constant for all the cure conditions

Table 2 Relative difference between the areas under the melting peaks in the DSC curve for different cure cases compared to the pre-polymer

PGS sample	Area under the melting peak (J/g)	Relative difference with pre-polymer (J/g)
Pre-polymer	49.57	–
130 °C	48.69	8.80E − 01
140 °C	45.26	4.31E + 00
165 °C, 4 h	28.50	2.11E + 01
165 °C, 48 h	27.94	2.16E + 01

higher cure temperatures and times, exemplified by the 165 °C 48 h case, a significant drop in the crystallization peak suggests that the chain mobility is lower and thus the material cannot form crystals. Conversely, when the material has a lower degree of crosslinking, the chains still retain some ability to realign themselves at the crystallization temperature. This is evidently observed by comparing the crystallization peaks of the 165 °C 48 h to the 4-h cure. The crystallization peak heights of the 130 and 140 °C case are not significantly different. The slight shift between the peaks may be attributed to imperfections in the crystals or differences in lamellae thickness. Observation of the curves reveals that the material is fully amorphous above 35 °C.

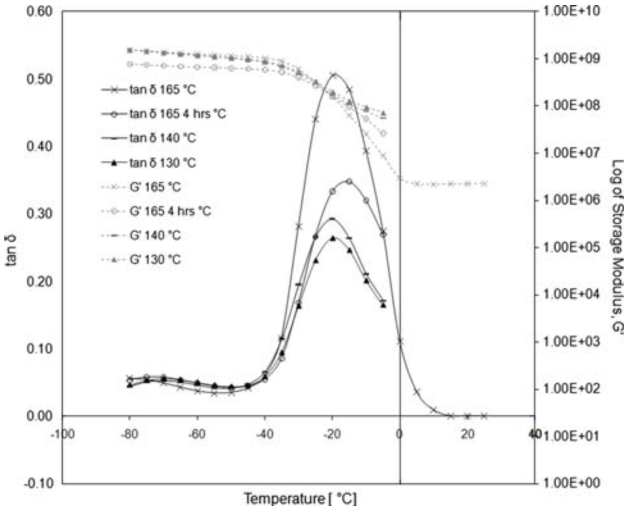

Fig. 3 Loss factor (tanδ) curves for PGS cured at 130 (24 h), 140 (24 h), and 165 °C (4 and 24 h). The curves were not continued beyond 0 °C for the 130, 140 °C, and 165 °C (4 h) cured samples since these became too pliable to register a reading on the DMA torque transducer. The curves show that the peaks coincide at approximately −20 °C for all conditions, which signify that the glass transition temperature does not change with respect to degree of crosslinking. Also, the peak heights appear to point to the material being more elastic at lower cure temperatures. However, this is not the case as shown in Fig. 4. We conjecture the decrease in peak heights at lower cure temperatures (and time) is due to a higher degree of crystallinity (and a lower amorphous phase)

A separate DSC study focusing on the pre-polymer was conducted with the temperature ramp going up to 200 °C. Interestingly, no exothermic peak was observed to signify curing of the pre-polymer. This may be due to its slow cure rate and/or due to the fact that hermetically sealed pans used did not allow for water to be drawn out of the pre-polymer during polycondensation. This will be examined further in the ongoing study.

The loss factor (tanδ) curves obtained from DMA at 1 Hz and 5 °C/min for PGS cured at 130, 140, and 165 °C for 4 and 24 h are plotted in Fig. 3. The position of the peaks suggest, as in the DSC analysis, that the glass transition temperature remains constant regardless of the degree of cure. As shown in Fig. 3, the curves were not continued beyond 0 °C for the 130, 140 °C, and 165 °C (4 h) cured samples since these became too pliable to register a reading on the DMA torque transducer. The storage modulus curves were also terminated beyond this point due to this same reason. Interestingly, the tanδ peak heights unexpectedly increase with the degree of cure. This can be explained by the noting that the degree of crystallinity of the 130 and 140 °C cured samples is significantly higher compared to the 165 °C sample. In this case, the amorphous phase constitute a smaller fraction, hence the tan δ peaks for the glass transition are smaller.

Step tensile tests were conducted to determine the equilibrium moduli of the various PGS samples studied. The specimens were 50 × 12 × 2.5 mm PGS rectangular slabs of cures as noted in Table 1. The equilibrium Young's modulus increases with increase in cure temperature. Specifically, the equilibrium Young's modulus is approximately 0.07, 0.12, 0.43, 2.02 and 2.30 MPa for the 120, 130, 140, 150, and 165 °C cured samples, respectively. It is noted that Chen et al. [3] reported a more rigid PGS cured at 130 °C with a mean stiffness of 1.20 MPa. This may be due to the differences in synthesis parameters as well as apparatus and method for mechanical testing. In this study, the samples were axially stretched by applying tension in steps of 5 g. At each step, the elongation of each sample is recorded. The tension was increased in this way until a percentage strain of approximately 6% is achieved. The slope of the linear stress–strain curve, as shown in Fig. 4 denotes the sample's equilibrium modulus. Since we have ascertained the ATR-FTIR spectral ranges that undergo significant peak height changes as PGS is cured, the relationship between maximum ATR-FTIR peaks within these ranges and the respective sample equilibrium modulus is quantified. Figure 5 plots the relationship between the PGS equilibrium modulus achieved at the respective cures and the corresponding ATR-FTIR peak ratios (i.e. the O–H stretch peak height at $\sim$3470 cm^{-1} to the –CH2 stretch at $\sim$2855 cm^{-1}).

To establish the crosslink density of PGS at each cure condition, the molecular weight between crosslinks, M_c (g/mol), was determined. Based on the theory of rubber elasticity [8], the equation used was $M_c = q\rho RT/G_\gamma$; where the front factor q was assumed as 1 for a shear modulus $G_\gamma << 10^7$ (Pa) at a temperature T (K), considering the material density ρ (g/cm^3) at that same temperature, and a universal gas constant R (kg m^2 s^2/K mol). The calculated M_c values are $6.93(10^4) \pm 5(10^2)$, $1.99(10^4) \pm 7(10^0)$, and $3.41(10^3) \pm 1(10^2)$ g/mol for the 130, 140, and 165 °C cure samples, respectively. These M_c values for the different samples were derived from room temperature data for ρ and G_γ. In comparison, Wang et al. [1] reported an M_c value of $1.83(10^4) \pm 1.62(10^2)$ g/mol for their PGS cured at 120 °C. The smaller M_c values allude to an increased number of crosslinks, confirming that the material's crosslink density increases with curing temperature.

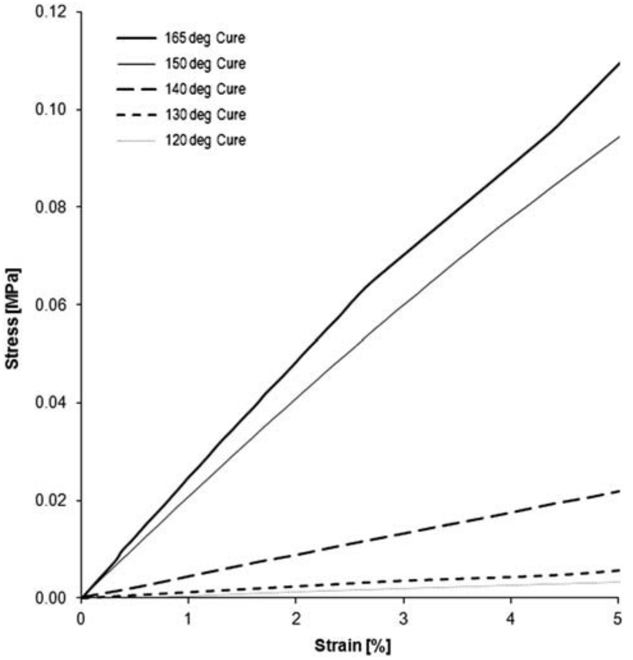

Fig. 4 Elastic region of stress–strain relationship for PGS cured at 120, 130, 140, 150, and 165 °C for 24 h. The curve slopes show that PGS increases in elasticity with increase in cure temperature. The equilibrium modulus for each respective cure temperatures is 0.07, 0.12, 0.43, 2.02, and 2.30 MPa

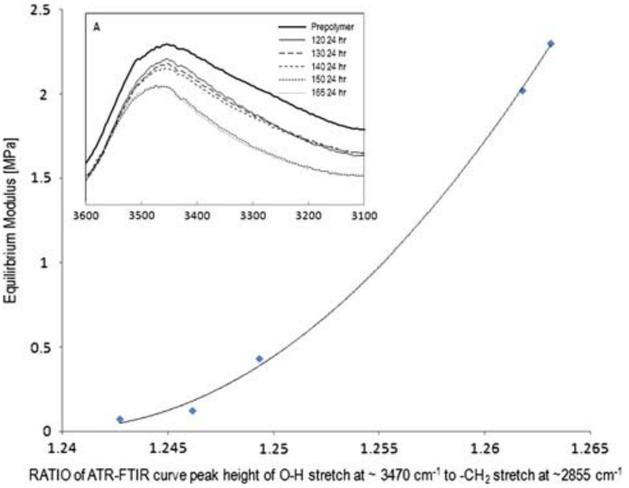

Fig. 5 Relationship between PGS equilibrium modulus and ratio between ATR-FTIR maximum peak heights of the O–H stretch at $\sim$3470 cm^{-1} and the –CH$_2$ stretch at $\sim$2855 cm^{-1}. Inset *A* shows the peaks for the PGS preoplymer and PGS samples cured for 24 h at 120, 130, 140, 150, and 165 °C. There is no equilibrium modulus data for the prepolymer as it is in a viscous liquid form

In summary, we have shown that PGS is a semi-crystalline elastomer that is fully amorphous above 35 °C. The material's ATR-FTIR spectra reveal that it contains polar groups in its molecular chains (hydroxyls). In addition to its biocompatibility, the presence of these hydroxyl groups contributes to its hydrophilicity, which may enhance in vitro cell culture. Our spectral analysis shows that its degree of crosslinking may be inferred from the change in its carboxylic acid bend at 1418 cm^{-1} and hydroxyl stretch at 3300 cm^{-1}. The degree of crosslinking has also been shown to influence the material's equilibrium Young's modulus. We have also quantified a relationship between the ATR-FTIR maximum peak height of the hydroxyl stretch for a given sample case and its respective equilibrium modulus. This study shows that for PGS synthesized from equimolar (1:1) amounts of glycerol and sebacic acid, the mechanical properties can be tuned depending on cure temperature and time. It is noted though that the material's glass transition temperature does not appear to be influenced by its degree of crosslinking. This requires further study and will be looked into in the ongoing work.

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