Effects of Water on the Curing and Properties of Epoxy Adhesive Used for Bonding FRP Composite Sheet to Concrete

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ABSTRACT: When a concrete surface is contaminated by water due to rain, saline water, ground water, and water jetty treatment, water, alkalis, and other contaminants on the concrete surface may interact with an epoxy adhesive used for bonding fiber-reinforced polymer composite sheets to concrete. This can influence both the curing rate and the degree of cure of the curing reaction. This in turn can affect the time required for field application. It can also influence the mechanical properties and durability of epoxy adhesives. In this paper, water effects on the curing and properties of two kinds of commercial adhesives were evaluated. Curing kinetics were studied using isothermal DSC analysis. Results showed that water accelerated the curing reaction. However, excess water offsets part of the accelerating effect. While water is typically considered to be harmful to properties of adhesives, it was seen that a small amount (less than 2%) of water improved degree of cure, mechanical properties, and durability of adhesives. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 2261–2268, 2004

Key words: adhesives; epoxy; kinetics; water; reinforcement construction; ageing

INTRODUCTION

In recent years there has been increasing interest in using fiber-reinforced polymer (FRP) composites to repair concrete structures. Epoxy resins are selected as adhesives for bonding FRP composite sheets to concrete due to their good adhesive ability to both concrete and FRP materials. In civil engineering applications, the concrete structures are often contaminated by different materials due to rain, saline water, ground water, and wet jetty treatment, while the concrete itself has high alkalinity and consists of different compositions. When epoxy adhesive is used to repair a concrete structure, water, alkalis, and other contaminants on the concrete surface may interact with the epoxy adhesive, and thus influence the curing reaction, both the curing rate and the degree of cure. Due to the restrictions of on-site processing, epoxy adhesives used in civil engineering applications are usually cured at room temperature. As a result, only a low glass transition temperature (T_g) can be obtained, which limits the service temperature and increases the sensitivity of the bond to environmental factors, such as humidity, temperature, etc. In addition, the mechanical properties and the durability of epoxy adhesives are greatly affected by the degree of cure. As the load is transferred to the FRP material by adhesives, the mechanical properties and the durability of this bond with concrete is critically important for the integrity and safety of the repaired structure. However, so far, most current research has focused primarily on mechanical properties of the whole system of concrete and composite reinforcing sheet. Information on the bond between concrete and the FRP sheet materials is relatively scarce.

Chen et al.[1] used near infrared (NIR) spectroscopy to study the curing reaction of two types of epoxy/hardener systems in the presence of water and found that water accelerated the curing reaction. The reaction rate constant increases linearly with water content up to a saturation point (about 0.06%) and then is invariant with the water content. The authors also evaluated the water effect on ultimate tensile strength, shear stress, impact strength, flexural strength, and compression strength and found that water deteriorated the mechanical strength of adhesives. This work showed that the presence of water can have an effect on the curing of the epoxy adhesives and their properties. However, there are aspects that this paper did not address:

1. The water used in that study was deionized water rather than regular water and concrete pore water, which may have different effects.
2. The quantity of water has an influence on its effect on the epoxy. The curing rate increases with water content for small amounts of water

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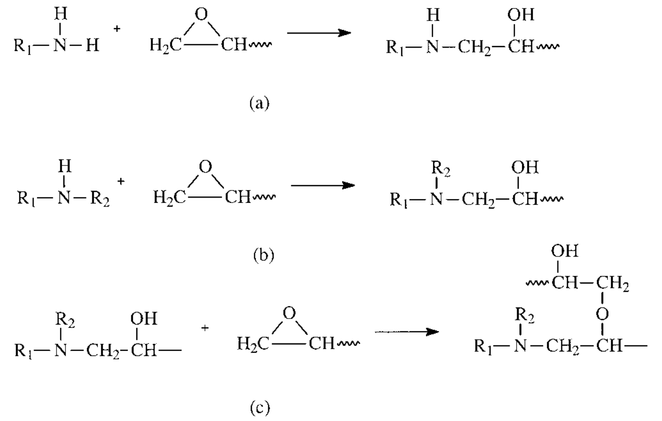


Scheme 1 Chemical reactions for a diepoxy–diamine system: (a) epoxide ring-opening reaction with primary amine; (b) epoxide ring-opening reaction with secondary amine; and (c) etherification reaction between reacted and unreacted epoxy groups.

(up to 0.06%), but an additional amount has no further effect. This effect should be examined more closely. In many field applications, the epoxy adhesives can be contaminated by a small amount of water on the concrete surface.

3. There was no evaluation of water effects on modulus and durability of epoxy adhesives. This is important in the design of using FRP to reinforce concrete.

The work described in this paper examined the effects of different issues arising from the application in the field, such as effects of water and concrete contaminants on the curing reaction, mechanical properties, and durability of adhesives, to provide a fundamental understanding of the performance and durability of the joint and also guidelines for the application of adhesive.

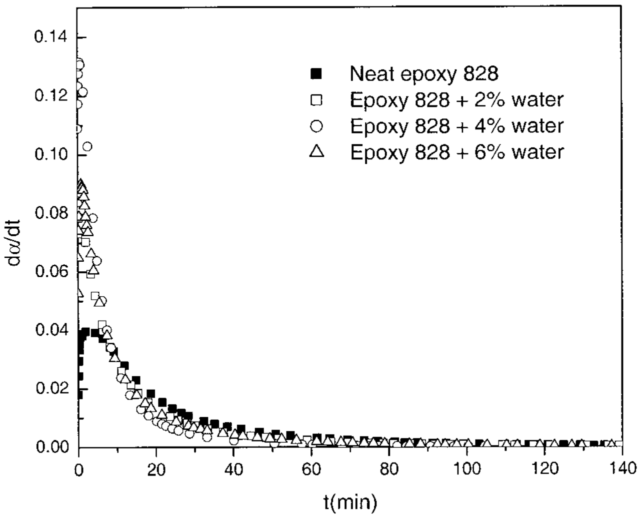


Figure 1 Plot of reaction rate versus time of the Epon 828 system with differing water contents curing at an isothermal temperature of 80°C.

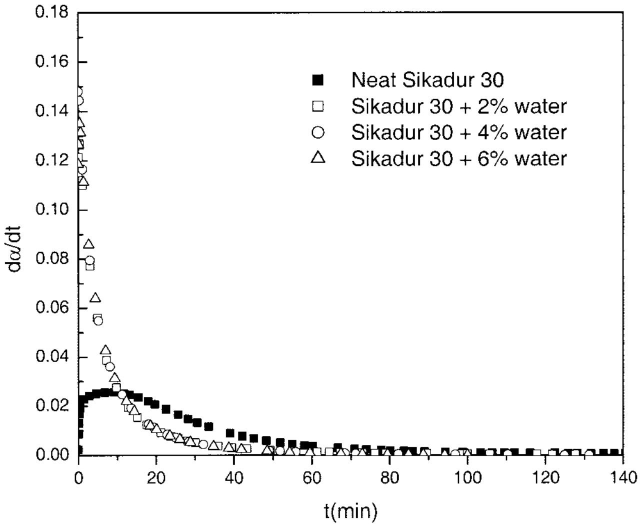
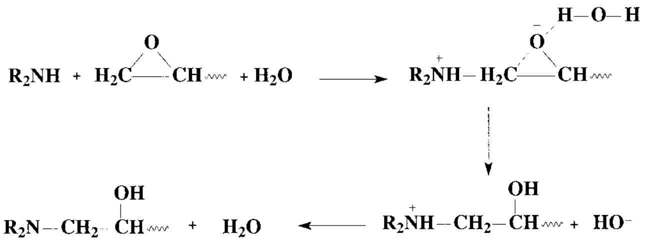


Figure 2 Plot of reaction rate versus time of the Sikadur 30 system with differing water contents curing at an isothermal temperature of 80°C.

EXPERIMENTAL

Materials

Two epoxy adhesive systems were used in this study. The Epon 828 system from Shell Co. consists of 1 part by weight EPON resin 828 and 0.47 part by weight EPI 3046. The Sikadur 30 system from Sika Co. consists of 3 parts by weight Sikadur 30A and 1 part by weight Sikadur 30B. Immediately after mixing the epoxy resin and hardener, distilled water or concrete pore water was added into the epoxy/hardener mixture at 2, 4 and 6% of total weight of epoxy resin and hardener, respectively, and mixed uniformly. The concrete pore water solution was formulated by immersing concrete in distilled water for 1 week and drawing the upper transparent solution. The pH of this solution was approximately 13.5.



Scheme 2 Ring opening polymerization in the presence of water.

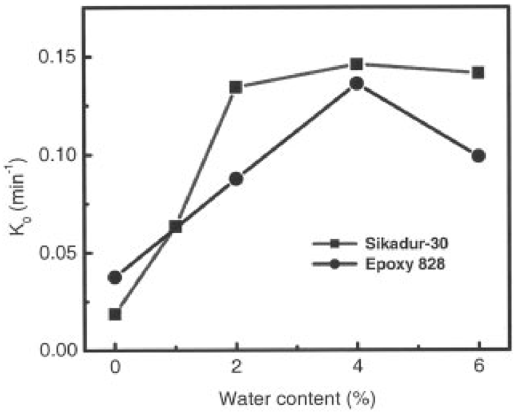


Figure 3 Plot of initial total rate constant versus water content for the Sikadur 30 systems cured at 60°C and the Epon 828 systems cured at 80°C.

Differential scanning calorimetry (DSC)

The differential scanning calorimeter (TA Instruments, DSC 2010) was operated in the isothermal mode to determine the kinetic parameters. The instrument was preheated to the isothermal temperature and kept stable before mixing epoxy, hardener, and water. From the bulk samples, 10- to 15-mg samples were used and sealed in aluminum pans before introducing them into the calorimeter.

Dynamic mechanical analysis (DMA)

The dynamic mechanical analysis was conducted using a TA Instruments DMA 983 in fixed frequency mode. The loading frequency was 1 Hz and the heating rate was 2°C/min.

Three-point bending test of FRP-reinforced concrete beam

The concrete beam used for the three-point bending test was 279.4 × 76.2 × 50.8 mm. The FRP used was a Sika CarboDur S512 with geometry of 228.6 × 50 × 1.2 mm. The three-point bending test of FRP-reinforced concrete beam was conducted at 0.2 mm/min by using an MTS-809 test system. The span was 254 mm.

RESULTS AND DISCUSSION

Effect of water on the curing reaction

The typical reaction between epoxy and amine hardener under room temperature is shown in Scheme 1.[2]

When the ratio of epoxide groups to amine hydrogens is 1:1, the etherification reaction is usually much slower than the amine-epoxy reactions and only becomes significant above 150°C.[3] To be consistent with the curing reaction in the field, the DSC isothermal temperatures were set at 60°C for the SikaDur 30 system and 80°C for the EPON 828 system to avoid the etherification reaction that occurs at high temperature.

Two experimental techniques exist for reaching a stable isothermal temperature: [3] In one, the calorimeter is preheated to the desired reaction temperature before the unreacted sample is placed in the calorimeter cell. In the other, the sample is placed in the calorimeter cell at a temperature at which no significant reaction will take place over a short time period, and the temperature is then raised as rapidly as possible to the predetermined reaction temperature. The time from placing sample to establish equilibrium by the preheating calorimeter method was about 1 min, while the other method took about 5 min to establish equilibrium. Since the curing reaction can happen at

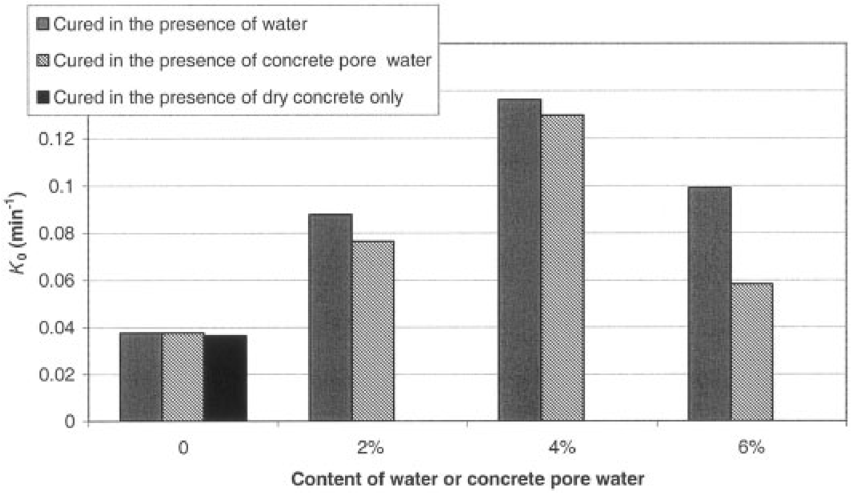


Figure 4 The comparison of initial total rate constants of the Epon 828 systems cured in the presence of water, concrete pore water, and dry concrete powder at an isothermal temperature of 80°C.

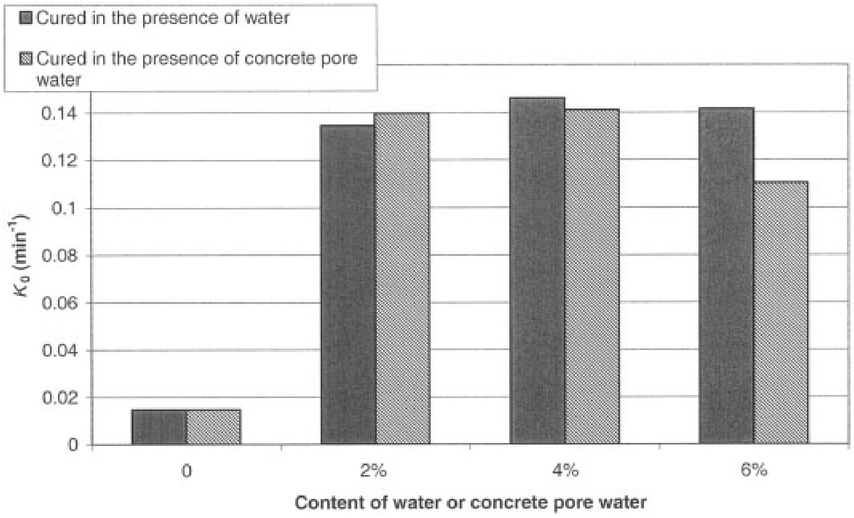


Figure 5 The comparison of initial rate constants of the Sikadur systems cured in the presence of water and concrete pore water at an isothermal temperature of 60°C.

room temperature, and becomes significant after heating, the reduction of equilibrium time is crucial to obtain precise results.

Effects of water on the curing rate

A general expression for degree of conversion α, is

$$\alpha = \frac{\Delta H_t}{\Delta H_0} \tag{1}$$

where ΔH_t is the heat evolved up to a certain time, in an isothermal experiment, and ΔH_0 is the total heat of reaction, obtained from ΔH_t at the end of test.

The reaction rate $d\alpha/dt$ was determined from DSC experiments using the equation

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0} \tag{2}$$

Figures 1 and 2 show the reaction rates corresponding to the different water contents. It can be seen that water can accelerate the curing reaction of the two epoxy adhesive systems. When epoxy cures in the presence of water, the additional ring-opening polymerization shown in Scheme 2 can occur.[4–6] It can be seen that water served only as a catalyst for the reaction.

According to Nunez et al.,[7] the curing reaction of epoxy can be expressed by the sum of two mechanisms: *n*th order and autocatalyzed. We found that the reaction obeyed the mechanism of the second-order reaction and the kinetic model proposed by Horie et al.[8] can be used to fit the combination effect of two types of mechanisms:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha)(1 - \alpha)^2 \tag{3}$$

where k_1 is the *n*th order rate constant, and k_2 is the autocatalyzed rate constant.

The k_1 term corresponds to the epoxy-amine reaction either uncatalyzed or catalyzed by water initially present in the system. The autocatalytic $k_2\alpha$ term corresponds to the same reaction but catalyzed by hydroxyl groups produced in the reaction. When there is no added water, the k_1 term is small and the curves of neat epoxy systems in Figures 1 and 2 show typical autocatalytic behavior, in which the reaction rate initially increases, reaches a maximum, and then drops off. When water is added, the k_1 term becomes much larger, so the $k_2\alpha$ term becomes relatively unimportant

TABLE I
T_g Measured by DMA for the Epon 828 System and the Sikadur 30 System after 1 Week of Curing

Resin system	Neat resin	+2% water	+4% water	+6% water	+6% Concrete pore water
Epon 828	58.6°C	64.7°C	62.9°C	58.0°C	58.7°C
Sikadur 30	64.1°C	64.9°C	65.1°C	76.3°C	75.2°C

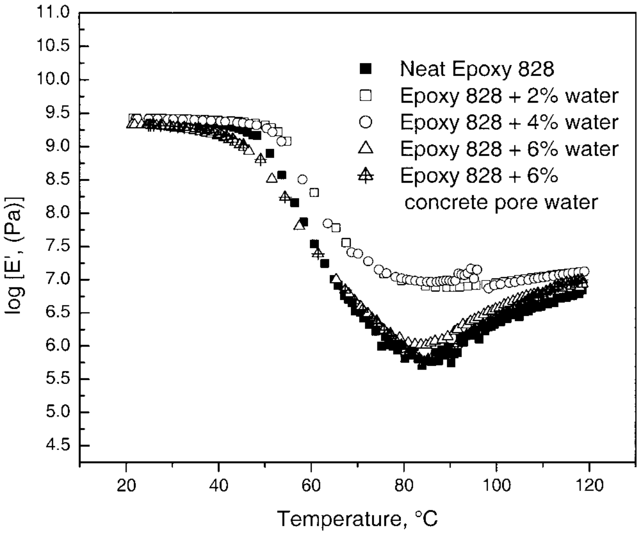


Figure 6 Comparison of the flexural storage modulus of the neat Epon 828 system and the Epon 828 system with water and concrete pore water after 1 week curing.

and the curves of epoxy + water systems in Figures 1 and 2 take on a shape more typical of an *n*th order reaction

The total rate constant is defined as

$$k = k_1 + k_2\alpha \tag{4}$$

Combining eqs. (1) and (4), the total rate constant can be calculated from DSC results by using eqs. (1), (2), and the following equation:

$$k = \frac{\frac{d\alpha}{dt}}{(1-\alpha)^2} \tag{5}$$

During the initial stage, the degree of conversion α is small. The total rate constant k approximately equals the *n*th order rate constant k_1. From eq. (4), the plot of total rate constant k versus the degree of conversion α is a straight line. The initial total rate constant k_0 can be obtained by extrapolating the straight line to $\alpha = 0$. Figure 3 is a plot of initial total rate constant versus water content for the Sikadur 30 system cured at 60°C and the Epon 828 system cured at 80°C. It can be seen that a small amount of water can greatly accelerate the curing reaction of both kinds of epoxy adhesive systems. However, when water content reaches a certain percentage of total weight of epoxy resin and hardener, the curing rate tends to be saturated or to decrease. The true solubility of water in the epoxy resin is limited. When the concentration exceeds the saturation limit, the excess water is no longer intimately mixed with the resin but exists in a phase-separated form (e.g., microdroplets) where it cannot take part in the curing reaction. In fact, it may even solubilize some components of the amine hardener and thereby slow down the reaction by removing them from contact with the epoxy molecules. This may explain the apparent drop in reactivity at 6% water for the Epon 828 system.

Combination effects of concrete and water

Figures 4 and 5 show the comparison of initial total rate constants of the two kinds of epoxy systems cured in presence of water, concrete pore water and dry concrete powder. Again, the concrete pore water can accelerate the curing reaction of both epoxy adhesive systems. It can be seen that the effect of concrete pore water on the curing reaction is less than the effect of the same amount of distilled water, especially at a high content. The high pH value of concrete pore water may deter the curing reaction and offset part of the water-accelerating effect on the curing reaction. In Scheme 2, the intermediate reaction results in hydroxyl ion. The higher hydroxyl ion content in concrete pore water may deter this reaction, resulting in slower reaction rate.

Degree of cure

The calorimetric method is not precise enough to measure the differences of degree of cure in the high degree of cure range. In the past decade, equations and models relating T_g to conversion have received widespread acceptance, establishing T_g as a primary measurement of degree of cure.[3] Unlike the residual heat of reaction, T_g displays increasing sensitivity to

TABLE II
Flexural Storage Modulus (in MPa) at Different Temperatures for the Epon 828 System With and Without Water and Concrete Pore Water

Temperature (°C)	Neat resin	+2% water	+4% water	+6% water	+6% Concrete pore water
30	2466	2616	2555	1948	2023
60	43.10	254.96	182.11	32.93	36.08
90	0.2150	7.5614	9.7250	1.5456	0.9178
120	21.95	13.04	13.56	42.76	12.09

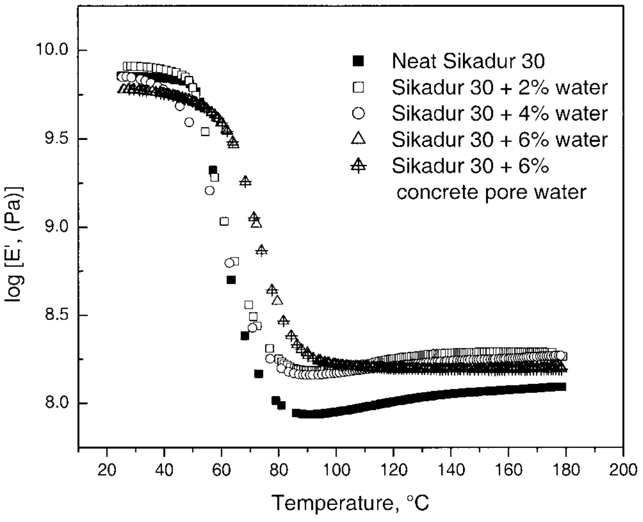


Figure 7 Comparison of the flexural storage modulus of the neat Sikadur 30 system and the Sikadur 30 system with water and concrete pore water.

cure with increasing conversion, thus allowing the final cure state to be more easily and accurately assessed. It was also reported that DMA is more sensitive than DSC in monitoring T_g. Thus, DMA is often employed to monitor the changes in cure degree, especially during durability tests.

After curing for 1 week at room temperature, DMA specimens were tested in the fixed frequency mode at 1 Hz of loading frequency and 2°C/min of heating rate. The glass transition temperatures were obtained using the temperature at peak of phase angle curves. The T_gs of the Epon 828 system and the Sikadur 30 system are listed the Table I.

Water can accelerate the curing reaction and increase the mobility of polymer chains. Higher degrees of cure and crosslink density are expected after epoxy resin is cured in the presence of water. However, excess water could result in more water remaining in the resin, which could not evaporate completely 1 week after curing. The plasticizing effect of water leads to a lower degree of cure for the Epon 828 system with 6% water. For the SikaDur 30 system, the high viscosity of epoxy and hardener, with a high content of filler, makes it difficult to achieve good mixing. Water improves the diffusion between epoxy and hardener, resulting in a somewhat higher degree of cure and T_g.

Effect of water on mechanical properties

Dynamical flexural storage modulus (E')

The flexural storage modulus curves of the neat Epon 828 system and the Epon 828 system with water and concrete pore water after 1 week curing are shown in Figure 6. Values of the flexural storage modulus at 30, 60, 90, and 120°C are listed in Table II. It can be seen that, in the room temperature range, a small amount of water increases the flexural storage modulus while a large amount of water decreases the flexural storage modulus. This can be due to the opposing effects of water: accelerating the curing reaction while also acting as a plasticizer. When temperature rises above 80°C, the samples with 0 and 6% water show an apparent increase in E'. This suggests that further curing took place above 80°C in the DMA experiment, thus providing evidence that the cure was not complete at room temperature for these samples. On the other hand, the samples with 2 and 4% water appear to be highly cured, resulting in much higher E' in the higher temperature range. At 90°C, the flexural storage modulus of the Epon 828 system plus 4% water was 45.2 times of the flexural storage modulus of the neat Epon 828 system.

The flexural storage modulus curves of the neat Sikadur 30 system and the Sikadur 30 system with water and concrete pore water after 1 week curing are shown in Figure 7. Values of the flexural storage modulus at 30, 60, 90, and 120°C are listed in Table III. Similar conclusions to those for the Epon 828 systems can be drawn.

Three point bending test of FRP-reinforced concrete beam

The ultimate strength of FRP-reinforced concrete beams bonded with the SikaDur-30 epoxy adhesives, which were cured in the presence of different contents of water, are shown in Figure 8. There is not a large variation, and all of the samples with reinforcement

TABLE III
Flexural Storage Modulus (in MPa) at Different Temperatures for the Sikadur 30 System With and Without Water and Concrete Pore Water

Temperature (°C)	Neat resin	+2% water	+4% water	+6% water	+6% Concrete pore water
30	7.1614	8.1300	6.9719	5.9826	6.0117
60	1.0456	1.2721	0.9075	3.8949	3.9482
90	0.0865	0.1534	0.1449	0.1938	0.1886
120	0.1019	0.1782	0.1629	0.1565	0.1584

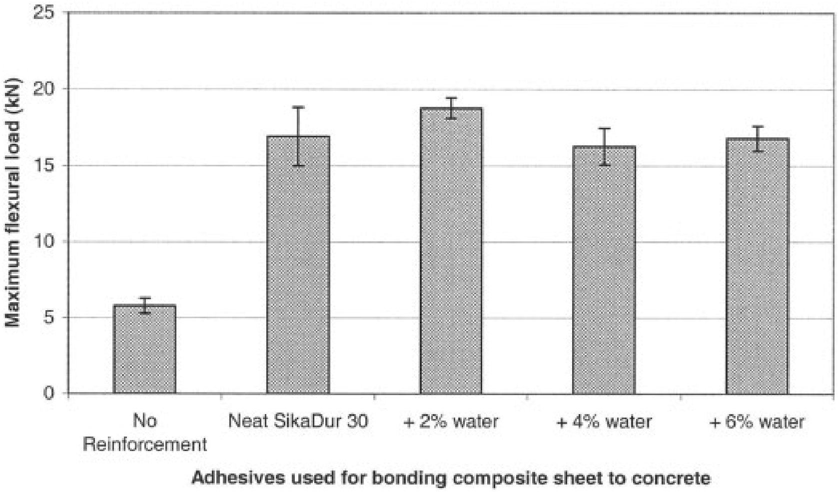


Figure 8 The ultimate strength of FRP-reinforced concrete bars bonded with expoxy adhesives, which were cured in the presence of different ratios of water.

are much better than the one without reinforcement. The maximum flexural load of the FRP-reinforced concrete beam bonded using SikaDur-30 + 2% water was the highest. This result is consistent with the dynamical flexural modulus result from DMA. Chen et al.[1] also show that the maximum shear stress, impact strength, flexural strength, and compression strength of epoxy adhesives are not those of neat epoxy, but those of epoxy cured in the presence of a small amount of water. It seems that a small amount of water not only accelerates the curing reaction, but also improves the mechanical properties.

Environmental exposure

Water uptake

The epoxy systems were cured at room temperature and cut to 1 × 1 in. squares. The specimens were kept at 50% humidity and room temperature until no weight change was observed. Specimens then were exposed in 45°C water to evaluate the durability. A minimum of five specimens was used for each condition. Specimens were weighed with an accuracy of 0.01 mg.

The 3-month water uptake results for the Sikadur 30 systems are shown in Figure 9. It can be seen that the Sikadur 30 systems cured in the presence of 4 and 6% water were prone to absorbing more water than the neat Sikadur 30 system. This can be explained by assuming that the excess water during the curing stage evaporated after cure and left more free volume in the resin, resulting in greater moisture absorption ability for the resin. However, the Sikadur 30 system cured in the presence of 2% water absorbed less water than the neat Sikadur 30 system. This can be explained on the basis that the small amount of water existing in

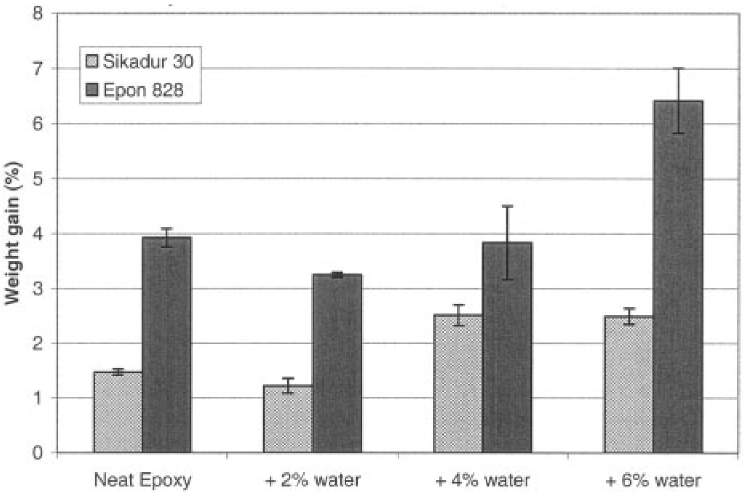


Figure 9 Plot of weight gain versus time for the Sikadur 30 and the Epon 828 systems after immersion in 45°C water for 3 months.

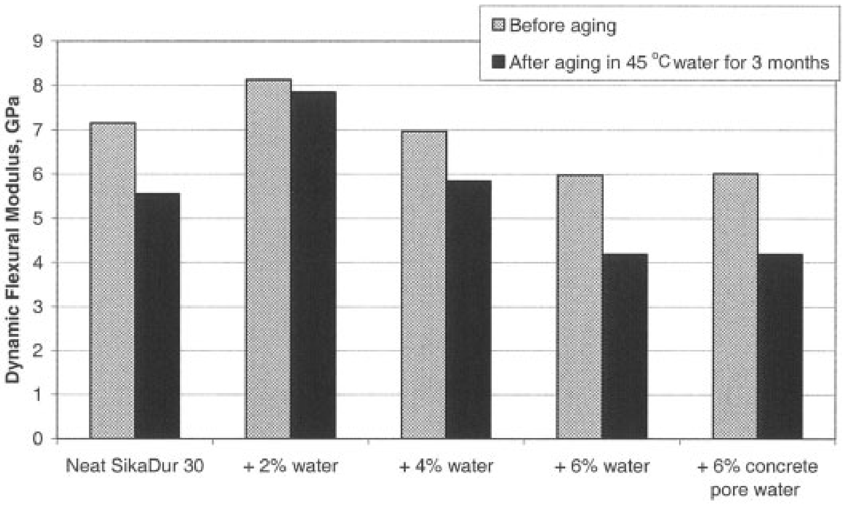


Figure 10 Comparison of the flexural storage modulus at 30°C of the Sikadur 30 systems after a 3-month immersion in 45°C water with those of unimmersed systems.

the curing stage increased the crosslink density, and thereby reduced the free volume in the resin, resulting in less water absorption. A similar tendency exists in the Epon 828 system. After 3 months of immersion, the SikaDur 30 + 6% water system absorbs 2.49% water and the SikaDur 30 + 6% concrete pore water system absorbs 2.65% water. The difference is within the error of measurement.

Dynamical flexural storage modulus

The dynamical flexural storage modulus results for the neat Sikadur 30 system and the Sikadur 30 system with water and concrete pore water after 3-months of immersion in 45°C water are shown in Figure 10 and are compared with those of unimmersed systems. It can be seen that after a 3-month immersion in 45°C water, the dynamical flexural storage modulus of the SikaDur 30 + 2% water system was highest. After 3-month immersion in 45°C water, the dynamical flexural modulus dropped 22.5% for the neat SikaDur 30 system, 3.4% for the SikaDur 30 + 2% water system, 16.1% for the SikaDur 30 + 4% water system, 30% for the SikaDur 30 + 6% water system, and 30.3% for the SikaDur 30 + 6% concrete pore water system. The degradation ratio of dynamical flexural modulus for the SikaDur 30 + 2% water system is smallest. The SikaDur 30 + 6% water system and the SikaDur 30 + 6% concrete pore water system degraded quickly. There is no obvious difference between water and concrete pore water systems.

CONCLUSION

Epoxy adhesives cured in the presence of water are significantly different from neat epoxy adhesives in terms of curing reaction, mechanical properties, and durability. A small amount of water (2%) accelerates the curing rate, increases the degree of cure, flexural modulus, and bonding strength, while it decreases water uptake and rate of degradation of the flexural modulus. However, excess water offsets part of the water effect on accelerating the curing reaction. Excess water also leads to worse mechanical properties and durability. The alkali content in concrete pore water can offset part of the water effect on accelerating the curing reaction. However, alkali content shows no obvious effect on degree of cure, flexural modulus, and durability.

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