DESIGN OF MICROCAPSULE SYSTEM USED FOR SELF-HEALING CEMENTITIOUS MATERIAL

M. Zhang [1], N. Han [1], F. Xing [1], **X. Wang** [1] and E. Schlangen [2]

[1] *Guangdong Provincial Key Laboratory of Durability for Marine Civil Engineering; Shenzhen Durability Centre for Civil Engineering; College of Civil Engineering, Shenzhen University, Shenzhen, P.R. China – e-mail: xingf@szu.edu.cn*
[2] *Faculty of Civil Engineering and GeoSciences, Delft University of Technology, Delft, The Netherlands*

Keywords: self-healing, microcapsule, in situ polymerization, activation energy, reaction order, curing kinetics

ABSTRACT

For a microcapsule based self-healing system in the cementitious material, a fundamental issue is to find and facilitate a suitable microcapsule system, concerning either the material selection or design and manufacture process. In this study, urea formaldehyde resin is used for the shell of microcapsule, and bisphenol – an epoxy resin E-51 diluted by n-butyl glycidy ether (BGE) is adopted as the heal-agent inside the microcapsule. The production process mainly includes pre-polymerization preparation, emulsification, acidification and curing stage. The fundamental reaction mechanisms with respect to the synthesis process and the properties of the obtained microcapsule are discussed in this paper. Meanwhile, the healing mechanism by means of catalyst MC120D is further explored. Results show that the microcapsule obtained with the adopted production process can be used for the self-healing system in the cementitious materials.

1. INTRODUCTION

Using organic microcapsules in making cementitious composites with a self-healing function is a novel technology. Considering the self-healing mechanism, microcapsules should not only store healing agent during period of storage, but also provide driving force during self-healing process when trigger is excited (e.g. the cement matrix cracks and the microcapsules broke). In addition, microcapsules should owe enough external sensibility; the healing agent should have high fluidity with low viscosity; the reaction energy of curing reaction of healing agent system should reach its minimum value. Thus as the trigger is turned on, the healing agent flows out from microcapsule and is cured quickly. In this study, an optimized proportion of healing agent with minimum activation energy is investigated with the help of differential thermal analysis and infrared analysis.

2. MATERIALS

Experimental materials in this study include: the healing agent - epoxy resin E-51 and diluent BGE; the catalyst MC120D.

3. METHODS

The thermal gravimetric analyzer (STA 409 PC) was adopted in order to carry out differential thermal analysis. The rate of temperature-rising was taken as 5 K/min, 10K/min, 15 K/min, 20 K/min, respectively. Spectrum BXⅡ was used for Fourier transform infrared spectroscopy (FTIR) analysis.

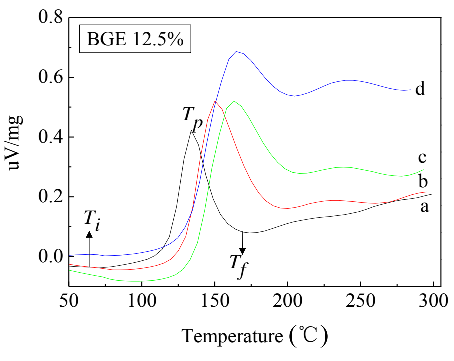
4. RESULTS

According to Kissinger equation [1] (eq. (1)) and Crane equation [2] (eq. (2)), the relation among the temperature-rising rate, the exothermic peak temperature with the activation energy and the reaction order are:

$$\frac{d\left(\ln(\beta/T_P^2)\right)}{d\left(1/T\right)} = -\frac{E}{R} \qquad (1)$$

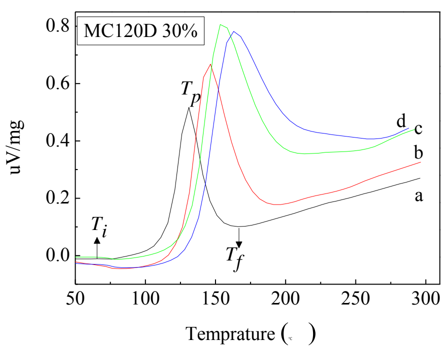
$$\frac{d(\ln\beta)}{d(1/T_P)} \approx -\frac{E}{nR} \qquad (2)$$

where β is the temperature-rising rate, T is the reaction temperature, T_p is the exothermic peak temperature, E is the activation energy, n is the reaction order.
Figure 1 shows differential thermal curves of a healing system with 20% MC120D and 12.5% of BGE. As seen from the figure, the curing reaction shows two exothermic peaks, which indicates that the curing-reaction proceeds step-wisely [1, 2, 3]. As the rate of temperature-rising increases, the initial temperature (T_i), the peak temperature (T_p) and the final temperature (T_f) of the healing agent system increase too. The total generated heat (the area under the exothermic peak temperature curve) increases with the increase of the rate of temperature-rising, which indicates that the curing reaction speed also goes up. Figure 2 illustrates the differential thermal curves of a healing system with 30% MC120D and 17.5% of BGE. As seen from the figure, the differential thermal curve only has one exothermal peak, which means that when MC120D content is higher than 30%, the curing reaction of healing agent is entirely dependent on the catalyst's functionality.



a. 5k/min, b. 10k/min, c. 15k/min, d. 20k/min

Figure 1: Differential thermal analysis of healing system with 12.5% BGE



a. 5k/min, b. 10k/min, c. 15k/min, d. 20k/min

Figure 2: Differential thermal analysis of healing system with 30% MC120D

Results related to the activation energy and the reaction order are shown in Table 1, which were obtained by using different contents of BGE and MC120D was kept at 20%. As seen from the table, activation energy and reaction order reach their minimum values when BGE content is 17.5%. In Table 2 results of the activation energy and the reaction order are shown which were obtained by using different contents of MC120D and BGE content was kept at 17.5%. As seen from the table, the activation energy and reaction order reach their minimum values when MC120D content is 20%. Based on systematic tests it was found that the optimal proportion of the healing agent system is: MC120D content 20% and BGE content 17.5%.

Table 1: Activation energy and reaction order for different diluents mass fraction

BGE fraction (%)	$-\ln(\beta/T_p^2)\sim 1000/T_P$ fitting $-\ln\beta\sim 1000/T_P$ linear fitting	Relative coefficient R^2	Activation energy E ($KJmol^{-1}$)	Reaction order n
10.0	y=-3.65469+5.72375x	0.998	47.59	0.870
	y=-17.76639+6.57637x	0.999		
12.5	y=-5.68331+6.55079x	0.969	54.47	0.885
	y=-19.78786+7.40054x	0.976		
15.0	y=-4.4576+6.06282x	0.998	50.41	0.877
	y=-18.56654+6.91445x	0.999		
17.5	y=-3.36634+5.61983x	0.998	46.73	0.868
	y=-17.4921+6.47836x	0.998		
20.0	y=-3.32175+5.62768x	0.998	46.79	0.868
	y=-17.44446+6.48505x	0.998		

Table 2 : Activation energy and reaction order for different mass fraction of catalyst

MC120D fraction (%)	$-\ln(\beta/T_p^2)\sim 1000/T_P$ fitting -lnβ～1000/TP linear fitting	Relative coefficient R^2	Activation energy E ($KJ\cdot mol^{-1}$)	Reaction order n
10	y=-4.81416+6.36782x	0.985	52.94	0.880
	y=-18.96889+7.23911x	0.989		
20	y=-3.36634+5.61983x	0.998	46.73	0.868
	y=-17.4921+6.47836x	0.998		
30	y=-6.91955+6.99507x	0.991	58.16	0.892
	y=-21.00677+7.83769x	0.993		
40	y=-5.98578+6.53037x	0.999	54.30	0.888
	y=-20.03786+7.35817x	0.999		
50	y=-11.31952+8.65504x	0.981	71.96	0.913
	y=-25.37057+9.48248x	0.984		

Figure 3 shows the Fourier transform infrared spectroscopy (FTIR) analysis of curing products by using different contents of BGE. It can be seen the main absorption peaks of epoxy resin, $771cm^{-1}$, $1035cm^{-1}$, $1184cm^{-1}$, $1361cm^{-1}$, $2928cm^{-1}$ are disappeared. The same phenomenon was observed for BGE, $913cm^{-1}$, $844cm^{-1}$, $761cm^{-1}$, which indicates the participation of BGE in the curing reaction [4, 5, 6].

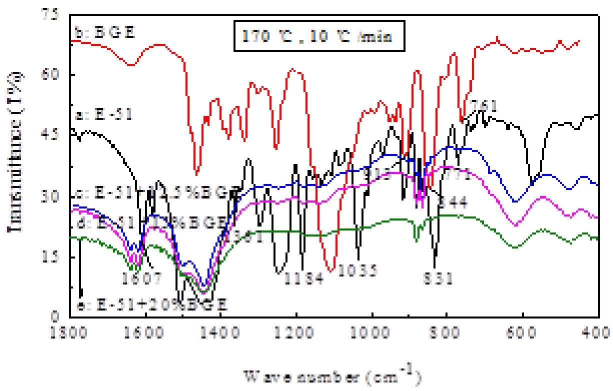


Figure 3 : FTIR spectra of cured epoxy resin E-51 (20%MC120D)

5. CONCLUSIONS

From this study, optimal proportion of healing agent is obtained. Results show that the microcapsule obtained with the adopted production process can be used for the self-healing system in the cementitious materials.

ACKNOWLEDGEMENTS

Financial support from the NSFC (Project No. 51120185002; No. 51078238, No. 50925829) is gratefully acknowledged.

REFERENCES

[1] Adalbert Farkas, Paul F. Strohm. Imidazole catalysis in the curing of epoxy resins. Journal of Applied Polymer Science, 1968, 12(1): 159-168.
[2] Yang Yanxu, Deng Guangqi, Pang Yaohua,et al. Study on the Curing Process of Epoxy Resins by FT-IR-the Curing Behavior and Kinetics of the E-51/2, 4 EMI System [J]. Journal of Xi'an Jiaotong University. 1989, 23(5): 65-70.
[3] F Ricciardi, W A Romanchick, M M Joullie. Mechanism of imidazole catalysis in the curing of epoxy resins[J]. Polymer Science. 1983, (21): 1475-1481.
[4] Junwei Gu, Qiuyu Zhang, Jing Dang, et al. Preparation and mechanical properties researches of silane coupling reagent modified β-silicon carbide filled epoxy composites[J]. Polymer Bulletin, 2009, 62(5): 689-697.
[5] Abdelkader, AF, White, JR. Curing characteristics and internal stresses in epoxy coatings: Effect of crosslinking agent[J]. Journal of Materials Science, 2005, 40(8): 1843-1854.
[6] Weng Shifu. Analysis of Fourier Transform Infrared Spectrometer [M], 2nd edition, Beijing : Chemical Industry Press 2010,389.