

Thermal Analysis of Glycerol Citrate/Starch Blends

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ABSTRACT: The reaction of glycerol and citric acid was studied by differential scanning calorimetry (DSC) and thermal gravimetric analysis. Reactions were performed in the DSC with a temperature oscillation of 1°C/min applied while scanning the range of 20–220°C. This modulated technique allowed separation of reversible and irreversible thermal effects. The energy associated with the esterification of glycerol and citric acid, 40 J/g, was calculated from

the irreversible component of the heat flow. When cornstarch was blended with glycerol and citric acid, the weight loss curves displayed prominent shifts in maxima values attributable to starch degradation. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1498–1501, 2008

Key words: glycerol; citric acid; cornstarch; polyesters; DSC

INTRODUCTION

Glycerol can react with polyfunctional acidic substrates, such as citric acid, phthalic anhydride, and succinic acid to produce linear polyesters or network polymers. The glycerol-based network polymers are the foundation of the alkyd resins that have numerous applications in protective, functional, and decorative coatings.^{1–3} In the recent past, the environmental concerns associated with the use of organic solvents and other volatile organic chemicals has increased. Modification to traditional solvent borne coating formulations, including the alkyds, has led to the development of high-solids and water dispersed coatings for many applications.⁴

Preliminary testing of coatings prepared from glycerol and citric acid indicated a potential benefit of combining these substrates with cornstarch to produce highly functionalized materials derived completely from renewable substrates. The structure of starch provides numerous sites for derivatization. For example, starch esters prepared by the reaction of starch with octenyl succinic acid anhydrides exhibit hydrophobic characteristics that change the sur-

factant properties of the product and can be used to stabilize oil/water emulsions.⁵ Starch may also be esterified with citric acid to produce materials with ion exchange applications.^{6,7} It would be difficult to prepare materials with comparable properties directly from the glycerol citrate polyesters due to the limited number of reactive sites available for derivatization. However, blending starch with glycerol and citric acid allows the formation of ester or ether linkages through the additional hydroxyl groups provided by the starch component.

Starch has been incorporated into synthetic polymers, such as starch-*g*-polyacrylonitrile, starch-*g*-poly-methylacrylate, and styrene-*co*-maleic anhydride.^{8,9} Starch can also form inclusion complexes that modify the thermal and mechanical properties of associated polymers.¹⁰ Microcellular foams have recently been prepared from starch, which can be compression molded.^{11,12} Starch is of particular interest in these applications because it is a renewable and biodegradable material available in high purity at relatively low cost.

Initial data on the reaction of glycerol and citric acid to form glycerol citrate polyesters were collected using modulated differential scanning calorimetry (DSC). This technique was then applied to blends of glycerol and citric acid with cornstarch. The influence of starch on the reaction was studied calorimetrically in a series of experiments at different blend levels. These materials are expected to find applications in the food and pharmaceutical industries.

EXPERIMENTAL

Materials

Glycerol, 99.5%, and citric acid, reagent grade were obtained from Sigma-Aldrich Co. (St. Louis, MO).

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Reagents were used as received. Cornstarch was obtained from A. E. Staley Co. (Decatur, IL) and was gravimetrically determined to contain 8 wt % moisture.

Reactions

Esterification of citric acid with glycerol or starch follows the scheme shown in Figure 1. The reaction of glycerol and citric acid was conducted with equimolar amounts of substrates by combining glycerol, 3 g, and citric acid, 6.26 g, in 30-mL glass vials. A magnetic stir bar was added to the vial and the reactants were stirred for 1 h at room temperature on a magnetic hotplate to produce a uniform mixture. Aliquots of the mixture, 5–10 mg, were removed, placed in tared aluminum pans, sealed, and submitted to DSC analysis. Reactions were analyzed using modulated DSC with a TA Instruments, Inc. (New Castle, DE) Model 2910 DSC. Scans were performed from 20 to 250°C with a heating rate of 10 and 1°C/min temperature oscillation. The reactions of glycerol and citric acid in the presence of cornstarch were prepared in a similar manner using equimolar quantities of glycerol, citric acid, with 1, 5, or 10 wt % starch added. Thermal gravimetric analyses were performed with a TA Instruments, Inc. (New Castle, DE) Model TGA-Q500 operated with a heating rate of 10°C/min over a temperature range of 25–400°C. Platinum pans of 100 μ L capacity were used. Infrared spectra were collected with a Nexus 470 FTIR spectrophotometer, Thermo Nicolet Corp. (Madison, WI) equipped with the ZnSe horizontal ATR. Spectra were processed using the accompanying OMNIC software.

RESULTS AND DISCUSSION

Calorimetric scans of the starting materials components are presented in Figure 2. Glycerol exhibits no significant thermal characteristics over the temperature range. The scan of citric acid shows a reversible endotherm beginning at 150°C with a peak temperature at 159°C. This is associated with the melting of citric acid, $T_m = 153^\circ\text{C}$. A second endotherm begins near 200°C with a maximum at 225°C. This was a nonreversible heat flow with an integrated value of

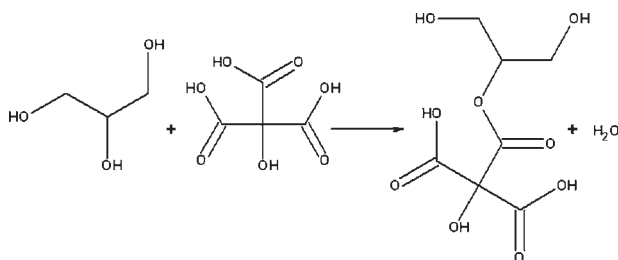


Figure 1 Esterification of citric acid with glycerol.

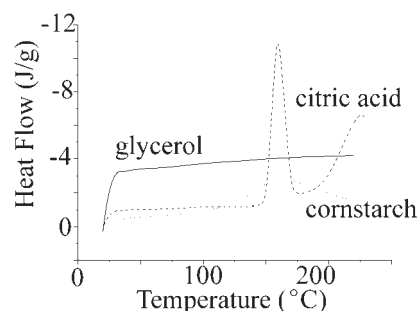


Figure 2 DSC heating curves for citric acid, glycerol, and cornstarch.

158 J/g and was attributed to the degradation of citric acid, which proceeds by decarboxylation and loss of water.

Cornstarch showed a broad endotherm beginning at 123.5°C and continuing to 220°C with a maximum centered at 162.4°C. This is typical of amylopectin melting and the onset temperature of these transitions in starch is sensitive to moisture content.¹³ Higher moisture levels typically shift the melting and degradation endotherms toward lower temperatures. Degradation would be expected to begin above 250°C for cornstarch with 10 wt % moisture or less.

The reactions of glycerol and citric acid were performed in the calorimeter as described above, which produced the scan shown in Figure 3. These are non-reversible and therefore related to reaction or degradation processes. The first endotherm has a peak temperature of 145°C. The energy associated with this endotherm was calculated to be 40 J/g by area integration. A second endotherm was detected with a peak temperature of 190°C and a calculated energy of 9.3 J/g. The third endotherm shows an onset temperature near 210°C and is assumed to be due to degradation of citric acid. The previously observed reversible endotherm related to the melting of citric acid was not detected.

The addition of 10 wt % starch to the reaction mixture resulted in the scan shown in Figure 4. The first endotherm has a peak temperature of 140°C

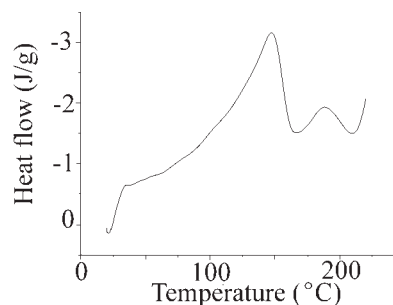


Figure 3 DSC heating curve for the reaction of equimolar amounts of glycerol and citric acid.

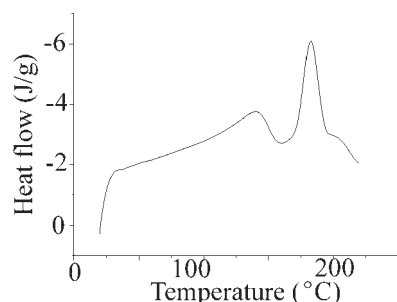


Figure 4 DSC heating curve for the reaction of equimolar amounts of glycerol and citric acid with 10 wt % cornstarch.

with an integrated energy of 30.7 J/g. The second endotherm exhibits a peak at 182.5°C and has both reversible and nonreversible components. The integrated values are 18.4 and 27.1 J/g, respectively. The reversible component is attributed to the cornstarch, which displayed a broad melting endotherm over the temperature range of 160–220°C. The nonreversible component is attributed to the continued reaction of the secondary hydroxyl group of glycerol as postulated for the esterification reaction in the absence of starch.

The reaction with starch was repeated in aluminum pans that were manufactured with a pin-hole in the lid. This was done to test the influence of sealed pans on the reaction progress. The reaction produces one mole of water per ester linkage formed and could potentially inhibit further reaction. When these reactions are performed on the laboratory bench at atmospheric pressure water vapor is allowed to vent freely. The scan performed with the pin-hole lid showed two prominent endotherms with peak temperatures at 139.5°C and 181°C. This is comparable to the peak values of 140°C and 182.5°C measured with the reactions in sealed pans.

FTIR analysis was performed on samples of reaction mixtures heated to 170°C to confirm the formation of ester bonds. Spectra of the starting materials

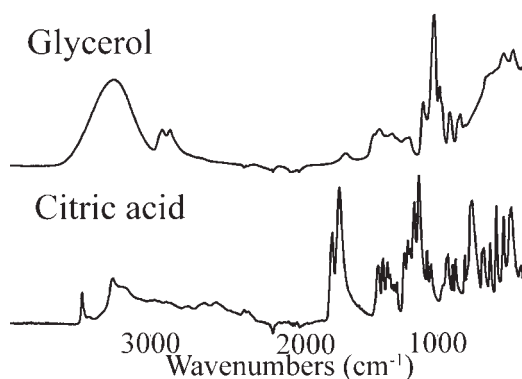


Figure 5 FTIR spectra of glycerol and citric acid.

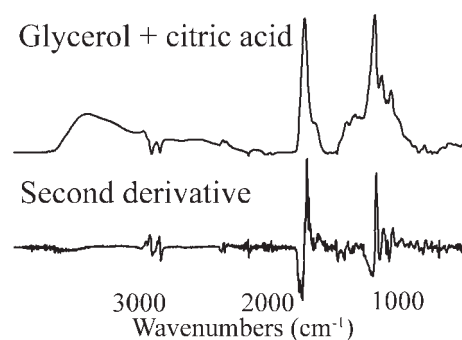


Figure 6 FTIR spectra and second derivative curve from the equimolar reaction of glycerol and citric acid at 170°C.

are shown in Figure 5 for comparison. The broad absorption band associated with the hydroxyl groups of glycerol appears at 3250 cm^{-1} with the carbon–oxygen absorptions characteristic of primary and secondary alcohols occurring at 1030 and 1100 cm^{-1} , respectively (Fig. 5). The spectra obtained for citric acid is shown below that of glycerol with the prominent carbonyl absorption band of the acid evident at 1700 cm^{-1} . The reaction of glycerol with citric acid produced the spectra displayed in Figure 6. This is presented with the corresponding second derivative curve to more accurately identify the absorption peaks. Formation of the ester is indicated by the prominent peak located at 1740 cm^{-1} . The small shoulder attached to this peak suggests the presence of unreacted acid groups. Similarly, the absorption band of the hydroxyl groups at 3250 cm^{-1} has decreased. This indicates a partial reaction of the available hydroxyls. The absorption at 1030 cm^{-1} due to the primary hydroxyl groups has disappeared but a small peak near 1100 cm^{-1} remains, which is attributed to the secondary hydroxyl groups of glycerol.

Spectra obtained for cornstarch and the reaction mixture of glycerol, citric acid, and cornstarch are shown in Figure 7. The spectra for the reaction with

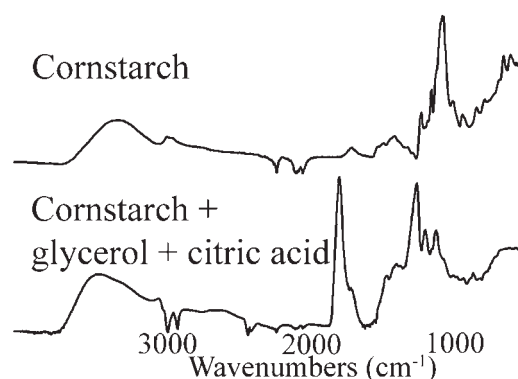


Figure 7 FTIR spectra from the reaction of glycerol and citric acid with 5% cornstarch.

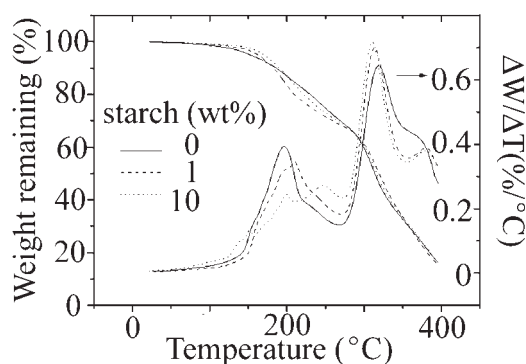


Figure 8 Weight loss and derivative curves for the reaction of equimolar amounts of glycerol and citric acid with cornstarch added at 0, 1, and 10 wt %.

5 wt % cornstarch and the reaction mixture without cornstarch are quite similar. The mixture with cornstarch shows an increase in the strength of the absorption band near 3250 cm^{-1} due to the contribution of the starch hydroxyls.

In addition to esterification, other possible reactions include the formation of ether linkages between the hydroxyl groups of two glycerol molecules, one glycerol and one citric acid molecule, or two citric acid molecules. These reactions would not occur without a suitable catalyst and the spectra of the reaction mixtures, both with and without cornstarch, do not indicate formation of ether bonds.

Thermal gravimetric analyses were also performed on mixtures containing equimolar amounts of citric acid and glycerol with varying amounts of cornstarch (0, 1, 5, and 10 wt %) to determine degradation or weight loss characteristics (Fig. 8). The derivative curves in Figure 8 show two prominent peaks for each sample tested. The maximum peak occurs between 303 and 317°C. A clear trend of increasing weight loss and slight decrease in peak temperature is observed with increasing level of added starch. The second set of peaks is centered near 200°C, which corresponds to the degradation peak seen in the DSC scans and is attributed to citric acid. As the starch level is increased, the peak associated with the degradation of citric acid decreases. At the highest level of starch, 10 wt %, an intermediate peak is evident near 250°C. This is expected to occur with the onset of starch degradation and becomes more pronounced as the starch level in the blend increases.

CONCLUSIONS

The esterification of glycerol and citric acid in the presence of cornstarch was investigated using modu-

lated DSC, TGA (thermal gravimetric analysis), and FTIR. These results confirmed that glycerol and citric acid reacted to form the glycerol citrate esters. The introduction of starch to the reaction mixture increased the number of hydroxyl groups available to form ester or ether groups with glycerol or citric acid. However, these starch derivatives were not observed at the chosen reaction conditions. The secondary hydroxyl groups of starch are less reactive than the primary hydroxyls of glycerol with respect to esterification by citric acid. The low reactivity of cornstarch in the glycerol-citric acid/starch blend suggests that the starch component could be derivatized in a subsequent reaction following the esterification of glycerol and citric acid.

The addition of cornstarch to the reaction mixture did produce measurable changes in the thermal behavior of the products. Thermal scans performed with the individual reactants allowed the identification of the reversible heat flows due to the phase transitions of citric acid and cornstarch. The nonreversible heat flows were attributed to either reaction or degradation processes. Nonreversible heat flows observed below 200°C were related to the formation of ester linkages between glycerol and citric acid. Heat flows above 200°C were attributed to thermal degradation. TGA of the reaction mixtures also showed that increasing the level of starch in the reaction mixtures decreased weight loss values at 200°C but increased weight loss values at 315°C.

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