DSC and curing kinetics study of epoxy grouting diluted with furfural -acetone slurry

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Abstract. The use of furfural-acetone slurry as active diluents of Bisphenol-A epoxy resin (DGEBA) groutings has been studied by dynamic and non-isothermal DSC for the first time. Curing kinetics study was investigated by non-isothermal differential scanning calorimetries at different heating rates. Activation enery (E_a) was calculated based on Kissinger and Ozawa Methods, and the results showed that E_a increased from 58.87 to 71.13KJ/mol after the diluents were added. The furfural-acetone epoxy matrix could cure completely at the theoretical curing temperature of 365.8K and the curing time of 139mins, which were determined by the kinetic model parameters.

1. Introduction

Crack is one of the most common deterioration problems of concrete dams, which can be caused by several factors, such as large temperature gradients, shrinkage, foundation deformation, and hydrostatic overload, etc. [1]. Some cracks emerge in construction period and some are formed during the operating period [2]. Cracks can not only affect the building appearance, but also can bring about a series of serious diseases, like leakage dissolution, environment water erosion, freeze-thaw damage and steel corrosion. Interacting with cracks, these problems cause a vicious cycle doing great harm to the durability of dam structures. Therefore, a scientific, reasonable and effective treatment of cracks is urgent for dam foundation improvement in order to solve these problems.

Because of their high mechanical strength, good adhesive properties, extremely low shrinkage and superior chemical resistance under corrosive conditions, at present, epoxy resin chemical grouting materials are the most widely used for reinforcement and anti-seepage projects of concrete structures and foundations in construction.

Although the addition of reactive diluents can reduce the viscosity of epoxy resin, such as butyl glycidyl ether [3], allyl glycidyl ether [4], and cyclohexanediol diglycidyl ether [5], they can't improve the low permeability of epoxy slurry, due to the high surface tension of the epoxy slurry itself. Acetone and furfural having low viscosity and epoxy resin can be well dissolved in them to form a homogeneous solution system. Under the action of alkali curing agent, acetone and furfural can react to generate furan resin, forming an interpenetrating network structure with epoxy resin.

Compared with general epoxy grouts, the furfural–acetone diluted epoxy grouting has a lower viscosity and small contact angle indicating a low surface tension properties, a privileged wetting and infiltration capacity, a long time for operation, and a high consolidation strength. Therefore this more effective acetone-furfural method has been widely applied into construction industry in China [6-7]. However, this promising material has not been drawing enough attentions, particularly with regard to the curing kinetics study of the epoxy grouting diluted by furfural -acetone slurry.

2. Material and methods

2.1. *Materials*

Bisphenol-A epoxy resin (DGEBA) was bought from the NanYa Resin Company with the epoxy equivalent of 187 g/mol and room temperature (25 ^{o}C) viscosity of about 12–15 Pa·s. The used curing agent was an Ancamine 2758 supplied by Air Products and Chemicals, Inc, which is a Mannich-Base polyamine. The furfural and acetone were bought from Sinopharm Chemical Reagent Company Ltd. and all materials were used as received.

2.2. *Preparation of epoxy grouting blends*

Two epoxy grouting systems were established. Sample A was prepared by mixing DGEBA and Ancamine 2758 at a mass rate of 100:43.9 at 25^{o}C under vigorous mechanical stirring for about 5mins. Sample B was obtained by blending DGEBA and Ancamine 2758 with furfural-acetone slurry under the same conditions. The mass rate of the four raw materials was 100:54.8:48:29. The curing samples were well mixed until a homogeneous system was obtained.

2.3. *DSC characterization*

Differential scanning calorimeters (DSC) was used to monitor the curing process of the epoxy resin and curing agent. The epoxy resin and curing agent should be mixed homogeneously by a vigorous stirring. About 9-11 mg of the above mixture was put into the DSC pan and put into the DSC sample chamber immediately. An empty DSC pan was selected as a reference when DSC was working. The epoxy resin and curing agent were non-isothermally cured in DSC at different heating rate of 5, 7.5, 10 or 15^{o}C/min, respectively. The temperature and heat was calibrated with high-pure indium standard beforehand [8-10].

3. Result and discussion

3.1. Dynamic DSC analysis

Curing kinetics parameters of epoxy matrix play an important role in understanding the curing reaction such as the activation energy and reaction order and so on. The apparent activation energy is a

parameter to determine whether the curing process can take place or not. The curing behavior can be carried out only when the involved molecules obtain greater energy than the apparent activation energy does. By calculating the reaction order, the curing mechanism of the epoxy matrix can be roughly estimated.

DSC is widely used in the kinetics analyzing thermosetting reaction [11-16]. The curing kinetics parameters can be analyzed by the following Eq. (1):

$$d\alpha/dt = \beta d\alpha/dT = k(T)f(\alpha) \quad (1)$$

where $d\alpha/dt$ is the rate of conversion, β is heat flow, T is the absolute temperature, $f(\alpha)$ is the function of the kinetic model, and k(T) is the function of the temperature which can be described by the Arrhenius Equation as Eq. (2):

$$k(T)=Aexp(-E_a/RT) \quad (2)$$

where A is the pre-exponential factor, E_a is the activation energy, R is the gas constant.

Various kinetic models can be used to describe the curing kinetics. The frequently used autocatalytic Kamal model [17-19] was applied in this work to analyze the cuing kinetics mechanism (see Eq. (3)).

$$f(\alpha)= (1-\alpha)^n \quad (3)$$

where n is the reaction order.

So the curing kinetic model equation can be easily changed into Eq. (4) based Eq. (1) and Eq. (2) and Eq. (3):

$$d\alpha/dt = Aexp(-E_a/RT) (1-\alpha)^n \quad (4)$$

As shown in Eq. (4) as mentioned above, calculation of the activation energy, reaction order and pre-exponential factor are prerequisite to determine the specific kinetic model. The two most common theories of activation energy are both Kissinger method [20-22] and Ozawa method [23, 24]. Both of them can be applied to give the activation energy E_1 and E_2, respectively, by the Eq. (5) and Eq. (6):

$$\ln(\beta/T_P^2) = \ln(AR/E_1)-E_1/RT_p \quad (5)$$

$$\ln\beta = -1.052E_2/RT_p + C \quad (6)$$

where C is a constant.

Fig. 1 and 2 show the dynamic DSC analysis curves measured for sample A and B, respectively, with four heating rates (β) 5, 7.5, 10, 15 K min-1. Compared with the two curves, it can be seen that the peak temperature (T_p) increased by the addition of furfural and acetone. This phenomenon is accordance with the coordinated reaction of the aldehyde or carbonyl groups and amino groups, which slow the curing rate and result into more heating energy if necessary.

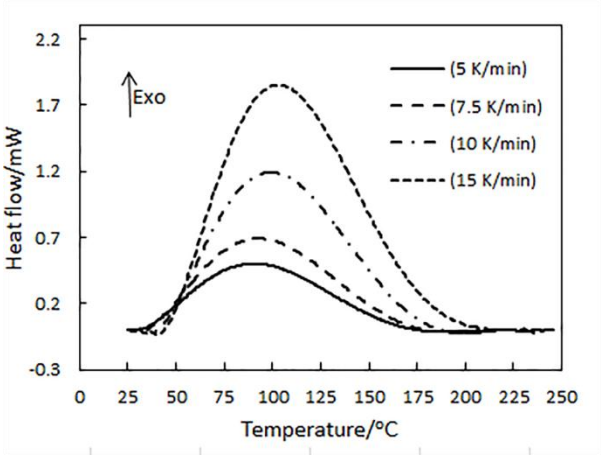

Figure 1. DSC curve of sample A.

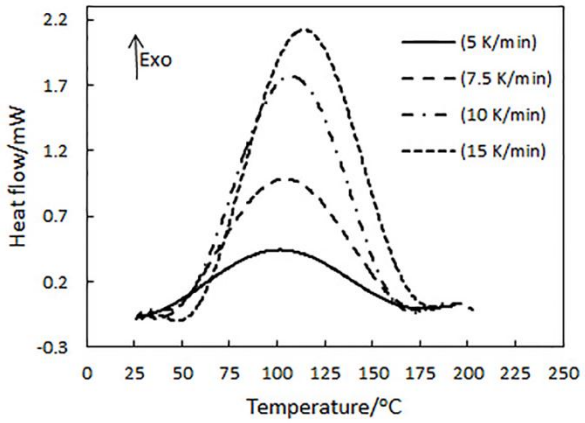

Figure 2. DSC curve of sample B.

Table 1. DSC analysis of curing process at different fates.

Curing system	β(K /min)	T_i(°C)	T_p(°C)	T_f(°C)	LN(β/T_p^2)	1000/T_p(K^{-1})
A	5	37.2	85.9	173.9	-10.16	2.79
	7.5	39.9	94.2	179.5	-9.80	2.72
	10	44.1	99.2	188.4	-9.54	2.68
	15	50.0	105.3	205.7	-9.16	2.64
B	5	39.8	100.6	176.5	-10.24	2.68
	7.5	41.6	105.2	182.1	-9.86	2.64
	10	45.5	111.0	191.2	-9.60	2.60
	15	51.1	117.6	199.6	-9.23	2.56

The main information about the dynamic DSC analysis curves is summarized as Table 1. Obviously, the heating rate has a great influence on the shape of the exothermic curves. With the increase of heating rate of the curing reaction, the thermal effect was enhanced and reacting time was shortened, causing a thermal lag. Therefore, shifting the initial curing temperature(T_i), peak temperature(T_p) and finishing temperature(T_f) to the high temperature zone were observed.

3.2. Average activation energy

According to Kissinger method, with Eq. (5), the peak temperature of different heating rates, E_1 can be obtained from the slope of the plot of $\ln(\beta/T_p^2)$ versus $1/T_p$, whereas sample A and sample B were 57.38 and 69.83kJ mol^{-1}, respectively. Fig. 3 shows the results. The E_2 can be estimated form the slope of the plot of lnβ versus 1/Tp according to Ozawa method with Eq. (6), whereas sample A and sample B were 60.36 and 72.42 kJ/mol, respectively. Fig. 4 shows the results.

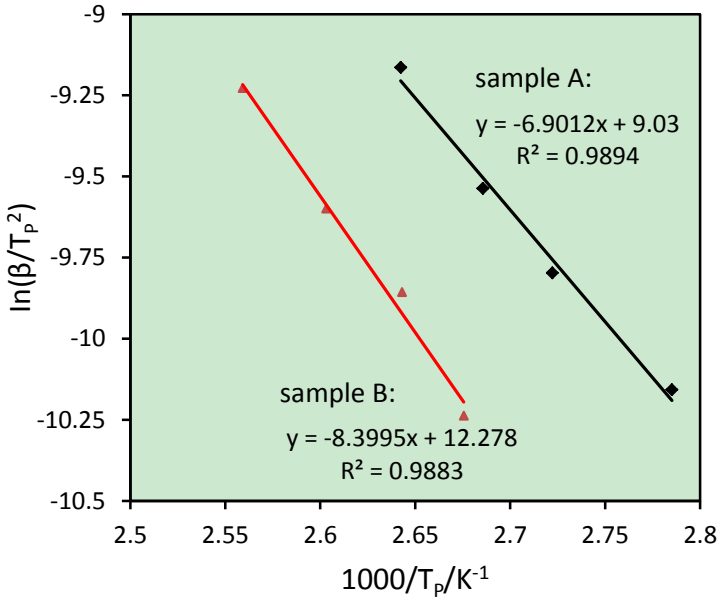

Figure 3. Kissinger's plot of $\ln(\beta/T_p)$ versus $1/T_p$ for sample A and B.

In this study, the final activation energy E_a is an average result of E_1 and E_2. Hence, the activation energy (E_a) of sample A and sample B were 58.87 and 71.13 kJ/mol respectively. The addition of the furfural acetone slurry made the activation energy increase a lot. This is the very reason that the set time of furfural acetone system is much longer, which does make an important contribution to the permeability of the grouting materials because of the long time for viscosity increase.

3.3. The kinetics equation of the curing reaction

Generally speaking, Crane kinetic model is used to determine the reaction order, which can be described by Eq. (7):

$$d(\ln\beta)/d(1/T_p) = -(E_a/nR + 2T_p) \quad (7)$$

The Eq. (6) can be changed into Eq. (8) by mathematical integration because of the ignored item $2T_p$ where $E_a/nR \gg 2T_p$.

$$\ln\beta = -E_a/nRT_p + C \quad (8)$$

where C is a constant. Hence, the reaction order n can be obtained from the slope of the plot of $\ln\beta$ versus $1/T_p$.

Fig. 4 shows the plot of $\ln(\beta)$ versus $1/T_p$ for sample A and B, while the reaction orders of sample A and B curing systems are 0.9270 and 0.9336, respectively, in accordance with the average activation energy calculated above. Both of them are underwent complicated reactions due to the non-integer reaction orders.

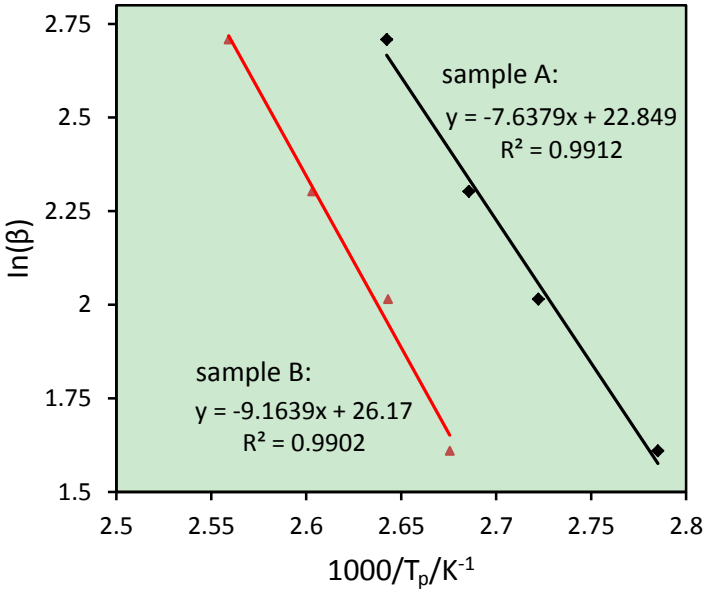

Figure 4. Ozawa's plot of ln(β) versus $1/T_p$ for sample A and B.

The pre-exponential factor(A) can be calculated approximately by Kissinger method from the intercept of the plot of $\ln(\beta/T_P^2$ p) versus 1/Tp as Eq. (5), while sample A and sample B are 5.76×107 and 1.56×109, respectively. Curing reaction kinetic equation of sample A and sample B can be described as Eq. (9) and Eq. (10):

$$d\alpha/dt = 5.76\times10^{7}\exp(-7.08/T)\,(1-\alpha)^{0.9270} \quad (9)$$

$$d\alpha/dt = 1.56\times10^{9}\exp(-8.56/T)\,(1-\alpha)^{0.9336} \quad (10)$$

3.4. The study of the curing process

Finally, T-β Extrapolation method was used to determine the curing process parameters including gelling temperature, curing temperature and post-curing temperature, which can be obtained from the intercepts of the plot of K versus β. According to the data given in Table 1, T-β fitting curve is shown in Fig. 5. The gelling temperature, curing temperature and post-curing temperature are 306.72K, 365.75K and 438.45K, respectively.

The curing time is also an important condition to determine the finally application of the products. Similarly, the theoretical curing time can be obtained from the kinetic model parameters by the way of Eq. (11):

$$\alpha(t) = 1-(A\exp(-E_a/RT)(n-1)t+1)^{1/1-n} \quad (11)$$

At the end of the curing reaction, the conversion rate α(t) was set as 100%. After the calculated parameters were put into Eq. (11), theoretical cure time was 139 mins at the curing temperature of about 365.8K.

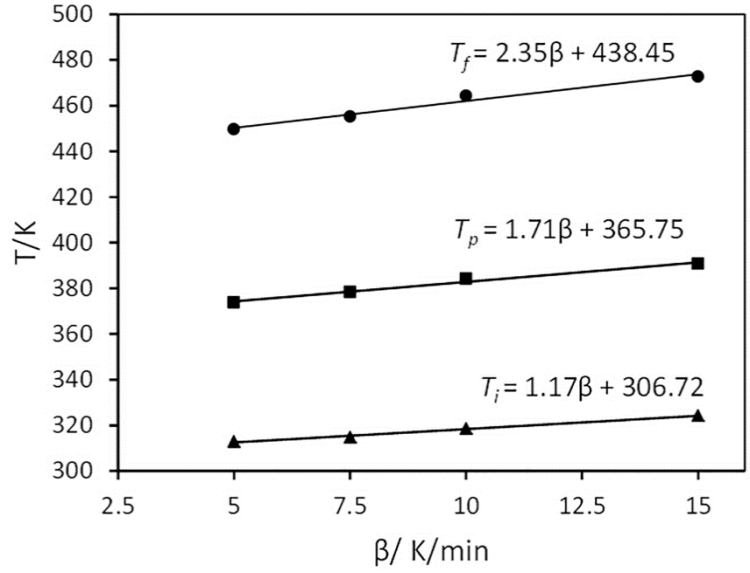

Figure 5. Relationship between curing temperature and heating rate in T-β Extrapolation method.

4. Conclusions

In this work, the differential scanning calorimetries have been applied to determine the kinetic parameters of furfural-acetone epoxy grouting for the first time. The results show the E_a of the DGEBA, Ancamine 2758 with and without furfural -acetone slurry are 71.13 and 58.87 KJ/mol, the reaction order are 0.9336 and 0.9270, the pre-exponential factor(A) are 5.76×10^9 and 1.56×10^7, respectively. The furfural-acetone slurry can improve the activation energy, exhibiting exactly the opposite point of the well-known active diluents based on glycerol ether, both curing reactions of them are complicated models, and then curing reaction kinetic equations are also described. The furfural-acetone epoxy matrix could cure completely with the theoretical curing temperature being 65.8K and the theoretical curing time being 139 mins, which are all determined by all the above kinetic model parameters.

Acknowledgement

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