ISSN 1997-1400 Int. J. Pavement Res. Technol. 4(3):140-146
Copyright @ Chinese Society of Pavement Engineering

A Curing Model for Epoxy Asphalt Concrete and Its Implementation for Construction

Xuejuan Cao[1], Yunbo Lei[2], Wei Wang[3], and Boming Tang[4+]

Abstract: The curing reaction kinetics of epoxy system in epoxy asphalt concrete was studied by means of non-isothermal analysis kinetics method combined with linear heating-up data of differential scanning calorimetry (DSC) at several scan speed rates. Taking advantage of Netzsch Thermokinetics Diffusion Control software, a precise model of this reaction was obtained by Friedman differential and nonlinear regression methods. The reaction energy and order can be solved with Kissinger equation and crane equation. Using this model, the conversion rate can be calculated under given conditions. The results show that temperature rise can greatly shorten the required curing time. The results also show that the time of conversion rate reaching 80 percent is much shorter than that of complete curing. The curing rate is over ten times when the pavement temperature is at 60°C than at 30°C. Therefore, it is recommended that epoxy asphalt concrete pavement be constructed in high-temperature season. Usually, the pavement temperature exceeds 30°C in a whole day and the maximum temperature can reach up to 60°C during hot summer season. Under this condition, the conversion rate reaches 80 percent in two weeks with the Marshall Stability value nearly reaching 40 kN, which is a value advised to open the pavement to traffic.

Key words: *Construction guidance; Epoxy asphalt concrete; Non-isothermal analysis; Reaction model; Thermal analysis kinetics.*

Introduction

Epoxy asphalt concrete has been used as a wearing surface material for steel bridge decks for many years. In the mid-1960s, after evaluation of several materials, the California Bay Bridge Authority of the United States (US) selected the epoxy asphalt concrete as the wearing surface for the construction of the San Mateo-Haywa Bridge [1, 2]. Advantages offered by epoxy asphalt concrete included cost, ride quality, placement with conventional construction equipment, high fatigue resistance, etc. [1] Since then, epoxy asphalt has been used extensively in the US and Canada, Europe and China for steel bridge deck construction, including San Francisco Joklan Bridge, Westgate bridge in Australia, London airport in England, Hageetein Bridge in Holland [2], and Runyang Bridge and Sutong Bridge in China [3, 4], and many others. Epoxy asphalt concrete generally consists of a well-graded aggregate, with 9-mm top size, and a 2-component epoxy resin system. After mixing, initial cure will take place in a few hours and the cure rate is temperature dependent. Full cure will take 30 to 60 days.

In general, epoxy asphalt binder is composed of epoxy resin, curing agent, asphalt and some other additives. Through curing reaction, the epoxy asphalt binder changes from a thermoplastic material to a thermosetting material [5]. Epoxy asphalt mixture generally possesses better physical and mechanical properties than ordinary asphalt mixture, such as strength, fatigue resistance, durability and aging resistance.

Since hot-mixed asphalt (HMA) concrete is constructed at a high temperature, which requires longer time for the epoxy system to gel and the curing process continues even after cooling. Therefore, it is very important to understand the curing rate of the epoxy system and to control the degree of curing. There have been some studies on construction process control of epoxy asphalt concrete. Cao and Lei studied and discussed the maximum operating time in higher temperature of epoxy asphalt concrete [6]. It was concluded that the operating time was reduced with increasing temperature. The operating time was only forty minutes at 140°C. In their study, Zhou, Chen and Zhao specified that the time required to open traffic for epoxy asphalt pavement would be forty-five days after placement [7], but no explanation was given about the requirement. Jiang *et al.* pointed out that a period of maintenance time after construction is required before opening to traffic [8]. However, no specific maintenance time is concluded in the study.

The strength of epoxy asphalt concrete increases with time and the curing time required to open traffic is dependent on the strength. Therefore, strength can be used as a criterion to determine the maintenance time. However, this strength testing requires longer time to draw a conclusion and the required time will vary since air temperature changes. So using this method is time consuming. Finding a quick and reliable prediction method for determination of the maintenance time is essential.

Thermal kinetics analysis is a systematic research method that analyzes reaction kinetics of materials. It has been widely used in researches studying the reaction mechanisms with changing rates of dehydration, decomposition, degradation of inorganic material; polymerization, solidification, crystallization and degradation of high polymer. It is also a rapid way to predict the time and rate of material’s curing reaction [9]. In this research, thermal kinetics analysis was used to study curing reaction of epoxy asphalt providing quick and accurate information. The results can be applied to develop guidance for construction of epoxy asphalt concrete.

---

[1] Chongqing Jiaotong University, Chongqing 40074, China.
[2] Logistical Engineering University, Chongqing 401331, China.
[3] Chongqing Jiaotong University, Chongqing 40074, China.
[4] Chongqing Jiaotong University, Chongqing 40074, China.
[+] Corresponding Author: E-mail leimiduo@qq.com

Note: Submitted November 30, 2009; Revised May 10, 2010; September 23, 2010.

Table 1. Properties of Epoxy Resin.

	Epoxy value (eq/100g)	Volatile Content	Viscosity (Pa.s 40°C)	Density (kg/m^3)
Epoxy Resin	0.48-0.54	≤1%	≤15	1.05-1.15

Table 2. Properties of Hardener.

	Amine Value (mg KOH／g)	Volatile Content	Viscosity (Pa.s 40°C)	Density (kg/m^3)
Hardener	300	≤2%	≤0.25	1.0-1.10

Materials Used and Test Methods

Materials

Epoxy asphalt binder is a blend of epoxy resin, curing agent, asphalt and some additives, while epoxy asphalt concrete is a mixture of the epoxy asphalt binder and aggregates. In this study, Bisphenol-A epoxy resin was used and the material parameters are listed in Table 1. A type of modified aromatic amines hardener was used to increase the speed of the reaction, and its properties are shown in Table 2. Zhong Hai AH-90 asphalt was used and its properties are listed in Table 3. Dense-graded aggregate, designated as AC-13, was used and the gradation is shown in Table 4. From previous experience, an Epoxy asphalt binder content of 6.3 percent was selected with a void content of the mix of 2.6%, as determined by based on ASTM D-3203.

Test Methods

Calorimetric measurements were conducted on specimens of epoxy asphalt binders, consisting of epoxy resins and curing agent, using NETZSCH DSC 204 device. To study the non-isothermal curing reaction of kinetics, 5-10 mg of the specimens were placed in a standard aluminum pan and scanned over a temperature ranging from 100°C to 300°C at constant heating rates of 15, 20 and 30 °C/min. Netzsch Thermokinetics Diffusion Control software (version 2000.6a) was utilized to analyze the differential scanning calorimetry (DSC) testing results. The analysis process included:

1. Importing the testing DSC data into the software.
2. Developing the relationship between temperature and conversion rate in the mode of model-free, using the Friedman analysis method.
3. Obtaining activation energy.
4. Developing the prediction model using non-linear regression method. Using the prediction model, the reaction time and reaction rate at any given temperature could be estimated easily and accurately.

After the epoxy asphalt concretes were well mixed, the hot mixtures were put into an oven at 120°C for half an hour. Then, the mixtures were removed from oven and were made into nine sets of standard Marshall Specimens and each set included three duplicates. The Marshall specimens were then cured in two different conditions. One was an accelerated curing process and the other was a thermostatic manner. One set of specimens were cured under the accelerated curing process in an oven for four hours at 120°C and others were cured in normal process for different times at a constant temperature of 30°C. Marshall testing on all the specimens was then conducted according to ASTM D 1559.

Results and Discussions

Marshall Testing Results

A set of Marshall Specimens was made from epoxy asphalt concrete at 120°C. Then, the specimens were conserved at 30°C. All the testing specimens have three duplicates and the results presented

Table 3. Material Parameters of ZhongHai AH-90.

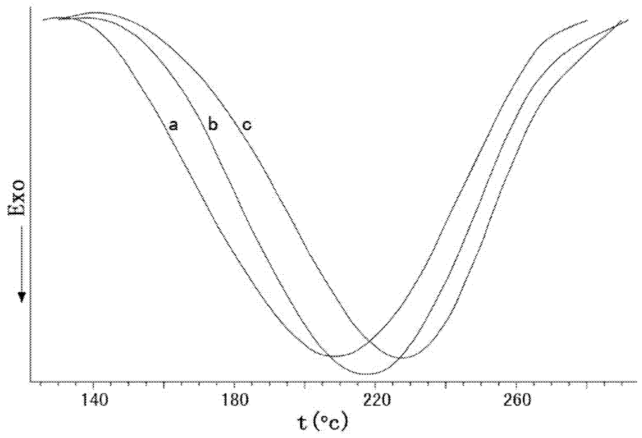
Test Items		Unit	Specification	Test Results	Test method
Penetration (25°C, 100 g, 5 s)		0.1mm	80 - 100	96.8	T 0604-2000
Penetration Index		-	-1.5 - +1.0	-1.12	
Softening Point (Universal Lw) TR&B		°C	≥44	46.0	T 0606-2000
Ductility	10°C	cm	≥30	>150	T 0605-1993
	15°C		≥100	>150	
Wax Content (Distillation Method)		%	≤2.2	1.5	T 0615-2000
60 ℃ Kinematic Viscosity		Pa.s	≥140	142	T 0620-2000
Flash Point (COC)		°C	≥245	249	T 0611-1993
Dissolubility (Trichloroethylene)		%	≥99.5	99.71	T 0607-1993
Density (15°C)		g/cm^3	-	1.012	T 0603-1993
TFOT (163°C, 5h)	Quality change	%	≤±0.8	-0.01	T 0609-1993
	Residual Penetration Ratio	%	≥57	64.3	T 0604-2000
	Residual Ductility 10°C	cm	≥8	22	T 0605-1993

Table 4. Gradation of Testing Aggregates.

Sieve Size, mm	16	13.2	9.5	4.75	2.36	1.18	0.6	0.3	0.15	0.075
AC-13 Sieving Rate (%)	100	97.2	76.2	54.9	35.1	25.7	17.2	12.2	9.0	6.0

Table 5. Marshall Stability during Different Curing Times at 30°C.

Curing Temperatures	Normal Curing at Temperature 30°C								Accelerated Curing at 120°C
Curing Time (d)	1	3	7	14	21	30	45	60	4 hrs
Marshall Stability of Specimen One (kN)	7.2	8.0	11.3	15.0	19.8	26.6	32.1	38.4	40.1
Marshall Stability of Specimen Two (kN)	7.2	8.3	11.5	15.1	20.4	26.8	32.8	38.6	41.5
Marshall Stability of Specimen Three (kN)	7.4	8.4	11.6	15.4	21.2	28.5	34.3	38.6	41.8
Mean Value (kN)	7.3	8.2	11.5	15.2	20.5	27.3	33.1	38.5	41.1



Heating rate: a: 15°C/min b: 20°C /min c: 30°C /min

Fig. 1. DSC Curves at Different Heating Rate.

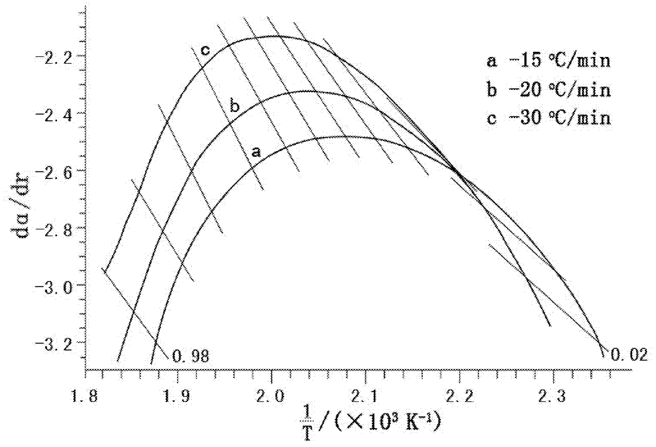


Fig. 2. 1/*T* - *dα*/*dt* Curves of Friedman-Analysis of Cure Reaction of Epoxy System.

are the mean values of three duplicates. The test results of the Marshall Stability are listed in Table 5.

From Table 5, it can be seen that the Marshall Stability value is lower with shorter curing time at 30°C. The value increases as curing time increases. After two months, the strength of the specimen is close to that of rapidly cured specimen.

Friedman Differential Method and DSC Curves of Epoxy System

Multiple curves at different heating rates were used to analyze the reaction kinetics of the specimens, including Flynn-Wall-Ozawa (FWO) integral method; Friedman differential method; and Kissinger-Akahira-Sunose differential method. Among them, Flynn-Wall-Ozawa (FWO) integral method [10, 11] and Friedman differential method [12] are most frequently used. Applying these methods, activation energy (*Ea*) values and reaction conversion rate (α) values were obtained, which, in turn, were used to calculate multi-step reaction and to obtain information of reaction mechanism [13, 14].

Previous researches have shown that, using Friedman differential method, in addition to *Ea* values and pre-exponential factor, other information could also be obtained, including reaction procedures, reaction order, and reaction type. For well mixed Epoxy resin and hardener at the prescribed proportions, the epoxy system curing reaction kinetics was studied by DSC and the curves are shown in Fig. 1.

Fig. 1 shows DSC curves of epoxy system at different heating rates. The heating rates of *a*, *b*, *c* are 15, 20, and 30°C/min, respectively. It shows that the curing of epoxy system is a typical exothermal reaction. With heating rate increasing, exothermic peak of curing reaction moves to high-temperature zone gradually.

Determination of Kinetic Parameters

In Friedman differential method, Friedman-Reich-Levi equation is as follows:

$$\ln\left[\frac{\beta d\alpha}{dT}\right] = \ln Af(\alpha) - \frac{E}{RT} \tag{1}$$

where β-heating rate

α-reaction conversion rate,
A-apparent preexponential factor
Ea (E in the eq.)-apparent activation energy (kJ/mol)
R-gas constant (= 8.314 J / (mol • K))
T-absolute temperature
$f(\alpha)$-differential mechanism function

Heating rate $\beta = \frac{dT}{dt}$ is a constant term, so Friedman-Reich-Levi equation can be converted to the following equation:

$$\ln\left[\frac{d\alpha}{dT}\right] = \ln Af(\alpha) - \frac{E}{RT} \tag{2}$$

With given α values, different DSC curves were obtained at different heating rates of 15, 20, 30 °C/min and a series of *T* value could be also obtained. In the Netzsch Thermokinetics Diffusion Control software, if model-free mode is applied and Friedman equation is selected at once, the 1/*T* - *dα*/*dt* curves can be obtained.

In Fig. 2, each straight line represents equal conversion rate. The

Table 6. Kinetics Parameters of Epoxy System.

β(°C/min)	Tp (°C)	Tp (K)	lnβ	-ln(β/Tp^2)	1/Tp (×10^{-3}/K)
15	207.48	480.48	2.71	9.72	2.081
20	218.94	491.94	3.0	9.40	2.032
30	226.42	499.42	3.40	8.95	2.002

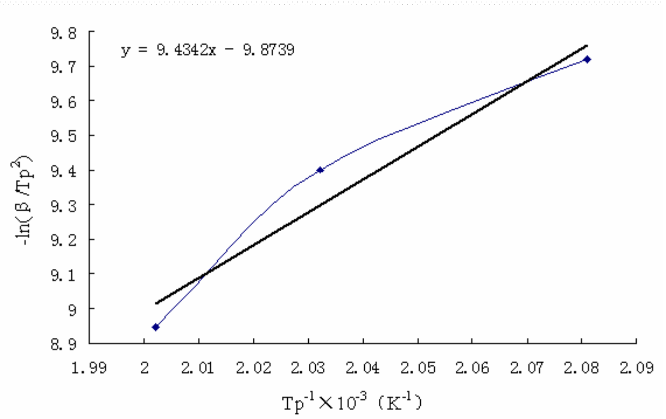


Fig. 3. Plots of ln *(β/Tp^2)* vs. 1/*Tp* of Epoxy System.

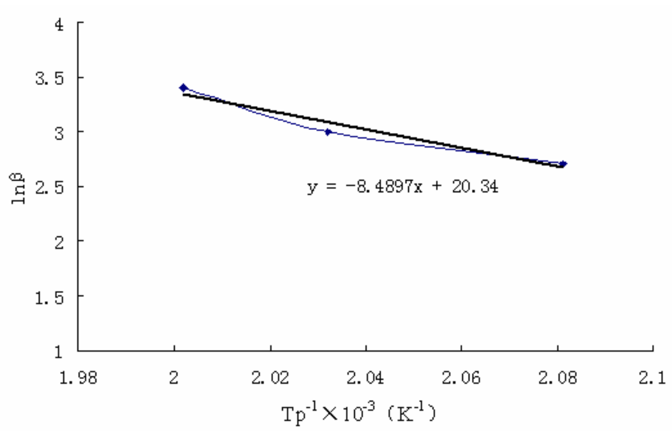
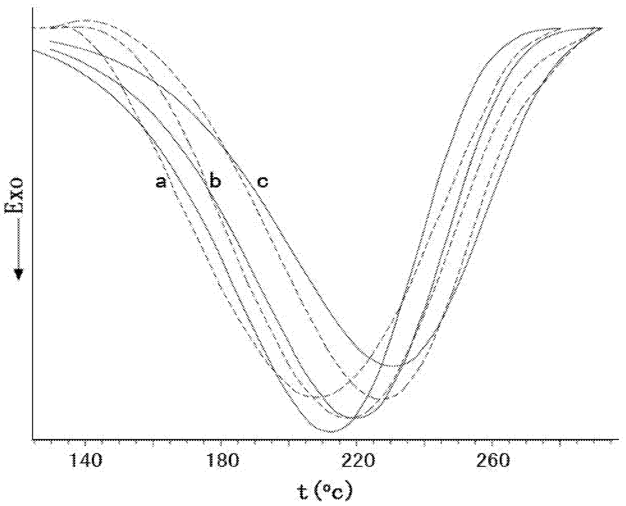


Fig. 4. Plots of lnβ vs. 1/*Tp* of Epoxy System.



Heating rate: *a*: 15°C/min *b*: 20°C/min *c*: 30°C/min

Fig. 5. Regression Curves of Epoxy System.

slope of the straight line represents the *E* and the intercept represents preexponential factor *A*. The three curves correspond to 1/*T* - *dα*/*dt* at each heating rate. When the reaction begins, i.e., when conversion rate is low (0.02), the slope of curves is lower than that of equal conversion rate, which indicates that the curing reaction of epoxy system is a typical of autocatalytic process.

Activation energy, presenting the barrier between the initial state and final state of the reaction, is an important index in the kinetics study. Currently, there are many experimental equations for determining the activation energy. Among them, Kissinger method is widely used because it is neither involved with the nature of the starting thermodynamics curve nor with its ending curve. Also, and it is not influenced by the baseline drift [15, 16]. The equation is as follows:

$$\ln(\beta/Tp^2) = \ln(AR/E) - (E/(R\cdot Tp)) \tag{3}$$

where,

β is the heating rate (°C/min);

Tp is the peak temperature (K);

A is the pre-exponential factor (min^{-1});

E and R are the same as those listed in previous equation.

From the equation, the kinetics parameters are to be calculated as shown in Table 6.

According to Kissinger equation, a direct line can be fitted between ln(β/Tp^2) and 1/*Tp*. The results are shown in Fig. 3.

From the equation on the figure, *E* and ln*A* can be calculated as 78.4 kJ/mol and 11.99 min^{-1}, respectively. After *E* value was obtained, the reaction order of epoxy system can be solved with Crane equation, which is given as follows [15, 16]:

$$d(\ln\beta)/d(1/Tp) = -(E/nR + 2Tp) \tag{4}$$

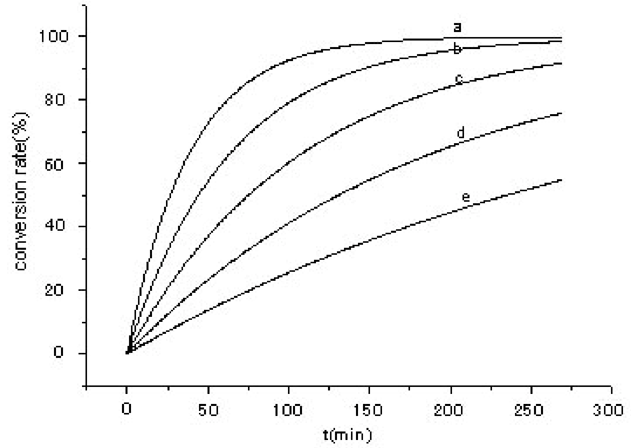
In the equation, n is reaction order. Based on the kinetics parameters presented in Table 6 and connected with Crane equation, when $-E/nR >> -2Tp$, the right hand side of the equation can be considered as constant; then the relation between ln β and 1/*Tp* can be represented as a straight line (Fig. 4). From the slope, order of the curing reaction of the epoxy system is 1.11, indicating a complex reaction and approximately following a first-order kinetics.

Model of Curing Reaction of Epoxy System

Because of the complex nature of the epoxy asphalt concrete curing reaction, nonlinear regression technique was used to develop the epoxy curing reaction models. The developed regression curves are shown in Fig. 5. The dotted lines are curves of measured DSC and solid lines represent curves of fitted (namely calculated using proposed model) DSC. It is shown in the figure that the calculated results are in good agreement with the actual results, indicating that the established model can predict testing results with good reliability and accuracy.

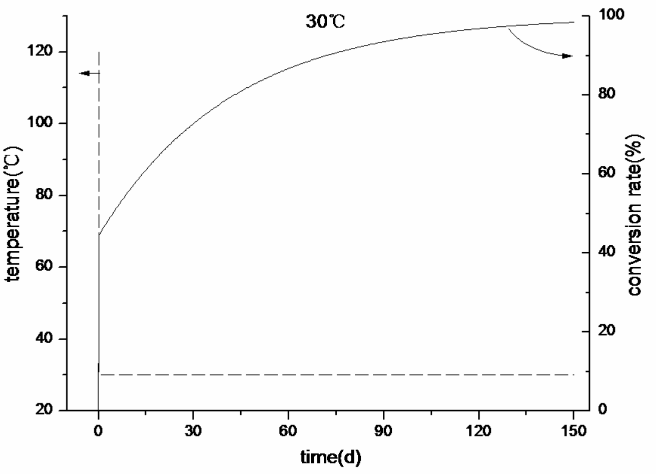
Implementation of the Models for Construction guidance

According to the prediction models, it is possible to estimate the influence of reaction time to the conversion rate at different

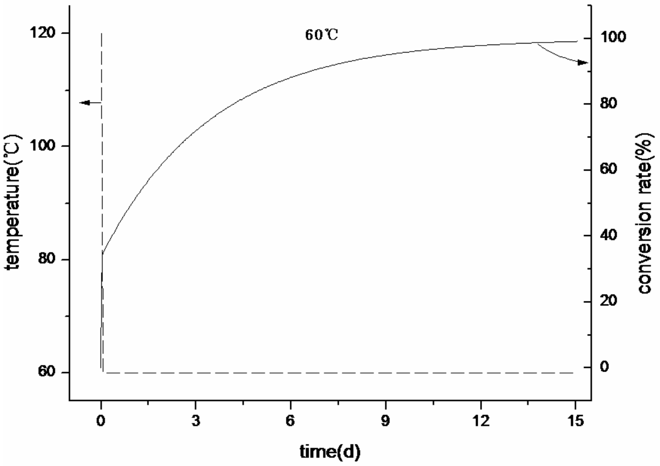


a: 140°C *b*: 130°C *c*: 120°C *d*: 110°C *e*: 100°C

Fig. 6. Curing Reaction Content at Different Temperatures.



(a) at 30°C



(b) at 60°C

Fig. 7. Conversion Rate with Time at Different Temperatures.

temperatures. Thus, they could be used as guidance for epoxy asphalt concrete construction. In field construction, temperature is controlled within 100 to 140°C. Within this temperature range, the corresponding reaction rates at different temperatures are shown in Fig. 6.

From Fig. 6, it can be shown that at a constant time, the reaction conversion rate increases as temperature increases. Similarly, at a constant temperature, the conversion rate increases as time increases. From Fig. 6, after curing at 120°C for four hours, the conversion rate of the epoxy asphalt concrete is about 90%. However, as presented in a previous section, Marshall testing results indicate that enough strength has been obtained under this curing condition.

Similarly, using the prediction models, reaction extents can be calculated in a set temperature program. Simulating the practical construction condition, the mixture is kept at 120°C for 30 minutes, the assumed time elapse from mixing to paving. The epoxy asphalt concrete is then cooled to ambient temperature for three hours. For pavement temperature of 30°C and 60°C, the curves of conversion rate with time are shown in Fig. 7.

In Fig. 7, the dashed lines represent temperature and the solid lines represent conversion rate. It can be seen that the reaction system requires nearly sixty days for the curing to reach 80 percent at 30°C, while it requires only four days if the pavement temperature is kept at 60°C. The time required for complete curing are 150 days at 30°C and 15 days at 60°C, respectively. The results show the reaction rate increases about ten times when temperature rises from 30°C to 60°C. It also shows that the time required is much longer for the conversion rate to increase from 80 percent to 100 percent. From Table 3 in Section 3.1 of this paper, at 30°C, the Marshall Stability of the epoxy asphalt concrete is 38.5 kN at sixty days. Therefore, the Epoxy asphalt concrete pavement can be opened to traffic when the conversion rate reaches 80 percent.

However, due to endothermic characteristic of asphalt concrete, the pavement temperature is usually higher than the air temperature. In summer times, the pavement temperature can reach 60°C. The daily temperature variations (cycles) also need to be considered. Therefore, a more reasonable analysis process taking into consideration of daily temperature variations was undertaken to evaluate the curing reaction. The analysis process was divided into seven stages:

1. At the start of the Epoxy asphalt concrete mixing, the temperature was set at 120°C;
2. Time required for mixing, transporting and paving, 30 minutes;
3. Time required for the pavement temperature to drop to 30°C at a rate of 0.5°C/min, 180 minutes;
4. The pavement temperature was kept a constant at 30°C from 0:00 am to 8:00 am;
5. The pavement temperature rises from 30°C to 60°C at a rate of 0.833°C/min, 360 minutes;
6. The pavement temperature decreases from 60°C to 30°C at a rate of 0.833°C/min, 360 minutes;
7. The pavement temperature was kept a constant of 30°C for 240 minutes.

Stages 4 to 7 represented daily pavement temperature variations after the pavement construction. The analysis process is shown in Table 7.

By repeating the Stages 4 to 7 for fourteen times, the pavement has undergone fourteen cycles of daily temperature variations. Fig. 7 shows conversion rate of reaction system according to the prediction model and setting temperature program.

In Fig. 8, the dash lines represent pavement temperature variations; the solid line represents the conversion rate. Fig. 8 shows

Table 7. A Given Temperature Program of Reaction System.

Stage	Mode	Final Temperature (°C)	Rate (°C/min)	Time (min)	Timeframe
1	Initial	120	-	-	-
2	Isothermal	120	-	30	Mixing, Transporting, Paving
3	Dynamic	30	-0.5	180	Cooling
4	Isothermal	30	-	480	0:00-8:00
5	Dynamic	60	0.833	360	8:00-14:00
6	Dynamic	30	-0.833	360	14:00-20:00
7	Isothermal	30	-	240	20:00-0:00

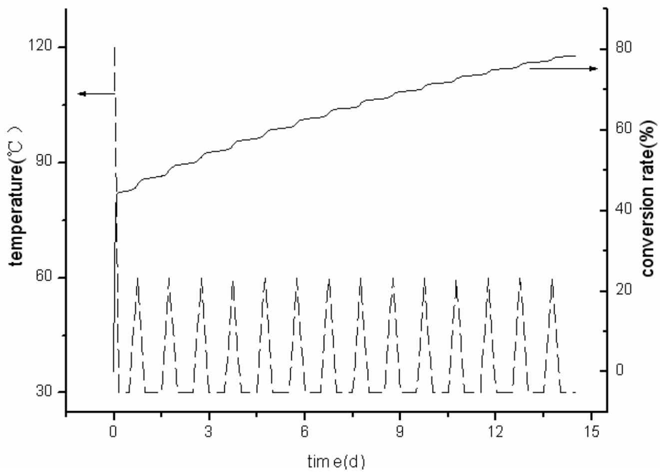


Fig. 8. Conversion Rate of Reaction System in Fifteen Days.

that the conversion rate has reached nearly 50 percent during mixing, storing and paving. Subsequently, conversion rate reaches 80 percent in about two weeks. It has been shown earlier, the pavement can be opened to traffic at a conversion rate of 80%; therefore, under this analysis, the Epoxy asphalt concrete pavement can be opened to traffic two weeks after the pavement construction. From this analysis, it is clear that, by construction of epoxy asphalt concrete pavement at a higher temperature will be of great help to open traffic earlier.

Summary and Conclusions

Taking advantage of Netzsch Thermokinetics Diffusion Control software, the curing reaction kinetics of epoxy system in epoxy asphalt concrete was studied by non-isothermal analysis kinetics method combined with linear heating-up data of DSC. A precise model of this reaction was obtained by using Friedman differential and nonlinear regression methods. Using this model, the time and content of the reaction were calculated. The following conclusions can be drawn from this study:

1. The reaction of epoxy system is a typical of autocatalytic process. The E and ln$A$ are 78.4 kJ/mol and 11.99 min^{-1}, and the order of reaction approximately follows first-order kinetics.
2. The time required for conversion rate to reach 80 percent is much shorter than that of complete curing.
3. When the reaction extent reaches 80 percent, the Marshall Stability value nearly reached 40 kN, considered to have enough strength to carry traffic.
4. The curing rate is over ten times when the pavement temperature is at 60°C than at 30°C.
5. It is recommended to pave epoxy asphalt concrete at high-temperature season because temperature rise can greatly shorten the required curing time of epoxy system.
6. In high-temperature season, if pavement temperature exceeds 30°C in a whole day and the maximum temperature reaches 60°C, the conversion rate reaches 80 percent in about two weeks. The time may be considered to open traffic.

References

1. Hicks, R.G., Dussek, J.I., and Seim, C., (2000). Asphalt Surfaces on Steel Bridge Decks, *Transportation Research Record*, No. 1740, pp. 135-142.
2. Huang, W. and Li, S.Q., (2001). Study on Steel Deck Paving Technology of the Second Large Bridge over the Yangtze River in Nanjing, *Highway*, Vol. 1, pp. 37-41 (in Chinese).
3. Cao, R.M., Zong, H., and Lu, B., (2001). Performance Evaluation of Epoxy Asphalt Mixture for Experiment Section of Runyang Highway Bridge over Yangtze River, *Communications Standardization*, Vol. 2-3, pp. 157-160.
4. Zhu, W., (2006). The Application of Epoxy Asphalt in Engineering Practice, *Soil Engineering and Foundation*, 20(1), pp. 33-35 (in Chinese).
5. Lv, W.M., (2001). *Design Principle and Method Asphalt Concrete,* Tongji University Press, Shanghai, China (in Chinese).
6. Cao, X.J. and Lei, Y.B., (2006). Main points of epxoy asphalt concrete construction technology, *Journal of China & Foreign Highway*, 26(2), pp. 189-191 (in Chinese).
7. Zhou, K., Chen, C.J., and Zhao, L.Z., (2009). Epoxy Asphalt Concrete Construction Technique of Sutong Bridge, *Modern Transportation Technology*, 6(2), pp. 18-21 (in Chinese).
8. Jiang, H., Li, T., and Peng, H.H., (2009). Application of Epoxy Asphalt Concrete on Yangluo Bridge Deck Pavement, *Transportation Science & Technology*, No. 235, pp. 100-102 (in Chinese).
9. Hu, R.G. and Shi, Q.Z., (2001). *Thermal Analysis Kinetics*, Beijing Science Press, Beijing, China (in Chinese).
10. Ozawa, T., (1965). A New Method of Analyzing Themogravimetric Data, *Bulletin of the Chemical Society of Japan*, 38(11), pp. 1881-1886.
11. Flynn, J.H. and Wall, L.A., (1966). General Treatment of the Thermogravimetry of Polymers, *Journal of Research of the National Bureau of Standards*, 70A(6), pp. 487-5231.
12. Brown Jr., J.F., (1986). Double Chain Polymers and Nonrandom Crosslinking, *Journal of Polymer Science*, 1(1), pp.

83-97.

13. Vyazovkin, S., (2000). Kinetic Concepts of Thermally Stimulated Reactions in Solids: A View from a Historical Perspective, *International Reviews in Physical Chemistry*, 19(1), pp. 45-60.
14. Vyazovkin, S., (1996). A Unified Approach to Kinetic Processing of Nonisothermal Data, *International Journal of Chemical Kinetics,* 28 (2), pp. 95-101.
15. Li, Z., Ren, D., Zheng Z., Zhu, Y., and Wang, W., (2007). Curing reaction of TDE-85/MeTHPA resin modified by polyurethane, *Journal of Central South University (Science And Technology)*, 38(2), pp. 213-217.
16. Pi, P., Lin, W., Zheng, D., Wang, Z., Wen, X., Cheng, J., and Yang, Z., (2010). Curing Behaviour of Polycyanate Ester/o-Cresol Formaldehyde Epoxy Resin Composite System, *Iranian Polymer Journal,* 19(6), pp. 469-477.