IOP Conference Series: Materials Science and Engineering

PAPER • OPEN ACCESS

Toughening Study of Epoxy Structural Reinforcement Adhesive in Concrete at Room Temperature

To cite this article: Lin Liu and Yiyi Chen 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **585** 012023

View the article online for updates and enhancements.

This content was downloaded from IP address 124.205.143.210 on 13/10/2019 at 21:01

IOP Conf. Series: Materials Science and Engineering **585** (2019) 012023 doi:10.1088/1757-899X/585/1/012023

Toughening Study of Epoxy Structural Reinforcement Adhesive in Concrete at Room Temperature

Lin Liu, Yiyi Chen

School of Materials Science and Engineering, Tongji University, 1239 SiPing Road, YangPu District, Shanghai, China
Email: 85418@tongji.edu.cn, 4c4h4c4h@tongji.edu.cn

Abstract. This paper selects liquid bisphenol A epoxy resin with different types of room temperature curing agent and different types of room temperature toughener. Comparing the energy per unit area combined with the tensile test, bending strength, compressive strength and steel-steel tensile shear strength, combination of the 10% amount of A2364 toughener and polyamide A350A curing agent shows best performance in various tests. Its bending strength is 96.9 MPa, shear strength is 23.2 MPa, and Tg is 74.6 ℃. The characteristic temperature of the epoxy strengthening system is calculated through DSC. The average apparent activation energy E= 63.79J/mol and the reaction order number n=0.93. The kinetic equation of the toughened epoxy curing system is obtained, which provided theoretical support for practical application.

1. Introduction

Polymer materials have been widely used in all aspects of life. Among them, epoxy resin has become an important part of them. In the construction field, epoxy is widely used as a structural reinforcement adhesive in the structural reinforcement of concrete. Adhesive used in the concrete field usually requires curing at room temperature, high strength performance, good adhesion to the corresponding substrate, low viscosity, no shrinkage and so on. As a kind of room temperature structural reinforcement adhesive, epoxy has excellent mechanical properties, good bonding performance, low price and easy to achieve. However, epoxy material is also brittle, and the properties after curing at room temperature are closely related to the curing agent [1]. The paper study on the adhesive properties effects of toughener, curing agent and epoxy resin, and the best toughening effect curing system would be studied for non-isothermal kinetics.

2. Experimental Part

2.1. Experimental Materials and Equipment

Dow Chemical DER331 is selected as standard liquid bisphenol-A epoxy resin. Room temperature curing agent, m-xylylenediamine MXDA of Mitsubishi Gas Chemical is selected as aromatic amine; Jeffamine D230 of Huntsman Chemical is selected as polyether amine, hereinafter referred as D230; Ancamide 350A of Air Products and Chemicals is selected as polyamide, hereinafter referred as A350A. The toughener, Ancarez 2364 of Air Products and Chemicals, hereinafter referred as A2364, which is a polyurethane resin toughener with acrylate functional groups; 52 toughener is a nano-reinforced epoxy toughener powder what is polymerized butyl acrylate capped with polymerized methacrylic co-monomer. MX toughener is a toughener based on core-shell rubber pre-dispersed in liquid epoxy resin, in which the core part is 50nm-1um styrene-butadiene rubber copolymer and the

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.
Published under licence by IOP Publishing Ltd

IOP Conf. Series: Materials Science and Engineering **585** (2019) 012023 doi:10.1088/1757-899X/585/1/012023

outer ring compound is good compatible with epoxy resin. ATBN 1300X16 toughener, hereinafter referred as ATBN, is a commonly used macroscopic phase separation type toughener.

Differential Scanning Calorimeter (DSC), Q2000, American TA Company; Electronic Universal Material Testing Machine, American Instron Corporation.

2.2. Experimental Methods

The glass transition temperature Tg of each curing agent and DER331 resin at different ratios is tested by DSC. In the test, the first ramp heating gives a complete cure reaction exotherm. Tg of the cured product is obtained at the second time. Test tensile strength, elongation at break, elastic modulus, bending strength, compressive strength, steel-steel tensile shear strength according to the requirements in the “Code for design of strengthening concrete structure (GB50367-2013)” (hereinafter referred to as the "Code for Design"). When the non-isothermal kinetic parameters are tested, epoxy strengthened and cured samples are heated at different ramp rates (5 K/min, 10 K/min, 15K/min, 20K/min) from 0 ℃ to 300 ℃ under N_2 purge.

3. Discussion of Results

3.1. Addition Ratio of Curing Agents and Toughener

For the same resin and curing agent, the larger Tg means the free movement of the polymer macromolecular segment requires the lower temperature and the cured product has the higher cross-linking degree. So, it is considered as the optimal amount of addition. The test showed that under the 100g DER331 epoxy resin, the optimal addition amount of MXDA is 18g; the optimum addition amount of D230 is 32g; the optimum addition amount of A350A is 55g.

The strengthen agent addition ratio is mainly determined according to the content of the active ingredients in the technical data sheet and the recommended dosage. Each of the toughener is selected to take experiment for toughening effect with three kinds of addition ratio.

3.2. Effect of Toughener on Strengthening Effect of Epoxy Curing Agents

Tensile strength generally refers to the ability of a material to resist elastic deformation and fracture under external forces. The energy per unit area is defined as the area integral of the displacement and the force during the stretching process from the beginning to the fracture. The greater the energy per unit area is, the greater the energy that requires to overcome to break the material is, which means the greater toughness of the material is. [2]

Table 1. A350A tensile test results

Toughener	Additive amount/%	Tensile strength/MPa	Elongation %	Elastic modulus/MPa	Energy per unit area/ $\times 10^{-1}$J/mm^2
Untoughened	0	57.2	4.20	2363	1.51
A2364	10	56.3	4.34	2678	1.79
	20	46.7	4.16	2288	1.34
	40	32.2	4.42	1489	0.13
52 Toughener	10	33.4	1.59	2776	0.31
	20	24.4	1.49	2424	0.21
	40	21.7	1.14	2262	0.13
ATBN	5	47.2	3.13	2351	1.10
	10	42.1	3.60	2228	0.90
	15	40.33	3.73	1996	1.13
MX Toughener	20	56.0	3.40	2544	1.12
	35	51.7	4.66	2496	1.69
	50	50.8	4.76	2429	1.72

IOP Conf. Series: Materials Science and Engineering **585** (2019) 012023 doi:10.1088/1757-899X/585/1/012023

Polyether amine D230 is a bifunctional primary amine with an average molecular weight at about 230. The molecule has a primary amine at both ends. MXDA has two secondary amines in the molecule and is the most widely used aromatic amine curing agent at room temperature. Polyamide A350A is produced by a polycondensation reaction from dimer acid and triethylenetetramine. The ratio of the epoxy resin and A350A is not strict and the tolerance range is large. It is found after test that A350A cured product has a higher energy per unit area than D230 and MXDA at room temperature. This is because the polyamide reacts more completely at room temperature curing. As seen in the Table 1, A2364 has the highest energy per unit area at 10% addition, and its elastic modulus is also the highest, indicating that the A2364 toughener has better strengthen effect on polyamide A350A at room temperature [3]. The effect of ATBN and 52 toughener both decreases. This is because the viscosity of polyamide is relatively large, while ATBN and 52 nano-toughener have a large effect on viscosity. Their compatibility after mixing is poor, and the toughening effect will also be poor. The MX toughener is pre-dispersed in the epoxy resin and has little effect on the viscosity. The toughening effect of the it is acceptable, but the elastic modulus is slightly lower.

3.3. Effect of Toughener on Steel-Steel Tensile Shear Strength

According to the "Appraisal Code", the requirements for Class I grade A adhesive in concrete load-bearing structure reinforcement, steel-steel tensile shear strength ≥ 15MPa. The tensile strength of the steel-steel can be used to judge the toughening effect. It can be seen from Table 2 that A2364 has obvious strengthening effect on the three curing agents, and the shear strength is improved. A350A polyamide and 10% A2364 toughener has the best result with 23.2MPa. The interpenetrating network can effectively improve the strengthening effect.

Table 2. Steel-steel tensile shear strength

Toughener	Addition amount/%	D230	MXDA	A350A
Untoughened	0	14.0	15.2	18.0
A2364	10	19.0	19.7	23.2
	20	18.8	19.2	19.5
	40	17.5	17.4	18.6

3.4. Effect of Toughener On Bending Strength

According to the "Appraisal Code", the requirements for Class I grade A adhesive in concrete load-bearing structure reinforcement, bending strength≥50MPa. It can be seen from Table 3 that the 10% addition of A2364 toughener on A350A has better toughening effect in the bending test. The bending strength is 96.9MPa.

Table 3. Test results of bending strength (MPa)

	Addition amount/%	A350A
Untoughened	0	84.1
A2364	10	96.9
	20	83.2
	40	65.1

3.5. Effect of Toughener on Tg of Cured Products

As shown in Table 4, the effect of A2364 toughener on Tg is little. Tg is 74.6 ℃, only -0.5 ℃ change. It can be seen that the formation of a good interpenetrating network does not affect the structure of the cured product, and the heat resistance is hardly affected.

Table 4. Tg (℃) change after room temperature curing after toughening

Toughener	Addition amount/%	Tg(A350A)/ ℃
Untoughened	0	75.1
A2364	10	74.6
Tg Change		↓0.5

3.6. Non-Isothermal Curing Kinetics Study

10% A2364 toughener is selected with A350A curing agent and DER331 epoxy resin for non-isothermal curing kinetics study. The curves at different ramp rates are determined by differential scanning calorimetry, and the DSC curves of the cured epoxy resin curing reaction are shown in Figure 1. It can be seen from Figure 2 that there is a significant difference between the initial temperature T_i, the maximum exothermic temperature T_p and the exothermic end temperature T_f of the toughened modified epoxy resin curing system at different ramp rates. By linear regression equations for the points of T_i, T_p and T_f, the linear regression equation of T_i is obtained: y = 0.876x + 303.4; the linear regression equation of T_p is obtained: y = 1.5016x + 378.68; the linear regression equation of T_f is obtained: y = 3.2082x + 473.08. Using the extrapolation method, the parameters, which are the intercepts of the fitting curve on the y-axis ordinate, are obtained at 0 ramp rate. T_i =303.4K, T_p =378.68K, and T_f = 473.08K. The initial temperature is 30.25℃, indicating that the reaction is relatively complete at room temperature. And the exotherm reaction will continue to increase the curing degree, so the performance of the toughened product after curing at room temperature is guaranteed.

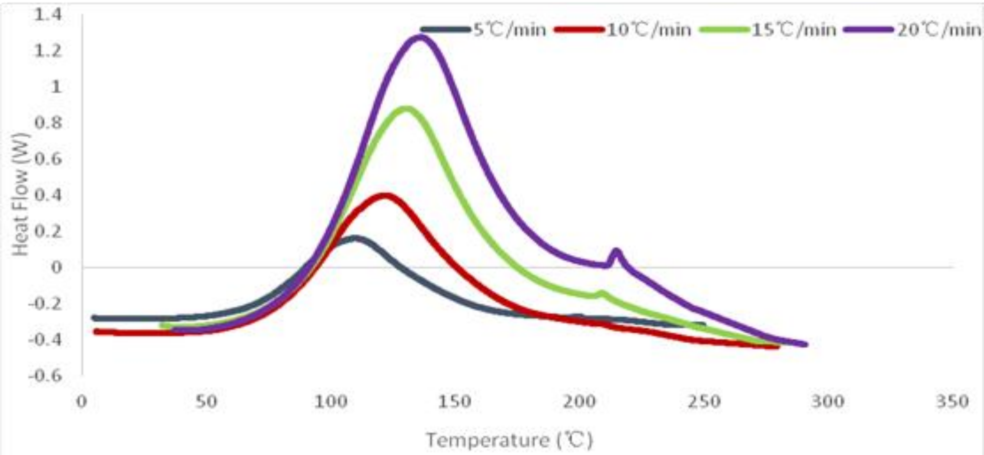

Figure 1. DSC graph of different heating rates

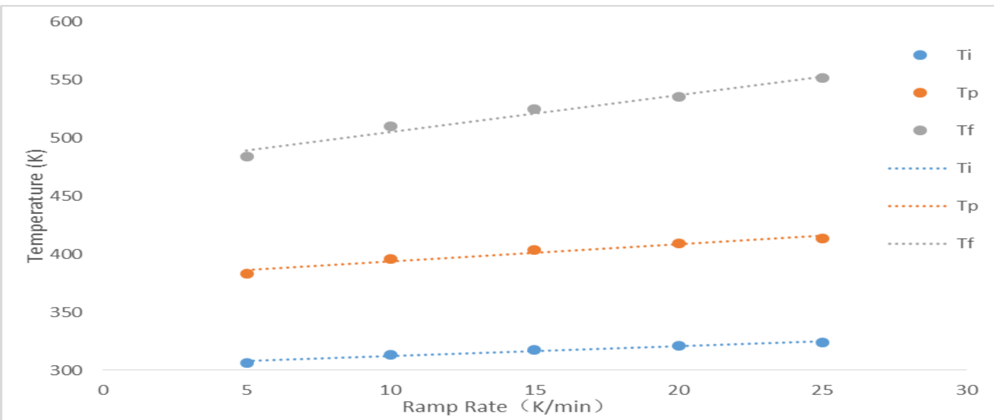

Figure 2. Curing temperature versus ramp rate

The activation energy E of the thermosetting resin system can generally be calculated by the Kissinger method [4] and the Ozawa [5] theory. The average value of E calculated by the two methods can be used as the E of the toughened modified epoxy resin system.

Kissinger is based on two assumptions: one is that the maximum rate of cure reaction is assumed to be the highest point of the exothermic peak of the curing reaction; the other is that the reaction order n remains constant throughout the curing reaction. Taking -ln(β/Tp^2) for 1/Tp×10^3 as shown in Figure 7, the equation fitting curve is a straight line. The linear regression equation of the toughening curing reaction system is y=7.479x-9.234, and the linear correlation coefficient is greater than 0.99. The slope of the line is 7.479. According to the Kissinger equation (1), Activation energy obtained by calculation E=62.18J/mol.

Ozawa's method is based on the mathematical relationship between ramp rate, maximum exothermic peak temperature and apparent activation energy. Taking lnβ for 1/Tp as shown in Figure 3, the equation fitting curve is a straight line. The linear regression equation of the strengthening curing system is y=-8.2745x+23.206, the linear correlation coefficient is greater than 0.99, and the linear slope is -8.2745. The equation is as in equation (2). The activation energy E = 65.39 J/mol is obtained. The average activation energy E = 63.79 J/mol.

$$\frac{d\left[\ln\left(\frac{\beta}{T_p^2}\right)\right]}{d\left(\frac{1}{T_p}\right)} = \frac{-E}{R} \tag{1}$$

$$\frac{d[\ln\beta]}{d\left(\frac{1}{T_p}\right)} = \frac{-1.052E}{R} \tag{2}$$

In the formula: β is the ramp rate, K/min; T_p is the highest temperature of the exothermic peak, K; R is the ideal gas constant, 8.314 J/mol K; E is the apparent activation energy, J/mol.

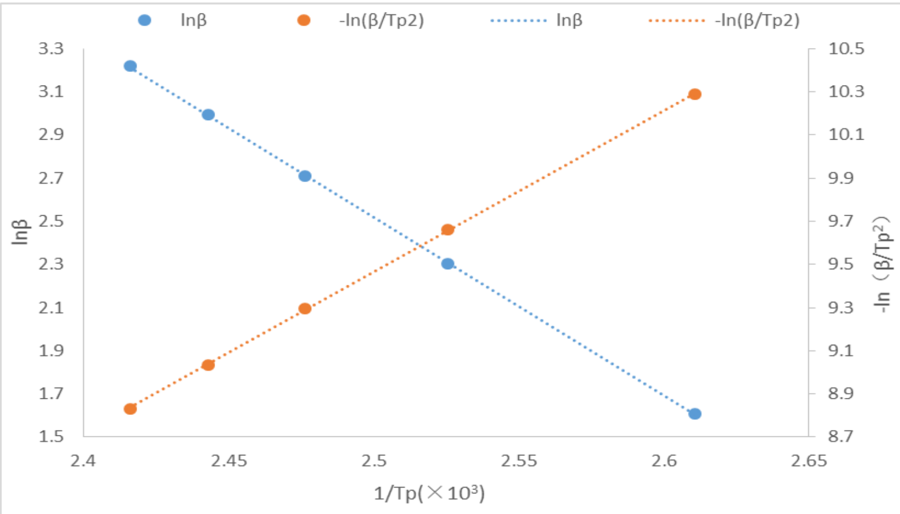

Figure 3. Kissinger and Ozawa equation fitting curve

Calculate the curing reaction order n of the toughened epoxy system by the activation energy using the Crane [6] equation (3). When E/(nR) is much larger than 2T_p, 2T_p can be neglected. Using lnβ and 1/T_p relation showed in Figure 7, the slope of the linear fitting straight line is -8.2745 and then the average activation energy is taken into the equation, and the reaction order number n=0.93 is calculated. The reaction order is not an integer, indicating that the toughened epoxy system is a near-stage 1 reaction.

$$\frac{d(ln\beta)}{d\left(\frac{1}{T_p}\right)} = -\left(\frac{E}{nR} + 2T_p\right) \tag{3}$$

IOP Conf. Series: Materials Science and Engineering **585** (2019) 012023 doi:10.1088/1757-899X/585/1/012023

In the formula: n is the reaction order.

Using the graph of -ln($\beta/T_p{}^2$) and $1/T_p$ showed in Figure 7, the slope of the linear fitting straight line is 7.479, and the pre-exponential factor A=7.86×10^7 s^{-1} is measured [7]. In practice, we can integrate the kinetic equation (4) as needed to obtain the relationship between curing temperature, curing time and curing degree in curing reaction which provides a theoretical basis to the curing process of the toughened epoxy system [8].

$$\frac{d\alpha}{dt} = 7.86 \times 10^7 \exp(\frac{-63787}{RT})(1-\alpha)^{0.93} \quad (4)$$

In the formula: R is the ideal gas constant, 8.314 J/mol·K; T is the reaction temperature, K; α is the reaction conversion rate.

4. Conclusion

DER331 is selected as the base resin for epoxy structural reinforcement adhesive in concrete. Firstly, the optimum addition amount of various curing agents is determined by Tg. Among them, 10% added A2364 toughener has a good improvement on the mechanical properties. The combination has a bending strength of 96.9 MPa, steel-steel tensile shear strength of 23.2 MPa, and a Tg of 74.6 ℃. The initial temperature is 30.25 ℃, indicating that the system could be completely reacted at near room temperature, and the average apparent activation energy is calculated as E=63.79 J/mol. The curing reaction order n = 0.93 is measured by the Crane equation. Using the obtained parameters, the toughened curing kinetic equation is determined, which provides a sufficient theoretical basis for practical application.

5. References

[1] Zhang Z, Evans D. Investigation of fracture properties of epoxy at low temperature[J]. Polym Eng Sci, 2003, 43: 1071-1080.
[2] Panagiotis I., Karkanas I.k., Patridge. Cure Modeling and Monitoring of Epoxy/Amine Resin System I, Cure Kinetics Modeling[J]. Journal of Applied Polymer Science, 2000, 77:1419-1431
[3] B B Johnsen,A J Kinloch,A C Taylor. Toughness of syndiotactic polystyrene/epoxy polymer blends:microstructure and toughening mechanisms[J]. Polymer, 2005, 46:7352-7369.
[4] Kissinger H E. Reaction kinetics in differential thermal analysis[J]. Analytical Chemistry,1957, 29(11): 1702-1706.
[5] Ozawa T. J Bull Chem Soc Japan,1965;38: 1881
[6] L W Crane. Analysis of curing kinetics in polymer composites [J]. Journal of Polymer Science: Polymer Letters Edition,1973(11): 533-540
[7] Kunz Douglass, Beaumont. Model for the toughness of poxyrubber particulate composite[J]. Mater Sci, 1980, 15: 1109-1123.
[8] Imanaka M, Takeuchi Y, Nakamura Y, et al. Fracture toughness of spherical silica-filled epoxy adhesives [J]. International Journal of Adhesion& Adhesives, 2001, 21:389-396.