JOURNAL OF MATERIALS SCIENCE 17 (1982) 2067–2076

Effect of zinc-levulinic acid chelate compounds formed in furfuryl alcohol polymer concrete

T. SUGAMA, L. E. KUKACKA
Process Sciences Division, Department of Energy and Environment,
Brookhaven National Laboratory, Upton, NY 11973, USA

As part of an experimental programme to develop high early strength water-compatible furfuryl alcohol (FA) polymer concrete (PC) composites, the polymerization heat resulting from the use of various mineral and organic acid initiators was measured using a differential scanning calorimeter. The results indicated that, of the several initiators evaluated, the use of 1,1,1-trichlorotoluene (TCT)–zinc chloride ($ZnCl_2$) system to cure a FA–water–saturated aggregate system yielded the highest early strength and the highest polymerization heat. The $ZnCl_2$ solution used as part of the two-component initiator systems had a significant effect on the rate of polymerization of the FA monomer and the thermal stability of the composite. The latter resulted from an increase in the stiffness of the polymer chains due to the formation of zinc–FA chelate compounds. These were formed through reactions between the bivalent metallic Zn^{2+} ions dissociated from the $ZnCl_2$ solution and the strongly ionized carboxyl groups of levulinic acid yielded by the cleavage of furan rings in an acidic medium. The thermal polymerization activation energy of FA monomer combined with the TCT–$ZnCl_2$ system was calculated to be 98.6 kJ mol^{-1}. The glass transition temperature, T_g, and thermal decomposition heat of the system were 62° C and 220 kJ kg^{-1}, respectively.

1. Introduction

In an early paper [1], the use of furfuryl alcohol (FA) monomer as a binder with wet aggregate to form a polymer concrete (PC) was described. Possible uses for the composite are as rapid all-weather repair materials for airport runways, bridge decks, and highways. FA–PC composites containing aggregate with a water content of up to 8 wt% yielded a compressive strength of greater than 13.78 MPa after a cure time of 1 h at temperatures ranging from − 20 to 30° C [2]. Constituents in the formulation included FA monomer, wet aggregate and dry silica flour (used as a moisture-absorbing filler). The condensation-type polymerization of the monomer was accomplished by the use of an acidic-type initiator consisting of 1,1,1-trichlorotoluene (TCT) as an organic acid and zinc chloride ($ZnCl_2$) as a mineral acid.

In preliminary studies to measure the polymerization rates of FA in the presence of wet aggregate at various TCT–$ZnCl_2$ concentrations, it was found that the $ZnCl_2$ had a significant effect on both the curing rate and the early strength. However, detailed studies using other acid or acid-releasing initiators, for use with $ZnCl_2$ in two-component systems, had not been performed.

The objective of the current study was to find an optimum acidic initiator for use in conjunction with $ZnCl_2$, from among water-soluble materials such as TCT, trichloroacetic acid (TCA), p-toluene sulphonic acid (TSA), aniline hydrochloride (AHC), sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and phosphoric acid (H_3PO_4). As part of this study, exothermic heat and kinetic analysis measurements of the thermal polymerization of FA initiated by various two-component systems were conducted using differential scanning calorimetry (DSC). Compressive strength measurements made 1 h after casting the FA–PC specimens at 24° C were used as an indication of the resulting mechanical properties of the composite.

In addition, on the basis of data obtained from

0022–2461/82/072067–10$03.70/0

infra-red spectroscopy (i.r.), X-ray diffraction (XRD), and DSC, hypothetical mechanisms for reactions occurring between FA and Zn^{2+} bivalent metallic ions released from the $ZnCl_2$ in an aqueous medium were developed. Also, the thermodyanmic properties of the reaction products were quantitatively examined.

2. Experimental procedure

2.1. Materials

Commercial-grade furfuryl alcohol (FA) monomer, supplied by the Quaker Oats Company, was used in this study. The vapour pressure of the FA was $133.322\,\mathrm{Nm^{-2}}$ at 31.8° C and the viscosity was about 5 cP at 25° C.

Anhydrous zinc chloride ($ZnCl_2$) was obtained from the Mineral Research Development Corporation. For use as an initiator for FA, 80 g of $ZnCl_2$ was dissolved in 20 g water.

The 1,1,1-trichlorotoluene (TCT), trichloroacetic acid (TCA), *p*-toluenesulphonic acid (TSA), aniline hydrochloride (AHC), sulphuric acid (H_2SO_4), hydrochloric acid (HCl), and phosphoric acid (H_3PO_4) reagents selected as candidates for acid-type initiators were commercial analytical-grade chemicals.

Commercial-grade silica sand, having a particle size of 1.19 to 0.149 mm, was used as an aggregate in the PC. Dry silica flour (SiO_2) of a particle size less than 62 μm was used as a moisture-absorbing reactive filler.

The procedures for the preparation of the PC specimens were identical to those described in an earlier publication [1].

2.2. Test methods

A Du Pont 910 differential scanning calorimeter (DSC) with a heating rate of $10°\,\mathrm{C\,min^{-1}}$ in N_2 gas was used for determining the thermodynamic properties of the FA samples. The area measurements of exothermic and endothermic peaks were made using an electronic-type planimeter.

Compressive strength tests were performed on four cylindrical specimens, of diameter 22 mm and length 44 mm. The standard deviation for the compressive strength results was 0.43.

A Perkin–Elmer model 257 spectrometer was used for infra-red (i.r.) analysis. The tests were performed by preparing KBr discs made by mixing 200 g of KBr with 3 to 5 mg of the sample that had been crushed to a size less than 0.104 mm. The spectra were recorded at an 8 min scanning rate over the frequency range of 4000 to $600\,\mathrm{cm^{-1}}$.

X-ray diffraction (XRD) analysis was performed using the powder diffraction pattern method. XRD patterns were measured in the diffraction range of 2.71 to 3.56×10^{-10} m.

3. Results and discussion

3.1. Exothermal heat of polymerization

The effect of active acidic initiators on the curing rates of FA monomer can be evaluated on the basis of heat derived by the thermal polymerization. The FA samples used in these heat-of-polymerization measurements were prepared by mixing FA with 1.0% of the acid initiator and 5.0% of a $ZnCl_2$ aqueous solution (80% $ZnCl_2$), by weight of FA, at a temperature of about 50° C. Approximately 30 mg of sample was then packed into an aluminum sample cell which was sealed tightly with an aluminum lid. A sealed empty sample cell was used as a reference for the measurement.

Measurements of the polymerization heat as a function of the curing temperature were conducted using DSC. A typical time-based thermogram is shown in Fig. 1. These were used for quantitative measurements of the area under the exothermic peaks as determined from the base line. A planimeter was used to measure the areas. Using these data the polymerization heat, ΔH, can be calculated from [3],

$$\Delta H = \frac{A}{m}(60\,BE\Delta qS), \qquad (1)$$

where A is the peak area ($645.2\,\mathrm{mm^2}$), m is the sample mass (mg), the factor of 60 is a conversion factor ($\mathrm{sec\,min^{-1}}$), B is the time-base setting ($2.362\,\mathrm{sec\,min^{-1}}$), E is the cell calibration coefficient at the temperature of the experiment (dimensionless) and ΔqS is the pen sensitivity ($0.165\,\mathrm{mJ\,sec^{-1}\,mm^{-1}}$).

The results from measurements of the ΔH, are given in Table I. The largest ΔH value, $329\,\mathrm{kJ\,kg^{-1}}$, resulted from the use of the TCT–$ZnCl_2$ system. Assuming that, if the ΔH obtained from this system is the total heat energy required to yield 100% conversion to polymer, then the value of $\Delta H = 297\,\mathrm{kJ\,kg^{-1}}$ resulting from the use of the one-component $ZnCl_2$ system corresponds to a conversion of about 90%. The remaining 10% is presumed to be unreacted monomer. The use of H_3PO_4–$ZnCl_2$ was also found to be very effective. In this case the ΔH value was $326\,\mathrm{kJ\,kg^{-1}}$.

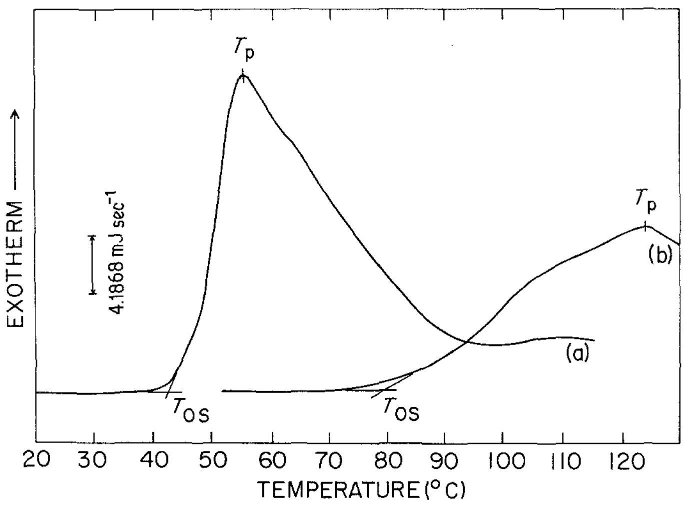

Figure 1 DSC thermograms for (Curve a) TCT–$ZnCl_2$-initiating FA monomers and (Curve b) $ZnCl_2$-initiated FA monomers.

Although the HCl–$ZnCl_2$ system results in initiation at approximately 31° C, the ΔH value of 315 kJ kg^{-1} is somewhat lower than that resulting from use of the TCT–$ZnCl_2$.

The results from measurements to determine the onset temperature of polymerization, T_{os}, and the peak exothermal temperature, T_p, for FA monomer polymerized using various initiators are also given in Table I. Using only $ZnCl_2$, the T_{os} value for FA is 80° C and the T_p value for FA is 123° C. These temperatures are higher than those resulting from the use of other acidic initiators in conjunction with $ZnCl_2$. Conversely, HCl–$ZnCl_2$ had the lowest T_{os} (31° C) and T_p (54° C) values, indicative that this system acts strongly to promote the condensation of FA at low temperatures.

The differences between T_{os} and T_p can be used to evaluate the degree of the propagation reaction and the extent of cure as a function of reaction time. This is useful for determining the effect of the initiators on the polymerization rate. For example, $T_p - T_{os} = \Delta T$, for the HCl–$ZnCl_2$ system was 23° C. This indicates that a temperature increase of 23° C above that needed to initiate the polymerization is required to give a complete cure. The most rapid propagation reaction resulted from the use of TCT–$ZnCl_2$. The ΔT value was 7° C. Very slow propagation reactions resulted from the use of $ZnCl_2$, TSA–$ZnCl_2$, and H_2SO_4–$ZnCl_2$ systems. In these cases, the ΔT value was greater than 40° C.

From the results described above, it appears that, of the initiators investigated for the polymerization of FA monomer, the TCT–$ZnCl_2$ system yields the highest conversion rate.

3.2. Compressive strength

Since early strength is a very important requirement for a rapid repair material, measurements of the compressive strength were used to evaluate candidate polymerization systems. In these tests, the strengths of specimens consisting of 14.3 wt% FA monomer, 68.6 wt% wet aggregate (water content 7.5 wt%) and 17.1 wt% dry silica-flour filler were measured 1 h after mixing the components at approximately 24° C. Curing was accomplished

TABLE I Heat of polymerization and exotherm temperatures for FA polymerized by two-component acidic reagents

Initiator	Exothermal temperature		Heat of polymerization, ΔH (kJ kg^{-1})
	Onset temperature, T_{os} (° C)	Peak temperature, T_p (° C)	
Zinc chloride	80	123	297
1,1,1-trichlorotoluene + zinc chloride	48	55	329
Trichloroacetic acid + zinc chloride	53	85	295
p-toluenesulphonic acid + zinc chloride	72	115	274
Sulphuric acid + zinc chloride	75	118	311
Hydrochloric acid + zinc chloride	31	54	315
Phosphoric acid + zinc chloride	39	68	326
Aniline hydrochloride + zinc chloride	61	84	302

TABLE II The effect of acidic initiators on the early compressive strength of polymer mortar consisting of 14.3 wt% FA monomer, 68.6 wt% wet sand (water content 7.5 wt%) and 17.1 wt% dry silica-flour filler

Initiator*	One-hour compressive strength at 24° C in air, (MPa)
Zinc chloride	†
1,1,1-trichlorotoluene + zinc chloride	16.40
Trichloroacetic acid + zinc chloride	7.58
p-Toluenesulphonic acid + zinc chloride	1.17
Sulphuric acid + zinc chloride	6.78
Hydrochloric acid + zinc chloride	10.67
Phosphoric acid + zinc chloride	12.29
Aniline hydrochloride + zinc chloride	3.17

*The amount of zinc chloride was 60.0% by weight of FA monomer; the amount of other initiators was 1.5% by weight of FA monomer.

†Too low to be measured.

using a mixture of 60% $ZnCl_2$ and 1.5% of the other acidic initiators, all by weight of the FA monomer. Strength data are summarized in Table II. The highest early strength obtained in this test series (16.4 MPa) was for FA–PC specimens polymerized by the use of TCT and $ZnCl_2$. The use of H_3PO_4–$ZnCl_2$ yielded the second highest strength (12.29 MPa), a value about 25% lower than that from the TCT–$ZnCl_2$. One-hour strengths that were less than 6.89 MPa were obtained when the $ZnCl_2$, TSA–$ZnCl_2$, H_2SO_4–$ZnCl_2$ and AHC–$ZnCl_2$ initiators were used. This is probably due to the high (> 60° C) onset of polymerization temperatures for these systems which result in low curing rates at 24° C.

An interesting correlation is apparent when the heat of polymerization of the FA initiator systems having a T_{os} value of less than 60° C, is compared with the compressive strength data. As indicated in Fig. 2, the PC strength increases non-linearly with an increase in the heat generation. These results suggest that the measurement of ΔH is a useful method for evaluating the effectiveness of various initiator systems and for predicting the early-age mechanical properties of the resulting PC composite.

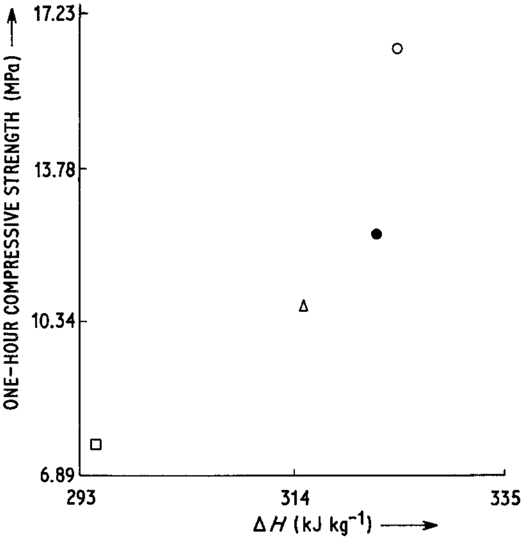

Figure 2 Compressive strength for FA–PC against polymerization heat for FA monomers; ○, TCT–$ZnCl_2$; ●, H_3PO_4–$ZnCl_2$; △, HCl–$ZnCl_2$; □, TAC–$ZnCl_2$.

3.3. Kinetics of thermal polymerization

In other experiments, the energetic condensation reactions occurring between FA monomer and the TCT–$ZnCl_2$ initiator were evaluated on the basis of results obtained from the activation energy of thermal polymerization. The kinetic parameters were determined from the DSC thermograms.

As shown in Curve a in Fig. 1, the typical thermogram indicates that the kinetic energy (4.1868 mJ sec^{-1}) increases rapidly with an increase in curing temperature. The energy of the maximum exotherm at 55° C was measured from the dynamic DSC curve to be 21.4 mJ sec^{-1}. This represents the energy needed to convert greater than 90% of the monomer to polymer.

As shown in Fig. 3, the value of the activation energy, E_a, for the condensation polymerization of FA monomer was determined from the slope of the curve of the Arrhenius plot of the logarithm of the polymerization rate constant, k, against the reciprocal of the absolute temperature, T^{-1}. The first-order activation energy for the thermal polymerization of FA containing 1% water by weight of monomer was calculated to be 98.6 kJ mol^{-1}.

3.4. Reaction mechanisms

The hypothetical reaction mechanisms of FA monomer initiated by the use of TCT and $ZnCl_2$ were investigated by use of i.r. spectroscopy and XRD. Three types of samples were evaluated: (a) FA monomer, (b) FA monomer containing 1 wt% TCT and 1 wt% water and (c) FA monomer containing 1 wt% TCT and 5 wt% of a $ZnCl_2$ solution (80% $ZnCl_2$). Samples (b) and (c) were

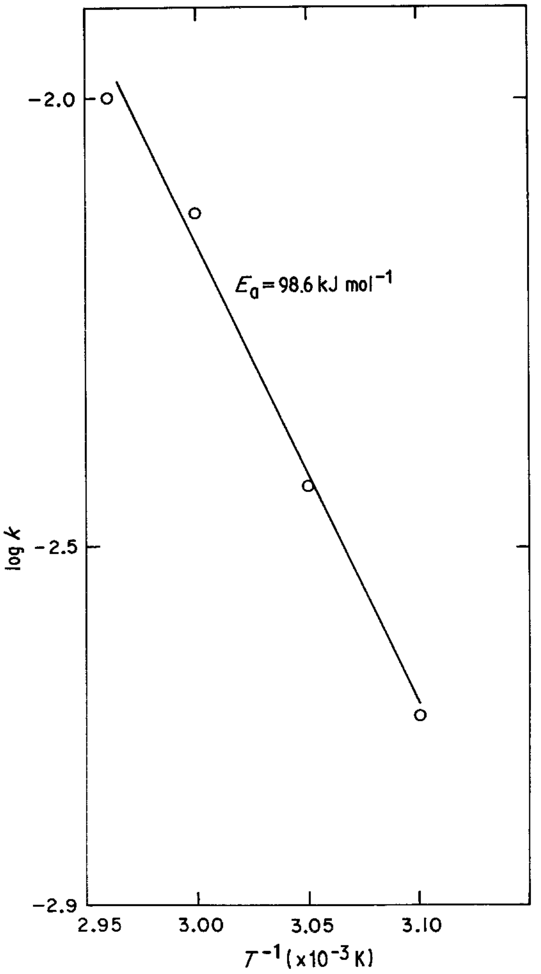

Figure 3 Arrhenius plot for the cure rate of FA monomer initiated with TCT and $ZnCl_2$.

post-cured in an oven at approximately 80° C in order to ensure complete polymerization.

The i.r. spectra of these samples are shown in Fig. 4. I.r. absorption frequencies of the FA monomer (see curve in Fig. 4) are characterized by a stretch vibration of bonded O–H at 3300 cm^{-1}, a stretch vibration of C–H in the furan ring at the 3100 cm^{-1} shoulder, a stretch vibration of C–H in the CH_2 groups at 2910 and 2860 cm^{-1}, a skeletal stretch vibration of C=C–C=C groups in the furan rings at 1600, 1500, 1405 and 1360 cm^{-1}, a vibration of deformed OH groups at 1250 cm^{-1}, an asymmetric and a symmetric stretching vibration of =C–O–C groups in 2-substituted furans at 1210 and 1000 cm^{-1} and a stretch vibration of C–OH groups of alcohol at 1150 cm^{-1}. Also, the band at 1210 cm^{-1} may be due to the C–H deformation of 2-substituted forms.

The spectrum of FA polymer in the presence of water phases initiated by adding the TCT catalyst (see Curve b in Fig. 4) showed the existence of three new bands at 1700, 1550, and 1390 cm^{-1}. The prominent absorption at 1700 cm^{-1} is due to a stretch vibration of carbonyl groups (C=O) of levulinic acid produced by a cleavage of furan rings. The cleavage of furan compounds in an acidic medium is not surprising in view of the nuclear configuration [4]. Levulinic acid may be yielded simultaneously in the condensation reaction process of furfuryl alcohol. Two other bonds of approximately equal intensity at 1550 and 1390 cm^{-1} indicate the absorption derived from the analogy of the ionized carboxyl groups (–C- - - -O) [5]. However, the degree of an intermediate double bond of carboxyl groups is not evident from the i.r. absorption shift analysis.

The production of levulinic acid can also be identified by the extreme reductions in absorbance intensity at 1600, 1500, 1405 and 1360 cm^{-1} which represents the frequencies of C=C–C=C groups in furan rings. This means that the double bonds of C=C–C=C groups were converted into single bonds. The spectrum also suggests the occurrence of a new weak band at 3370 cm^{-1}, which is attributed to slight changes in OH frequency due to the formation of water or to an OH group in a slightly different environment.

The spectrum of the FA–TCT system, combined with the $ZnCl_2$ acid-releasing catalyst which liberates an electropositive bi-valent metallic Zn^{2+} ion in an aqueous medium, shows very interesting absorption bands (see Curve c in Fig. 4); these include a new band at 3390 cm^{-1} and a prominent sharp band at 1550 cm^{-1}. The former may be due to water ligands co-ordinated in the zinc derivatives. The zinc cation from the zinc derivatives will complex up to six molecules of H_2O in the form of an octahedral structure [6]. The peak intensity at 1550 cm^{-1} for the FA–TCT–$ZnCl_2$ system is considerably stronger than that of the FA–TCT system. The difference in intensity between the frequencies of ionized carboxyl groups at 1550 cm^{-1} is considered to be due to the formation of a complex between the ionic carboxyl groups and the Zn^{2+} ions released from the $ZnCl_2$ solution.

The formation of Zn complex compounds can also be identified from a visible increase in the absorption at 1390 cm^{-1} which represents the second ionized carboxyl groups. In addition, the relative intensity of the carbonyl absorption at 1700 cm^{-1} is much less, when compared with that

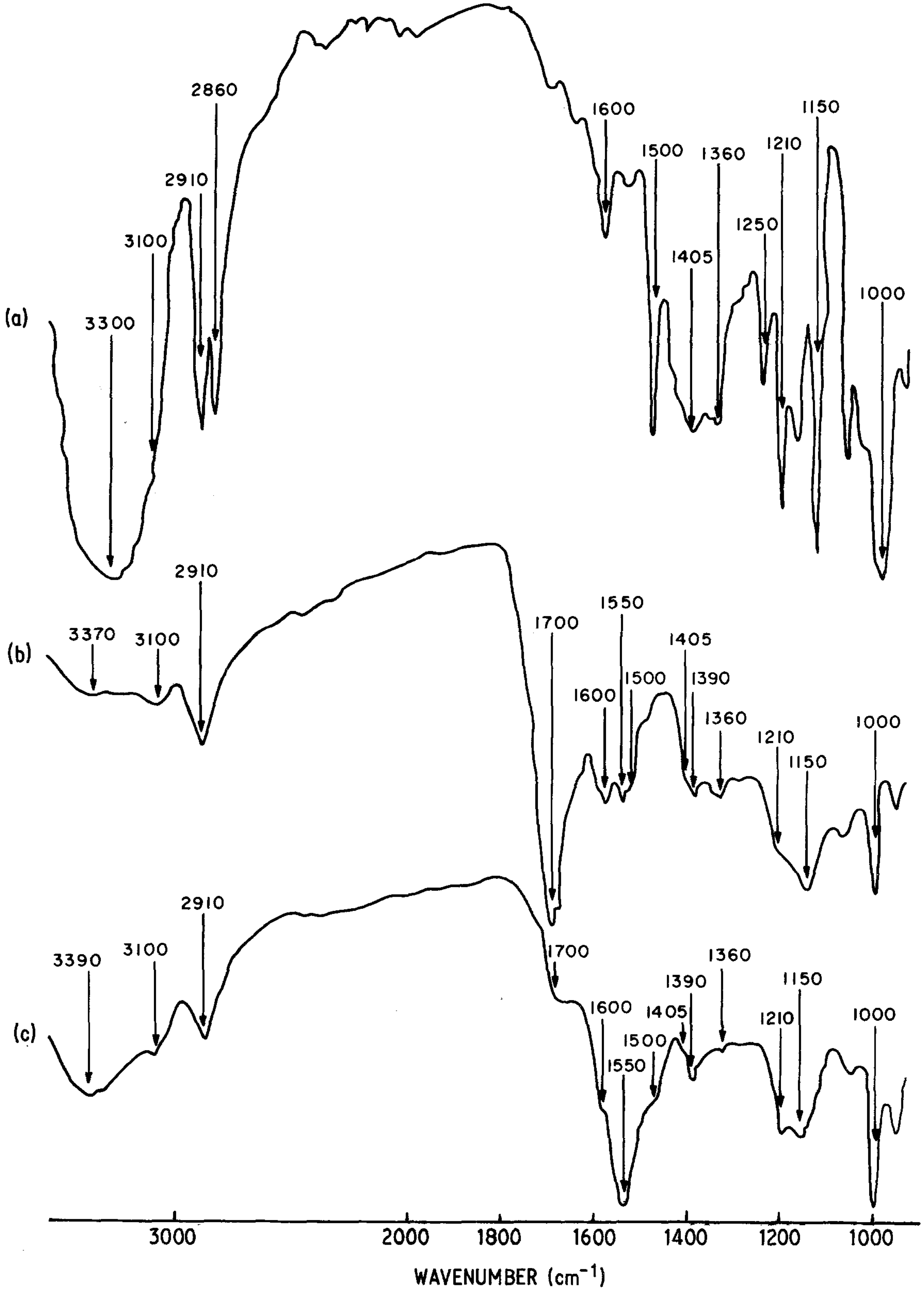

Figure 4 Infra-red spectra of (Curve a) FA monomer, (Curve b) TCT-intiated FA polymer and (Curve c) TCT–$ZnCl_2$-initiated FA polymer.

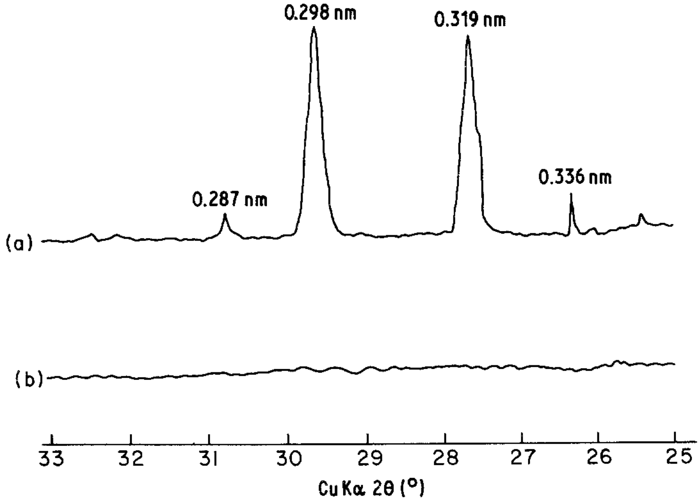

Figure 5 X-ray diffraction patterns of (Curve a) $ZnCl_2$ powder and (Curve b) TCT–$ZnCl_2$-initiated FA polymer.

from the FA–TCT system. This extreme reduction in carbonyl groups seems to demonstrate that a number of C=O groups were converted into ionic zinc complexes consisting of the chelate bond between the Zn^{2+} ions and the ionic carboxyl groups.

It is clearly evident from the XRD analysis that the reaction with levulinic acid is not due to the $ZnCl_2$ reagent, but is due to the Zn^{2+} ions produced by dissociation. As illustrated in Fig. 5, the XRD pattern for $ZnCl_2$ crystal powder (see Curve a in Fig. 5) in the diffraction range of 2.71 to 3.50×10^{-10} m shows strong bands at a spacing of 2.98 and 3.19×10^{-10} m and weak bands at 2.87 and 3.36×10^{-10} m. However, for the FA polymer fully cured using the TCT–$ZnCl_2$ initiator (see Curve b in Fig. 5), the existence of any specific deflections over the range 2.71 to 3.56×10^{-10} m is not revealed. Thus, it is assumed that the $ZnCl_2$ crystals combined with FA monomer are dissociated into Zn^{2+} and two Cl^- ions in the polymerization process. Consequently, they contribute to the zinc complex formation brought about by the chelate bonding between the Zn^{2+} ions produced by dissociation and the levulinic acid derived from the cleavage of furfuryl alcohol.

On the basis of the experimental evidence obtained from the i.r. and XRD analysis results described above, the hypothetical reaction mechanisms of TCT–$ZnCl_2$-initiated FA monomer is presumed to occur according to the reaction process shown in Fig. 6. The furfuryl alcohol monomer (Structure A) in an acidic aqueous medium is easily converted into the form of levulinic acid (Structure C), through a process of the formation of unstable intermediate cyclic hemi-acetal (Structure B) [4]. The cleavage of the furan resin ring in FA monomer to levulinic acid is initiated by the attack of a H^+ proton dissociated from an aqueous acid on the hydroxyl groups having electronegative characteristics, and subsequently causes the rupture of the furan ring accelerated by an acid-catalysed hydrolysis. The levulinic acid formed takes part in the predominant condensation reactions with FA monomer caused by the catalytic function of an active strong acid and simultaneously produces water molecules as by-products. Further reaction in the same manner leads to higher molecular-weight condensation products in which furan rings are linked together by bridge formations of methylene ($-CH_2-$) and ether ($-CH_2-O-CH_2-$) groups. For the final reaction process, the zinc chelate compounds (Structure D), consisting of Zn^{2+} salt bridge structures are synthesized by the formation of chelate bonding between the Zn^{2+} ions having six-co-ordinated H_2O ligands and the ionized carboxyl groups of levulinic acid. The chemical function of bi-valent metallic Zn^{2+} ions may be presumed to be intermolecular cross-linking, acting to connect two chains of FA polymers. It is further assumed that the chemically co-ordinated H_2O molecules may produce elastic behaviour of the dynamic molecular mobility occurring between the layers of Zn–FA complexes.

Leitheiser *et al.* [7] have reported that the final FA compounds consist of the four homologous types including a difurylmethane, difurfuryl ether, furfuryl alcohol and polyfunctional polymer containing the levulinic acid. They also reported that the homogeneous formations of both the furfuryl alcohol and the polyfunctional polymer constitute

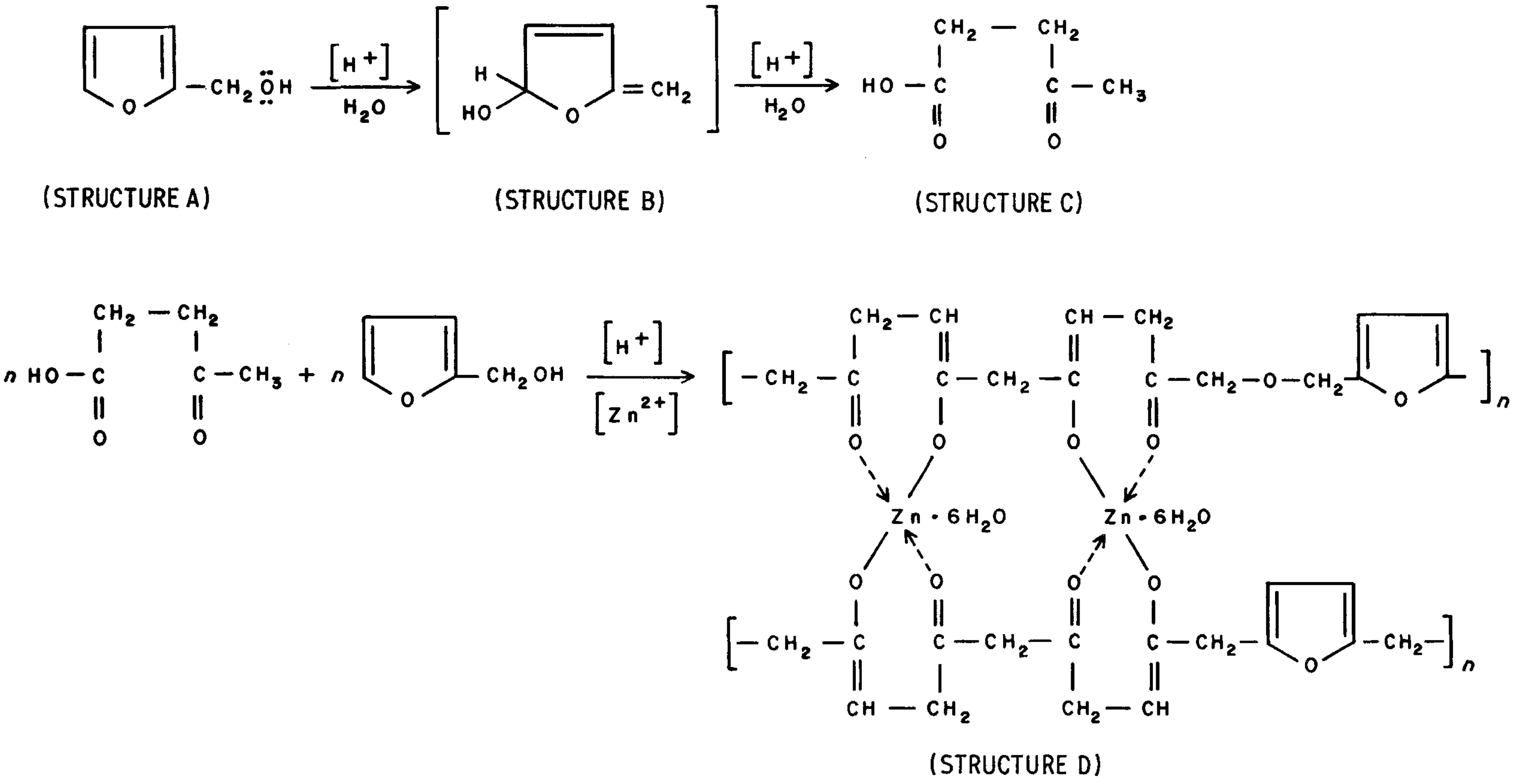

Figure 6 Hypothetical reaction mechanism between $ZnCl_2$ and FA in acidic medium.

greater than 85% of the total quantity of FA compounds. Unfortunately, the data obtained from the i.r. study are not sufficient for use in the quantitative evaluation of the formative elements of FA polymers. However, if the quantity of chemical structure is estimated by a comparison of i.r. absorption intensities, it appears from the strong intensity bands at 1550, 1210, 1150 and 1000 cm^{-1} that the major compounds of FA polymer in the presence of TCT–ZnCl$_2$ initiator may consist of furfuryl alcohol and Zn–levulinic acid complexes.

3.5. Thermodynamic analysis of thermal decomposition

A thermodynamic characterization of the TCT–ZnCl$_2$-initiated FA polymer system is necessary for a better understanding of the effect of ZnCl$_2$ on the rate of polymerization and the product quality. Therefore, measurements of the glass transition temperature, T_g, and the heat of decomposition, ΔH, were performed to obtain information with regard to the thermodynamic kinetics of FA polymers cured with TCT alone and cured with the TCT–ZnCl$_2$ system. These thermodynamic parameters were determined from the DSC thermograms illustrated in Fig. 7. The DSC curves for the FA–TCT (Sample a) and FA–TCT–ZnCl$_2$ (Sample b) systems show two regions of energy change. In the first region, the small endothermic peaks which range from 50 to 65° C are due to the glass transition temperature of the polymer. In the second region, which ranges from a peak temperature of 145° C for the FA–TCT system to 165° C for the FA–TCT–ZnCl$_2$ system, the larger endothermic peaks are caused by thermal decomposition of the polymer. The heat of decomposition, ΔH, was measured from the total area of the latter curve enclosed by the base-line, as shown in Fig. 7.

The results of T_g and ΔH measurements are given in Table III. Generally, the T_g values of the amorphous polymers can be used to determine the degree of the chain mobility and segmental jumping frequency. T_g also depends on the forces applied during the test, the molecular weight, the cross-linking and the cohesive forces between chains.

The data indicate that the T_g value of TCT-initiated FA polymer was 51° C, a value which is about 11° C lower than that of the FA–TCT–ZnCl$_2$ system. The high T_g value of 62° C, obtained by the addition of ZnCl$_2$ to the FA–TCT system, is believed to be due to the greater chain stiffness and the higher polymer molecular weight compared to those of the FA–TCT system. The restraint on the mobility and flexibility of the FA molecular chains results in a cross-linking structure formed by the chelate bonding between the Zn^{2+} and the ionized carboxyl groups of levulinic acid.

Results of the heat of decomposition indicate that the ΔH value of the FA–TCT–ZnCl$_2$ system

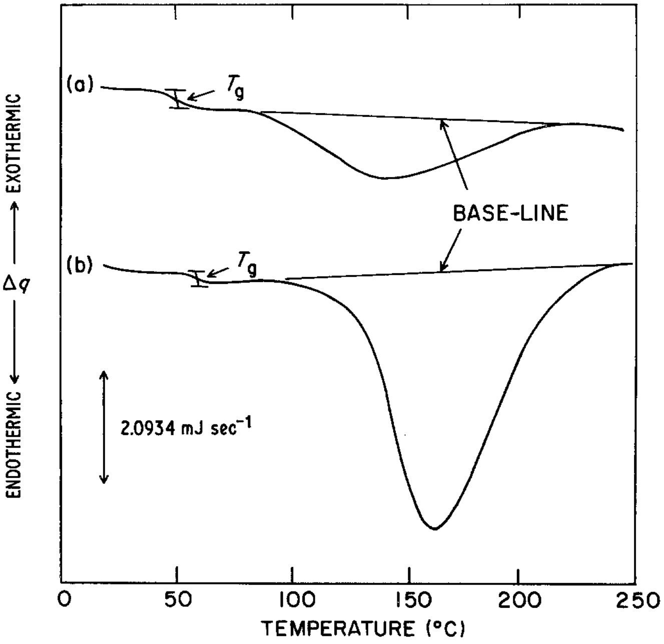

Figure 7 DSC curves for thermal decompositions of (Curve a) FA–TCT and (Curve b) FA–TCT–ZnCl$_2$ polymer systems.

TABLE III T_g and heat of decomposition, ΔH for FA–TCT and FA–TCT–$ZnCl_2$ systems

System	T_g (° C)	Peak temperature of thermal decomposition (° C)	Heat of decomposition, ΔH (kJ kg^{-1})
FA–TCT	51	145	26
FA–TCT–$ZnCl_2$	62	165	220

is considerably higher (220 compared with 26 kJ kg^{-1}) than that of FA polymer in the presence of TCT alone. This means that the addition of $ZnCl_2$ has a significant effect on the degree of cross-linking of the FA monomer. The complex formation between the Zn^{2+} ion and the levulinic acid is also considered to be closely related to the accelerative effect. Thus, the active inorganic $ZnCl_2$ acts as a promotor which causes the rate of polymerization to accelerate.

4. Conclusions

The 1,1,1-trichlorotoluene (TCT)–zinc chloride ($ZnCl_2$) system, selected from among various two-component acidic initiator candidates, had a very significant effect on the early strength characteristics of furfuryl alcohol (FA) polymer concrete (PC) compositions consisting of FA monomer, water-saturated aggregate and dry silica-flour filler. The heat of polymerization and the activation energy of the acidic 1 wt% TCT–5 wt% $ZnCl_2$ solution (80% $ZnCl_2$) used to polymerize the FA monomer were calculated to be 329 kJ kg^{-1} and 98.6 kJ mol^{-1}, respectively. Results from DSC analysis suggest that the use of the DSC in the quantitative analysis of polymerization heat can be a good method for selecting appropriate initiator systems for PC for use over a reasonable temperature range.

The bi-valent metallic Zn^{2+} ions liberated from the $ZnCl_2$ solution formed chelate bonding with the ionized carboxyl groups of levulinic acid resulting from the cleavage of furan rings in an acidic medium. The zinc–levulinic acid chelate compounds formed in FA polymer structures contribute significantly to restrain the mobility and flexibility of the polymer chains as a result of intermolecular cross-linking. The heat energy of thermal composition of FA polymer combined with the TCT–$ZnCl_2$ catalyst system was considerably higher than that when TCT was used alone. Thus, it seems to demonstrate that $ZnCl_2$ used as an acid-releasing reagent acts as a promoter to increase the rate of condensation reactions of the FA monomer.

Acknowledgement

This work was performed under the auspices of the US Department of Energy under contract number DE–AC02–76CH0016.

References

1. T. SUGAMA, L. E. KUKACKA and W. HORN, *Cem. Concr. Res.* **11** (1981) 495.
2. *Idem,* "Water-Compatible Polymer Concrete Materials for Use in Rapid Repair Systems for Airport Runways" Final Report, BNL 51390, March 1981 (Brookhaven National Laboratory, New York, USA, 1981).
3. Instruction Manual, 990 Thermal Analyzer and Modules, E.I. duPont de Nemours and Co. Inc., Instrument Products Division, Wilmington, DE, USA, 1974, p. A-10.
4. A. P. DUNLOP and F. N. PETERS, "The Furans" (Reinhold Publishing Corporation, New York, 1953) p. 640.
5. L. J. BELLAMY and R. F. BRANCH, *J. Chem. Soc.* (1954) 4491.
6. A. D. WILSON and R. J. MESLEY, *J. Dent. Res.* **51** (1972) 1581.
7. R. B. SEYMOUR (ED.), "Plastic Mortars, Sealants, and Caulking Compounds", ACS Symposium Series 113, 177th ACS National Meeting, Honolulu, Hawaii, 3 April 1979 (ACS, Washington, D.C., USA, 1979) p. 7.

Received 2 October
and accepted 16 December 1981