

# Glycerol Citrate Polyesters Produced Through Heating Without Catalysis

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**ABSTRACT:** The influence of various heating methods without catalysis to prepare polyesters from citric acid : glycerol blends was studied. In the presence of short-term microwave treatments, i.e., 60 s at 1200 W, blends of glycerol and citric acid invariably formed solid amorphous polyesters. Fourier transform infrared spectroscopy showed that citric acid and glycerol blends can form highly stable polymers composed of ester bonds. The glycerol citrate polyester polymers exhibited the least degradation in water, more in acid solu-

tions (0.1–1.0M HCl), and the most deterioration in strong alkaline solutions (0.1–1.0M NaOH) after 72 h soakings. Polyesters of glycerol and citric acid were studied with differential scanning calorimetry and thermal gravimetric analysis. The polyesters were found to be thermally stable (up to 313°C). © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

**Key words:** biopolymers; blending; differential scanning calorimetry; esterification; thermogravimetric analysis

## INTRODUCTION

Numerous issues such as price uncertainty, manufacturing costs, environmental disposal, and geo-political concerns are affecting the petroleum-based polymer industry. As an alternative, since 1980s there is an increasing interest in the development of biodegradable nonpetroleum-based polymers.<sup>1–4</sup> However, the price of these nonpetroleum-based polymers [e.g., poly(lactic acid), PLA] is high and not competitive with petroleum-based polymers (e.g., polyethylene terephthalate, PET).<sup>4</sup> Therefore, the development of lower cost nonpetroleum-based polymers is needed. Polyesters can be prepared using polyfunctional acids and alcohols such as citric acid and glycerol, respectively.<sup>1–4</sup>

Citric acid is relatively inexpensive and is the most commonly produced organic chemical obtained by fermentation.<sup>4,5</sup> Citric acid is a weak organic acid that naturally occurs in a variety of vegetables and fruits.<sup>5</sup> In 2007, ~ 1,700,000 million tons of citric acid was produced with as much as 50% manufactured

in the People's Republic of China. About 50% of the citric acid is used in beverages, 20% in food applications, 20% in detergent applications, and 10% in nonfood-related applications such as cosmetics, pharmaceutical, and chemical industrial products.<sup>5</sup>

The production of biodiesel has resulted in an enormous excess of glycerol.<sup>4,6–8</sup> Biodiesel is commonly produced from the transesterification of vegetable oil or animal fat feedstocks with glycerol generated as a co-product. For every ton (i.e., 1000 kg) of biodiesel manufactured, 100 kg of glycerol is produced.<sup>4,6–8</sup> The 2000 market price for glycerol has plummeted to only 1/10th of that price by 2009.<sup>2,7,8</sup> We can presume in the future that the price of glycerol will continue to remain low and perhaps even continue to decline as biodiesel production escalates.<sup>2,7</sup> Industrial producers of glycerol are actively seeking new uses for this excess glycerol to increase the value for this product.<sup>2,9</sup> Several investigators have sought to use glycerol as a feedstock for microorganisms to produce high-value chemical products such as succinic acid, propionic acid, ethanol, butanol, and hydrogen terephthalate.<sup>8</sup>

Normally, citric acid and glycerol are considered plasticizers and are used to increase the fluidity of the material to which they are added (e.g., plastics, concrete, wallboard, and clay). Glycerol may be combined with tricarboxylic acids such as citric acid to

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form a corresponding ester.<sup>1-4</sup> Polymers derived from glycerol and citric acid are relatively benign and biodegradable.<sup>3,4</sup> The importance of heating to achieve glycerol citric acid polyester polymerization has been previously demonstrated.<sup>1,4</sup> Budhavaram and Barone<sup>4</sup> prepared polyesters by blending various molar ratios of glycerol and citric acid to obtain a 15 mL solution in a beaker coupled with 9 mL of distilled water, and then stirred for 10 min while heating at 25–140°C to drive off the water. Subsequently, the reaction continued for 2 to 3 days to achieve polymerization at 75°C using 1.2 : 1 molar ratio of citric acid : glycerol blend, and even lower polymerization rates were achieved by heating blends at 45°C for 6 days.<sup>4</sup> Pramanick and Ray<sup>1</sup> mixed glycerol and citric acid in various molar ratios with *p*-toluene sulfonic acid within a flask and then incubated at 170°C under nitrogen for 12 h. After the elimination of the water by-product, the blend (i.e., glycerol citrate polyester) was further heated for an additional 4 h under the same temperature and conditions. A solid amorphous polyester was collected from the reaction vessel, which was purified by leaching several times with boiling ethanol.<sup>1</sup> This amorphous solid polyester was insoluble in water and other common organic solvents, suggesting this polymer was “sufficiently cross linked.”<sup>1</sup>

In this study, we sought to obtain solid polyesters of glycerol and citric acid blends through various heating methods without addition of any external catalysts. We examined the response of various ratios of citric acid and glycerol blends using hotplate heating, autoclaving, oven convection heating, and microwaving. Our aim was to produce solid glycerol citrate polyesters quickly, inexpensively, and without complicated synthesis procedures. These polyesters could then be used and evaluated in various polymer applications (i.e., molding).

## EXPERIMENTAL

### Reagents

Three different anhydrous citric acid sources were used: food grade (Duda diesel LLC, Madison, AL), 99% reagent grade (Sigma–Aldrich, St. Louis, MO), and 99.5% reagent grade (Acros Organics, Morris Plains, NJ). Unless otherwise indicated the 99% reagent grade (Sigma) was used in all experiments. Glycerol, 99+% reagent grade (Acros) was used in all tests.

### Preparation of blends and experiments

The following citric acid : glycerol molar ratio blends were prepared for heating tests: 2 : 1, 1.4 : 1, 1 : 1, 0.7 : 1, 0.5 : 1, 0.34 : 1, 0.25 : 1, 0.16 : 1, and 0.12 : 1 respectively. Each formulation consisted of 12 g of

reagents and was mixed thoroughly together by hand with the aid of stainless steel spatula within their respective heating vessels. For microwaving, a silicone muffin pan (70 mm diam. × 30 mm H; 80 mm<sup>3</sup> cap.) (Wilton Industries, Woodridge, IL) was used. Microwave heating was conducted with an Ethos EX microwave Labstation (Milestone Inc., Shelton, CT). The microwave was equipped with internal IR-temperature sensor (not used as a feedback control for regulating microwave intensity) and ATC-FO fiber optical probe. This microwave oven was rated 1200 W with a 41,906 cc cap. and was equipped with a turntable. A single silicone pan was heated within the microwave using the 100% power level intensity per treatment. Vessels were microwaved for 60 s. In some cases, samples were heated for 48 s and compared with 60 s samples. In other heating methods, citric acid : glycerol blends of 12 g were prepared in aluminum weighing pans (7.62 cm diam × 1.51 cm D; 80 mm<sup>3</sup> cap.) (Cole Parmer, Chicago, IL). Samples were heated in laboratory oven (Model 1329-2, Sheldon Manufacturing Inc., Cornelius, OR) at a constant temperature of 100°C for 12, 72, 96, and 120 h. Hotplate heating was conducted on a Hotplate/stirrer (Model PC-320–575 watt, Corning, Lowell, MA,) preheated to 270°C. Blends in pans were heated on the hotplate until bubbling ceased, e.g., 4 : 44 min, achieving a polymer surface temperature of 223°C. Surface polymer temperatures of the blends were measured with an infrared laser sighting thermometer (Model WD-39644-00, Oakton, Vernon Hills, IL) when appropriate. Autoclave heating was conducted for 45 min at 121°C at 0.103 mPa by placing pans inside a polycarbonate Nalgene Biosafe box (7 L × 18.4 H × 17 W cm) (Thermo Fisher Scientific Intern., NY). At the end of heating treatments, citric acid : glycerol blends were cooled to room temperature and then rated for their physical appearance, weighed and analyzed by Fourier transform-infrared (FTIR) spectroscopy.

The physical stability of 2 : 1, 1.4 : 1, 1 : 1, 0.7 : 1, and 0.5 : 1 molar ratio of citric acid : glycerol blends obtained from microwaving were tested in alkaline and acid environments. Three replicates were conducted for each treatment. A 0.2 g polymer sample was immersed in 10 mL of 0.0, 0.1, 0.5, or 1.0M HCl or NaOH and incubated at 25°C for 72 h. Samples were filtered through Whatman filter paper dried at 40°C for 5 days and then weighed to determine weight loss and percent degradation calculated.

To demonstrate the influence of the vessel type used in a microwave experiment, 12 g of 1 : 1 molar ratio of citric acid : glycerol blend was prepared and microwaved for 60 s in a muffin pan, a miniature Bundt pan (70 mm diam. × 30 mm H; 80 mm<sup>3</sup> cap.), or a cake baking pan (22.5 cm diam × 5.0 cm H; 1800 cm<sup>3</sup> cap.). In some cases, citric acid : glycerol

molar ratios of 2 : 1, 1 : 1, 0.7 : 1, and 0.5 : 1 were microwaved for 60 s and kept at laboratory room temperature for 1 year and then analyzed by FTIR and differential scanning calorimetry (DSC) and compared to 1-day-old samples.

### Fourier transform-infrared spectroscopy

FTIR spectra were measured on an Arid Zone FTIR spectrometer (Model ABB MB-Series, Houston, TX) equipped with a DTGS detector. Absorbance spectra were acquired at  $4\text{ cm}^{-1}$  resolution and signal-averaged over 32 scans. Interferograms were Fourier transformed using cosine apodization for optimum linear response. Spectra were baseline corrected, scaled for mass differences, and normalized to the methylene peak at  $2927\text{ cm}^{-1}$ .

### Determination of gel content

The gel content analysis was conducted to determine the degree of cross linking in citric acid : glycerol blends with molar ratios of 2 : 1, 1.4 : 1, 1 : 1, 0.7 : 1, and 0.5 : 1. Gel content was determined gravimetrically, according to the ASTM D2765-01 procedure using a 16 h extraction cycle with *p*-xylene as the solvent heated at  $150^\circ\text{C}$ .<sup>10,11</sup> Approximately, 1 g of the polymer samples was cut into small pieces and placed in a preweighed stainless steel fine wire mesh pouch. Pouches were sealed to prevent polymer loss during the extraction process. After extraction cycle, the sample was air dried in the ventilation hood for 24 h then placed in a vacuum oven at the temperature of  $80^\circ\text{C}$  for 2 h. The percentage of gel content of the blends was calculated based on the following eq. (1).

$$\% \text{ Gel Content} = ((W_2 - W_1)/S) * 100 \quad (1)$$

where  $S$  is the weight of the original polyester sample,  $W_1$  is the weight of the stainless steel pouch, and  $W_2$  is the weight of the extracted pouch and polyester sample.

### Thermal analysis

#### TGA and Degradation Kinetics

TGA was performed using a Model 2050 TGA (TA Instruments, New Castle, DE). Pure citric acid and a 1 : 1 molar ratio of citric acid : glycerol blend were heated in a platinum pan from 25 to  $800^\circ\text{C}$ . For decomposition kinetics analysis, each sample (10–20 mg) was heated under a nitrogen atmosphere at three different heating rates: 10, 15, and  $20^\circ\text{C}/\text{min}$ , to  $800^\circ\text{C}$ . This data were analyzed using the TA Advantage Specialty Library software (TA Instruments), which operates in accordance with ASTM

Standard E1641, "Decomposition Kinetics by TGA" and the activation energy ( $E_a$ ) values were obtained at 50% conversion. The derivative TGA (wt %/min) of each sample was obtained from the software using the  $10^\circ\text{C}/\text{min}$  run.

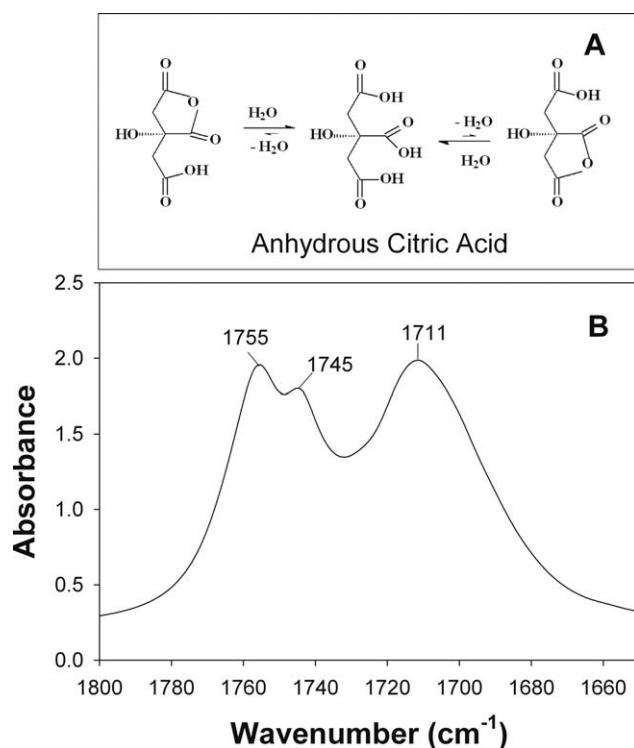
#### Differential Scanning Calorimetry

All experiments were performed on a TA Instrument DSC, Model Q2000 (TA Instruments) with RCS cooling system (New Castle, DE, USA). Baseline was calibrated with sapphire disk. Samples weighed to within 5–8 mg were encapsulated in Tzero aluminum pans. The DSC was purged with dry nitrogen at 50 mL/min. The conventional heat/cool/heat cycling experiment was done at  $10^\circ\text{C}/\text{min}$  for heating and  $5^\circ\text{C}/\text{min}$  for cooling at the temperature range of  $-40$  to  $180^\circ\text{C}$ . The modulated DSC was done with modulation temperature of  $1^\circ\text{C}$ , modulation interval of 60 s, and ramp rate of  $3^\circ\text{C}/\text{min}$  at the temperature range of  $-40$  to  $180^\circ\text{C}$ . The data resulting from the thermal transitions were obtained using the Universal Analysis software (TA Instruments).

## RESULTS AND DISCUSSION

### FTIR studies

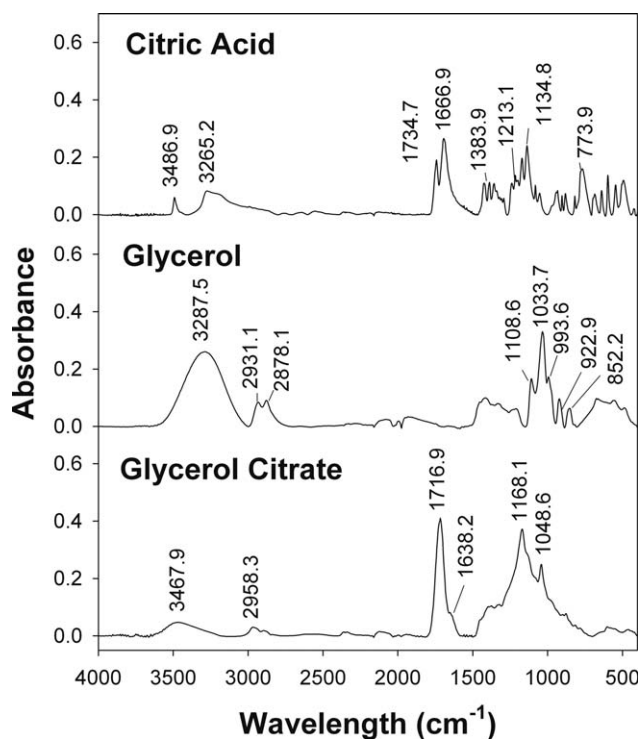
A close examination of the  $1800\text{--}1550\text{ cm}^{-1}$  region of the FTIR spectrum of the anhydrous citric acid used in these reactions exhibited bands which could aptly be interpreted as consisting of a small conformational mixture of its anhydride  $1755\text{ cm}^{-1}$  and  $1745\text{ cm}^{-1}$  and the mainly free carboxylic acid conformer  $1711\text{ cm}^{-1}$  bands as schematically depicted in Figure 1(A) and represented in the spectrum in Figure 1(B). This spectral interpretation is consistent with that of unconjugated cyclic anhydrides.<sup>12</sup> With this observation in mind, it becomes more understandable how citric acid readily reacts with glycerol in the absence of a strong acid catalyst usually necessary to affect esterification of alcohols with other weaker carboxylic acids. As esterification is a reversible reaction, one can invoke Le Châtelier's Principle to rationalize the rapid reaction with the alcohol by the initially small amount of the reactive anhydride component of citric acid present. This is essential to drive the reaction forward and eventually to completion as more anhydride is produced coupled especially to the condensation by-product, water, driven off under microwave reaction conditions. Shogren et al.<sup>13</sup> had reported use of citric acid without a catalyst to esterify D-sorbitol, thus one could surmise by inference that citric acid was autocatalytic in that process. Of course citric acid anhydride can be produced from a variety of methods for use in polymer coatings, paints, resins, and adhesives.<sup>14</sup> Although in



**Figure 1** Conformational forms of anhydrous citric acid reagents as per FTIR, and B 1800-1550  $\text{cm}^{-1}$  spectral region of anhydrous citric acid from commercial sources.

an earlier study, Pramanick and Ray<sup>1</sup> had suggested that the 3449  $\text{cm}^{-1}$  broad band to be unreacted internal carboxyl and tertiary hydroxyl groups of citric acid, in our hands or under microwave radiation, the only discernible unreacted component seems to be the tertiary hydroxyl groups of citric acid that are sterically encumbered to be reached even in this reaction environment (Figs. 2–4).

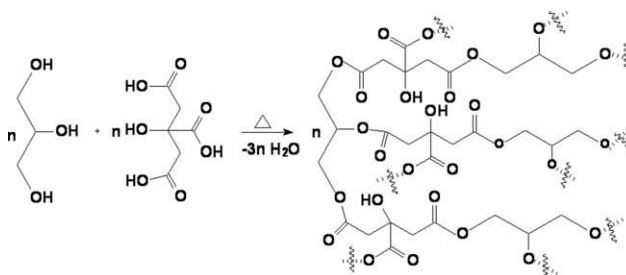
The method of reacting citric acid : glycerol blends resulted in products with different physical properties (Table I). When an autoclave is used as the method of heating, usually only a liquid or sticky gel was obtained from the citric acid : glycerol blends. In many cases, the undissolved citric acid was visibly present in these gels (Table I). Clearly, there was not enough heat to drive the reaction to completion. An alternative explanation may lie in the reversibility of esterification reaction. In a steam environment, the forward reaction is thwarted, again in accordance with Le Châtelier's principle. Examination of the FTIR of 1 : 1 molar ratio citric acid : glycerol blends from the autoclaved treatments exhibits the ester peak at 1739.15  $\text{cm}^{-1}$  and a carboxylate peak at 1694.29  $\text{cm}^{-1}$  (Figs. 4 and 5). This suggests that an incomplete reaction was obtained. Autoclave heating was clearly inadequate to produce polymerization but did result in preliminary polymerization as shown by the FTIR. Using the hotplate to heat the citric acid : glycerol blends resulted poly-



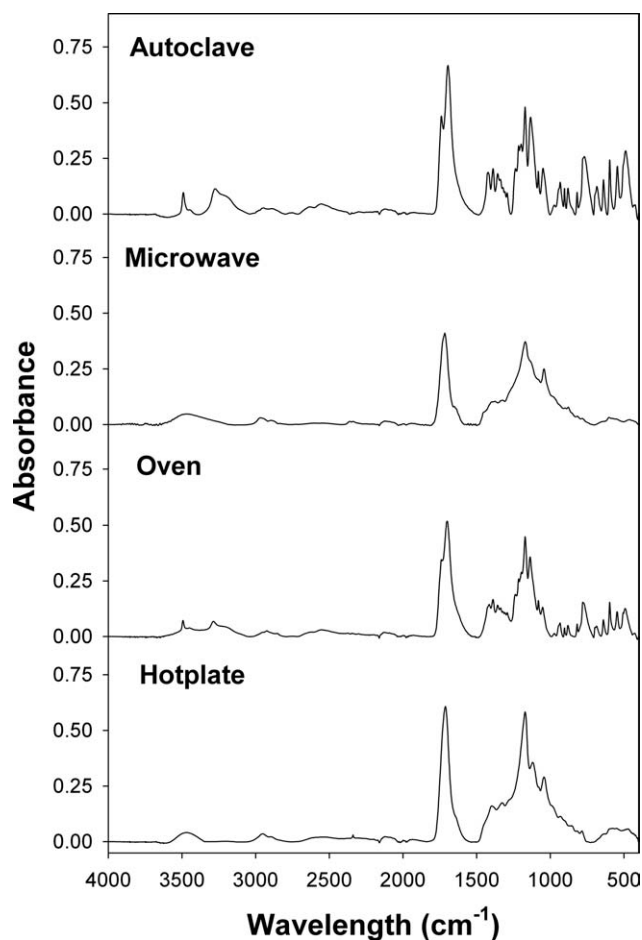
**Figure 2** FTIR spectra: anhydrous reagent grade citric acid, glycerol, and 1 : 1 molar ratio of citric acid : glycerol blend microwaved for 60 s.

mers with in entirely different physical properties. These products were essentially rubbery gels punctuated with a myriad of air bubbles. When using an oven, the resultant blends were usually hardened into a brittle translucent plastic-like film after 120 h of heating at 100°C. Less heating times resulted in a sticky rubber-like gel, indicating incomplete polymerization. Use of convention oven heating at 100°C has been previously used to obtain similar physical constructs.<sup>3</sup> Regardless of the method of heating, FTIR analysis revealed the presence of the glycerol citrate polyesters in all resultant products (Figs. 4 and 5).

Citric acid : glycerol blends with molar ratios of 2 : 1, 1.4 : 1, 1 : 1, 0.7 : 1, and 0.5 : 1, produced distinct white foam structures when microwaved for 60 s (Figs. 6 and 7; Table I). During the microwaving



**Figure 3** Stoichiometric reaction of glycerol with citric acid to produce glycerol citrate polyester employing microwave heating (proposed structure of polymeric foam).



**Figure 4** FTIR spectra for 1 : 1 molar ratio of citric acid : glycerol blend prepared as follows: autoclaved at 121°C for 45 min at 0.103 mPa; microwaved for 60 s; oven at 100°C for 120 h; and hotplate 4.44 min. Note that the oven heating retains peaks of the citric acid indicating the citric acid did not react as completely as in the hotplate and microwave heating.

process, considerable bubbling was observed. We attribute this to the vaporization of the water as steam which also results in vigorous mixing of the formulations. Microwaving the various citric acid : glycerol blends resulted in foams that conformed to the shape of the pan used (Figs. 6 and 7). However, when using the large surface area cake pan (i.e., 1800 mm<sup>3</sup> cap.), the blend failed to solidify and only formed a sticky liquid. FTIR examination of these citric acid : glycerol blends revealed the occurrence of distinct esters (Figs. 4 and 5). It should be noted that by increasing the microwave reaction time from 48 to 60 s results in the formation of larger foams, suggesting that a more complete reaction occurred. About 25 to 30% of the original blend weight was lost in the 48 s microwave treatment, whereas 35 to 45% of original blend weight was lost in the 60 s microwave treatment (data not shown). We attributed this weight loss to the by-product, water-steam, generated and lost in the condensation reaction of

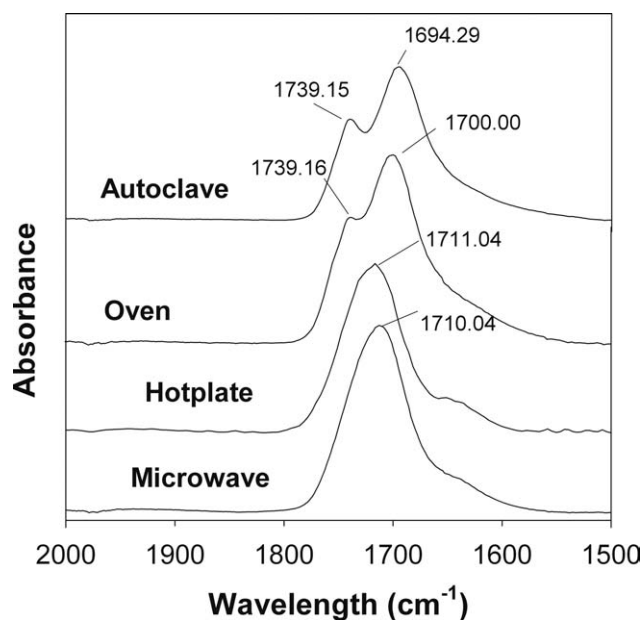
ester formation. This water by-product loss by vaporization in microwave heating drives the reaction to completion in accordance with Le Châtelier's principle as mentioned earlier. However, prolonged microwave treatment results in burning and discoloration of the foam.

### Degradation studies

When the microwaved glycerol citrate polyester foams were immersed in water they behaved in a sponge-like manner. Depending on the formulation, water immersion could result in considerable flaking and foam rupture, but little loss of the original material weight occurred (Table II). However, depending on the formulation used, treatment with

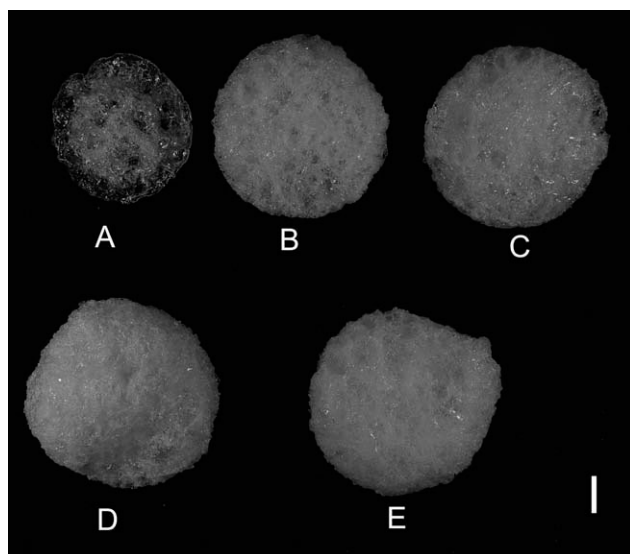
**TABLE I**  
Responses of Citric acid : Glycerol Molar Ratio Blends to Different Heating Treatments

Citric acid : Glycerol	Heating (sec)	Wt <sub>final</sub> (%)	Temp. (°C)	Ht. (mm)	Description
Microwave					
2 : 1	60	52.4%	212	52	Foam
1.4 : 1	60	55.6%	213	43	Foam
1 : 1	60	58.2%	211	32	Foam
0.7 : 1	60	57.7%	208	27	Foam
0.5 : 1	60	59.8%	208	18	Foam
0.34 : 1	60	60.5%	212	7	Gel
0.24 : 1	60	64.2%	209	4	Liquid
0.16 : 1	60	68.9%	213	3	Liquid
0.12 : 1	60	72.2%	217	3	Liquid
Oven at 100°C					
2 : 1	432,000	95.9%	100	3	Gel
1.4 : 1	432,000	93.7%	100	3	Gel
1 : 1	432,000	93.0%	100	3	Gel
0.7 : 1	432,000	89.2%	100	3	Sticky gel
0.5 : 1	432,000	86.1%	100	3	Sticky gel
0.34 : 1	432,000	86.5%	100	3	Sticky gel
0.24 : 1	432,000	80.9%	100	3	Sticky gel
0.16 : 1	432,000	88.9%	100	3	Sticky liquid
0.12 : 1	432,000	60.1%	100	3	Liquid
Autoclave					
2 : 1	2700	101.6%	121	3	Sticky gel
1.4 : 1	2700	101.5%	121	3	Sticky gel
1 : 1	2700	101.1%	121	3	Sticky gel
0.7 : 1	2700	100.4%	121	3	Sticky gel
0.5 : 1	2700	101.3%	121	3	Liquid
0.34 : 1	2700	101.1%	121	3	Liquid
0.24 : 1	2700	101.3%	121	3	Liquid
0.16 : 1	2700	102.3%	121	3	Liquid
0.12 : 1	2700	100.0%	121	3	Liquid
Hotplate					
2 : 1	368	87.4%	224	9	Foam
1.4 : 1	307	84.5%	215	12	Foam
1 : 1	307	81.8%	224	11	Foam
0.7 : 1	383	83.1%	240	10	Foam
0.5 : 1	359	72.3%	236	8	Foam
0.34 : 1	379	77.0%	242	4	Sticky gel
0.24 : 1	413	72.2%	231	3	Liquid
0.16 : 1	430	76.9%	224	3	Liquid
0.12 : 1	428	77.6%	228	3	Liquid



**Figure 5** FTIR spectra (1500 to 2000 wavenumbers) for 1 : 1 molar ratio of citric acid : glycerol blend prepared as follows: Autoclaved at 121°C for 45 min at 0.103 mPa.; microwaved for 60 s; oven at 100°C for 120 h; and hotplate 4.44 min.

acid (i.e., 0.05 to 1.0 molar ratio HCl) caused various degrees of degradation the polyesters after 72 h. For example, the 1 : 1 molar ratio citric acid : glycerol blend only exhibited 8% degradation in 1 molar ratio HCl, whereas the 2 : 1 molar ratio blend exhibited 70.5% degradation (Table II). In comparison, alkaline treatment with 0.5 and 1.0 molar ratio NaOH caused visible foam deterioration and yellowing of the solution, a situation which was not observed using lower alkaline or in any acid concentrations. For example,



**Figure 6** Top view of the polyester foams obtained after microwaving for 60 s from different molar ratios of citric acid : glycerol (A) 0.5 : 1; (B) 0.7 : 1; (C) 1 : 1; (D) 1 : 4 : 1; and (E) 2 : 1. Bar = 10 mm.



**Figure 7** Side view of the polyester foams. Height comparisons between two citric acid : glycerol molar ratios, 0.5 : 1 (left) and 1.4 : 1 (right) given 60 s microwaving. Bar = 10 mm.

1.4 : 1 and 1 : 1 molar ratio citric acid : glycerol blends in 0.5 molar ratio NaOH exhibited 97 and 96% deterioration, respectively. These results clearly show that the polyester composition which mirrored the degree of polymerization could greatly influence its biodegradability.

#### Gel content of citric acid : glycerol blends

The percent gel content or degree of cross linkable polymers generated from microwaving heating various citric acid and glycerol polyester blends are presented in Table III. It is evident from the results that the % gel content was high (e.g., 93.3–92.5%) for citric acid : glycerol blends above 0.7 : 1M citric acid : glycerol. The 0.5 : 1M citric acid : glycerol blend had a significantly lower % gel content (i.e., 82.8%).

#### TGA studies

Citric acid and glycerol have melting points of 153°C and 17.8°C and boiling points of 175°C and 290°C, respectively. The resultant 1 : 1 molar ratio citric acid : glycerol blend did not have an observable melting point, even after heating to 325°C. The TGA scan of pure citric acid exhibited one major peak at 214°C [Fig. 8(A,B)]. A minor shoulder peak occurs at 160°C for the citric acid TGA, which may be attributed to the loss of water by a condensation reaction with itself. The 1 : 1 molar ratio citric acid : glycerol blend, the polyester glycerol citrate polymer, showed a different profile compared to the pure citric acid. The 1 : 1 molar ratio glycerol citrate blend exhibited a profile that gradually lost weight as temperature increased; unlike pure citric acid which exhibited a sharp drop in weight as temperature increased. It is clear that the glycerol citrate blend resists temperature degradation making it more heat stable than citric acid. It is also clear from Figure 8(B) that the presence of three new species appeared in the blend degrading at 156, 313, and 396°C. It is also important to mention that two of these newly formed materials started degrading at a

**TABLE II**  
**Degradative Responses of Glycerol Citrate Polyesters prepared from various Citric acid : Glycerol Molar Ratio Blends to Acid and Base Concentrations after 72 h<sup>a</sup>**

Citric acid : Glycerol	HCl				NaOH		
	0	0.1	0.5	1	0.1	0.5	1
2 : 1	43.6a	49.6a	64.0b	70.5c	81.6d	94.0e	94.7e
1.4 : 1	8.0a	8.9a	6.0a	44.0b	29.7c	96.9d	97.6d
1 : 1	4.5 <sup>a</sup>	4.3a	12.3b	8.1b	38.8c	95.5d	90.2d
0.7 : 1	7.6 <sup>a</sup>	9.8a	12.5b	10.2b	59.4c	95.5d	88.5d
0.5 : 1	5.0a	20.8b	28.5c	17.4b	63.5d	94.6e	92.1e

<sup>a</sup> Percent degradation of the original materials is reported. Three different replicates are presented for each mean. Values with different letters in the same row were significant at  $P \leq 0.05$ .

temperature much higher than pure citric acid as shown in the Figure 8(B). This indicates some sort of unique interaction between citric acid and glycerol occurs that needs to be further investigated.

Additionally, TGA data were used to determine the degradation kinetics of neat citric acid or the 1 : 1 molar ratio citric acid : glycerol blend. Three heating rates, 10, 15, and 20°C/min, were used to calculate the activation energy of degradation ( $E_a$ ) according to Flynn and Walls<sup>15</sup> based on the following eq. (2).

$$\log \beta \cong 0.457 \left( -\frac{E_a}{RT} \right) + \left[ \log \left( \frac{AE_a}{R} \right) - \log F(a) - 2.315 \right] \quad (2)$$

where  $\beta$  is the heating rate,  $T$  is the absolute (Kelvin) temperature,  $R$  is the gas constant,  $a$  is the conversion,  $E_a$  is the activation energy,  $F(a)$  is the function of degree of conversion, and  $A$  is the pre-exponential factor. According to this equation at the same conversion,  $E_a$  can be obtained from the slope of the plot of  $\log \beta$  versus  $1000/T$  (K). The  $E_a$  was calculated using the software provided by the TGA manufacturer (TA Instruments). The degradation mechanism of both samples can be obtained by plotting the percent degradation conversion versus  $E_a$  as shown in Figure 9, where a horizontal line means a one-step degradation; otherwise it is a multistep process.

**TABLE III**  
**Percent Gel Contents of Microwaved Citric acid : Glycerol Molar Ratio Blends<sup>a</sup>**

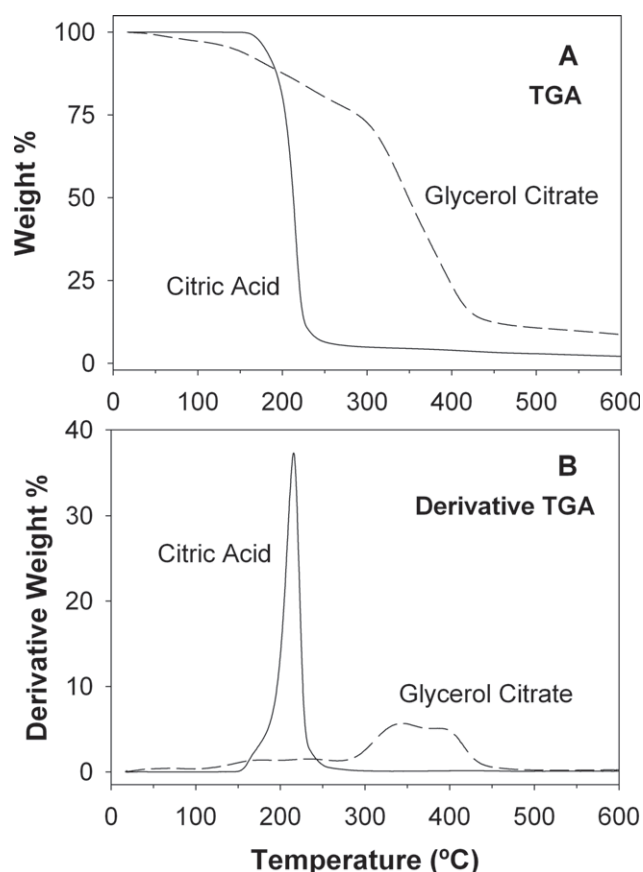
Citric acid : Glycerol	Gel content (%)
2 : 1	92.5a
1.4 : 1	92.4a
1 : 1	93.3a
0.7 : 1	92.7a
0.5 : 1	82.8b

<sup>a</sup> Three different replicates are presented for each mean. Values with different letters in the same column were significant at  $P \leq 0.05$ .

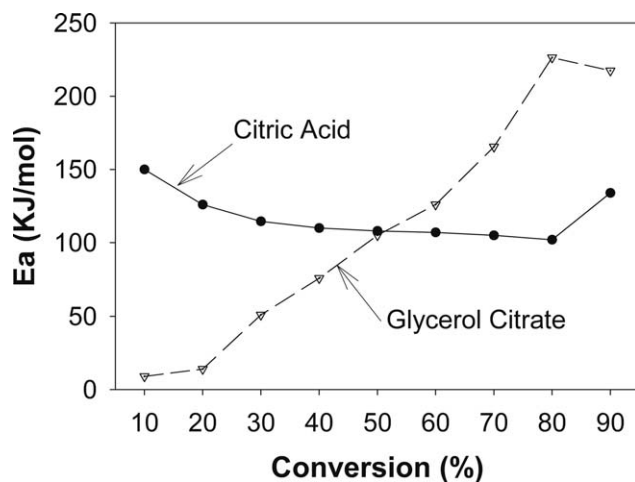
Although with varying  $E_a$  values for each percent conversion, pure citric acid exhibited a one-step degradation mechanism (Fig. 9), whereas the 1 : 1 molar ratio glycerol citrate polyester showed multi-step process indicating interaction. It is also clear from the profile that the citric acid : glycerol blend gives a higher  $E_a$  at higher percent conversion.

#### DSC studies

The DSC profile of citric acid was done by subjecting the sample for two cycles, heating and cooling

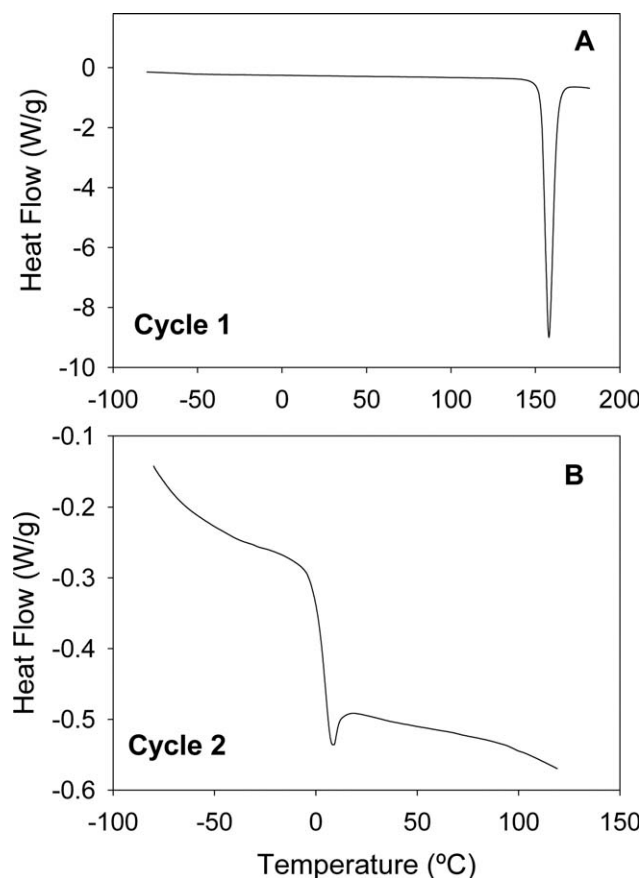


**Figure 8** TGA analysis. A: TGA profile of citric acid and 1 : 1 molar ratio of citric acid : glycerol blend. B: TGA derivative of citric acid and blend.

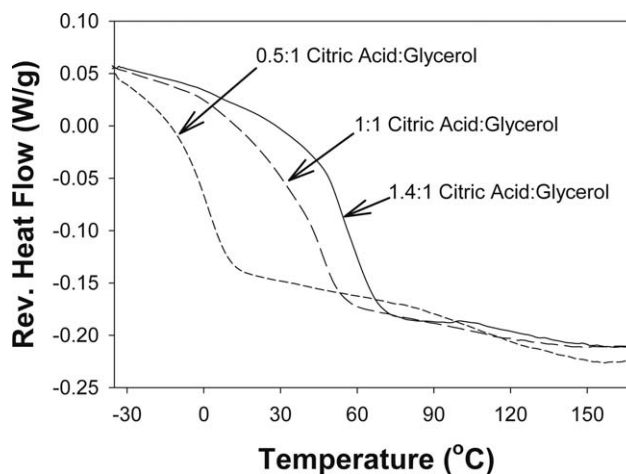


**Figure 9** Degradation kinetics of citric acid and 1 : 1 molar ratio of citric acid : glycerol blend.

[Fig. 10(A,B)]. The first cycle (heating) of pure citric acid showed a melting peak at  $155.1^{\circ}\text{C}$  ( $\Delta H = 223.1 \text{ J/g}^{\circ}\text{C}$ ), whereas the second cycle (cooling) exhibited a glass transition ( $T_g$ ) at  $2.47^{\circ}\text{C}$  ( $\Delta C_p = 1.3 \text{ J/g}^{\circ}\text{C}$ ). It is clear that citric acid was crystallized under different specific processing conditions, which explains why it did not crystallize during the cooling cycle



**Figure 10** DSC of citric acid. (A) Cycle 1-heating. (B) Cycle 2-cooling.



**Figure 11** DSC of glycerol citrate polyesters. Reversible heat flows of 1.4 : 1, 1 : 1, and 0.5 : 1 molar ratios of citric acid and glycerol from the modulated DSC.

[Fig. 10(B)]. There is a dip under the  $T_g$  that resembles a melting peak, but in reality it is an enthalpic relaxation [Fig. 10(B)]. The melted material relaxed to the most stable thermodynamic state, its lowest energy level and was brittle (relaxation). In accordance with the TGA analysis which showed a shoulder occurring around  $160^{\circ}\text{C}$  indicating a condensation reaction with citric acid itself (Fig. 8), our DSC runs clearly indicate a confirmatory polymerization process/reaction based on the  $T_g$  observed in the second cycle (Fig. 10). This polymerization reaction could be a condensation reaction between carboxylic acid group and the hydroxy group, but it is apparently masked in the DSC citric acid melting peak.

The conventional heat/cool/heat cycling test of the polymer obtained from 1 : 1 molar ratio of the citric acid : glycerol blend was conducted and compared with citric acid. No citric acid melting peak was observed in the DSC curve for the various citric acid : glycerol blend after microwave heating indicating that citric acid was entirely reacted to produce this polymer. The DSC curves of the polymer during the first and second heating cycles did not show much difference implying that the polymerization was substantially completed (data not shown). The reversible heat flow in the modulated DSC confirmed the transition found in the conventional DSC was the glass transition. The reversible heat flow thermograms from modulated DSC experiments of the polymers with three different molar ratios (1.4 : 1, 1 : 1, and 0.5 : 1 molar ratio of citric acid : glycerol) are shown in Figure 11. The  $T_g$ s and  $\Delta C_p$ s of 1.4 : 1, 1 : 1, and 0.5 : 1 molar ratio blends were measured at  $56.6 \pm 3.2$ ,  $47.6 \pm 0.7$ , and  $-4.98 \pm 0.4^{\circ}\text{C}$ , and  $0.62 \pm 0.05$ ,  $0.57 \pm 0.01$ , and  $0.49 \pm 0.13 \text{ J/g}^{\circ}\text{C}$ , respectively. The polymer of 1.4 : 1 molar ratio showed higher  $T_g$  than others presumably due to a high level of cross-linking. The lowest  $T_g$  of 0.5 : 1



molar ratio polymer may attribute to unreacted glycerol and less cross-linking.

### GENERAL REMARKS

The 2 : 1, 1 : 1, 0.7 : 1, and 0.5 : 1 molar ratio citric acid : glycerol polyester blends were found to be stable after a year when maintained at room temperature in the laboratory environment from FTIR analysis. These molar blends did not physically deteriorate, discolor, or take up moisture when compared to 1-day-old molar blends. In addition, FTIR and DSC analysis of 1-year-old polyester blends revealed it to be similar to the 1-day-old blends (Data not shown).

Microwave radiation accelerates the chemical reaction processes by electromagnetic energy radiation rather than by using heat conduction and obtains higher chemical conversions than by conventional heating (e.g., gas burners, hotplates, convection ovens, or autoclaving).<sup>16–19</sup> Microwave chemistry may reduce reaction times by a factor of 10 to 10,000X.<sup>16–19</sup> Microwave heating has several advantages over conventional heating such as: accelerated reaction rates, milder reaction conditions, higher chemical yields, lower energy use, different reaction selectivity, and uniform heating.<sup>18,19</sup> An advantage of the microwaved glycerol citrate polyester is that it is produced without a catalyst or complicated synthesis. The microwave method of producing glycerol citric acid polyesters that have unique physical properties that cannot be readily produced by other heating methods (Table I). In addition, we readily obtained a solid polymer with a number of citric acid : glycerol blends rather than a liquefied polymer as some investigators obtained.<sup>3,4</sup> The solid amorphous polymer obtained by Pramanick and Ray<sup>1</sup> mimicked that obtained in our study but was produced through a considerably more complicated synthesis procedure when compared to ours. Microwave heating apparently heats and mixes reactants and appears to give rise to a relatively uniform polymer product. In using open container vessels in the microwave, the steam generated

is constantly removed by the microwave fan during the heating processes and appears to allow for the reaction to proceed more rapidly than other heating methods. Therefore, numerous polymer compositions can be prepared quickly for subsequent evaluation (i.e., FTIR, TGA, DSC).

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