

A New Strategy to Characterize the Extent of Reaction of Thermoset Elastomers

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ABSTRACT: A new method for determining the extent of reaction of thermoset elastomers was developed based on equilibrium swelling and dynamic mechanical analysis (DMA). The extent of reaction was defined based on the molecular weight between crosslinks (M_c) of a polymer sample in relation to M_c at the onset of gelation and at complete reaction. The molecular weight between crosslinks was measured using equilibrium swelling, whereas rheology and DMA were used to determine the exact point of gelation and reaction completion, respectively. The extent of reaction of poly(1,8-octanediol-co-citrate) at various polymerization conditions was investigated and this method was used to study the relationship between mechanical properties, molecular weight between crosslinks, and extent of reaction. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 1318–1328, 2008

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INTRODUCTION

The worldwide use of biodegradable polymers has been steadily increasing each year with an estimated consumption of 68 million kilograms in 2001.¹ In particular, for the past 20 years the research and use of biodegradable polymers has increased as they have played a significant role in the improvement of health care and have had a positive impact on the environment.^{2–4} To date, polyesters make up the bulk of biodegradable polymers used in healthcare and the fabrication of environmentally “friendly” consumables.^{5–7} Although poly(α -hydroxyesters) have

been suitable to make traditional medical devices such as sutures and orthopedic fixation devices, new therapeutic modalities such as regenerative medicine have created a demand for new materials with a wide range of biodegradation and mechanical characteristics.^{8–13} In particular, the emerging field of tissue engineering often requires the use of temporary scaffolds to guide and promote tissue regeneration. The mechanical properties of the scaffold should be consistent with the target tissue to be replaced as several researchers have demonstrated the importance of substrate mechanical properties on cellular processes.^{14–18} In the case of tissue that displays elasticity such as that found in blood vessels, heart, skin, and lung, the use of elastomeric scaffolds is warranted.¹⁹

Toward that end, we have developed a new family of biodegradable elastomers based on citric acid, a natural metabolite of the body.^{20–23} When reacted with a diol, a network of polyester

J. Yang's contribution to the work was performed while he was a post-doctoral associate at Northwestern University.

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crosslinks is generated, resulting in a thermoset elastomer. The elastomer, generally referred to as poly(diols citrate), has been shown to be biocompatible with several tissues *in vivo* and can support the adhesion, proliferation, and differentiation of many cell types.^{20–23} The synthesis conditions for the prepolymer are simple and do not involve exogenous catalysts. Furthermore, the prepolymer can be processed into a variety of shapes with defined microarchitectures that are useful for tissue engineering scaffolds.^{20,21} However, for crosslinked thermoset elastomers such as poly(diols citrates), the degree of postpolymerization and resulting mechanical properties can be affected by the geometry and dimensions of the sample. Therefore, reporting mechanical properties based on the time and temperature of polymerization may not be appropriate. An improved method would be to report mechanical properties along with an extent of reaction. Although the extent of reaction for crosslinked thermoset elastomers can be estimated from Fourier transform infrared (FTIR) spectra, this method is unreliable for large polymer samples or samples with complex geometries such as tissue engineering scaffolds. Furthermore, although near infrared (NIR) spectroscopy has been used to monitor conversion in larger polymer samples, we chose not to use this method due to the added complexity in identifying overlapping hydroxyl, carboxyl, and water peaks present within a narrow spectrum. Herein, we present a new method by which the extent of reaction can be calculated based on equilibrium swelling and dynamic mechanical analysis (DMA). We use this new method to calculate the extent of reaction of poly(1,8-octanediol-co-citrate) (POC) and examine the relationship between tensile mechanical properties, molecular weight between crosslinks, and extent of reaction.

EXPERIMENTAL

Synthesis of Poly(diols citrate) Prepolymer

All chemicals were purchased from Sigma-Aldrich (Milwaukee, WI). POC was used for all experiments. Equimolar amounts of citric acid and 1,8-octanediol were added to a 250-mL three-neck round-bottom flask, fitted with an inlet and outlet adapter. The mixture was melted under a flow of nitrogen gas by magnetic stirring at 160–165 °C in a silicon oil bath and

then the temperature of the system was lowered to 140 °C. The mixture was stirred for another 30 min at 140 °C to create a prepolymer. Following this, the prepolymer was purified to remove unreacted monomers by dissolution in ethanol and precipitation in water. The purification process was repeated twice and prepolymer collected, freeze-dried, and dissolved in ethanol to a concentration of 30% (w/v). For crosslinked films, the prepolymer was poured into a glass Petri dish and the ethanol evaporated in a fume hood. The polymers were cast to a thickness of ~1.5 mm and postpolymerized at either 80 °C without vacuum for 2–7 days or 80 °C without vacuum for 2 days followed by 120 °C under high vacuum (2 Pa) for 1–6 days.

Determination of Molecular Weight Between Crosslinks and the Polymer/Solvent Interaction Parameter via Equilibrium Swelling

The number-average molecular weight between crosslinks, which describes the average molecular weight of polymer chains between two consecutive crosslinks, and Flory–Huggins polymer/solvent interaction parameter were determined by equilibrium swelling in solvent.^{24–26} Thermodynamically, the swelling behavior of a polymer is governed by the additive effect of the chemical potential of mixing and the chemical potential of elasticity. When placed in a solvent, the liquid diffuses into the network driven by the difference of the chemical potential of solvent between the network inside and outside. Finally, the swollen polymer reaches the equilibrium state in which the elastic contributions to the overall chemical potential balance the chemical potential of polymer/solvent mixing. Therefore, at equilibrium the following equation holds true:

$$\Delta\mu_{\text{mix}} + \Delta\mu_{\text{el}} = 0 \quad (1)$$

The mixing term can be expressed using the Flory–Huggins polymer/solvent interaction equation where R is the equilibrium gas constant, T is the temperature, v_{2m} is the volume fraction of polymer at equilibrium swelling, and χ is the dimensionless Flory–Huggins polymer/solvent interaction parameter.^{27–30}

$$\Delta\mu_{\text{mix}} = RT [\ln(1 - v_{2m}) + v_{2m} + \chi v_{2m}^2] \quad (2)$$

The elastic contribution to the overall chemical potential is defined by the James and Guth

phantom network model using eq 3.^{31,32} In the phantom network model, polymer chains are assumed to have a Gaussian distribution with the ends of the network chains attached to each other at crosslinks with some of these junctions at the surface of a nonfluctuating elastic medium and others in space, free to fluctuate over time.^{31–36} The junctions that are attached to the surface transmit the macroscopic deformations to the bulk of the network chains that are freely fluctuating in space. With the phantom network model, the crosslinks not directly attached to the surface can fluctuate freely and are unaffected by macroscopic deformation. However, in real networks, crosslinking and entanglements with other chains can affect chain fluctuations. Despite this limitation, the phantom network model was chosen because in the highly swollen state, it has been shown that real network exhibits properties closer to those of the phantom network model than other constrained junction theories.^{24,26,37,38}

$$\Delta\mu_{\text{el}} = RT \left[\frac{(1 - (2/\phi))V_1\rho v_{2c}^{2/3} v_{2m}^{1/3}}{M_c} \right] \quad (3)$$

In the above equation, ϕ is the average functionality of the network, V_1 is the molar volume of solvent, ρ is the polymer density, v_{2c} is the volume fraction of polymer present during network formation, and M_c is the molecular weight between crosslinks. Combining eqs 1, 2, and 3 gives

$$\ln(1 - v_{2m}) + v_{2m} + \chi v_{2m}^2 + \frac{(1 - (2/\phi))V_1\rho v_{2c}^{-1/3} v_{2m}^{1/3}}{M_c} = 0 \quad (4)$$

The above equation can be rearranged into a linear form $y = mx + b$, where

$$y = - \left[\frac{\ln(1 - v_{2m})}{v_{2m}^2} + \frac{1}{v_{2m}} \right] \quad (5)$$

$$m = \frac{1}{\text{Abs}(M_c)} \quad (6)$$

$$x = \left(1 - \frac{2}{\phi} \right) V_1 \rho v_{2c}^{-1/3} v_{2m}^{-5/3} \quad (7)$$

$$b = \chi \quad (8)$$

Using the linear form of eq 4, both the molecular weight between crosslinks and χ can be determined by measuring the volume fraction of polymer samples at equilibrium swelling (v_{2m}) and plotting the data to determine the slope and intercept. The volume fraction of polymer at equilibrium swelling was determined using the following equations:

$$v_{2m} = \left[1 + \frac{(q_w - 1)\rho_{\text{polymer}}}{\rho_{\text{solvent}}} \right]^{-1} \quad (9)$$

$$q_w = \frac{\text{mass of polymer at equilibrium swelling}}{\text{mass of polymer before swelling}} \quad (10)$$

In the above equations, the density of the polymer was measured using a Mettler-Toledo AX205 analytical balance with a density determination kit (Mettler-Toledo, Columbus, OH). Polymer samples were then accurately weighed and swollen in dimethyl sulfoxide (DMSO) at room temperature. Samples were blotted dry and weighed every 24 h for 2 days to ensure equilibrium swelling was reached.

Rheological Determination of the Gel Point

A network polymer at the gel point is in a transition state between liquid and solid. At this point, it has been shown that the relaxation behavior of a crosslinked network polymer follows a power law,^{39–42}

$$G(t) = St^{-n}; \quad p = p_c \quad (11)$$

where S is the gel strength, t is time, n is the relaxation exponent ($0 < n < 1$), and p is the extent of reaction. The frequency (ω) dependence of the dynamic moduli (G' and G'') can be calculated using:

$$G'(\omega) = \Gamma(1 - n) \cos\left(\frac{n\pi}{2}\right) S\omega^n \quad (12)$$

$$G''(\omega) = \Gamma(1 - n) \sin\left(\frac{n\pi}{2}\right) S\omega^n \quad (13)$$

$$G' \sim G'' \sim \omega^n \quad (14)$$

From the above equations, it can be seen that the storage (G') and loss moduli (G'') depend on frequency in an identical manner and as such are parallel in a log–log plot versus frequency. In addition, the loss tangent ($\tan \delta$) becomes independent of the frequency at the gel point.

$$\tan(\delta) = \frac{G''}{G'} = \tan\left(\frac{n\pi}{2}\right) \quad (15)$$

The gel point of poly(diols citrate) prepolymer was determined using a TA Instruments ARES rheometer (TA Instruments, New Castle, DE). POC prepolymer in ethanol was cast to a thickness of ~ 0.5 mm onto 25-mm stainless steel plates and the solvent allowed to evaporate in a fume hood. The plates were then polymerized at 120 °C without vacuum for times ranging from 30 to 150 min and then cooled to room temperature prior to testing. The plate was then covered with a second uncoated plate, loaded into the rheometer, and a dynamic frequency sweep performed at 8% strain and frequencies ranging from 1 to 100 rad/s. Polymers at the gel point were removed from the rheometer and the molecular weight between crosslinks measured using equilibrium swelling as described earlier. The gel point was defined as 0% extent of reaction.

Determination of Reaction Completion Using DMA

POC samples were cast into a flat sheet and polymerized as described earlier. Solid specimens were cut into thin strips (2 mm wide \times 38 mm long) and DMA data recorded on a MTS 831.21 Elastomer Test System (MTS, Eden Prairie, MN) operated at room temperature in tension with a strain amplitude of 5% and frequencies ranging from 1 to 15 Hz (6.28–94.25 rad/s). From these tests the complex dynamic modulus (E^*) was determined. The reaction was determined to be complete when the complex modulus no longer varied with frequency and the molecular weight measured as described earlier. The reaction completion point was defined as 100% extent of reaction.

Determination of the Extent of Reaction

The extent of reaction was defined based on the molecular weight between crosslinks as measured by equilibrium swelling in DMSO. The following equation was used where M_c is the measured

molecular weight between crosslinks, $M_{c,0}$ is the measured molecular weight between crosslinks at the onset of gel formation, and $M_{c,100}$ is the measured molecular weight between crosslinks at complete reaction:

$$p = \frac{M_{c,0} - M_c}{M_{c,0} - M_{c,100}} \quad (16)$$

Characterization of the Mechanical Properties

Tensile tests were conducted according to ASTM D 412a on an Instron 5544 mechanical tester equipped with 500-N load cell (Instron, Canton, MA). The specimen size recommended in ASTM D 412a was modified to conserve the amount of polymer that was needed to fabricate the samples. Briefly, dog-bone-shaped samples (26 mm \times 4 mm \times 1.5 mm, length \times width \times thickness) were pulled at a rate of 500 mm/min until failure. From these tests, the ultimate tensile strength and Young's modulus were recorded.

Statistical Methods

Data are expressed as mean \pm standard deviation with $n = 6$ for mechanical testing. Swelling experiments were performed in triplicate with a total of six samples used per experiment. The statistical significance between two sets of data was calculated using two-tail Student's t -test. Analysis of variance and *post hoc* analysis using the Tukey test was used to determine significant differences among three or more means. Data were taken to be significant, when a p -value of 0.05 or less was obtained.

RESULTS AND DISCUSSION

Poly(diols citrates) are synthesized through the polycondensation of citric acid and a linear aliphatic diol (Fig. 1). For the reaction to proceed, water molecules produced during the formation of ester bonds must be removed. The rate of this reaction can be increased through application of vacuum or by increasing the polymerization temperature. However, the geometry and dimensions of the sample can affect the rate of water removal. For example, a thin poly(diols citrate) prepolymer film cast into a Petri dish will polymerize faster than a thicker one cast into an identical Petri dish. This difference is not only

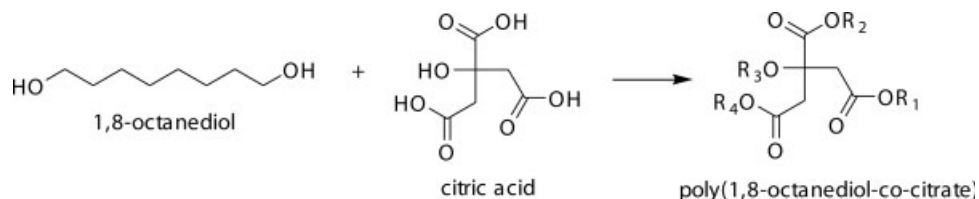


Figure 1. Poly(diols citrate) reaction scheme. R_1 , R_2 , R_3 , and R_4 can be citric acid, 1,8-octanediol, or another polymer chain.

due to the greater volume of water that must be removed from a larger volume of prepolymer, but also due to the increased distance that water molecules must travel through the polymer to escape from the bottom of the Petri dish to the surface. Likewise, for prepolymer cast into molds to form complex shapes or tissue engineering scaffolds, the reaction rate may be different than that of a flat film. Therefore, polymerizing a complex tissue engineering scaffold with the same polymerization conditions as a flat film used for tensile testing may yield vastly different properties. For that reason, defining crosslinked thermoset elastomer properties based only on polymerization conditions may not be appropriate.

An alternative method by which the mechanical properties of poly(diols citrates) and other crosslinked thermoset elastomers can be categorized is to define an extent of reaction. The extent of reaction can be determined by monitoring FTIR spectra as the reaction proceeds.^{43–45} For instance, in the case of a condensation polymerization, a hydroxyl group and a carboxyl group react to form an ester bond. As the reaction proceeds, the absorption intensity of the hydroxyl signal at 3460 cm^{-1} decreases while the intensity of the methylene signals at 2960 cm^{-1} remain unchanged. As a result, the change in absorption intensity ratio of the hydroxyl to methylene groups could be used to estimate the extent of reaction.^{43–45}

Unfortunately, because this method requires the use of very thin sections of polymer to obtain FTIR spectra, it is best suited for polymers that can be cast into thin films and FTIR spectra taken through the full thickness specimen.^{43–45} Although poly(diols citrates) can easily be cast into thin films, the mechanical properties at identical polymerization conditions would be vastly different than that of thick films for tensile testing or tissue engineering scaffolds. In addition, for these samples the use of FTIR spectra to monitor the extent of reaction may not be applicable due to the difficulty in obtaining thin

sections. Furthermore, we have also found this method to be unreliable due to gradients in the extent of polymerization throughout thick polymers caused by temperature gradients during polymerization or difficulty in removing water from complex geometries.

To overcome the limitations of FTIR spectroscopy, NIR spectroscopy can be used to monitor the conversion of thick polymer samples.^{46,47} NIR is beneficial because it requires little or no sample preparation and can penetrate much deeper into samples than infrared or visible light.⁴⁸ Although hydroxyl groups produce measurable bands in the NIR region and can potentially be used to monitor the extent of reaction, the spectra can become very convoluted with hydrogen bonding, carboxylic acid groups, alcohols, multiple $-\text{OH}$ compounds, and water, all appearing within a similar range.⁴⁹ In addition, sample preparation, branching, and end groups may affect the spectra.⁵⁰ Although these limitations can be overcome by using multivariate calibration algorithms and statistical methods,^{51,52} we chose not to use this technique due to the added complexity in discerning overlapping bands. Therefore we sought to define a new method by which an extent of reaction can be calculated based on equilibrium swelling and DMA. We sought to use this new method to report the mechanical properties of POC.

Determination of Molecular Weight Between Crosslinks and the Polymer/Solvent Interaction Parameter via Equilibrium Swelling

To determine the molecular weight between crosslinks of poly(diols citrates), equilibrium swelling in DMSO was used. DMSO was selected as the swelling agent, also referred to as solvent, to minimize the amount of solvent evaporation and deswelling during polymer measurements. Using eq 4, polymer swelling data were plotted and the molecular weight between crosslinks and polymer/solvent interaction

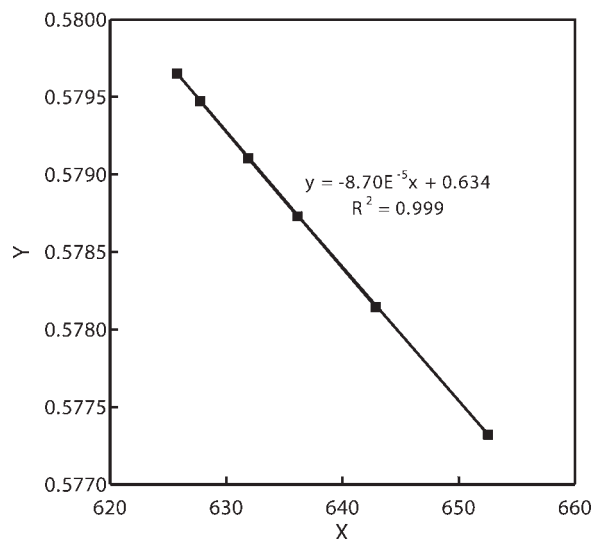


Figure 2. Typical equilibrium swelling data plot used to calculate molecular weight between crosslinks (M_c) and polymer/solvent interaction parameter (χ). Y and X are calculated using eqs 5 and 7, respectively. Each point represents a single swelling measurement.

parameter determined from the slope and intercept, respectively (Fig. 2). As noted earlier, the M_c values were calculated using the phantom network model of rubber elasticity. It is important to note that this model neglects many aspects of nonideal network formation such as chain entanglement, dangling ends, and cyclization. However, in the highly swollen state, real networks exhibit properties closer to the phantom network model than other constrained junction models.^{24,26,37,38} With increasing polymerization, the molecular weight between crosslinks decreases while the Flory/Huggins polymer/sol-

Table 1. Molecular Weight Between Crosslinks and Polymer–Solvent Interaction Parameter for POC Swelling in DMSO

Polymerization Condition*	M_c (g/mol)	χ
80-2	14,000 ± 300	0.622 ± 0.007
80-3	11,600 ± 100	0.634 ± 0.003
80-5	9700 ± 200	0.642 ± 0.001
80-7	8400 ± 300	0.651 ± 0.002
120-1	5500 ± 600	0.689 ± 0.009
120-2	4000 ± 100	0.709 ± 0.010
120-4	3400 ± 200	0.717 ± 0.005
120-6	1100 ± 400	0.866 ± 0.042

*80-X = polymerized at 80 °C for X days without vacuum, 120-X = polymerized at 80 °C for 2 days without vacuum followed by 120 °C for X days with vacuum.

vent interaction parameter increases (Table 1). The decrease in M_c was expected as increased polymerization should lead to greater ester bond formation between copolymer chains and branches. The polymer/solvent interaction parameter values are consistent with DMSO being a swelling agent for POC.⁵³ In addition, the values are similar to that of crosslinked natural rubber in various solvents and also show a similar increase with crosslinking.⁵⁴

Rheological Determination of Gel Point

Poly(diols citrates) were coated on 25-mm stainless steel plates and polymerized outside the rheometer prior to sandwiching between a second parallel plate and measurement.^{55–57} This was done to ensure that the polymerized materials were homogenous throughout. It was found that sandwiching the prepolymer between parallel plates and performing the polymerization during rheology yielded a material that was more polymerized on the perimeter of the plate where water molecules could more easily escape.

As shown in Figure 3, the viscous behavior of the oligomeric prepolymer dominates at early polymerization times with the loss modulus (G'') being significantly larger than the storage modulus (G'). As polymerization proceeds, the molecular weight and the loss modulus increase while the storage modulus rises sharply until it intersects and eventually exceeds the loss modulus. This behavior is typical of viscoelastic materials

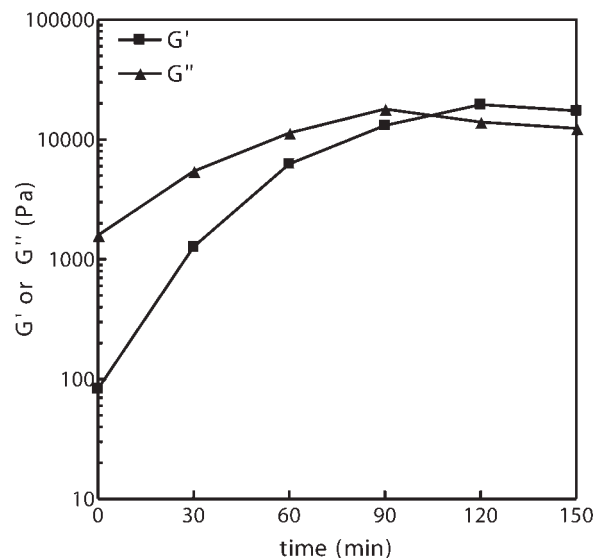


Figure 3. Storage (G') (squares) and loss (G'') (triangles) modulus of poly(1,8-octanediol-co-citrate) as a function of polymerization time and a frequency of 1 rad/s.

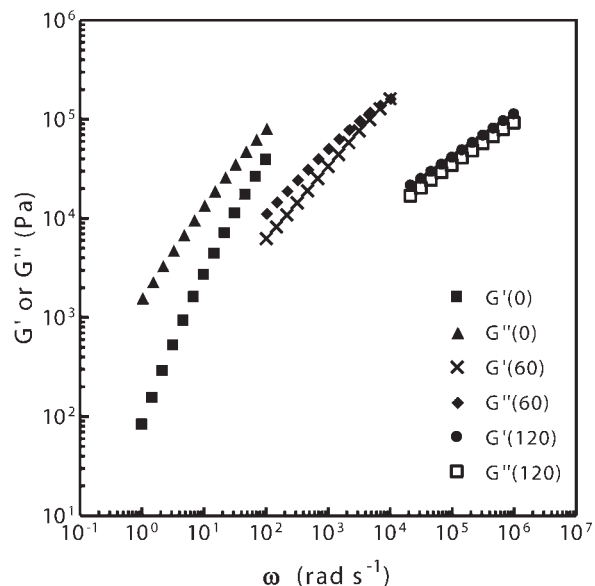


Figure 4. Storage (G') and loss (G'') moduli of poly(1,8-octanediol-co-citrate) as a function of frequency (1–100 rad/s) and times of 0, 60, and 120 min of polymerization at 120 °C without vacuum. For clarity, the 60 and 120 min curves are shifted right by 10^2 and 10^4 rad/s, respectively.

that undergo gelation.⁴¹ The intersection between G' and G'' coincides with the gel point for stoichiometrically balanced networks and yields a relaxation exponent (n) of 0.5.⁵⁸ For networks with an imbalance in crosslinker monomers, n can be greater or less than 0.5. A relaxation exponent greater than 0.5 indicates a deficiency of crosslinker molecules. In this case, gelation would occur before the crossover point.⁵⁸ Likewise, $n < 0.5$ indicates an excess of crosslinker and gelation would occur after the crossover point.⁵⁸

The exact point of gelation, regardless of stoichiometric ratio, occurs at the instance that the storage modulus and loss modulus have the same slope (Winter criterion).⁵⁸ For POC, this occurred after 120 min of polymerization (Fig. 4) and the relaxation exponents (n) given by the slope of G' and G'' are 0.455 and 0.457, respectively. These values are consistent with the gel point occurring after the G' – G'' crossover (Figs. 3 and 4). It should be noted that although an equimolar ratio of citric acid and linear aliphatic diol was used in the polymerization and should yield a stoichiometric balance of carboxyl to hydroxyl groups, the value of the relaxation exponent indicates an excess of crosslinker. This could be caused by steric hindrance making it

difficult or impossible for the hydroxyl group of one citric acid molecule to react with the carboxyl groups of other citric acid molecules.⁵⁹ This leads to an excess ratio of citric acid carboxyl groups to diol hydroxyl groups and could cause a value of $n < 0.5$.

The gel point can also be estimated from curves of $\tan \delta$ versus time with each curve corresponding to a different frequency. The curves intersect at the point at which the loss tangent becomes independent of frequency and corresponds to the gel point. As shown in Figure 5, at 120 min of polymerization, the loss tangent is the same over a wide range of frequencies. The value of n at this point calculated using eq 15 is 0.453. This value is similar to that obtained from the slopes of G' and G'' and confirms that the gel point was reached, and that the Winter criterion is applicable for our system. After determining the gel point, the polymer was scraped from the parallel plates and swollen in DMSO to measure the molecular weight between crosslinks. The gel point was defined as 0% extent of reaction and the measured molecular weight between crosslinks was $\sim 135,000 \pm 10,000$ g/mol.

Determination of Reaction Completion Using DMA

Fully crosslinked samples were prepared from the same prepolymer used to determine the gel point by polymerizing at high temperature

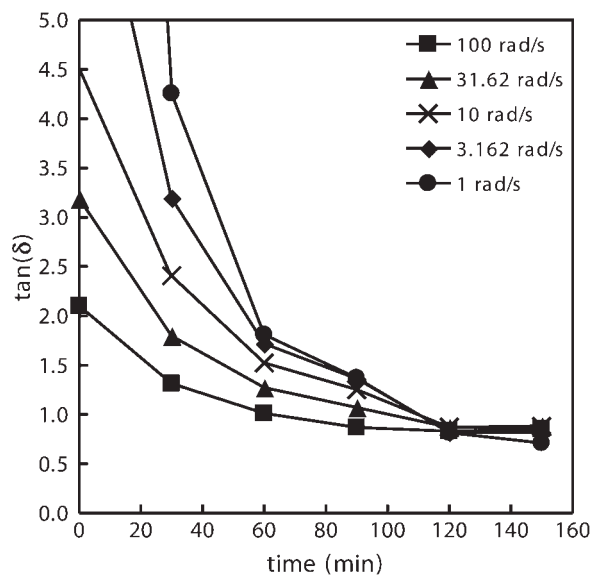


Figure 5. Loss tangent of poly(1,8-octanediol-co-citrate) as a function of polymerization time at 120 °C without vacuum. Each curve corresponds to a different frequency.

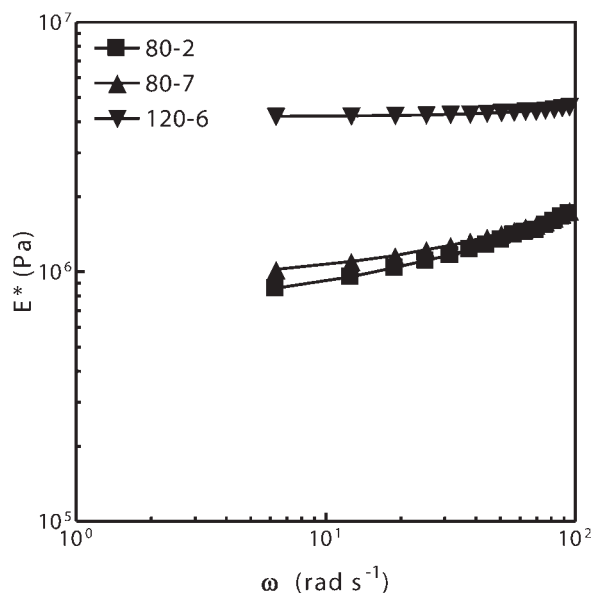


Figure 6. Dynamic complex modulus of poly(1,8-octanediol-*co*-citrate) versus frequency. 80-2 = polymerized at 80 °C for 2 days without vacuum; 80-7 = polymerized at 80 °C for 7 days without vacuum; 120-6 = polymerized at 80 °C for 2 days without vacuum + 120 °C for 6 days under high vacuum.

under high vacuum for several days. Like other rheological experiments, complete crosslinking was defined as the point at which the dynamic moduli no longer change over a wide range of frequency.^{60,61} However, because the polymerization could not be performed in the rheometer due to the inability to obtain a homogenous material, the dynamic mechanical properties of polymerized solid materials were analyzed using DMA. As seen in Figure 6, at early polymerization times the complex modulus increases with increasing frequency. However, after polymerizing at 120 °C for 6 days under high vacuum (2

Pa), the complex dynamic modulus no longer changes with frequency. This point was defined as 100% extent of reaction and the molecular weight between crosslinks measured as described earlier. At this point, the measured molecular weight between crosslinks was 1100 ± 400 g/mol.

Determination of Extent of Reaction and Mechanical Properties

The extent of reaction of polymerized POC sheets was determined using the measured molecular weight between crosslinks and eq 16. Although the method of determining the extent of reaction was only used for POC, it should be applicable to other thermoset elastomer systems in which the FTIR method may not be appropriate.⁶² Once the molecular weight at the gel point and at complete reaction are known, the extent of reaction of polymer samples can be determined with a simple and nondestructive swelling measurement. Furthermore, because the extent of reaction was calculated using equilibrium swelling data from a bulk piece of polymer, it should eliminate the variability in monitoring the extent of reaction of large samples with FTIR spectra from thin sections of polymer. In addition, unlike sectioning of polymer samples for FTIR, the swelling method is nondestructive because the polymer can easily be swollen in solvents that do not hydrolyze the polymer bonds and deswollen prior to use. Using this new method, the relationship between molecular weight between crosslinks, extent of reaction, and tensile mechanical properties can be examined.

The ultimate tensile strength, Young's modulus, and extent of reaction for POC are summarized in Table 2. Thermal properties were not

Table 2. Extent of Reaction and Mechanical Properties of POC

Polymerization Condition*	Extent of Reaction (%)	Tensile Strength (MPa)	Young's Modulus (MPa)
80-2	90.4 ± 0.7	1.64 ± 0.07	1.48 ± 0.08
80-3	92.2 ± 0.6	1.51 ± 0.08	1.59 ± 0.13
80-5	93.6 ± 0.5	1.77 ± 0.19	1.74 ± 0.13
80-7	94.6 ± 0.4	2.31 ± 0.16	2.20 ± 0.05
120-1	96.8 ± 0.2	1.73 ± 0.11	2.45 ± 0.14
120-2	97.8 ± 0.2	2.13 ± 0.15	2.52 ± 0.19
120-4	98.3 ± 0.1	3.37 ± 0.12	3.04 ± 0.15

*80-X = polymerized at 80 °C for X days without vacuum, 120-X = polymerized at 80 °C for 2 days without vacuum followed by 120 °C for X days with vacuum.

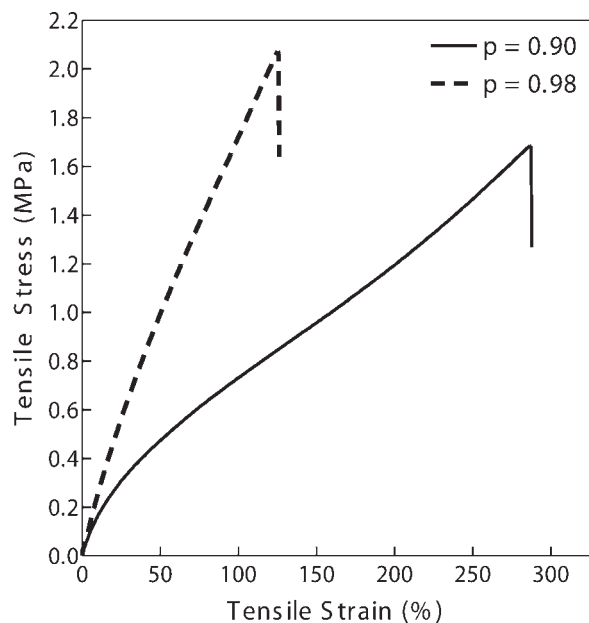


Figure 7. Typical stress–strain curves of POC at low (90%) and high extents (98%) of reaction.

examined as they have been previously reported.^{20,21} The extent of reaction ranged from 90 to 98% for the polymers tested. Polymers below 90% extent of reaction were sticky and difficult to test mechanically and thus were not used in this study. Tensile tests produced stress–strain curves characteristic of elastomeric materials with a low initial modulus and high strain at failure (Fig. 7). In addition, no permanent deformation was found during tensile me-

chanical tests despite elongations at break of up to 300%. In general, with increasing extents of reaction, the mechanical properties increased. There is a significant difference ($p < 0.05$ for 90% versus 98% extent of reaction) between low and high extents of reaction for both tensile strength and modulus, indicating that increased polymerization temperature or time can significantly impact the mechanical properties. These results were expected as an increased extent of reaction is indicative of increased crosslinking and a lower M_c . The lower the value of M_c , the more tightly crosslinked the network and more polymer chains are affected during elongation. As a result, with a larger number of crosslinks, the polymer will be stiffer and have a higher Young's modulus. Likewise, the tensile strength will be greater with the increased number of crosslinks and polymer bonds that must be broken prior to failure.

Figure 8 shows the ultimate tensile strength and Young's modulus of POC as a function of extent of reaction. Although the general trend is an increase in tensile strength or Young's modulus with increasing extent of reaction and decreasing M_c , Young's modulus [Fig. 8(b)] correlates better with the extent of reaction than the ultimate tensile strength [Fig. 8(a)] which can vary significantly. Although both mechanical properties depend on the number of crosslinks and M_c , the tensile strength can also be influenced by strain-induced crystallization. Strain-induced crystallization is a high elongation phe-

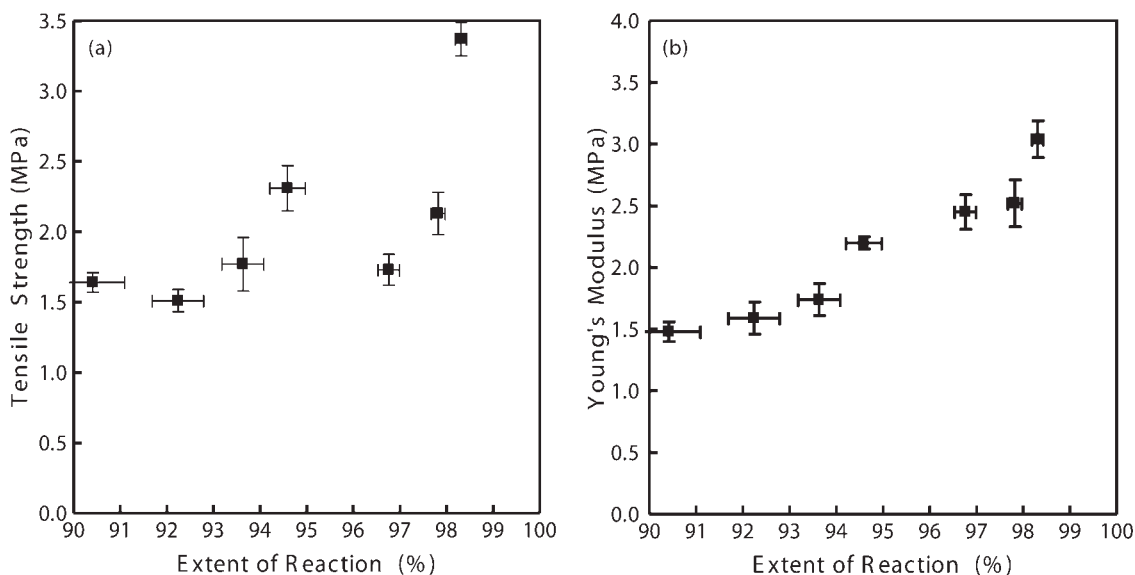


Figure 8. (a) Tensile strength and (b) Young's modulus of poly(1,8-octanediol-co-citrate) versus extent of reaction.

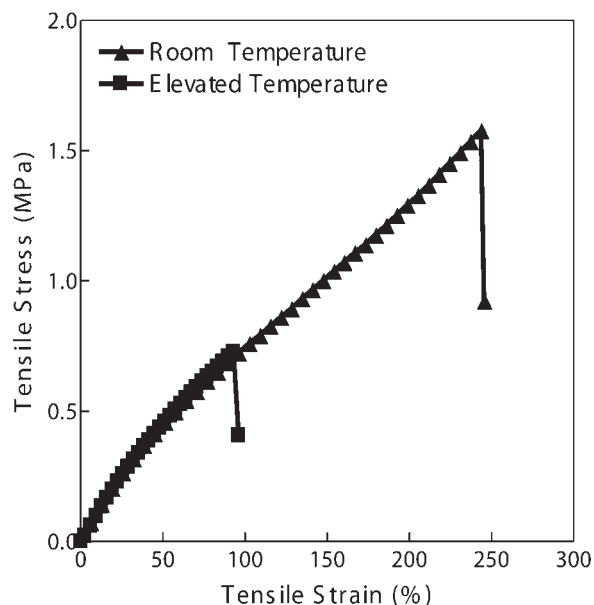


Figure 9. Stress–strain curves of POC (extent of reaction = 90%) tested at room and elevated temperatures.

nomena in which long polymer chains group together in the direction of elongation into crystalline domains that act as additional crosslinks. It is believed that at low extents of reaction (90–95%), the high molecular weight between crosslinks (Table 1) allows the long and flexible polymer chains to group into crystalline domains and act as additional crosslinks to increase the tensile strength. However, as the reaction progresses, the molecular weight between crosslinks decreases (Table 1) and the shorter polymer chains cannot easily group into crystalline domains. Because the increase in number of crosslinks prevents the grouping of hydrophobic chains into crystalline domains, the strength is caused by the breaking of individual crosslinks. It is these two competing factors that cause the ultimate tensile strength to vary significantly.

When comparing the stress–strain curves of POC (Fig. 7), at low extents of reaction there is a noticeable upturn in the stress–strain curve at high elongations. We hypothesized that this upturn was caused by strain-induced crystallization. To test this hypothesis, tensile tests of POC were conducted at room (25 °C) and elevated (100 °C) temperatures. The elevated temperatures provide the energy to melt any crystalline domains formed at high strains but should not change the initial portion of the stress–strain curve.^{26,63–65} As shown in Figure 9, at elevated temperatures, the ultimate tensile

strength dropped significantly while Young's modulus and the low elongation portion of the stress–strain curves were identical. Therefore, the ultimate tensile strength of POC can be affected by strain-induced crystallization and cause the variability seen in Figure 8(A).

CONCLUSIONS

Herein we describe a new method to characterize the extent of reaction of thermoset elastomers such as POC. The method is simple, non-destructive, and can be applied to samples of any size or shape. Increasing the extent of reaction of POC resulted in an increase of the Young's modulus and ultimate tensile strength. However, the Young's modulus had a better correlation with extent of reaction, probably due to the effects of strain-induced crystallization on the ultimate tensile strength of POC.

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