



Synthesis and Characterization of Poly(glycerol sebacate), Poly(glycerol succinate) and Poly(glycerol sebacate-co-succinate)

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Abstract

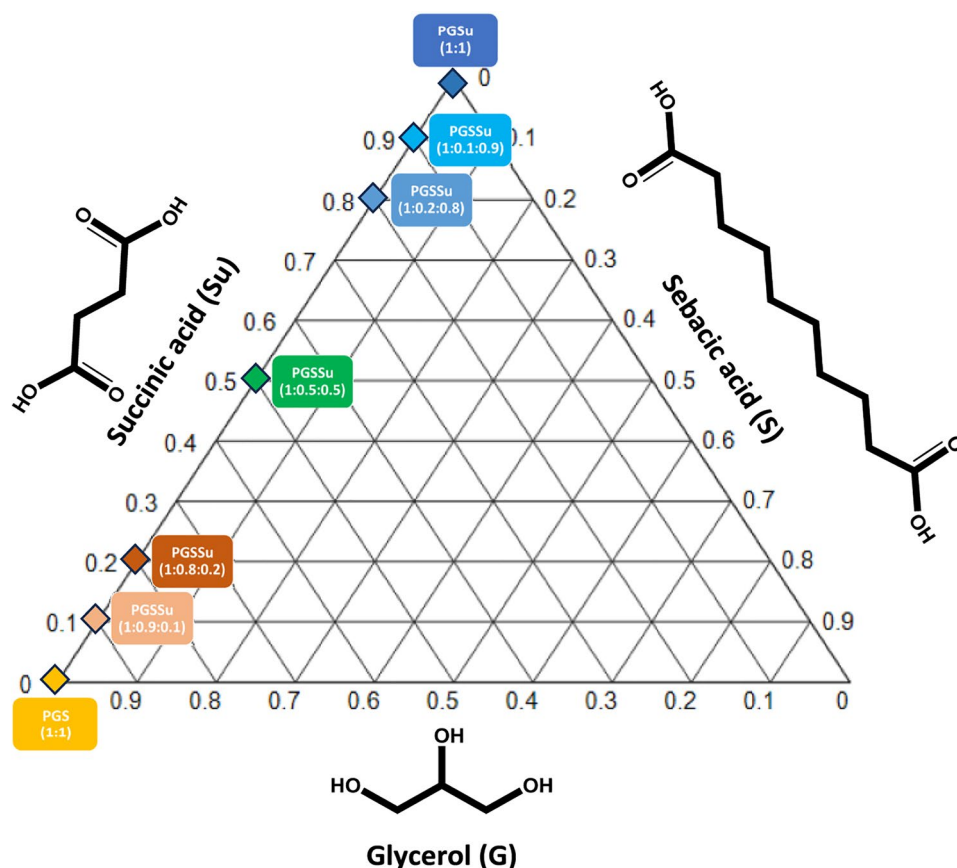
In recent years, thermoset elastomers, particularly polyesters derived from the polycondensation of glycerol and non-toxic diacids, have garnered significant interest. This study focuses on the synthesis of poly(glycerol-co-diacids) polymers using varying molar ratios of glycerol (G), sebacic acid (S), and succinic acid (Su). Seven distinct ratios were investigated (PGS (1:1), PGSSu (1:0.9:0.1), PGSSu (1:0.8:0.2), PGSSu (1:0.5:0.5), PGSSu (1:0.2:0.8), PGSSu (1:0.1:0.9) and PGSu (1:1)). The resulting polymers were analyzed using Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), dynamic mechanical analyses (DMA), tensile tests, scanning electron microscopy (SEM), gel fraction and degree of swelling determination. Among the synthesized polymers, PGS (1:1) and PGSu (1:1) exhibited superior mechanical robustness than the polymers obtained by mixing diacids. The results show that the incorporation of succinic acid in the synthesis of the polymers progressively led to rougher surfaces and a reduction in thermal resistance compared to PGS (1:1). PGSu (1:1) showed the highest surface roughness and the lowest thermal resistance. The glass transition temperature (T_g) for these elastomers ranged from -30 °C to 30 °C. Additionally, higher ratios of succinic acid led to increased polymer density and less degree of swelling. The gel fraction of these polymers ranged from 70 to 95%. PGS (1:1) with the lowest and PGSu (1:1) with the highest gel fraction, respectively.

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Graphical Abstract



Keywords Poly(Glycerol sebacate) · Poly(Glycerol succinate) · Poly(Glycerol sebacate-co-succinate) · PGS · Polycondensation

Introduction

In recent years, glycerol-based polymers, particularly polyesters formed through the polycondensation of glycerol and non-toxic diacids, have attracted significant interest. Glycerol, a building block of triglycerides in the human body, is widely regarded as a safe molecule. To date, several glycerol-co-diacids polyesters have been explored, primarily for biomedical applications, as they typically exhibit biocompatibility, biodegradability, and tunable properties. Poly(glycerol sebacate) (PGS) is the most extensively studied polymer in this family and several reviews have been published about this polymer and its derivatives [1–10].

Numerous studies have assessed various aspects of PGS synthesis, based on glycerol and sebacic acid esterification, and their effects in the polymer properties, in order to better understand and optimize the process, such as heat generation (microwave vs. conventional heating) [11, 12], temperature [11, 13–19], reaction time [11, 13–17, 20, 21], reagents ratio

[17, 19, 22–24], atmosphere [25], solvents [19], and catalysts [19, 26–28]. It is possible to find PGS with significantly distinct values of Young modulus (0.017–6.86 MPa), tensile strength (0.1–1.96 MPa) and elongation (10–448%) based on several publications [3, 17, 18, 26, 27, 29–37]. In bibliography, it is possible to find a mimetic polymer of PGS called poly(sebacoyl diglyceride) (PSeD) that has a well-defined linear structure produced by ring-opening reaction of diglycidyl sebacate with sebacic acid. Its mechanical properties are in range with the ones for PGS, with a Young modulus of 1.57 MPa, an elongation of 409% and a tensile strength of 1.83 MPa [38].

To improve its properties, PGS has been conjugated with other materials forming copolymers and blends/composites. Copolymerization of PGS with urethane units (PGSU) used for cross-linking allows to obtain stronger materials. For example, PGSU have a Young modulus between 0.1–20 MPa, tensile strength around 0.14–12.1 MPa, and an elongation between 10–516% [39–41]. This represents

an improvement in the hardness and elasticity of the PGSu when compared to PGS. Copolymerization of PGS with acrylate moieties (PGSA) also increases the Young modulus (0.05–30 MPa) and tensile strength (0.01–1.36 MPa) of resulting polymers, but its elasticity (5–200%) is not superior than that of PGS [42–44]. The use of citric acid to co-polymerize with PGS (PGSC) permits an improvement of the Young modulus (6.9 MPa) and tensile strength values (2.7 MPa) [45]. The greater elasticity of the PGS copolymer was achieved in PGS-b-PTMO—Hytrel 3078 with 2574% of elongation [26]. The blending of PGS with other polymers like polycaprolactone [46, 47] or polyethylene glycol [29], and materials as carbon structures [36, 45, 48, 49], cellulose [40, 50] and glass [2, 51, 52] have also been explored to obtain a different range of material properties.

Poly(glycerol succinate) (PGSu) is another polyester that can be synthesized by polycondensation of glycerol with succinic acid, a dicarboxylic acid. However, PGSu has been less studied compared to PGS. So far, only a few publications used glycerol and succinic acid to produce PGSu polymer structures [33, 53–61]. Therefore, information about the mechanical properties of PGSu is currently very limited. Nagata et al. [53] prepared a low degree polymerization PGSu-based polymer named “Yg4” by doing a polycondensation at very high temperatures (≥ 200 °C). In Cai et al. [54], PGSu was synthesized by polycondensation at 150 °C to create internal fixation bone screws. The registered values for bending strength and tensile strength reached 122.01 ± 8.82 MPa and 31.41 ± 2.76 MPa respectively, for a polymer produced with 1:1 reactant groups ratio (OH:COOH). Using different proportions of reagents to synthesize the polymer, it was possible to conclude that increasing the number of OH leads to a less resistant and inherently softer material. This phenomenon is consistent with findings from PGS studies that have examined the impact of reagent ratios [17, 23]. It's highly probable that some of the knowledge acquired from PGS studies can be applied to PGSu. Other areas of interest in PGSu can also be found in the literature, such as the characterization of oligomers [55, 57, 58, 61], applications of surfactants [56], and blending component with other polymers [60]. Valerio et al. [59] produced PGSu at 180 °C using different sources of glycerol, and tested some polymer properties but conventional mechanical parameters as Young modulus, tensile strength and elongation were not performed. Additionally, there are studies that have successfully synthesized PGSu structures utilizing alternative reagents [62–66]. In summary, the production of PGSu, using glycerol and succinic anhydride, was mathematically described [66] and a PGSu eco-friendly plasticizer was tested [62]; PGSu nanogels for dermal delivery were produced from glycidol and succinic anhydride; [65] dendritic macromolecules with PGSu structures were produced with benzyldiene glycerol and succinic anhydride

[63, 64]. However, none of these publications have studied the mechanical properties of a PGSu polymer.

Like PGS, some studies have shown that PGSu can also be modified through copolymerization. In one such process, PGSu is combined with maleic anhydride to create a copolymer, poly(glycerol succinate-co-maleate) (PGSMA), and then used to produce blends with other polymers [67–70].

Nagata et al. [33] prepared copolyester films from glycerol, sebacic acid, and succinic acid with different acid ratios, called Yg-10/4. A prepolymerization step was performed at 200 °C with significant differences in reaction time for each ratio of diacids. These times ranged from 32 to 90 min with no clear pattern. For instance, the sebacic/succinic ratios of 90/10, 80/20, and 70/30 took 58, 34, and 46 min respectively, while Yg-10 (PGS) and Yg-4 (PGSu) prepolymers required 43 and 90 min. The cure step for all films took 4 h at 230 °C. The films obtained revealed different degrees of reaction (78–90%). Replacing sebacic acid with succinic acid produced denser films with increased degradation resistance, stiffness, and a higher Young's modulus.

More recently, Godinho et al. [61] prepared prepolymers of poly(glycerol-co-diacids) based on sebacic and succinic acid mixtures by polycondensation at 150 °C. In this work, a detailed characterization by NMR and mass spectrometry of the obtained oligomeric structures was performed. However, no final polymers were produced and, as such, the influence of the acid mixtures on the mechanical properties was not studied.

Considering the existing literature, this study aims to evaluate the synthesis of poly(glycerol-co-diacids) using two diacids simultaneously, an approach not found in recent publications. Polycondensation reactions of glycerol with sebacic and succinic acids were performed to produce poly(glycerol-sebacate-co-succinate) (PGSSu), employing different diacid ratios. PGS and PGSu were also synthesized as reference materials. A total of seven polymers were obtained under similar conditions, except for the diacid ratio. Polymers were characterized through tensile tests, dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). This study enables the observation of the effects of progressively replacing sebacic acid with succinic acid in the synthesized polymers, thereby expanding the knowledge on PGSu mechanical properties, which have been scarcely reported in previous research.

Experimental Section

Materials

Glycerol, sebacic acid, succinic acid and solvents were purchased from Sigma–Aldrich with 99% purity.

Synthesis of Prepolymers (Prepolymerization Step)

Several reactions were performed at 1:1 molar ratio of glycerol (G) to diacids (sebacic (S) and/or succinic (Su) acid), using seven different diacid ratios—PGS (1:1), PGSSu (1:0.9:0.1), PGSSu (1:0.8:0.2), PGSSu (1:0.5:0.5), PGSSu (1:0.2:0.8), PGSSu (1:0.1:0.9), PGSu (1:1). Reactions were carried out in batch mode using a PARR reactor with a 300 mL stainless-steel vessel and a PARR 4843 controller for heating and temperature control. The agitation system was modified to work with a CAT R100 with RPM and torque monitoring.

The reactor system was programmed to perform a temperature ramp of 42 min until reaching 150 °C (t₀). Agitation began at 70 RPM until 100 °C, and then increased to 100 RPM until the end of the reaction. All reactions were performed under a nitrogen flux to avoid oxidation and to remove any water produced. The reactions were stopped when the degree of esterification (DE) reached approximately 55% (tend), as measured by the water collected (7.5 mL) in a 20 mL graduated cylinder.

Synthesis of Final Polymers (Cure Step)

The cure step of each polymer was done in a VT 6025 vacuum oven (Thermo Scientific) coupled with a ILM-VAC MP 601 T vacuum pump (full capacity: ultimate exhaust < 1 mbarr). Prepolymers were cured in dog-bone shaped geometry Teflon molds, previously carved using a CNC machine according to DIN EN ISO 527-2, as Bue et al. [71]. These tensile testing specimens have a volume of 0.6 cm³.

Before the cure, a step of degasification was performed to remove any dissolved gas in the obtained prepolymers. The prepolymers were heated at 90 °C in the same oven and vacuum pump for an easy degasification, since it allows the maintenance of a low viscosity liquid state, while the vacuum pump worked at full capacity. After 2 h, all prepolymers ceased bubbling. This crucial step helps to prevent bubbles in the cured dog-bone pieces and any instability during the curing process.

Following degasification, the prepolymers were transferred into pre-heated molds at 90 °C to avoid filling difficulties due to increased viscosity upon contact with a cold surface. The filled molds were placed back in the oven at 90 °C with the vacuum at full capacity. The system was sealed to maintain the vacuum, and the pump was switched off. The filled molds remained in these conditions overnight to remove any residual gas. Subsequently, the curing step commenced. The vacuum pump was turned on at full capacity, and the temperature was gradually increased to 150 °C at a rate of 12 °C/h, starting from 90 °C. Once the temperature reached 150 °C (after 5 h), the vacuum pump was turned off,

and the oven system was sealed to preserve the vacuum for the next 19 h, totaling a 24-hour curing process. This progressive heating procedure is essential for preventing bubbles in the final dog-bone pieces, allowing bubbles formed during the process to escape the mold. At 150 °C, all polymers were found to be stable and bubble-free. Finally, after removal from the molds, all specimens were weighed on a KERN ACJ 320-4 M scale for quality control.

Fourier-Transform Infrared Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) spectra were collected on a Perkin Elmer FTIR System Spectrum BX Spectrometer equipped with a single horizontal Golden Gate ATR cell. Prepolymers and cured polymers were analyzed, and data were recorded at room temperature, in the range of 4000–400 cm⁻¹ by accumulating 32 scans with a resolution of 4 cm⁻¹.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out using a SETSYS Evolution 1750 thermogravimetric analyzer (Setaram) over a temperature range from 25–800 °C, with a heating rate of 10 °C/min under an air atmosphere.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) of the final polymers was carried out using a Tritec 2000 equipment (Triton Technologies) in tension mode using a strain factor of 200. Samples with dimensions of 5 × 3.7 × 2 mm³ were analyzed over a temperature range from –80–80 °C, with a constant heating rate of 2 °C/min, and frequencies of 1 and 10 Hz.

Mechanical Testing

Tensile tests of PGS, PGSSu, and PGSu cured specimens were conducted on a Hegewald & Peschke universal testing machine Inspekt solo, equipped with a 2.5 kN load cell, in accordance with DIN EN ISO 527. Tensile tests were performed at a speed of 10 mm/min up to the breaking point, to determine the following parameters: ultimate tensile strength (UTS), elongation at break and the Young's modulus. The Young's modulus of each sample was calculated by the linear fitting of stress–strain curves at low strain (until 20%). At least five replicas were tested for each polymer, and only the three most concordant replicas were selected.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) analyses were conducted using a SU-70 (Hitachi) scanning electron

microscope. The samples were vacuum coated with carbon to prevent electrostatic charging during examination and were analyzed at an accelerating voltage of 5.0 kV.

Gel Fraction and Degree of Swelling Determination

The gel fraction and swelling determination experiment was performed using tetrahydrofuran (THF) as solvent and the ends of dog-bones (between 220 and 320 mg weight) as test pieces. Briefly, the samples ($n=3$) of each polymer were immersed in 10 mL of THF at room temperature (≈ 23 °C) for 72 h [18, 30], using screw-top vials (Fig. S5). The swollen samples were dried in a vacuum oven at room temperature for the first 48 h and at 35 °C for the last 24 h, in a total process of 72 h, with the vacuum pump at maximum capacity. This change in temperature in the last 24 h was due to the difficulty in removing the solvent from the PGSSu (1:0:1:0.9) and PGSu (1:1) samples. In the last 12 h, all the samples showed a stable weight.

The gel fraction (%) is the percentage of insoluble polymer mass from initial sample, while the degree of swelling (DS) is the ratio of solvent mass retained by the mass of gel fraction. These values are determined by:

$$\text{Gel Fraction}(\%) = \frac{W_d}{W_o} \times 100$$

$$\text{DS}(\%) = \frac{W_s - W_d}{W_d} \times 100$$

where W_o is the initial weight of the sample; W_d is the weight of the dry insoluble part of sample; W_s is the weight of the insoluble swollen part of sample.

Previously, 700 mg of each prepolymer was added to 10 mL of THF to check solubility. All the prepolymers dissolved perfectly within a few seconds. This guarantees that the amount of solvent used has more than enough capacity to dissolve the soluble fraction in the samples. All masses were obtained on a KERN ABT 100-5NM scale for greater precision.

Results and Discussion

Polymer Synthesis and Quality Control of Dog-Bone Testing Specimens

The syntheses of PGS, PGSu, and PGSSu were achieved by polycondensation of sebacic acid (S), succinic acid (Su), or a combination of both acids, with glycerol (G). Figure 1 shows the chemical representation of these three monomers and the generic structures of the resulting polymers. The seven polymers synthesized are consistently represented by the same

color scheme throughout this document: PGS (1:1)-yellow, PGSSu (1:0.9:0.1)-light pink, PGSSu (1:0.8:0.2)-dark orange, PGSSu (1:0.5:0.5)-green, PGSSu (1:0.2:0.8)-blue, PGSSu (1:0.1:0.9)-light blue, PGSu (1:1)-dark blue.

The polymer synthesis was conducted in two steps. The first step involved a prepolymerization process until reaching a DE of 55%. Figure 2 shows the time required to achieve this DE for each prepolymer. A correlation ($R^2=0.9819$) was observed between the time required and the diacids ratio, where substitution of sebacic acid with succinic acid leads to a reduction in the time necessary to achieve a DE of 55%, as previously reported [61].

This specific DE (55%) prevents the gel point and enables the production of prepolymers with low viscosity at 90 °C, which eases their transfer into Teflon molds and allows for gas release.

During the synthesis, some N_2 that is used to prevent oxidation gets absorbed into the prepolymers. As a result, it is crucial to perform gas removal on the prepolymers before proceeding to the final cure step, particularly for prepolymers produced with higher amounts of succinic acid. Fig. S1 (bottom mold) displays the outcome after curing PGSu (1:1) without a prior degassing process, resulting in test samples with numerous bubbles and defects that rendered them unsuitable for analysis. PGS (1:1) is easier to degas and does not necessitate 2 h for this process. However, to maintain consistent procedures for all prepolymers, the methodology that allowed for obtaining flawless PGSu (1:1) test samples was adopted. In fact, PGS (1:1) is a much easier and simpler material to work with than PGSu (1:1) or any of the mixtures.

Figure S1 (top mold) shows the result of synthesizing PGS (1:1) without a controlled atmosphere, leading to test specimens with yellowing. In contrast, Fig. 3 presents test specimens obtained with full atmosphere control, which are completely colorless and transparent. Fig. S2 shows perfect test specimens of all polymer ratios, and an amplification of PGS test specimens without any trace of yellowing. Conejero-Garcia et al. [17] used N_2 during the prepolymerization step but the cure process took place in a forced ventilated oven rather than a vacuum oven, which resulted in yellowish PGS, as evidenced by their figures. The yellow color associated with PGS in the literature is undoubtedly related to oxidation phenomena.

The dog-bone specimens produced were weighed to verify the reproducibility of the process. Fig. S3 displays the results from weighing five test specimens of each polymer. The methodology employed to create these specimens proved to be effective, yielding similar objects with low standard deviation (%) between replicates. These mass results also indicate that polymers synthesized using a larger ratio of sebacic acid tend to have lower mass, and consequently, less density compared to those created with a

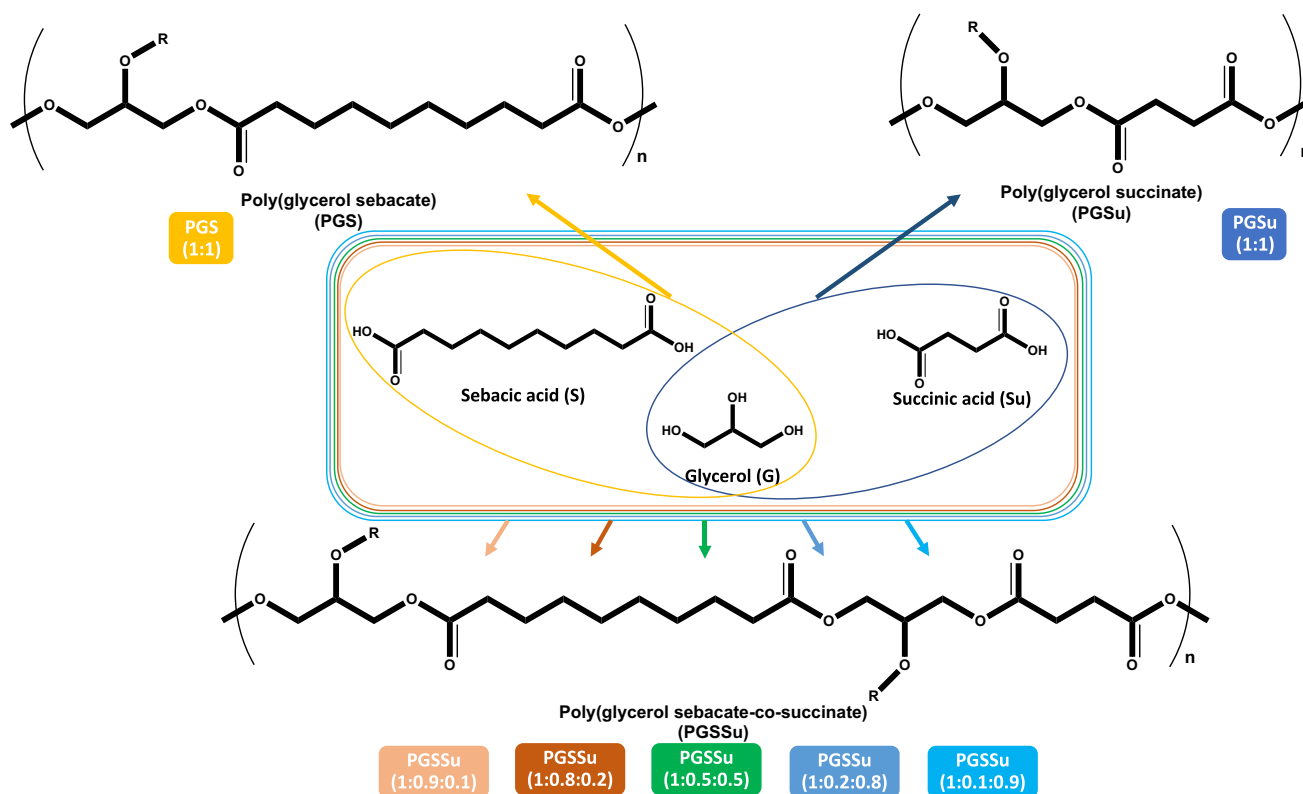
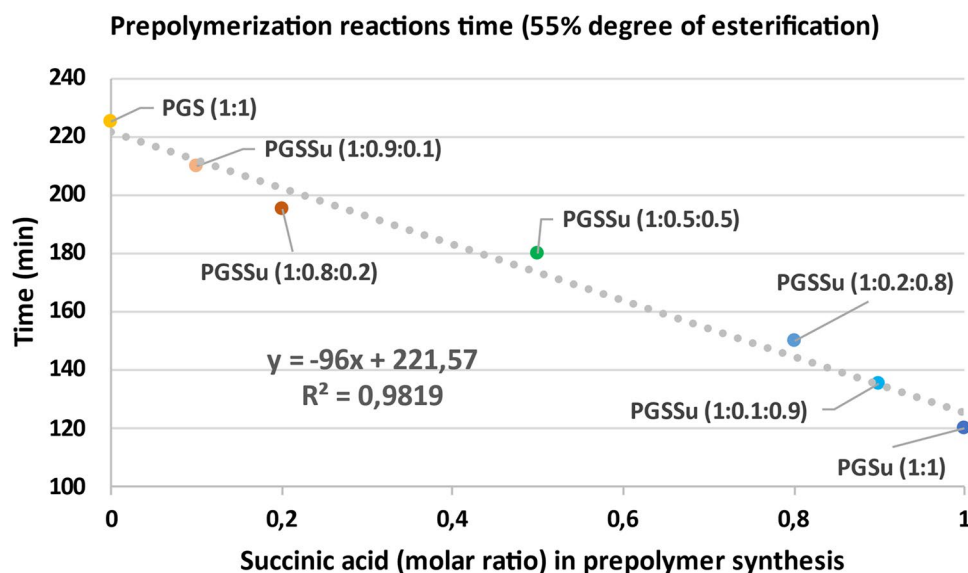


Fig. 1 Chemical structure representations of monomers used, and polymers formed, where “R” is an undetermined chain. Monomers: glycerol (G), succinic acid (Su) and sebacic acid (S). Polymers: PGS

(1:1)-yellow, PGSSu (1:0.9:0.1)-light pink, PGSSu (1:0.8:0.2)-dark orange, PGSSu (1:0.5:0.5)-green, PGSSu (1:0.2:0.8)-blue, PGSSu (1:0.1:0.9)-light blue and PGSu (1:1)-dark blue (Color figure online)

Fig. 2 Time required for each prepolymer ratio to achieve degree of esterification (55%) and correlation between time and succinic molar ratio used in prepolymers synthesis (Color figure online)



higher concentration of succinic acid. This is consistent with Nagata et al. [33] where PGSu and PGS presented densities of 1.375 and 1.106 g/cm³, respectively.

Considering the volume of the dog-bone molds used (0.6 cm³), and the average mass of the specimens, it is possible to

estimate the densities for PGSu and PGS as 1.329 and 0.941 g/cm³, respectively. These values are lower than the previously reported ones, a discrepancy that may be attributed to the mass loss that can occur during the curing process [11, 13, 72]. Upon completion of the curing step, the 0.6

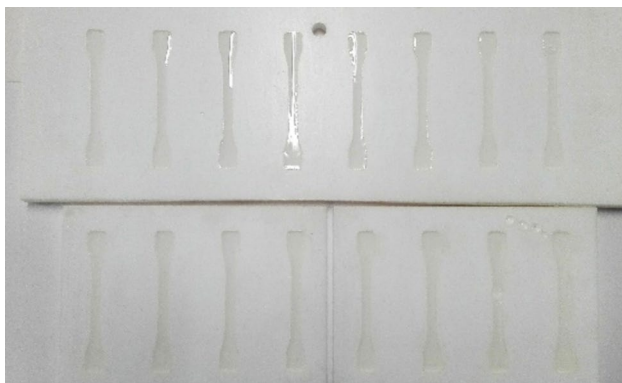


Fig. 3 Teflon molds filled with properly cured PGS (1:1) polymer

cm^3 mold might not be completely filled, resulting in dog-bone specimens that are slightly smaller. This discrepancy likely introduces a measure of inaccuracy into the calculated density values.

FTIR

Figure 4 shows the FTIR spectra of prepolymer and final polymer sample for PGSSu (1:0.5:0.5), as example. The spectra

of the other ratios tested can be seen in Fig. S4 of the supporting information. To aid interpretation, certain regions of interest in the spectra have been marked. Starting from lower wavenumber values, the first region, $1000\text{--}1050\text{ cm}^{-1}$, indicates the primary alcohol C–O stretching. As expected, the cured polymers exhibit a significant reduction in this peak when compared with their respective prepolymers. A similar decrease in intensity is observed in the $3200\text{--}3600\text{ cm}^{-1}$ region, indicating undefined alcohol C–O stretching. This broad peak also decreases in intensity in cured polymers. Furthermore, the signals from the carboxylic acid groups diminish in the spectra of the cured polymers. At around 1400 cm^{-1} (carboxylic acid O–H bending), a visible decrease in the signal is observed between prepolymers and polymers. The region near 1700 cm^{-1} represents esters and carboxylic acid C=O stretching. In the prepolymers' spectra, it is possible to see the presence of both signals (ester- 1730 cm^{-1} and acid- 1695 cm^{-1}), especially in those with more sebacic acid. However, as sebacic acid is replaced with succinic acid, this distinction becomes less clear, and the peak becomes wider, spanning the range of $1695\text{--}1730\text{ cm}^{-1}$, indicating the coexistence of ester and acid groups. In the spectra of the cured polymers, a distinct and sharp peak at 1730 cm^{-1} , representing ester groups, is observed.

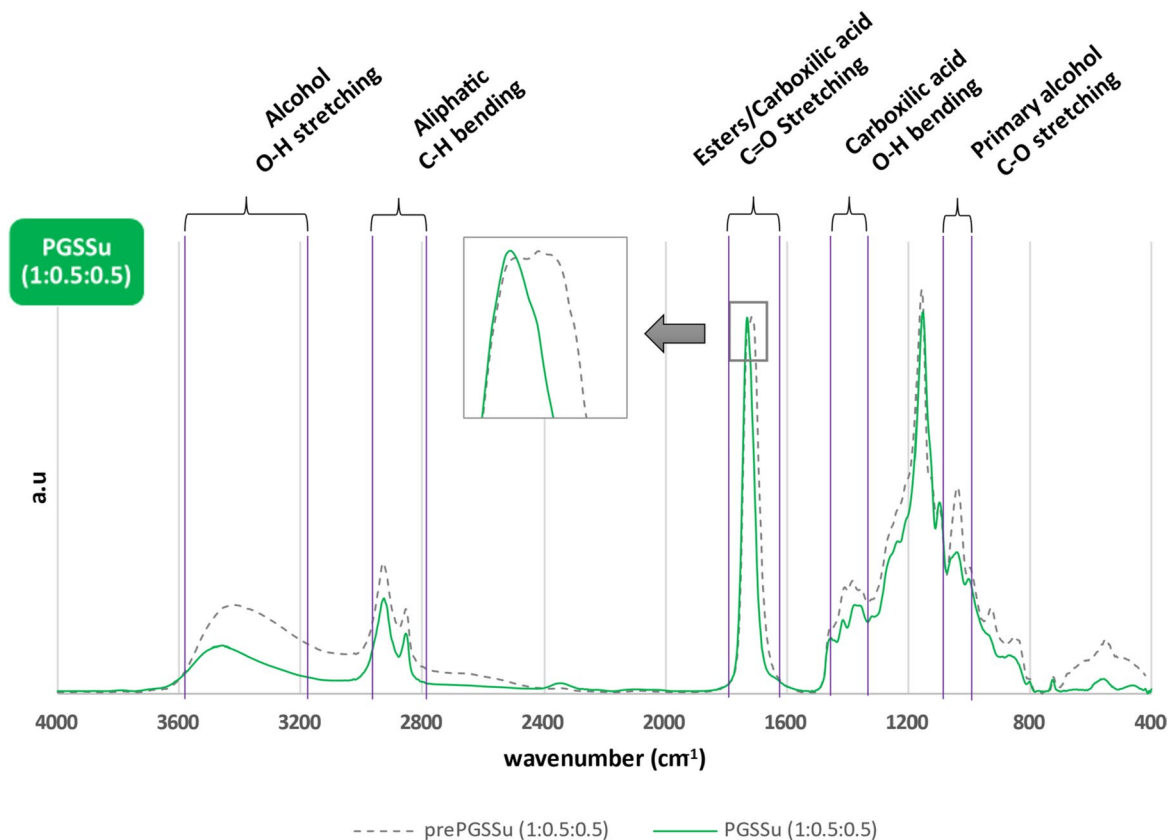


Fig. 4 FTIR spectra of prepolymer (dot line) and cured polymer (solid line) for PGSSu (1:0.5:0.5), as example (Color figure online)

These observations validate that the curing process involves the consumption of acid and hydroxyl groups to produce ester groups, as anticipated.

Lastly, the alkane groups (C–H) of the polymer backbone appear as two characteristic sharp peaks at 2855 cm^{-1} and 2927 cm^{-1} . A gradual decrease in these signals is observed with the substitution of sebacic acid by succinic acid, as expected, given that succinic acid is a smaller molecule and thus has fewer C–H bonds.

Morphology

Figure 5 shows the SEM images obtained of the surfaces of the seven synthesized polymers. The surface of PGS (1:1) has a smooth undulating appearance similar to that already reported by other authors [73]. The progressive replacement of sebacic acid by succinic acid has visible effects on the evolution of the surface appearance. Figure 5a and b clearly show that PGS (1:1) and PGSSu (1:0.9:0.1) have the smoothest surfaces, while PGSu (1:1) and PGSSu (1:0.1:0.9) (Fig. 5g and f) have the roughest and most irregular surfaces. This rougher appearance of the PGSu surface was also observed in Cai et al. [54].

The polymers with intermediate ratios, PGSSu (1:0.8:0.2), (1:0.5:0.5) and (1:0.2:0.8), have intermediate roughness. The increase in succinic acid in the synthesis of these polymers seems to contribute to an increase in their surface roughness. The surface appearance of each polymer confirms the tactile perception felt by us. PGS (1:1) is very soft and smooth, with little friction between the surface and the fingers, like glass. PGSu (1:1), on the contrary, provides better grip and offers a more rubber-like feel.

Some surfaces have small lumps, which is normal for this type of materials, and this observation has also been reported in previous works [20, 74, 75].

Thermal Analysis

The thermal stability evaluation of polymers using TGA is depicted in Fig. 6. Below $300\text{ }^{\circ}\text{C}$, all polymers exhibit relatively high stability, retaining over 95% of their initial weight. However, as the temperature surpasses $350\text{ }^{\circ}\text{C}$, differences in thermal stability among the polymers become apparent. Specifically, reducing the amount of sebacic acid and substituting it with succinic acid leads to a reduction in the thermal stability of the polymers.

Looking at where the weight cross 80% of their initial value, one can clearly see that PGS (1:1) is thermally more stable than PGSu (1:1), confirming what has been previously reported for each of these materials (PGS [10], PGSu [54]). The thermomechanical analysis carried out by Nagata et al. [33] also revealed that PGS has a slightly higher thermal resistance than PGSu. All other five tested ratios are perfectly in order among themselves, according to the respective amount of each diacid. Figure 7 shows correlation between the temperature recorded at 50% weight loss and the proportion of diacids used in the synthesis of the polymers ($R^2 = 0.9571$). Polymers synthesized with more succinic acid lost 50% of their mass at temperatures below $400\text{ }^{\circ}\text{C}$, while polymers synthesized with less succinic acid lost 50% of their mass at temperatures above $400\text{ }^{\circ}\text{C}$. PGSSu (1:0.5:0.5), synthesized with equal parts of both acids, is in the middle, losing 50% of its mass near $400\text{ }^{\circ}\text{C}$. Polymers containing lower amount of succinic acid are more resistant to temperature. These differences in thermal stability among

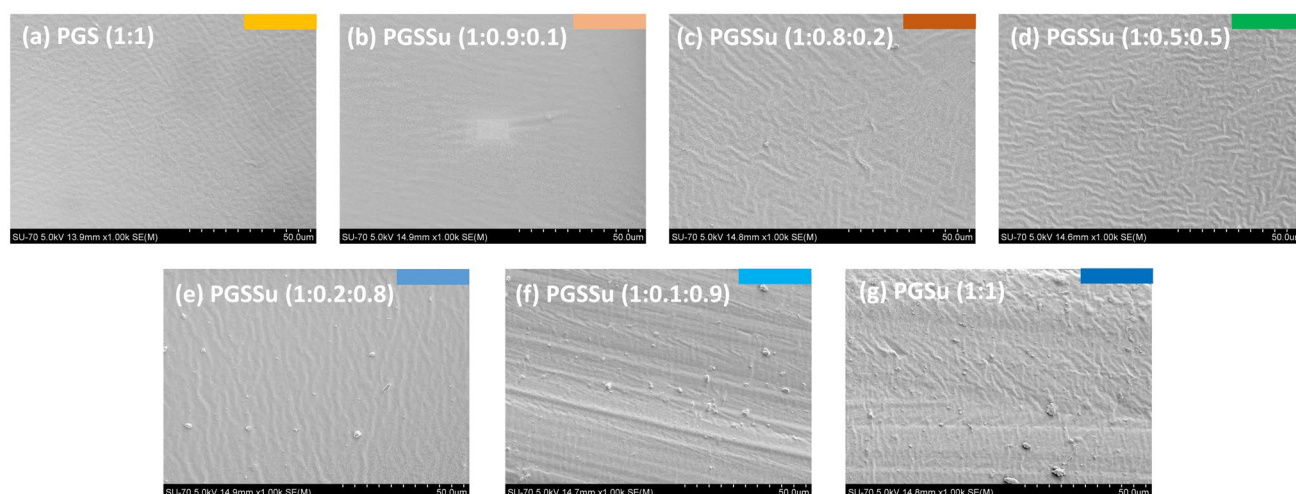


Fig. 5 SEM images (scale $50\text{ }\mu\text{m}$) of the polymers' surfaces: **a** PGS (1:1), **b** PGSSu (1:0.9:0.1), **c** PGSSu (1:0.8:0.2), **d** PGSSu (1:0.5:0.5), **e** PGSSu (1:0.2:0.8), **f** PGSSu (1:0.1:0.9) and **g** PGSu (1:1) (Color figure online)

Fig. 6 TGA thermograph of all seven polymers tested, with detail of the TGA analysis for the region 250–500 °C (Color figure online)

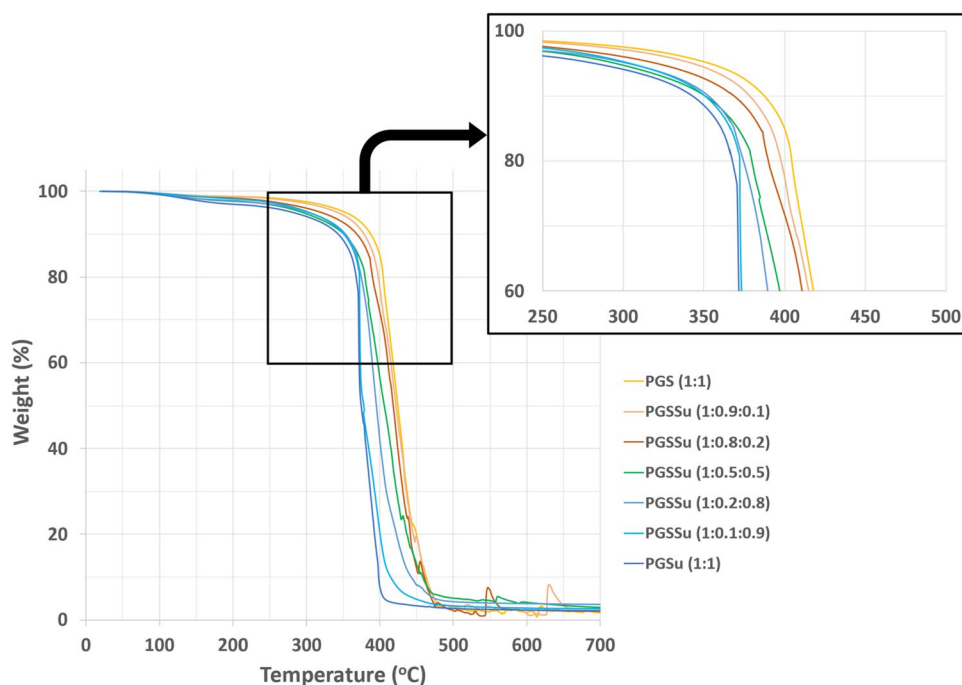
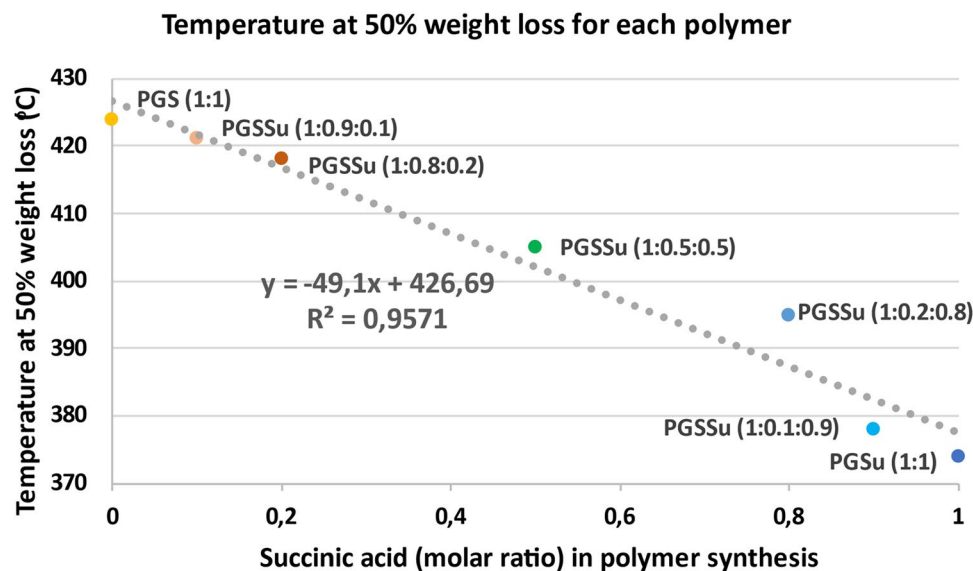


Fig. 7 Temperature at 50% weight loss for the seven polymers, collected from the TGA data and correlation between these temperatures and molar ratio of succinic acid in polymer synthesis (Color figure online)



the obtained polymers may be attributed to the thermal stability characteristics of the respective diacids. By consulting the physicochemical properties of each diacid, it can be seen that sebacic acid has a boiling temperature of around 365°C and a flash point of 220 °C [76]. Succinic acid has a boiling point of 235 °C (also degradation point) and a flash point of 160 °C [77]. These values show that sebacic acid is more thermally resistant than succinic acid, which helps to justify the differences in the thermal stability of the polymers analyzed.

It should be noted that slight variations in TGA results may arise across different studies due to variances in the

atmospheric conditions used during the analyses. The utilization of oxygen, air, or an inert atmosphere can influence the thermal stability outcomes for the same polymer. For instance, the PGSu produced in this study demonstrated a 90% weight loss at 400 °C under an air atmosphere, while in Cai et al. [54] the same PGSu exhibited a 90% weight loss after 450 °C under an inert atmosphere (nitrogen).

Dynamic Mechanical Analysis

The DMA results for all samples are presented in Fig. 8, aiming to investigate the mechanical performance and behavior

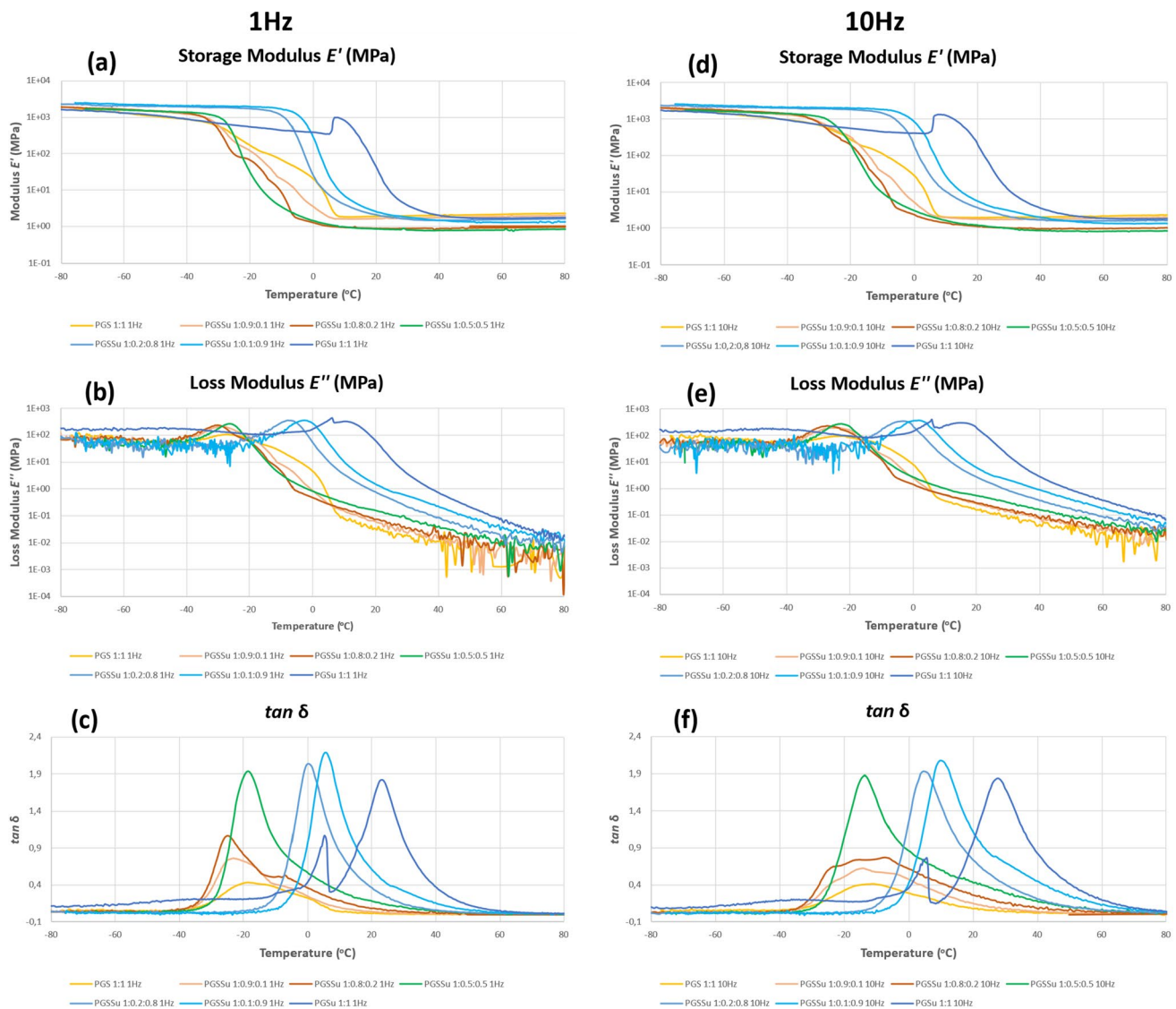


Fig. 8 DMA curves of the seven polymers synthesized: **a** Modulus/storage modulus E' , **b** Loss modulus E'' , **c** $\tan \delta$ at 1 Hz and **d** Modulus/storage modulus E' , **e** Loss modulus E'' , **f** $\tan \delta$ at 10 Hz (Color figure online)

of the synthesized polymers, including the glass transition temperature (T_g). After prepolymerization, the materials underwent the same curing process and were stored under identical conditions until analysis was conducted.

The storage modulus, as a function of temperature, was compared and shown in Fig. 8a and d for frequencies of 1 and 10 Hz, respectively. The loss modulus, in function of temperature, is presented in Fig. 8b and e for 1 and 10 Hz, respectively. The $\tan \delta$ factor represents the ratio, E''/E' , of the loss modulus (E'' , indicating hysteresis energy dissipation) over the storage modulus (E' , representing recoverable strain energy). Variations in peak temperature of $\tan \delta$ and in the slope of the storage modulus are related to T_g . Figure 8c and f show the graphs of $\tan \delta$ used to identify the T_g of the

polymers. T_g was measured by the highest peak value of the respective $\tan \delta$ curves, and these results are presented in Table 1.

T_g is the transition temperature from the glassy state to the rubber state of a polymer.

Based on the storage modulus curves, it is possible to identify a glassy region, in which all the polymers have a storage modulus close to 1000 MPa, a glass transition region, in which the storage modulus decreases significantly, and a rubber state region, in which all the polymers have a storage modulus close to 1 MPa.

Increasing the frequency from 1 to 10 Hz led to a shift in T_g at higher temperatures in all the samples. A higher frequency corresponds to shorter times for the response of

Table 1 Glass transition temperatures (T_g) and respective $\tan \delta$ values for the polymers tested by DMA at both frequencies (1 and 10 Hz)

Samples	T_g (°C) $\tan \delta$ (max at peak)		$\tan \delta$ value	
	1Hz	10Hz	1Hz	10Hz
PGS (1:1)	-18.5	-10.9	0.43	0.41
PGSSu (1:0.9:0.1)	-23.0	-14.4	0.77	0.62
PGSSu (1:0.8:0.2)	-24.8	-7.8	1.07	0.76
PGSSu (1:0.5:0.5)	-18.6	-13.3	1.94	1.87
PGSSu (1:0.2:0.8)	0.1	4.4	2.04	1.92
PGSSu (1:0.1:0.9)	5.8	10.3	2.19	2.07
T_g PGSu (1:1)*	23.3	27.5	1.83	1.84
*Previous transition	5.2	5.6	1.07	0.77

the materials to the deformation caused by the external force applied. Thus, at a higher frequency, the macromolecular polymer chains need more energy to relaxation process, which explains the observed difference in T_g [78].

Differences in T_g were also observed between the samples. Several factors may explain the differences observed. Previous work has already reported that PGS materials can have a semi-crystalline nature, especially when curing times are short and there is less cross-linking, which results in T_g variations [20, 21]. In addition to the degree of crystallization and cross-linking, the establishment of hydrogen bonds and other factors that may affect the mobility and organization of the polymer chains may explain the change in T_g , but also the damping capacity ($\tan \delta$ value) [21, 68].

For example, it is known that the longer methylene chain enhances the mobility of polymeric networks [53], which in general helps to explain the differences observed between the materials presented here with the variation in diacids. We can be observed that the polymers synthesized with more sebacic acid (longer methylene chain) have lower T_g , which indicates greater mobility and elasticity.

A more detailed analysis shows that PGS (1:1) exhibits a T_g within the previously reported range, close to -20 °C [16, 17, 20, 21, 79, 80]. Comparatively, PGSSu (1:0.9:0.1) and PGSSu (1:0.8:0.2) show a slight decrease in T_g due to the incorporation of succinic acid, rendering them softer than PGS (1:1). This may seem contradictory since longer methylene chains generally promote mobility. However, the substitution of sebacic acid with succinic acid (shorter methylene chain) in small amounts may result in a disorganized polymer structure, consequently allowing for increased freedom of movement. The different behavior of the $\tan \delta$ graphs at various frequencies for these polymers precisely indicates that the polymer network is not well-defined because the transition from glassy to rubbery state is wider and more irregular, especially at 10 Hz. This type of effect, in which irregular humps are observed in the transition zone of the $\tan \delta$ graph, has also been observed in samples less cross-linked, in reported work [20, 21]. This confirms that these

two polymers may indeed have a more disorganized and heterogeneous structure with several fractions with different melting points.

PGSSu (1:0.5:0.5), with equal molar parts of both acids, appears to have a more organized structure than the previous polymers. There is a well-defined T_g between -20 and 0 °C. Its T_g is like that observed for PGS, however, the $\tan \delta$ value is around four times higher in PGSSu (1:0.5:0.5) at both frequencies (Table 1), which indicates that the progressive introduction of succinic acid up to 50% led to an increase in damping capacity.

PGSSu (1:0.2:0.8) and PGSSu (1:0.1:0.9) were synthesized with a higher proportion of succinic acid and show a well-defined T_g . These polymers are less flexible than the previous ones as they consist mostly of short chains of succinic acid. The transition from a glassy to a rubbery state occurs at positive temperatures (Table 1), indicating reduced mobility of the polymeric structures. The difference in T_g between these two is justified by the amount of succinic acid used in their synthesis. A higher proportion of succinic acid leads to less mobility in the polymeric network, resulting in an increased T_g . Like PGSSu (1:0.5:0.5), these two polymers also show an increase in damping capacity.

PGSu (1:1), synthesized exclusively with succinic acid, exhibits the highest T_g among the polymers, indicating a less mobile polymer network. This observation is consistent with its higher density, resulting in reduced free volume within the network. Its T_g occurs near of room temperature (25 °C). Although Cai et al. [54], reported slightly higher values, it should be noted that they employed a longer curing period, leading to increased cross-linking and higher T_g . Wrzecionek et al. [66], on the other hand, utilized succinic anhydride instead of succinic acid for synthesizing PGSu and found that the T_g of this polymer structure ranged from -10 to 40 °C, depending on the reactant ratio. Higher T_g values were achieved with a greater proportion of succinic anhydride due to enhanced cross-linking. In their study, the 1:1 ratio resulted in a T_g range of $10-20$ °C, which is near our result. Considering that during the cure there is always some loss of glycerol (a problem already reported [11, 13, 72]), a T_g of 25 °C is in line with ratios where succinic anhydride is slightly higher than glycerol [66].

Apart from the T_g peak, our study observed a second $\tan \delta$ peak around 5 °C for both frequencies. Although this peak does not represent a true T_g since there is no significant shift between frequencies, its presence remains unexplained. An increase in modulus during temperature increase is not common, but can happen when cold penetration into the samples is insufficient, leading to a temperature inconsistency between the surface and the inside of the sample, as previously reported [20]. This justification is acceptable at an early stage of the temperature increase, but after such a long period of ascent, an increase in modulus at room temperature

does not seem plausible. Liang et al. [81] also reported a much smaller peak in $\tan \delta$, but in the PGS they synthesized, for which they couldn't find a cause either.

We note that this less pronounced peak in our PGSu (1:1) coincides with the temperature at which water reaches its maximum density (4 °C). The denser and more strongly cross-linked polymeric network of PGSu may have some water retained, which can establish hydrogen bonds with the polymeric network. When the water reaches its maximum density, the resulting decrease in volume can lead to the whole polymer becoming denser and harder, thus increasing the modulus momentarily. However, this is only a theoretical assumption to justify this unusual behavior.

Tensile Tests

Tensile tests were performed using dog-bone specimens of the seven produced polymers, as shown in Figure S2. The data obtained from these tests are compiled in Fig. 9. The stress-strain curves (Fig. 9d) were used to determine the ultimate tensile strength (UTS) (Fig. 9a), Young's modulus (Fig. 9b), and elongation at break (Fig. 9c). All tested polymers exhibited stress-strain curves typical of elastomers.

The highest UTS is observed for PGSu (1:1) with a value over 0.6 MPa, followed by PGS (1:1) with a value close to 0.5 MPa. The polymers synthesized with a diacid mixture have a lower UTS, which means that using sebacic acid and succinic acid combined, even in small percentages, results in polymers with lower strength.

PGS structure proves to be more sensitive to small compositional changes, when in comparison with PGSu structure. When sebacic acid was substituted with succinic acid at 10% and 20%, the UTS values significantly decreased for PGSSu (1:0.9:0.1) and PGSSu (1:0.8:0.2) in comparison to PGS (1:1). With each 10% replacement, the UTS value decreased by approximately 50% of the previous value. Among these polymers, PGSSu (1:0.8:0.2) exhibited the lowest UTS. The PGSu structure appeared to be more stable with sebacic acid incorporations, but even PGSSu (1:0.9:0.1) and PGSSu (1:0.2:0.8) showed a significant decrease in UTS value (around 35% when compared to PGSu (1:1)).

The Young's modulus, which represents the tensile stiffness of materials, was measured. Once again, PGSSu (1:0.8:0.2) displayed the lowest value (less than 0.2 MPa), followed by PGSSu (1:0.5:0.5) with 0.3 MPa. PGS (1:1), PGSu (1:1), and PGSSu (1:0.2:0.8) showed similar stiffness levels (around 0.8 MPa) considering the error bars. The stiffness values decreased significantly from PGSu (1:1) to PGSSu (1:0.1:0.9), with PGSSu (1:0.2:0.8) exhibiting a value close to that of PGSu (1:1). The observed variation in Young's modulus is not easily understood but remains consistent across multiple samples. This suggests that it may arise from a different organization of the polymer structure in these mixtures, which is not yet fully understood.

The elongation at break (%) provides valuable information about the material's ability to stretch from its initial length until failure occurs. As with UTS, PGS is more sensitive to small incorporations of another diacid than PGSu.

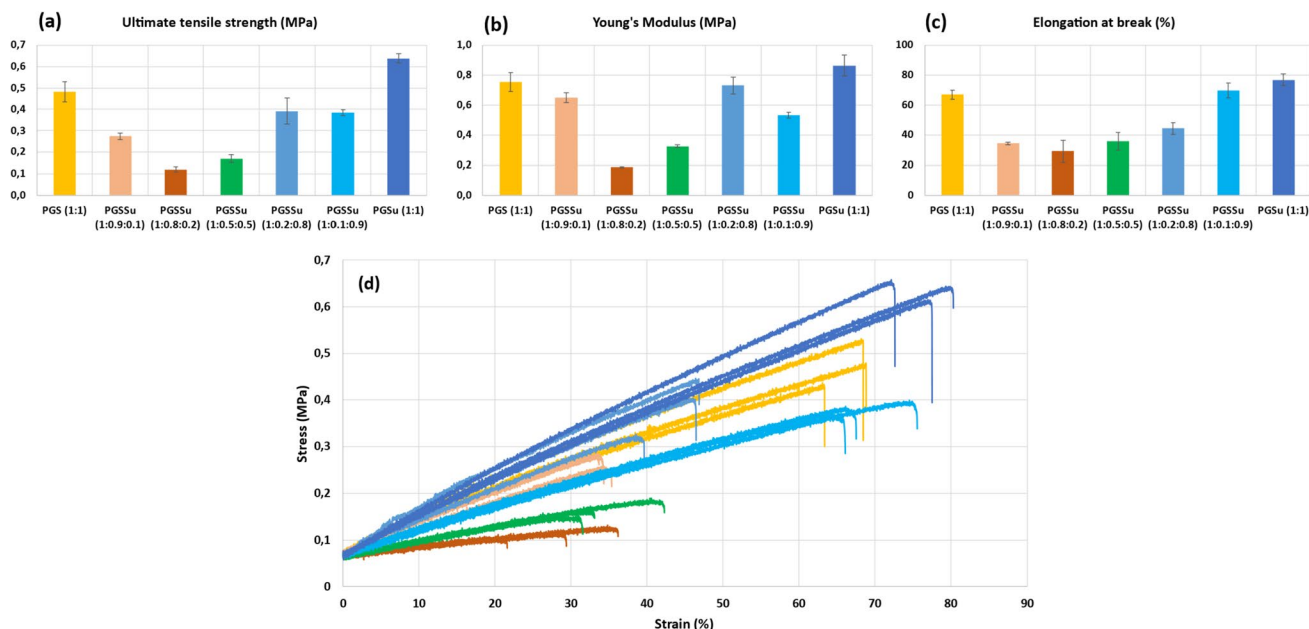


Fig. 9 **a** Ultimate tensile strength (MPa), **b** Young's Modulus (MPa), **c** Elongation at break (%) and **d** Stress-strain curves of the seven polymers tested. The error bars corresponding to the standard deviation

in **a**, **b** and **c** resulted from the data analysis of the three replicas of each polymer shown in **d** (Color figure online)

PGS (1:1) exhibits an elongation of 65%, whereas PGSSu (1:0.9:0.1) only achieves 35%. This substantial decrease in elongation is significant when compared to the difference between PGSu (1:1) and PGSSu (1:0.1:0.9), which is almost negligible considering the error bars. The elongation values for PGSSu (1:0.9:0.1), PGSSu (1:0.8:0.2), and PGSSu (1:0.5:0.5) range between 30% and 40%. PGSSu (1:0.2:0.8) exhibits an elongation of 45%, representing a significant reduction compared to the 70% and 75% values of PGSSu (1:0.1:0.9) and PGSu (1:1), respectively. This implies that a 20% replacement of succinic acid by sebacic acid already induces a significant change in the polymer's structure.

These results diverge from those demonstrated by Nagata et al. [33], when they progressively substituted sebacic acid with succinic acid in the polymers synthesis. Unlike our results, the replacement of sebacic acid with succinic acid resulted in an increase in the UTS and in the Young's modulus values, while the values for elongation did not change significantly, except for PGSu.

Overall, the results indicate that the mixture of diacids produces more brittle and softer polymers with reduced mechanical performance. This is likely due to the destabilization of the polymeric network caused by the incorporation of units with significantly different lengths. Sebacic acid has a linear chain of 10 carbons, while succinic acid has only 4 linear carbons. This difference of 6 carbons in length may be creating difficulties in the formation of a uniform and well-cross-linked polymeric network. Mixing acids is disadvantageous and contributes to the deterioration of mechanical properties. Considering all the analyzed parameters, it

is evident that PGS (1:1) and PGSu (1:1) exhibit superior mechanical capacity faced to polymers produced by diacid mixing.

Gel Fraction and Degree of Swelling (DS)

The degree of swelling (DS) and the gel fraction were obtained based on procedures previously carried out for this type of elastomers (PGS [13, 18, 23, 30] and PGSu [54]). These parameters provide insight into the behavior and robustness of the polymer network when subjected to interaction with solvents, and provide important information for the processing, formulation, and applicability of polymers.

Figure 10 shows the DS (%) obtained for each of the synthesized polymers, as well as the physical appearance of one of the respective replicas, after 72 h of immersion in THF. Figure 11 shows the gel fraction (%) obtained from each polymer (bottom) and the final appearance of the respective replicas after the 72-hour drying process (top). Before the immersion in THF and drying process, all the polymers look similar and are indistinguishable to the eye (Fig. S2), so one reference is enough to represent the initial appearance in Figs. 10 and 11.

PGS (1:1) and PGSSu (1:0.9:0.1) have a significantly higher DS than other polymers with DS 712% and 652% respectively. From PGSSu (1:0.9:0.1) to PGSSu (1:0.8:0.2) and other polymers, there is a significant decrease in swelling, which is also perceived visually (Fig. 10 top). PGSSu (1:0.8:0.2) has a DS of 311%, and as succinic acid replaces sebacic acid in the polymer formulation, there

Fig. 10 Degree of swelling (%) obtained for each polymer (bottom) with standard deviation as error bars, and the appearance of one of the respective replicas after 72 h of immersion in THF (top). The reference represents the initial appearance of the polymers (Color figure online)

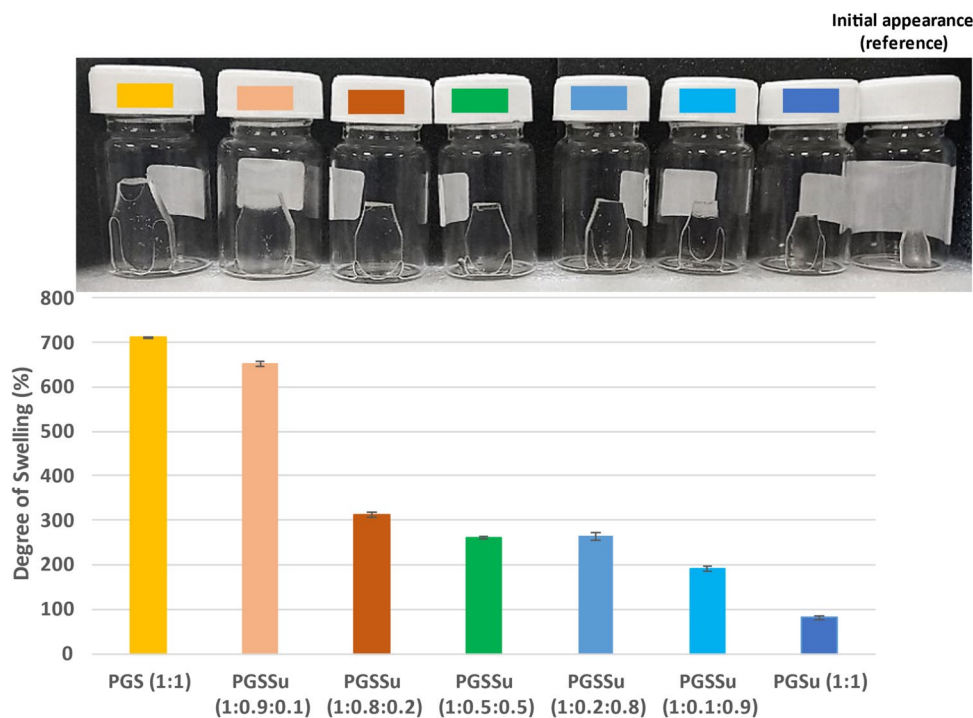
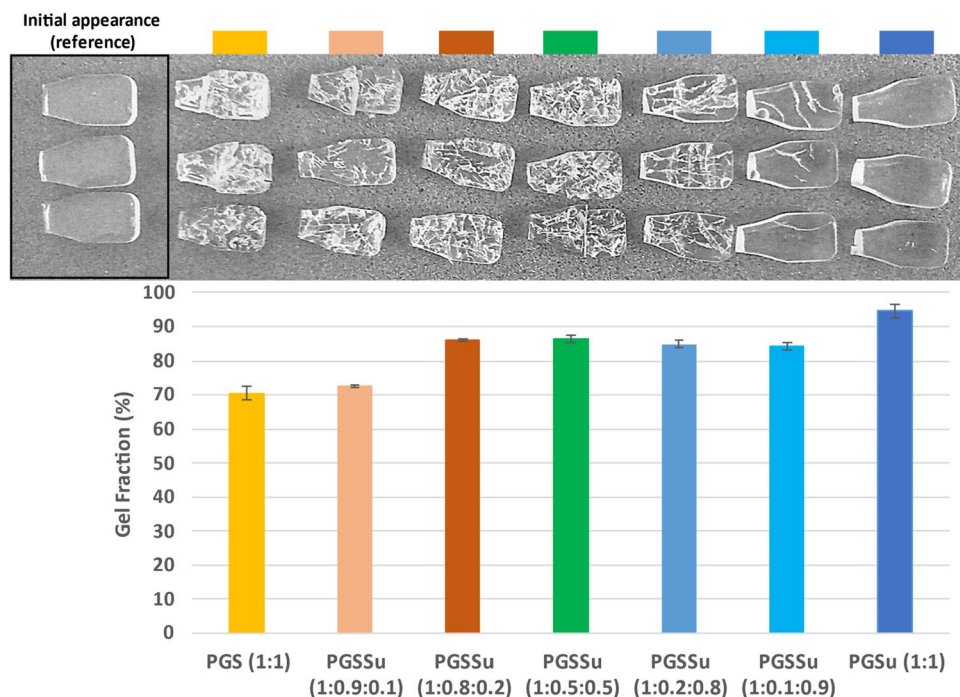


Fig. 11 Gel fraction (%) determined for each polymer (bottom) with standard deviation as error bars, and the appearance of the respective replicas after the 72-h drying process to remove THF (top). The reference represents the initial appearance of the polymers (Color figure online)



is a progressive reduction in swelling. PGSSu (1:0.5:0.5) and PGSSu (1:0.2:0.8) have a similar DS of 260%, PGSSu (1:0.1:0.9) has a DS of 191% and PGSu (1:1) has the lowest DS with 81%. When compared directly, PGS (1:1) and PGSu (1:1) behave very differently when it comes to incorporating and releasing the solvent. Although PGS (1:1) absorbs more solvent, it also releases it more easily. Although PGSu absorbs less solvent, it is more resistant to its release, requiring more drying time and an increase in temperature. The results indicate that replacing sebacic acid with succinic acid in the synthesis tends to produce polymers that are less permeable to THF.

PGS (1:1) and PGSSu (1:0.9:0.1) have the lowest gel fraction with approximately 72%. PGSSu (1:0.8:0.2), PGSSu (1:0.5:0.5), PGSSu (1:0.2:0.8) and PGSSu (1:0.1:0.9) have a gel fraction close to 85%. PGSu (1:1) is the most solvent-resistant and has a gel fraction of 95%.

The appearance of the samples after drying (Fig. 11 “top”), shows that PGSu (1:1) maintained a physical appearance very similar to the initial one. Although PGSSu (1:0.8:0.2), PGSSu (1:0.5:0.5), PGSSu (1:0.2:0.8) and PGSSu (1:0.1:0.9) have a similar gel fraction, their appearance after drying shows that the polymer structure becomes less robust as the succinic quantity in the synthesis decreases. PGSSu (1:0.1:0.9) has only a few internal fissures, but PGSSu (1:0.2:0.8) has clearly more damage. In the other polymers, with a gel fraction of $\approx 85\%$, the structural damage is greater, and external cracks can be seen. It is not possible to make a visual distinction between them. The polymers with a gel fraction close to 70% show

a lot of structural damage after drying. PGS (1:1) appearing to be slightly more damaged than the rest.

The results observed here largely corroborate what was observed in the mechanical tests. PGSu (1:1) is the most mechanically and structurally robust polymer. Polymers obtained by mixing acids progressively lose their physical and mechanical integrity, indicating structural disorganization. Although they have a similar gel fraction, this is apparently less interconnected when less succinic acid is used in the synthesis.

PGS (1:1) is an exception, as it has opposing results between mechanical performance and the solvent resistance of its polymeric network. PGS (1:1) is the lowest density polymer and its synthesis kinetics are the slowest, so it makes sense that it has the highest DS and the lowest gel fraction. This explains the greater susceptibility of the polymeric network to the solvent. However, in mechanical tests it has the 2nd best UTS and the 2nd best elasticity, along with PGSSu (1:0.1:0.9). This can be theoretically justified. PGS (1:1) produced with only one diacid has a homogeneous and molecularly equidistant structural assembly. Despite having the lowest gel fraction, non-covalent bonds (e.g. hydrogen bond and Van der Waals forces) may be favored in PGS (1:1) due to its spatial-molecular homogeneity. In this way, the soluble fraction can be well incorporated into the gel fraction and act as an efficient filler/plasticizer, allowing PGS (1:1) to have superior mechanical performance, despite being less cross-linked (lower gel fraction). This allows us to conclude that a higher gel fraction in these polymers with different

compositions may not be associated with better mechanical performances.

Conclusions

In the present work, seven elastomers were produced by different ratios of glycerol, sebacic acid and succinic acid: PGS (1:1), PGSSu (1:0.9:0.1), PGSSu (1:0.8:0.2), PGSSu (1:0.5:0.5), PGSSu (1:0.2:0.8), PGSSu (1:0.1:0.9) and PGSu (1:1). These polymers were synthesized without employing catalysts or solvents. It was possible to produce these colorless and perfectly transparent polyesters by controlling the atmosphere using N₂ flow in the prepolymerization step and vacuum in the cure step. The polymers' density is related to the amount of succinic acid used in the synthesis, with higher amounts of succinic acid yielding polymers of greater density. Incorporation of succinic acid results in rougher and more irregular polymer surfaces. Polymers synthesized with higher succinic acid content exhibit lower thermal resistance than those with a higher sebacic acid content. The T_g of these elastomers ranges from $-30\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$. Polymers synthesized with more succinic acid have positive T_g values, while those synthesized with more sebacic acid or equal amounts of diacids have negative T_g values. Mechanically, PGS (1:1) and PGSu (1:1) are more robust than the polymers produced by mixing diacids. A higher gel fraction may not be associated with better mechanical performance in this group of polymers. The swelling of polymers tends to be lower if more succinic acid is used in their synthesis, but it is not directly proportional. These findings expand our understanding of poly(glycerol-co-diacids) synthesis, particularly for PGSu, a topic that has not been extensively explored in existing research.

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Declarations

Competing Interests The authors declare no competing interests.

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