Effect of CaO in the thermal crosslinking of maltodextrin and citric acid: A cooperative action of condensation and ionic interactions

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ABSTRACT: The study of the effect of CaO in the thermal crosslinking of maltodextrin with citric acid demonstrates that the addition of small amount of this compound enhances the crosslinking of the cured system under processing conditions. This enhancement of the crosslinking leads to a noticeable improvement of the mechanical properties. The mechanism of the enhanced crosslinking reaction has been deeply analyzed by rheology, FT-IR, and TGA. The rheological results show that CaO contributes to the crosslinking. This contribution would allow decreasing 10 °C the temperature of curing process. The enhancement of the crosslinking and consequent improvement of mechanical properties is explained by the contribution of the interactions between the Ca^{2+} and citric acid and the polycondensate network formed between maltodextrin and citric acid. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 44203.

INTRODUCTION

The crosslinking normally refers to the formation of a polymer network. In principle, any type of chemical reaction between compounds bearing suitable functional groups (i.e., monomers) may be used to form a polymer network. The chemical and physical properties of the polymer network strongly depend on the chemical nature of the monomers involved and the crosslinking density. As a consequence, it is possible to design crosslinked polymeric materials with a wide variety of physical properties according to the requirements of its final application.[1] Most crosslinking processes take place by covalent bond formation, like for instance sulfur vulcanization, peroxide curing, radiation curing, or by amine, epoxy bonds. Yet, another reported way of crosslinking is the ionic crosslinking.[2–4]

In recent years crosslinked binder systems based on polysaccharides and polycarboxylic acids have been developed for their application in the glass fiber and nonwoven industry.[5–7] The crosslinking in these polymeric systems takes place by polycondensation, due to the esterification reaction between the hydroxyl groups of the polysaccharides and the carboxyl groups of the polycarboxylic acids. One of the weak points of these binder systems is their slow crosslinking reaction and poor polymer network. This makes these systems to deliver limited mechanical performance especially upon weathering conditions

(temperature, humidity). The system containing maltodextrin and citric acid have been studied in previous work.[8] It was demonstrated that the polycondensation reaction between maltodextrin and citric acid can deliver a thermoset system under processing conditions at 140 °C. However, when comparing this system with traditional petrol based systems like, for instance, phenolic resins for its application in glass fiber materials, mechanical performance of this last are still the best. Improvement of the mechanical performance is linked to the polymer network formed between the polysaccharide and polycarboxylic acid, therefore to the crosslinking density of the system. For that reason, it is intended to improve the crosslinking density of this system.

One alternative to increase the crosslinking density might be by generating additional covalent bonds. This would require the modification of the polysaccharide; for instance, by appending new reactive groups.[9,10] This approach might imply important modifications on the processability of these systems. Another alternative is introducing additional ionic bonds to the existing covalent bonds. The ionic crosslinking look interesting as an alternative because it does not require major modifications to process the systems based on polysaccharides and polycarboxylic acids. Interaction of starch with metal ions have been reported,[11,12] particularly the formation of complexes of metals with starch and maltodextrin.[13–17] Interaction of metal ions

Additional Supporting Information may be found in the online version of this article.

Table I. Compositions Containing Maltodextrin (MAL) and Citric Acid (CA) with CaO

Composition	MAL (% dry weight)	CA (% dry weight)	CaO (% dry weight)
MC	60.0	40.0	—
MC1Ca	59.4	39.6	1.0
MC3Ca	58.3	38.8	2.9

with carboxylic acids is well described and applied in different fields. For instance, it has been reported the use of metal ions as crosslinkers in polymer compositions containing poly(acrylic acid),[18,19] by the interaction between the metal ions and the carboxyl groups of the poly(acrylic acid).[20,21] It is also well known the interaction of polycarboxylic acids with metal ions[22–24] in water treatments and wine industry.

Considering these previous works, it has been considered the introduction of calcium ions in the systems containing maltodextrin and citric acid in order to improve the polymer network. Interactions between maltodextrin and Ca^{2+} could take place, as well as between the citric acid and the Ca^{2+}; both contributing to improve the mechanical properties of the crosslinked systems. Whenever metal ions are introduced as crosslinkers, they are introduced as salts, like for instance calcium chloride. However, the counterion of the salt could generate some drawbacks in final application like for instance corrosion in the steel facilities due to chloride ion. For that reason it is preferable to use a metal oxide, and not metal salt.

The aim of this work is to study the use of Ca^{2+}, by the addition of CaO, as enhancer of the polymer network formation in the binder systems containing maltodextrin and citric acid. The study of the system has been carried out considering under thermal treatment, reproducing the process of final applications (i.e., wood and glass fiber materials).

EXPERIMENTAL

Materials
Powdered maltodextrin (MAL) Maldex 120 (dextrose equivalent, DE 11 to 15), manufactured by spray-drying of liquid maltodextrin, derived from edible corn starch hydrolysis was provided by Tereos Syral. Citric acid (CA) reagent and CaO were purchased from Sigma-Aldrich. The products were used without additional purification.

Crosslinking Systems
Different compositions containing MAL and CA, with CaO were prepared by mixing them in water at different ratios (Table I). MAL was dissolved in distilled water under mechanical stirring and then the CA was added keeping the stirring until the solution was homogeneous. Finally CaO was added keeping the same stirring conditions until it was completely dissolved. Additional mixtures were prepared containing only CA and CaO in the same proportion as in the compositions containing MAL (Table II). Unless otherwise stated, all the mixtures in water were prepared with 50% dry content. Freeze-dried samples were

prepared to avoid the influence of water in the thermogravimetrical analysis.

Mechanical Properties Measurements
Mechanical properties measurements were carried out on glass paper "Whatman GF/A 8 × 10 ins" impregnated with the corresponding composition and cured by heating treatment. A glass paper sheet was soaked in a water solution with 20% solid content of the different compositions. The treated sheet was pressed between the squeezing rolls of a laboratory padder (Mathis) at 3 mm/min speed of the rolls and pressure between the rolls at 2.5 bars. Heating treatment on the impregnated glass paper was applied in a Labdryer oven (Mathis) at 140 °C. Specimens were cut from the cured glass paper sheet with size 75 × 25 mm. Cured specimens were treated with accelerated weathering conditions in a climate chamber (Ineltec) at 50 °C and 95% humidity for 24 h. Tensile strain measurements were carried for the specimens previous to the treatment with accelerated weathering conditions and after the application of accelerated weathering conditions. The tensile strain measurements were carried out in an Instron Universal Testing Machine equipped with a 500 N load cell. The cross-head speed applied was 2.3 m/min and the gauge length was 50 mm. The data was taken from the average of at least six specimens.

Rheological Measurements
Rheological measurements were carried out with an AR1000 rheometer (TA Instruments). Disposable plate-plate geometry with diameter 25 mm was used. Dynamic measurements in oscillatory mode were performed for approximately 1 mL sample in 2000 μm gap, applying frequency mode at 1 Hz and a fixed torque value (tests were performed previously to ensure that the response was in the viscoelastic region). Rheological behavior of water solutions of the compositions in Table I was monitored at isothermal conditions at 130, 135, 140, and 145 °C until maximum modulus plateau was achieved, previously heating up to the isothermal temperature with ramp rate of 3 °C/min. The measurements were done by duplicate.

Attenuated Total Reflectance-Fourier Transform-Infrared (ATR-FT-IR) Spectroscopy
ATR-FT-IR spectra were measured in a Spectrum One FT-IR Spectrometer (Perkin Elmer) with a split pea accessory for ATR. Absorbance spectra were acquired at 4 cm^{-1} resolution and signal-averaged over 10 scans recorded from 4000 cm^{-1} to 650 cm^{-1}. The spectra were baseline corrected and normalized to the most intense absorbance peak. FT-IR spectra were measured for the different compositions upon curing at 140 °C. In order to assure the interpretation of the spectra of the compositions after thermal treatment, spectra were measured for the

Table II. Compositions Containing Citric Acid (CA) and CaO

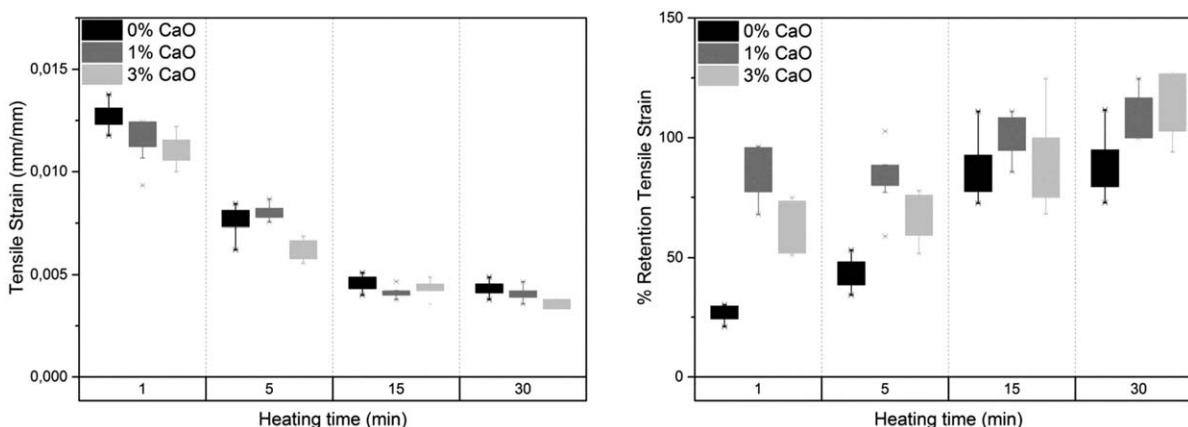| Composition	MAL (% dry weight)	CA (% dry weight)	CaO (% dry weight)
C1Ca	0.0	97.6	2.4
C3Ca	0.0	93.0	7.0

Figure 1. Tensile strain and its retention upon accelerated weathering conditions for glass paper impregnated with the compositions (0% CaO) MC, (1% CaO) MC1Ca, and (3% CaO) MC3Ca, cured at 140 °C and different curing times (1, 5, 15, and 30 min).

resulting samples before and after purification. The cured compositions were purified by membrane dialysis, placing approximately 2 g of composition in a 1000 Da membrane, in 2 L of water for 20 h, renovating the water after 10 h. The purified polymer was dried under vacuum at 40 °C for 24 h. By this purification the citric acid moieties not participating in the esterification reaction are dissolved in water.

Thermogravimetric Analysis (TGA)

TGA was performed using a TGA Q500 (TA Instruments). Different freeze-dried samples of the compositions were heated in a platinum pan from 25 to 600 °C, under a nitrogen atmosphere at a heating rate of 10 °C/min. The derivative TGA (wt %/ °C) of each sample was obtained from the software TA Universal Analysis.

Scanning Electron Microscopy (SEM) and Electron Dispersion X-ray (EDX) Analysis

A microscope US8000 (Hitachi) with EDX system was used for SEM/EDX analysis of different compositions after the curing process. An accelerated voltage of 1 and 5 kV was applied to carry out the SEM analysis and 15 kV for the EDX analysis.

RESULTS AND DISCUSSION

The Effect of CaO on the Mechanical Properties of the Composite Material

By mechanical characterization has been found that the performance of the cured system MC can be improved by adding CaO. The glass paper impregnated with the different compositions in Table I, and cured at 140 °C for different curing times (1, 5, 15, and 30 min) behaves as a stiff thermoset because it breaks, but the deformation is elastic[25,26] (see Supporting Information). More flexible behavior is perceived in short curing time (i.e., 1 min). In this case the yield point is well-defined after elastic region and the composite material breaks with the plastic deformation. The flexible behavior is less noticeable when curing time is 5 min and, becoming completely stiff after 15 min curing. According to the analysis done, the effect of CaO on the crosslinking is more relevant at short treatment times, with a remarkable increase in the slope of the curve. This suggests that, when a small amount of CaO is added to the system, its crosslinking density is increased.

A deeper analysis on the mechanical characterization has been made based on the tensile strain data and Young's modulus data. The results on tensile strain and its retention upon accelerated weathering conditions are shown in Figure 1. The tensile strain decreases when curing time increases, reaching a minimum plateau after 15 min curing. This is due to the increase of the crosslinking density when curing process is longer, leading to a stiffer material.[26,27] The retention of tensile strain upon accelerated weathering conditions is also increased, going from lower than 50% retention in short curing times to a maximum around 80% after a thermal treatment of 15 min. When CaO is added to the system containing MAL and CA, tensile strain is decreased, particularly in short curing times. The positive effect of the addition of CaO on the stiffness (i.e., decreasing tensile strain) is also seen upon accelerated weathering conditions. The retention of tensile strain is higher than 50% independently of the curing time for the compositions containing CaO, reaching a maximum around 100% after 15 min curing. In general, the effect of CaO is statistically relevant ($p < 0.05$) when 3% of CaO is added. This proves that CaO helps to improve the thermoset character of the system containing MAL and CA, most likely as a consequence of the higher crosslinking density.

In Figure 2 is shown the data of Young's modulus and its retention upon accelerated weathering conditions. It can be observed that the Young's modulus increases with the curing time; and its retention after accelerated weathering conditions asymptotically decreasing to 100% after 15 min curing. The addition of CaO significantly increases ($p < 0.05$) the modulus at any curing time. More remarkable is the fact that at short curing times (i.e., 1 or 5 min), when modulus is strongly modified upon weathering conditions in the composition MC, CaO prompts a retention of about 100%. This proves that CaO addition helps to preserve the mechanical properties of the cured material under weathering conditions, as consequence of the increased crosslinking density, especially when cured for shorter times.

The mechanical characterization of the cured system containing MAL and CA shows a positive contribution of CaO on the material stiffness especially when shorter curing times are applied. Furthermore, the addition of CaO helps to the
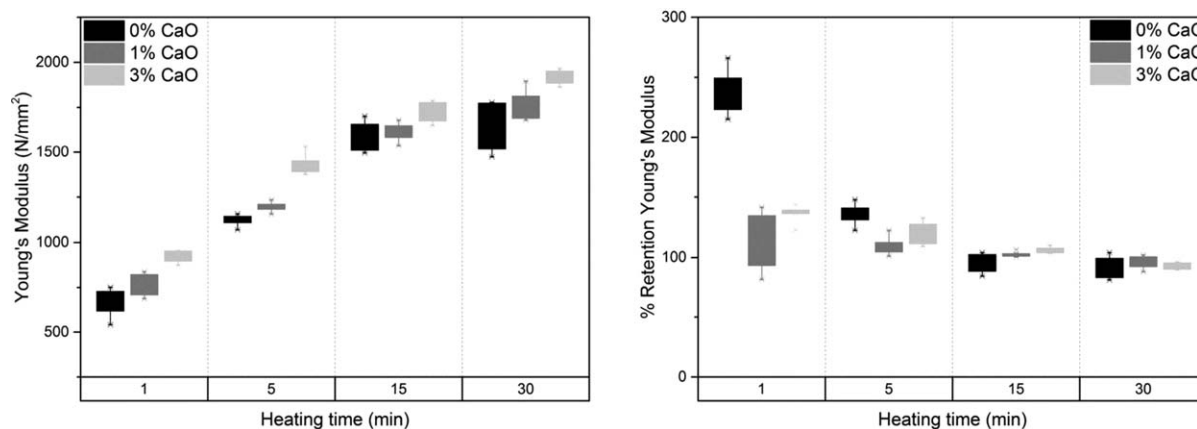
Figure 2. Young's modulus and its retention upon accelerated weathering conditions for glass paper impregnated with the compositions (0% CaO) MC, (1% CaO) MC1Ca, and (3% CaO) MC3Ca, cured at 140 °C and different curing times (1, 5, 15, and 30 min).

preservation of the mechanical properties upon weathering conditions, what is a typical behavior of thermoset systems.

SEM/EDX Analysis

Scanning electron microscopy (SEM) micrographs of the glass-paper impregnated with the different compositions used for the mechanical characterization are shown in Figure 3. The surface of the glass fiber paper is homogeneously impregnated independently of the composition. In the cross-section pictures, it can be observed that the composition is partially covering the fibers and gluing different fibers together. This indicates the good adhesion of the crosslinked system to the glass fibers.

Furthermore, the distribution of Ca^{2+} in the cured compositions at 140 °C was analyzed by EDX. As representative examples, in the Supporting Information are shown the SEM/EDX
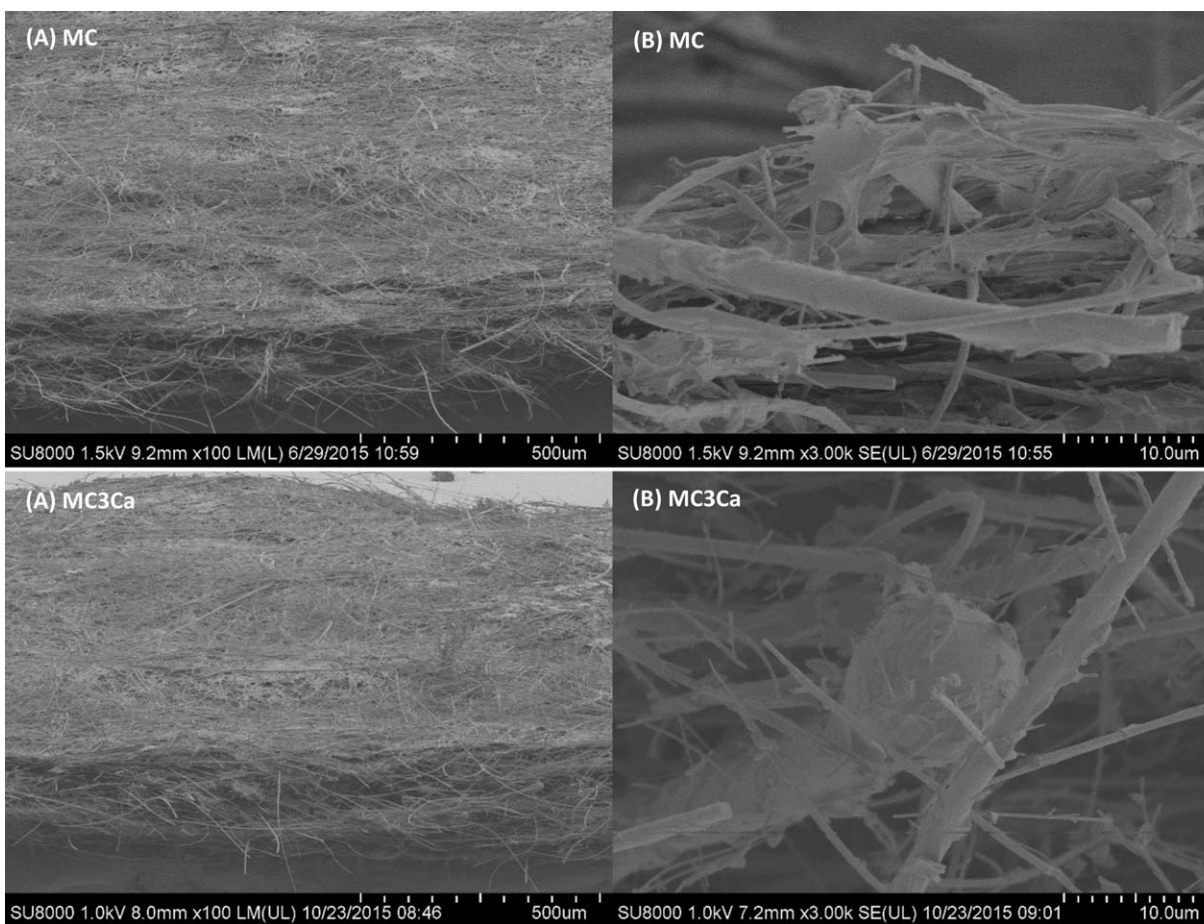

Figure 3. SEM micrographs of glass paper impregnated with composition MC, MC3Ca upon heating treatment for 15 min, after tensile strength test on the (A) surface and (B) cross-section fibers.
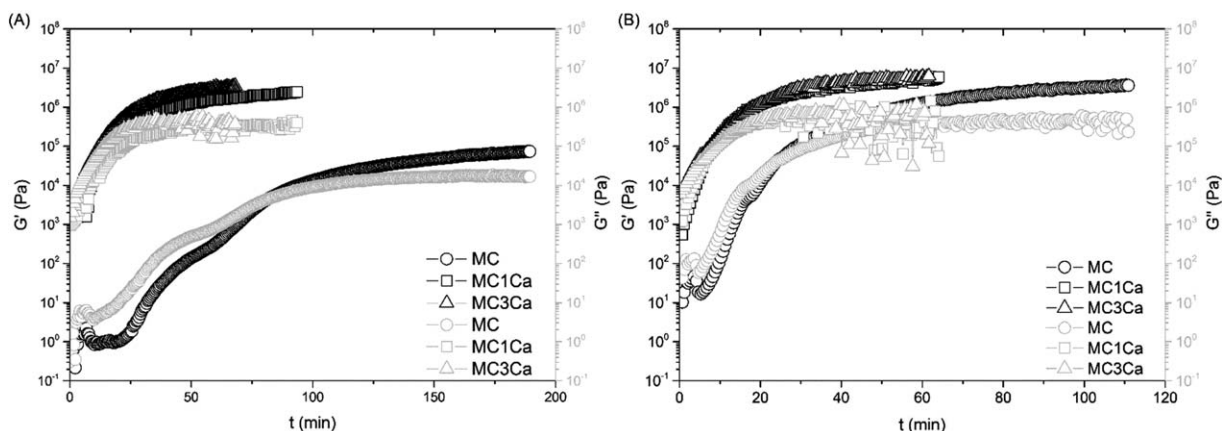
Figure 4. Log G and log G'' against time upon isothermal treatment at 130 °C (A) and 140 °C (B) for the compositions MC, MC1Ca, and MC3Ca.

diagrams of the composition MC3Ca. In the corresponding SEM micrograph of the surface of MC3Ca it cannot be identified any fractures but fairly flat surface. In EDX diagram it can be observed that Ca^{2+} are homogeneously distributed all over the surface of the cured composition.

The Effect of CaO on the Crosslinking Process

The impact of the addition of CaO on the crosslinking of the systems containing MAL and CA has been studied by rheology. Isothermal treatment was applied at different temperatures (130, 135, 140, and 145 °C) for the different compositions in Table 4. Figure 4 shows the evolution of storage modulus (G') and loss modulus (G'') against time, at temperature 130 and 140 °C. Both moduli increase since the beginning of isothermal treatment due to the crosslinking process.[28] Furthermore it can be observed that the maximum modulus achieved at 130 °C for the composition MC is lower than at 140 °C. However, the addition of CaO prompts faster increase of the moduli,[29] leading to a maximum modulus around 10 MPa independently of the testing temperature. This indicates that, when CaO is added, the same level of crosslinking can be achieved with curing temperature 10 °C lower.

The gel time for the different compositions in Table I has been also determined from these experiments. For that it has been considered that the gel time is the time at which storage modulus and loss modulus cross-over.[30,31] The values obtained for the different compositions are shown in Figure 5. The gel time for the composition MC at 130 °C is approximately four times higher than the gel time at 140 °C. Therefore the processing temperature has a strong impact on the gel time. Nevertheless, the addition of CaO dramatically decreases the gel time independently of the processing temperature, giving rise to similarly low values at 130 and 140 °C.

Experimental calculation of apparent activation energy (Ea) has been done in order to evaluate the effect of 3% CaO addition on the kinetic of the system containing MAL and CA. For its calculation the Arrhenius law [eq. (1)] has been applied. Considering that the chemical conversion of the system at the gel time is constant,[31] apparent kinetic constant (k') would be related to the gel time (tg) according to the eq. (2). By replacing eq. (2) in eq. (1), eq. (3) can be obtained. By plotting ln (tg) against the inverse of the temperature corresponding slope is obtained (Fig. 6), and from the slope the apparent activation energy (Ea) can be calculated. The calculation has been done based on the gel time data obtained by measurements run at temperature of 130, 135, 140, and 145 °C.
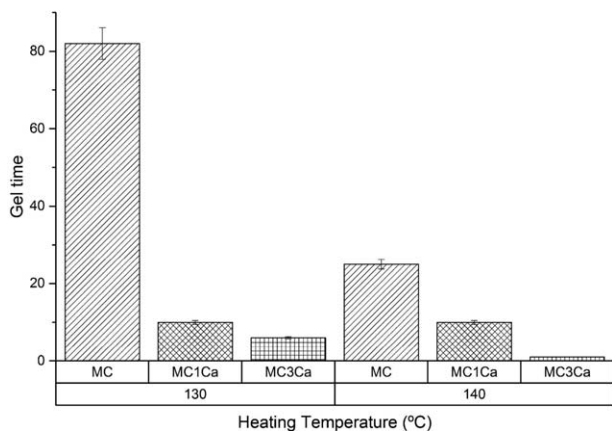

Figure 5. Gel time of the compositions MC, MC1Ca, and MC3Ca when testing at different temperatures, 130 °C and 140 °C.
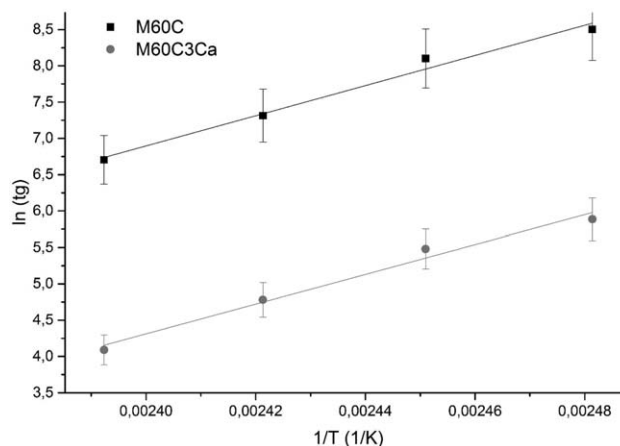

Figure 6. Plot of ln(tg) against the inverse of corresponding temperature.

Table III. Activation Energy of Composition M60C, M60C1SHP, and M60C3SHP

Composition	Ea (kJ/mol)
M60C	172.8
MC3Ca	170.2

$$\text{Arrhenius law, } \ln k' = \ln A - E_a/RT \tag{1}$$

$$\text{Relation between apparent kinetic constant} \\ \text{and gel time, } tg = \frac{cte}{k'} \tag{2}$$

$$\text{Relationship between gel time and inverse} \\ \text{of temperature, } \ln tg = \ln cte' + E_a/R \cdot T \tag{3}$$

In Table III, is collected the resulting Ea from the calculation explained above. The results show that activation energy of the system containing MAL and CA is slightly reduced when 3% CaO is added.

This rheological study demonstrates that CaO contributes to the crosslinking formation of the system containing MAL and CA. This contribution to the crosslinking is detectable independently of the processing temperature in the range of 130 to 145 °C. However the apparent activation energy of the system would be just stlightly affected by the addition of CaO.

The Interactions of Ca Ion with the System Based on MAL and CA

IR Study. According to previous work,[8] the evolution of the polycondensation reaction between MAL and CA can be followed by IR. The C═O stretching band, assigned to the ester bond between the hydroxyl groups of MAL and the carboxyl group of CA, and the OH stretching band evolve as the esterification reaction is progressing. In Figure 7 is shown the IR spectra for the different compositions in Table I after curing treatment for different periods of time at 140 °C. The C═O stretching band at 1712 to 1720 cm^{-1} evolves similarly in all the compositions. The OH band at 3331 to 3398 cm^{-1} shifts to different wave numbers when CaO is added to the composition MC. This may be assigned to the different evolution of the hydrogen bond interactions of the MAL and CA when Ca^{2+} is in the media.[11,15,17] Furthermore, new bands in the range of 1630 to 1637 and 1546 to 1547 cm^{-1} can be identified in the system containing 3% of CaO (MC3Ca). These bands have been further investigated.

As representative example, in Figure 8 can be observed the C═O stretching band related to the ester bond at 1721 to 1728 cm^{-1}, after 4 h thermal treatment at 140 °C and later purification, for the compositions MC, MC1Ca, and MC3Ca. In this way it is assure that the intensity of C═O stretching band correspond solely to the ester bond, therefore it is proved that the ester bond between the hydroxyl groups of MAL and the carboxyl groups of CA still remains after leaching with water.
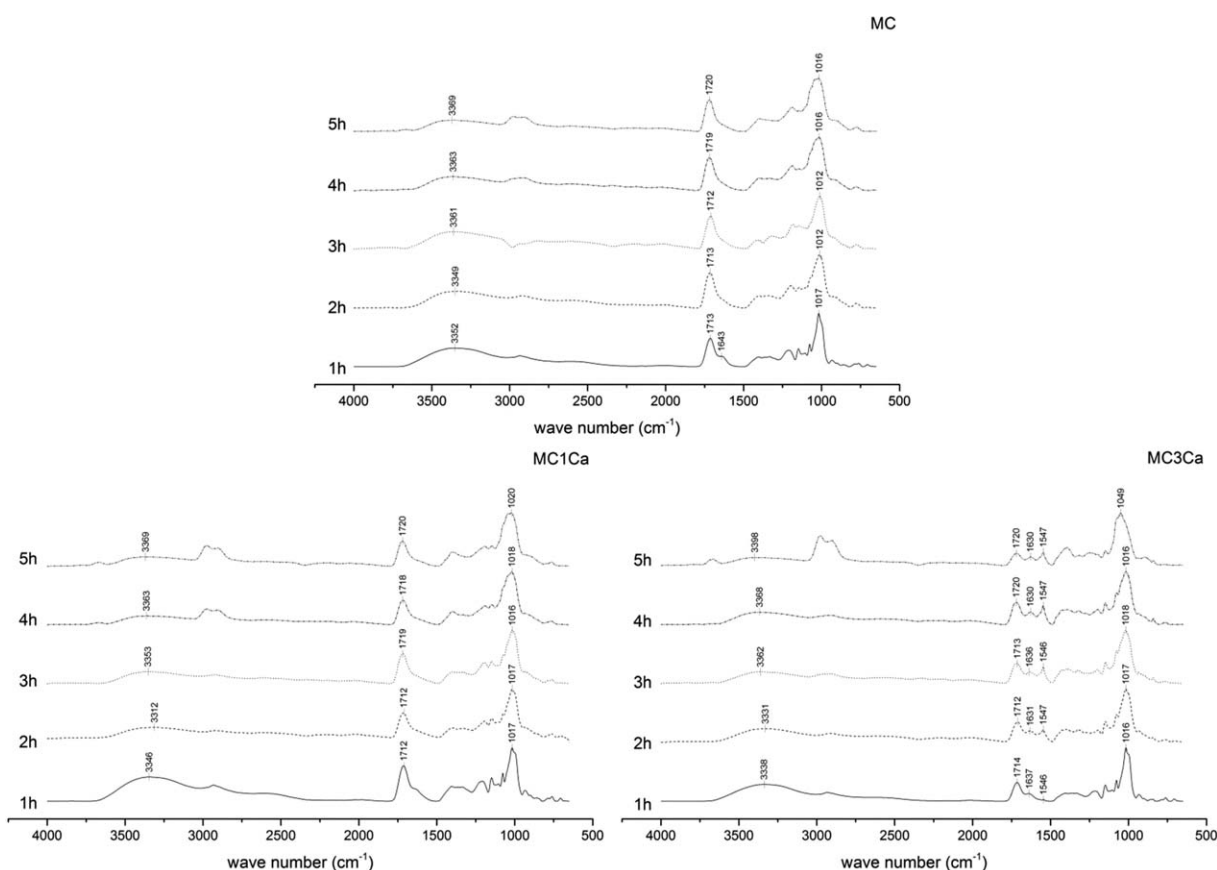

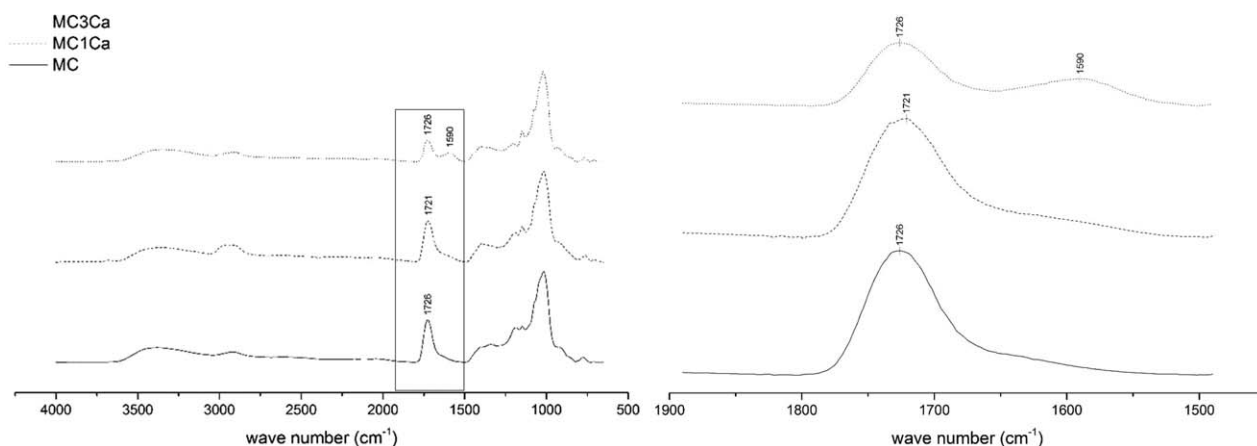**Figure 7.** IR spectra of the compositions MC, MC1Ca, and MC3Ca upon curing at 140 °C for different curing times.

Figure 8. IR spectra of the binder systems MC, MC1Ca, and MC3Ca after 4 h curing at 140 °C and later purification.
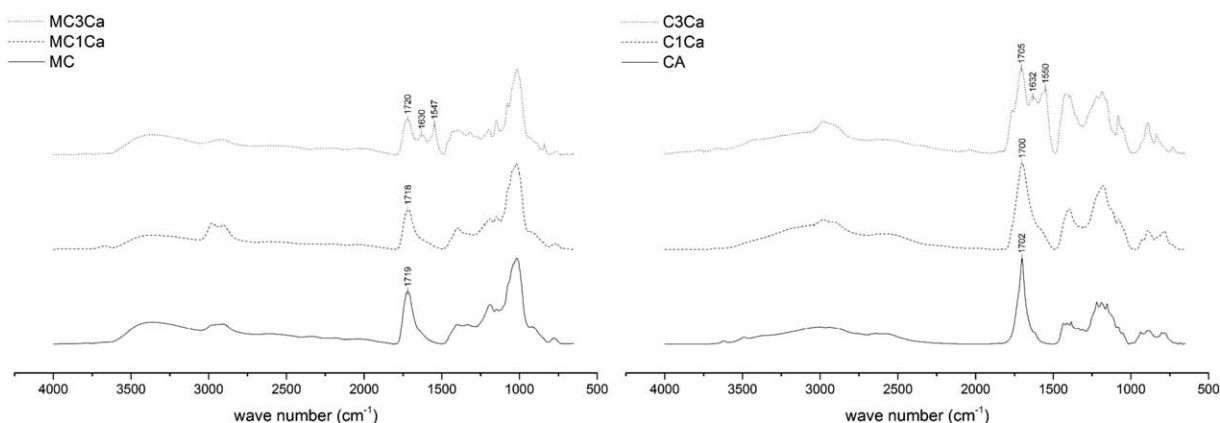

**Figure 9.** IR spectra of the compositions in Tables I and II after 4 h curing at 140 °C, no purified.

Quantitative comparison of the intensity of C=O stretching band due to ester bond for the different compositions is shown in the Supporting Information. The intensity of the band decreases when CaO is added to the system containing MAL and CA (MC). This may be a consequence of the ionic interactions between the Ca^{2+} and the carboxyl groups of CA not involved in the ester formation with MAL.[24,32] Apart from the C=O stretching band, a new band at 1590 cm^{-1} assigned to carboxylate form[33,34] can be clearly identified for the composition containing 3% of CaO. This band may be assigned to the interaction of carboxyl groups of CA with Ca^{2+}, still remaining after purification. To further understand the interactions leading to these results, mixtures without MAL were studied.

In Figure 9 are compared the spectra of the systems containing MAL and CA with CaO after curing 4 h with the spectra of cured (4 h) mixtures containing only CA and CaO. It can be observed that the bands at around 1550 and 1630 cm^{-1} identified in the spectra of cured mixtures containing only CA and Ca can also be identified in the spectra of the composition MC3Ca. This proves that interactions between CA and Ca take place in those systems containing MAL, CA, and Ca leading, for instance, to the formation of complexes CA—Ca.[35,36] As it can be observed in in Scheme 1, CA has two equivalent carboxyl groups and one different carboxyl group. Considering this, the

band at 1590 cm^{-1} may be assigned to the carboxylate form of one of the carboxyl groups, and the band at 1630 cm^{-1} may be assigned to the other carboxyl group. This has been proved by comparison of the spectra in Figure 8 with the spectra of precipitate of mixture C3Ca and the water solution of the composition M60C3Ca shown in the Supporting Information.

Comparing the spectra in Figure 8 with the spectra in Figure 7, it can also be observed that the band at 1630 cm^{-1} disappears after purification, as a consequence of leaching of CA non-reacted with MAL. However the band at 1590 cm^{-1} indicates that still carboxylate forms remain in the polycondensate system.

Overall, IR study demonstrates the existence of ionic interactions, between Ca^{2+} and CA, which are partially resistant to the humidity. In the final cured systems these ionic interactions
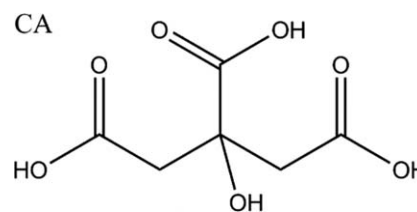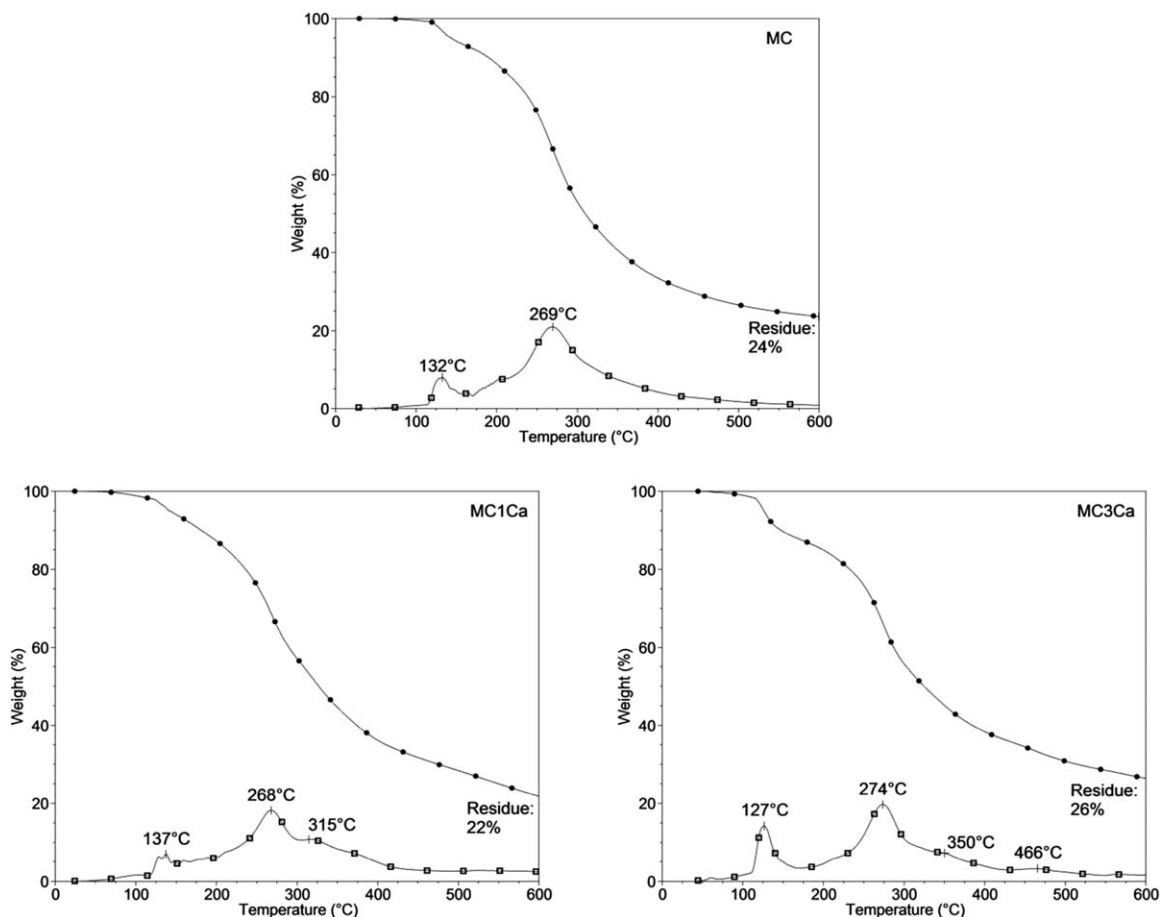

Scheme 1. Citric acid.

Figure 10. TGA and its first derivative for all he compositions MC, MC1Ca, and MC3Ca.

contributes to the improvement of the mechanical performance. The additional crosslinking generated by ionic interactions should be expected not to be humidity resistant; however it might still positively contribute to the polymer network as shown above, because it could be embedded (i.e., protected) in the polycondensate network formed by the reaction between the hydroxyl groups of MAL and the carboxyl groups of CA. This would lead to a synergetic effect of the two types of crosslinking, covalent and ionic.

TGA Study. The esterification reaction between carboxyl groups of CA and hydroxyl groups of MAL has been analyzed by TGA as reported in previous work.[8] In Figure 10 are compared the TGA and corresponding first derivative for the compositions in Table I. The weight loss due to the water released by the esterification reaction around 130 °C is identified[37] in all the compositions. The second weight loss step around 270 °C, related to the decompositions of the esterification derivatives can be also identified in all the compositions. Still, a third weight loss step is found at 315 °C
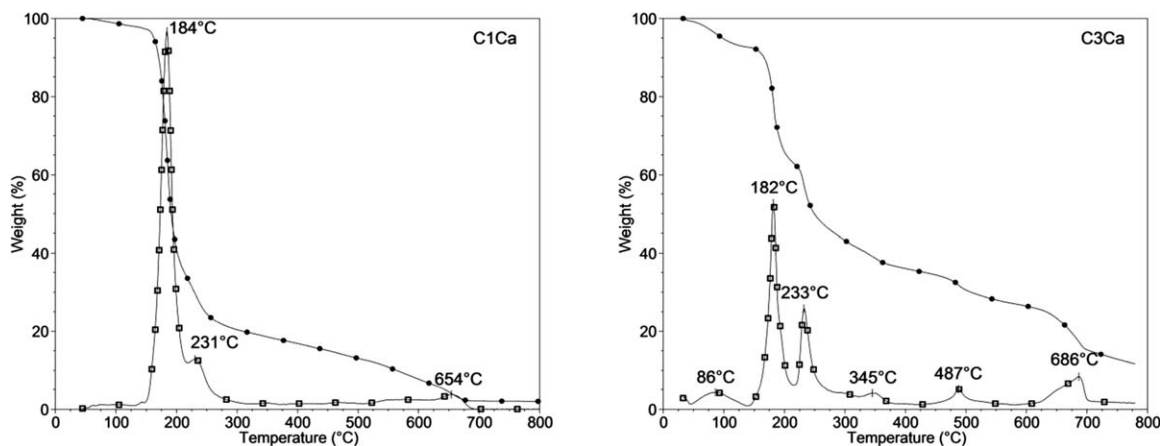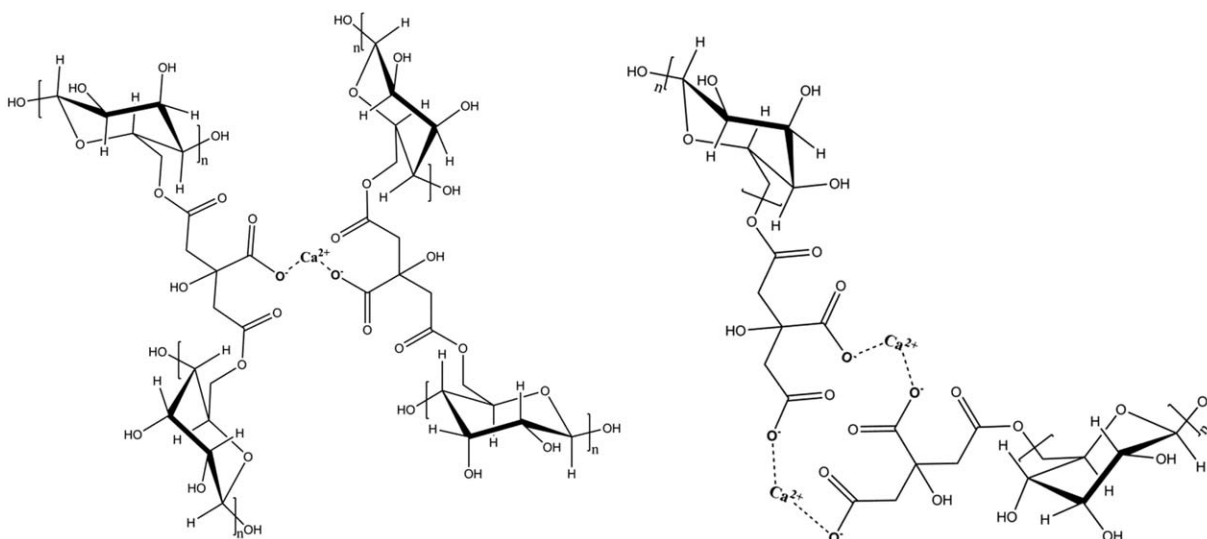

Figure 11. TGA and its first derivative for the mixtures C1Ca and C3Ca.

Scheme 2. Possible interactions of Ca^{2+} with CA attached to MAL chains.

and 350 °C for the compositions MC1Ca and MC3Ca respectively, which is assigned to the decomposition of the polycondensation derivatives. And even a fourth weight loss at 466 °C can be detected for the composition MC3Ca, which is due to the decomposition of compounds result of interaction of CA with Ca^{2+}. The assignment of this weight loss has been proved by the analysis of the mixtures containing CA and CaO quoted in Table II.

In Figure 11 is shown the TGA and corresponding derivative curve of the mixtures containing CA and CaO. In the mixture C3Ca several weight loss steps are identified which are related to the decomposition of calcium citrate tetrahydrate as reported previously by Mansour,[38] result of the complexes formation between CA and Ca^{2+}. Additional weight loss steps at 182 to 184 °C and 231 to 233 °C appear in both mixtures, C1Ca and C3Ca. The relation between their decomposition rates is different depending on the percentage of CaO. This means that the ratio of compounds causing these decompositions is different depending on the CaO content. This suggests that the compounds related to these decompositions are due to the interaction of CA with Ca; not generating complexes which lead to calcium citrate tetrahydrate, but just interacting, for instance, one single carboxyl group of CA with Ca^{2+}.

Based on the IR and TGA results it is proposed that the crosslinking enhancement of the system containing MAL and CA by the addition of CaO is due to the Ca^{2+} interacting in different ways with CA and MAL-CA polycondensates. According to the chelation activity of CA reported by Welling *et al.* a portion of Ca^{2+} would form Ca-Cit^{3-} complexes which later become calcium citrate tetrahydrate.[24,32] The rest of Ca could interact with CA in the form of $HCit^{2-}$ and H_2Cit^-. Furthermore, although it was not possible to prove, it is proposed that, as shown in Scheme 2, other interactions of Ca takes place with the free carboxyl groups of CA molecules which are attached to MAL chains by another carboxyl group. All these different interactions would contribute to the crosslinking formation, therefore to the mechanical properties delivered by the polymer network formed by MAL and CA.

CONCLUSIONS

Improvement of the mechanical properties of the crosslinking system containing maltodextrin and citric acid has been provided by the addition of CaO. The improvement refers not only to the mechanical performance of the system just after curing but also upon weathering conditions. This means a system with stronger thermoset character. It has been demonstrated the existence of interactions between citric acid and Ca^{2+}. These interactions are the reason for the enhancement of the crosslinking formation. In fact the crosslinking reaction in the system containing maltodextrin and citric acid could be carried out at 10 °C lower than normally used for industrial processes (i.e., 140 °C). Based on the results, a mechanism of interaction of Ca^{2+} with citric acid has been proposed. The interactions would take place not only with single citric acid molecules but also with the citric moieties of the polycondensate derivatives from maltodextrin and citric acid. This would help to the reinforcement of the original polymer network formed between maltodextrin and citric acid.

ACKNOWLEDGMENTS

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