Curing of Epoxy Resin Contaminated with Water

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ABSTRACT: Epoxy resins used for reinforcement of bridges and buildings are explored in the light of both curing rates and mechanical properties when resins are contaminated with water in outdoor construction. The developed resin is composed of a conventional resin of bisphenol A diglycidyl ether and a hardener with a polyoxipropyldiamine base. Curing rates were obtained by time variation of the near infrared absorbance of amine groups in the hardener at various water contents. They obeyed the second-order reaction law with respect to the hardener, of which the activation energy was 70 kJ mol^{-1}. Water increased the reaction rate. Mechanical properties such as ultimate tensile strength, adhesive shear stress, and flexural strength were measured at various water contents for the developed epoxy resin and the commercially available low-temperature epoxy resin. The developed cured resin shows not only higher mechanical strengths but also much less deterioration by water than the conventional cured resin. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 214–220, 2001

Key words: epoxy resin; hardener; water; curing rates; reinforcement constructions

INTRODUCTION

Epoxy resins have been used recently for a repairing material of reinforcing buildings, bridges, and highways that were deteriorated for overage use or damaged by natural disasters such as earthquakes. Since construction for the reinforcement is usually made outdoors, environment at a construction site imposes some restrictions on the use of epoxy resins. Crucial restrictions are as follows:

1. environmental temperature in the curing process not only because of difficulty in heating uniformly at outdoor work but also of avoiding thermal strain by local heating;
2. rapid curing rates in order to reduce a construction period;
3. contamination by water because of soak of rain- and groundwater.

A strategy of satisfying condition (1) is to use polyoxipropyldiamine, [H$_2$NCH(CH$_3$)CH$_2$–(OCH$_2$CH(CH$_3$))$_{2.6}$–NH$_2$][1] as a low-temperature hardener. Although this hardener provides the cured epoxy resin with good enough mechanical properties for repairing materials, it takes more than one week to attain the expected strength. Thus, condition (1) conflicts with condition (2) from the viewpoint of chemical kinetics. In order to solve this incompatibility, it is necessary to decrease the activation energy of the curing reac-

tion, with maintaining mechanical properties. Finding an activation step leads to the study on reaction mechanisms, which has been done by means of viscosity,[2] ^{1}H NMR,[3] Fourier transform infrared (FTIR),[4] and size exclusion chromatography.[5] The overall activation energy, however, not only includes the activation energy of the elementary reaction but also depends on auxiliary variables such as solvent, concentrations, viscosity, and mixing rates, and contamination. In particular, contamination with water is practically important for the reinforcement construction.

Condition (3) is not directly relevant to the curing reaction mechanism itself, but may block the reaction and deteriorate mechanical properties in terms of formation of the aqueous microphase. Although several techniques of detecting water content have been developed, e.g., FTIR,[6] NMR,[7] fluorescence,[8] and near-infrared spectra,[9] applicability of the epoxy resin contaminated by water has not been well discussed yet,[9–11] to our knowledge. We have found a possibility of improving mechanical properties of water-included epoxy resin by means of trial and error preparation of a hardener. This paper is devoted to evaluating quantitatively a relationship of a water content with the reaction rate as well as mechanical properties.

EXPERIMENTAL

Materials

The epoxy resin used here was the conventionally used bisphenol A diglycidyl ether (Epoxy-828, Yuka Sieru, Tokyo), which is insoluble in water. We developed a hardener by blending polyoxipropyldiamine (EA-230, Dainippon Inki, Tokyo), cyclohexan-diamine (Wako, Tokyo), adipic acid dihydrazide (Wako, Tokyo), and phenols (Wako, Tokyo) at various fractions by trial and error. EA-230 is commercially available for a low-temperature hardener. Cyclohexandiamine was used for enhancement of addition reactions in the curing process as well as of complex formation with metals.[12] Adipic acid dihydrazide, being a hardener insoluble in water, is predicted to cure the epoxy resin in the organic phase, regardless of the presence of water. Phenols are not only solvents but also cross-linking reagents. We call this synthesized hardener EP-NT97. A control experiment was made by use of EA-230.

Water used was deionized water. Organic reagents and solvents for preparation were of analytical grade.

Measurements of Curing Rates

The epoxy resin, the hardeners and water were thermostated at a given temperature. The hardener to which a known amount of water was added was mixed with the epoxy resin until the solution looked a uniform phase. The mixture was transferred to a spectroscopic plastic cell, which had been thermostated in advance. Since the exothermic reaction raised the temperature at the rate 0.5°C per 10 min, the thermostat was controlled manually so that a given temperature was kept within ±0.5°C. The mixture was stirred gently during the experimental run. Near infrared (NIR) spectroscopy was made with a V570 spectrophotometer (JASCO, Tokyo) after a given lapse of time starting from the mixing time. The reference cell contained the epoxy resin without the hardener.

Measurements of Mechanical Properties

In order to evaluate the influence of the water on mechanical properties, we examined the ultimate tensile strength (JIS K7113), the adhesive shear stress (JIS K6851), the compression surrender strength (JIS K7208), the compression elasticity coefficient (JIS K7208), the flexural strength (JIS K7203), the impact strength (JIS K7111), and the hardness (JIS K7215), according to the procedures by Japanese Industrial Standards (JIS). The epoxy resin including water was cured at room temperature in a silicon cast with a specified geometry. A test sample was kept at 20°C for 7 days.

RESULTS AND DISCUSSION

Curing Rates

The NIR spectra of the hardener showed (Fig. 1) a sharp absorbance at 1540 nm for amines,[9,13,14] which can be distinguished clearly from the spectrum of the epoxy resin without hardeners [Fig. 1(a)]. The base-corrected absorbance decreased as the crosslinking reaction proceeded. This absorbance was used for determination of the concentration of amines that had not yet participated in the curing reaction. Curing rates of epoxy resins have been obtained often by use of differential
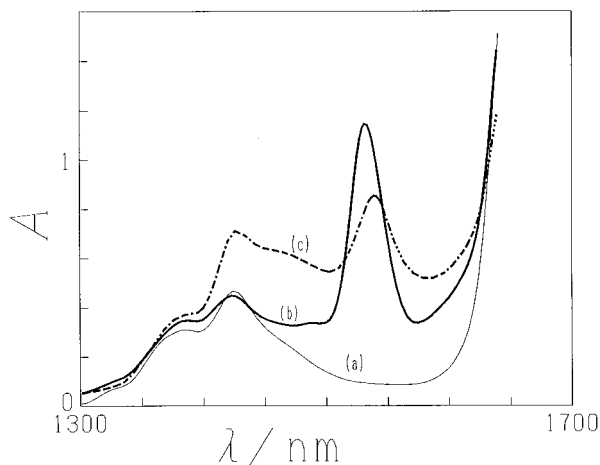
Figure 1 NIR spectra of (a) the epoxy resin without hardener, and (b) 8 min and (c) 30 min after mixing with hardener, EP-NT97-epoxy, at 60°C.

scanning calorimetry measurements,[15–17] the dielectric measurements,[18,19] FTIR,[20] and the NIR technique.[13,14] Since the attention is paid only to determination of an amount of the amines left in the resin, the NIR technique is convenient for the kinetic analysis with temperature dependence. Water could dissolve in two kinds of hardeners up to 50% of the water content (w, defined by the weight ratio of water to the hardener), whereas it could not in the epoxy resin at all. It dissolved easily in the mixture of the epoxy resin and the hardener when $w < 0.1$. Therefore, water is apt to contaminate the epoxy resin.

Figure 2 shows time variations of the amount of the amines left behind the curing reaction when no water is involved in the hardener. The base-corrected absorbance A decayed monotonically with the time at every temperature. The decay was more rapid with an increase in the temperature. The reaction rate was slow a few minutes after the mixing, probably because of insufficient mixing by the stir. In order to find a rule of controlling the curing reaction, we made various kinds of plots for the relation between the amount of the left amines and the time.[21] Then, we found that the reaction obeyed the mechanism of the second-order reaction with respect to the amines, expressed by

$$1/c = kt + 1/c_0 \qquad (1)$$

where c and c_0 stand for the concentrations of the amines at any time and at the initial time, respectively, and k is the reaction rate constant. The
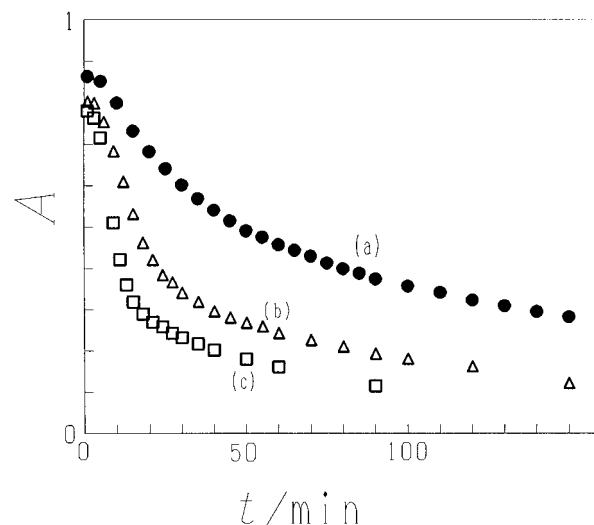

Figure 2 Time variations of the absorbance at 1540 nm for the mixture of the epoxy resin and EP-NT97 at (a) 50, (b) 60, and (c) 70°C without water.

plot of c_0/c or A_0/A against t is shown in Figure 3, indicating a straight line except for the short time response, where A_0 is the absorbance at $t = 0$. The second-order reaction suggests the mechanism that the epoxy ring is opened and bound by two amines. The slope of the line gives the quasi-reaction rate constant $c_0 k$. The Arrhenius plot of the rate constant gave the activation energy, $E_a = 70$ kJ mol^{-1}. Since the reaction rate is proportional to $\exp(-E_a/RT)$, the reaction rates at 20 and 30°C are, respectively, 7 and 18% of the rate at 50°C. In other words, the curing time at 20 and
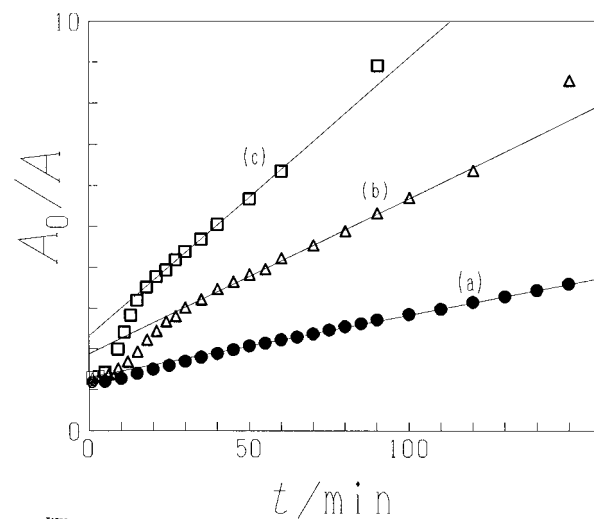

Figure 3 Plots of the data of Figure 2 for the second-order reaction mechanism.
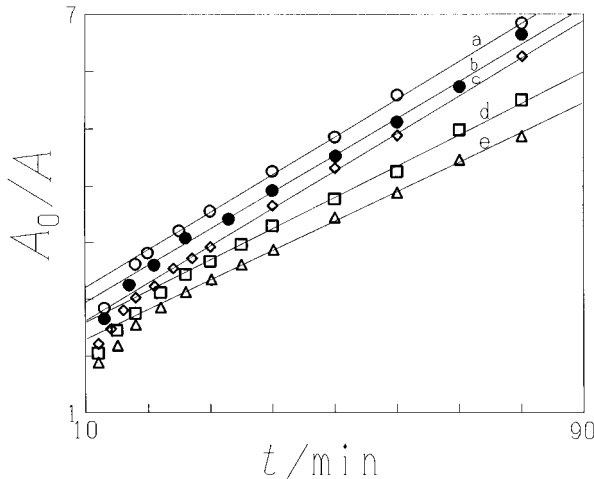
Figure 4 Variation of A_0/A with t for water contents, w = (a) 0.083, (b) 0.063, (c) 0.048, (d) 0.032, and (e) 0.020 at 30°C.

30°C are, respectively, 28 and 11 h if the curing time at 50°C is assumed to be 2 h (see Fig. 2). These periods are acceptable for actual construction periods of the outdoor reinforcement.

The value of the activation energy is close to the reported values.[14,22] However, the comparison is not meaningful because the kinetic analysis, the time domain, and the temperature domain are different from those of other experiments. Similar kinetic measurements were made for EA-230 (the conventional hardener). The curing rate was 10 times smaller than that of EP-NT97.

When water is contained in the hardener, variations similar to those in Figure 3 were observed, as shown in Figure 4. The more the water content, the faster the reaction is. Therefore, water catalyzes the curing reaction. The mechanism of the second-order reaction is still valid for the addition of water. Not only the slope but also the intercept increased with an increase in the water content. Therefore, the second-order reaction mechanism is not rigorously valid with an increase in the water content. Values of the reaction rate constant are plotted against the water content in Figure 5. The rate constant increases linearly with the water content up to w = 0.06, and then is invariant to the water content. The uncured epoxy resin at $w > 0.08$ was colloidal with aqueous microphase, indicating that the organic phase should be saturated with water. Further addition of water may increase the amount of the aqueous microphase, keeping the water content in the epoxy phase. Thus, the catalytic activity of water is constant for $w > 0.08$, as demonstrated in Figure 5.

Mechanical Properties

Several mechanical properties of the epoxy resin cured with EA-230 (called EA-230-epoxy) and that cured with EP-NT97 (called EP-NT97-epoxy) were examined in the light of variations of the water content. The following questions are interesting:

1. Which is stronger, the EP-NT87-epoxy or the EA-230-epoxy?
2. How much does the mechanical strength vary with the water content?
3. Is there a limitation of the water content for a practical use?

Figure 6 shows variations of the ultimate tensile strength. The EP-NT97-epoxy is stronger than the EA-230-epoxy for any value of w. The strength of the EA-230-epoxy decreased by as much as 70% for w = 0.08, exhibiting large deterioration for the water content. On the other hand, the strength of the EP-NT97-epoxy was not so influenced by the water content. When $w > 0.08$, the EP-NT97-epoxy is three times stronger than the EA-230-epoxy.

When two plates adhered with the cured epoxy are stretched into disruption, destruction occurs generally either at the epoxy, at a part of the plates, or at the interface between the plate and the epoxy. It was at the interface that the iron plates adhered with the EA-230-epoxy were de-
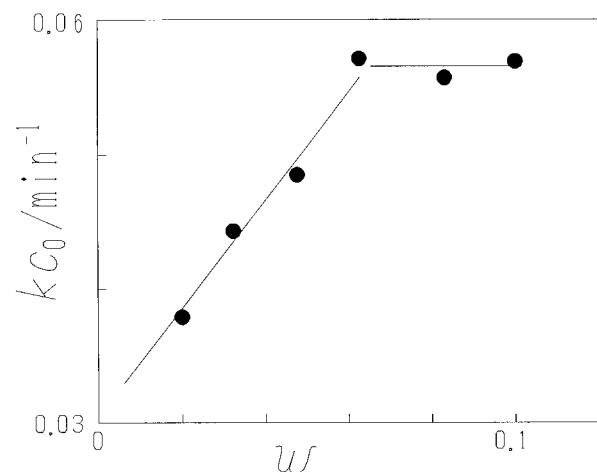

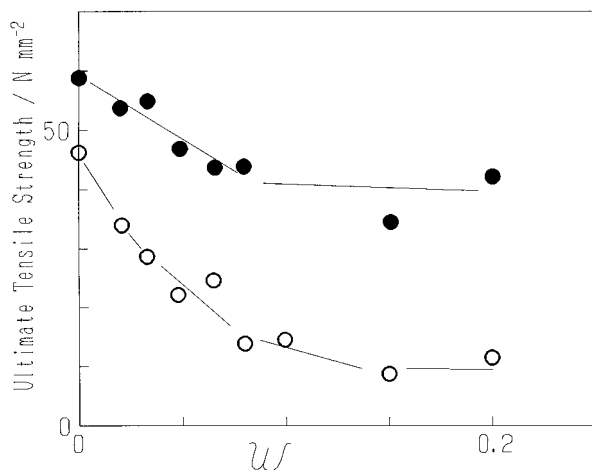**Figure 5** Dependence of the rate constant on the water content at 60°C.

Figure 6 Variation of the ultimate tensile strength with the water content for the EP-NT97-epoxy (full circles) and the EA-230-epoxy (open circles).

stroyed; i.e., the cured epoxy was attached on either surface of iron plate. Figure 7(A) shows a scanning electron microscopy (SEM) photograph of the surface of the epoxy from which the iron plate was detached. Various black, flat domains are surfaces that were adhered with the iron surface. On the other hand, the iron plates adhered with the EP-NT97-epoxy were destroyed mostly at the cured epoxy. Therefore the adhesion to the iron surface is stronger than that of the EA-230-epoxy. The SEM photograph of the destroyed sur-

face [Fig. 7(B)] shows a number of stretched and split pieces of the epoxy, as if the epoxy were sticky. When the EP-NT97-epoxy contained water, the destruction occurred also at the epoxy rather than at the interface. The destroyed surface [Fig. 7(C)] shows many small spots. Since the number of the spots increased with the water content, the spots are the aqueous microphase. No stretched and split pieces appeared, indicating that the water inclusion may make the epoxy brittle.

In order to see quantitatively the adhesive strength, we plotted in Figure 8 variations of the adhesive shear stress with the water content. The EP-NT97-epoxy exhibited higher stress than the EA-230-epoxy for any water content. The higher adhesive stress of the EP-NT97-epoxy accords with the durability of the interfacial destruction, as shown in Figures 7(A) and 7(B). Even when the water content increased, the stress decreased only slightly and was kept 90% at $w = 0.2$. This durability may be ascribed to the ability of cyclohexandiamine to form complexes with metals.[12] On the other hand, the adhesive stress of the EA-230-epoxy decreased drastically with the water content, and then vanished at $w = 0.1$ (no adhesion).

Figure 9 shows dependence of the flexural strength on the water content. The strength of the EP-NT97-epoxy is three times larger than that of the EA-230-epoxy for any value of the water con-
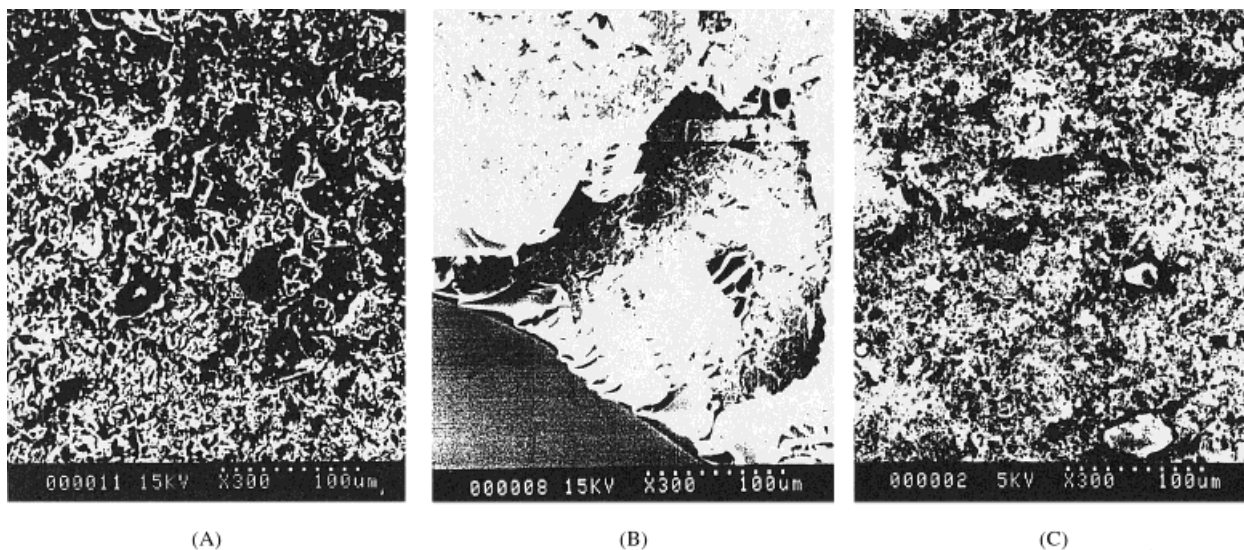

(A)   (B)   (C)

Figure 7 Photographs of surfaces of the steel plates peeled with the shear stress. The plates were cured with (A) EA-230-epoxy at $w = 0.009$. (B) EP-NT97-epoxy without water, (C) EP-NT97-epoxy at $w = 0.2$.
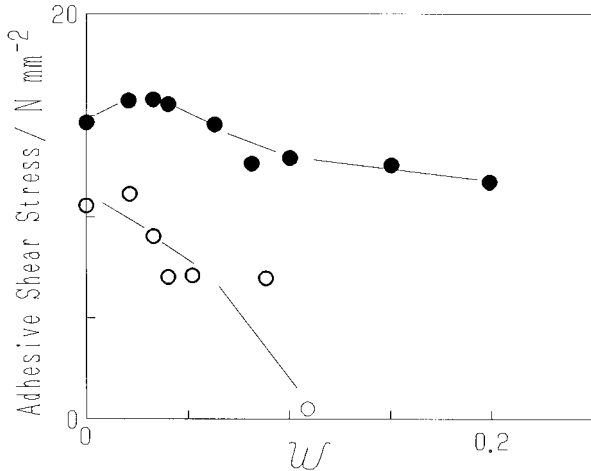
Figure 8 Variation of the adhesive shear stress with the water content for the EP-NT97-epoxy (full circles) and the EA-230-epoxy (open circles).

Figure 10 Variation of the impact strength with the water content for the EP-NT97-epoxy (full circles) and the EA-230-epoxy (open circles).

tent. Both the epoxies show gradual decreases in the strength with an increase in the water content.

The impact strength for the EP-NT97-epoxy has no influence of the water content for $w < 0.05$, as shown in Figure 10, and is three times larger than that for the EA-230-epoxy. However, it decreases to 1/3 drastically at $w = 0.05$. For $w > 0.06$, the EP-NT97-epoxy has similar values of the impact strength as EA-230-epoxy.

The compression surrender strength (Fig. 11) shows a small variation with the water content for both kinds of the epoxy. However, the EP-
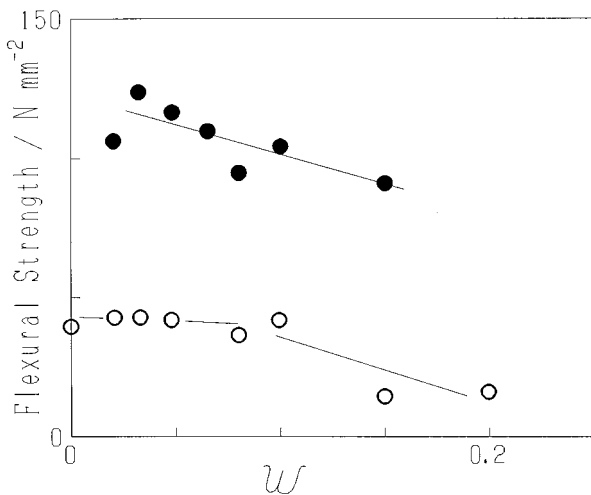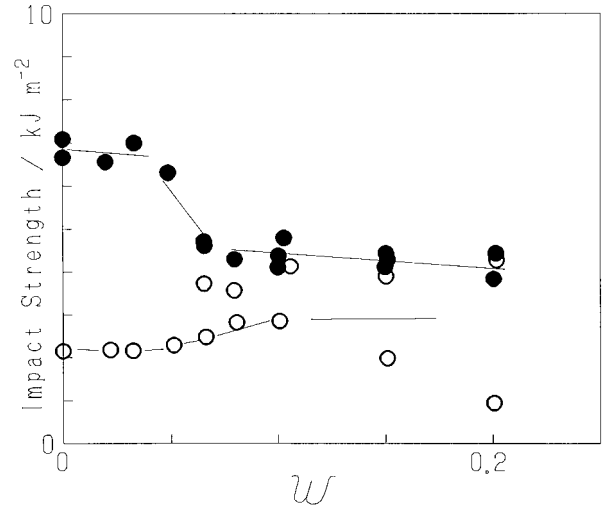
NT97-epoxy is more or less stronger than the EA-230-epoxy, especially for $w < 0.05$. A similar variation can also be seen in the compression elasticity coefficient. The hardness did not vary with the water content at all, and the values for the EP-NT97-epoxy was identical with those for the EA-230-epoxy.

Mechanical properties of both epoxies are summarized in Table I in the light of the water content. Table I also shows a degree of the predominance of EP-NT97-epoxy over EA-230-epoxy.

Figure 9 Variation of the flexural strength with the water content for the EP-NT97-epoxy (full circles) and the EA-230-epoxy (open circles).
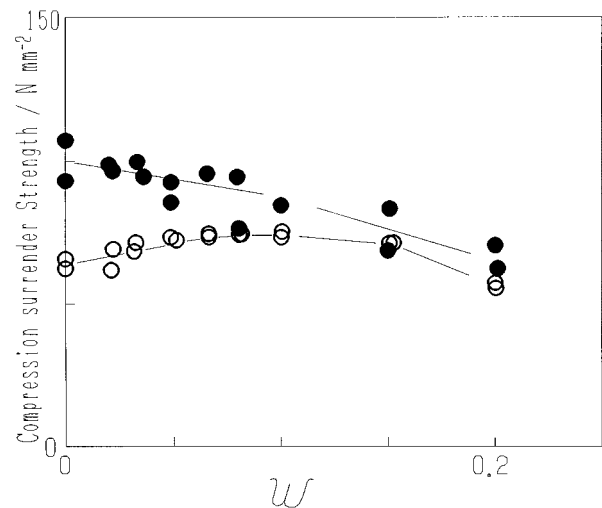

Figure 11 Variation of the compression surrender strength with the water content for the EP-NT97-epoxy (full circles) and the EA-230-epoxy (open circles).

Table I Summary of Variations of Mechanical Properties with Water Contents

Mechanical Strength	Deterioration of EA-230-Epoxy	Deterioration of EP-NT97-Epoxy	Predominance of EP-NT97-Epoxy
Ultimate tensile	70% ($w > 0.06$)	30%	Much more
Adhesive shear stress	100% ($w > 0.09$)	10%	Much more
Flexural	Gradual decrease	Gradual decrease	Three times larger
Impact	1/3 ($0.05 < w < 0.06$)	Constant	More
Compression surrender	Gradual decrease	No variation	Same
Hardness	No variation	No variation	Same

With an increase in the water content, all the strength decreased for both epoxies. However, the EP-NT97-epoxy does not suffer so remarkably from water as the EA-230-epoxy.

CONCLUSIONS

The epoxy resin, EP-NT97-epoxy, designed for the outdoor construction for the reinforcement, can satisfy the three requirements mentioned in the Introduction. It shows higher mechanical performance, especially for the ultimate tensile strength and the adhesive shear stress, than EA-230-epoxy. It also exhibits smaller variations with water content than EA-230-epoxy. It has curing times of a few hours and 1 day at 60°C and at room temperature, respectively. Water accelerates the curing reaction. If the temperature increases to 60°C, it takes a few hours to cure the resin. These advantages are suitable for outdoor constructions of the reinforcement.

REFERENCES

1. Guide for the selection of polymer adhesives with concrete. ACI Mater J 1992, 89(1), 90.
2. Poy, T.; Holm, J. Paint Technology 1967, 39, 385.
3. Barton, J. N.; Buist, G. J.; Hamerton, I.; Howlin, B. J.; Jone, J. R.; Liu, S. Poly Bull 1994, 33, 215.
4. Don, T.-M.; Bell, J. P. J Polym Sci Part A Polym Chem 1996, 34, 2103.
5. Urbaczwski, E.; Pascault, J.-P.; Sautereau, H.; Riccardi, C. C.; Moschiar, S. S.; Williams, R. J. J. Makromol Chem 1990, 191, 943.
6. Hartauer, K. J.; Matheson, L. E.; Guillory, J. K. Appl Spectros 1988, 42, 699.
7. Moy, P.; Karasz, F. E. Polym Eng Sci 1980, 20, 315.
8. Sung, C. S. P.; Sung, N. H. Mater Sci Eng A 1993, 162, 241.
9. Calvert, P.; George, G.; Rintoul, L. Chem Mater 1996, 8, 1298.
10. Champion, J. V.; Dodd, S. J. IEE Conf Publ 1996, 430, 206.
11. Haga, T.; Nakajima, T.; Mishima, S.; Hirai, M. Nippon Kagakukaishi 1996, 12, 1045.
12. Salaam, A.-B.; Roman, P.-S.; Abdul, R. K. J Coord Chem 1993, 26, 1.
13. St. John, N. A.; George, G. A. Polymer 1992, 33, 2679.
14. George, G. A.; Cole-Clarke, P.; St. John, N. A.; Friend, G. J Appl Polym Sci 1991, 42, 643.
15. Barral, L.; Cano, J.; Lopez, A. J.; Lopez, J.; Nog Ueira, P.; Ramirez, C. J Appl Polym Sci 1996, 61, 1553.
16. Ghaemy, M.; Riahy, M. H. Eur Polym J 1996, 32, 1207.
17. Lin, S.-T.; Huang, S. K. J Appl Polym Sci 1996, 62, 1641.
18. Levita, G.; Livi, A.; Rolla, P. A.; Culicchi, C. J Polym Sci Part B, 1996, 34, 2731.
19. Levita, G.; Livi, A.; Rolla, P. A.; Gallone, G. Polym Adv Technol 1996, 7, 873.
20. Lim, S.; Su, Y.-F.; Ma, C.-C. M.; Chen, J.-L.; Lu, M.-S.; Chang, F.-C. Polymer 1996, 37, 3899.
21. Atkins, P. W. Physical Chemistry, 6th ed.; Oxford University Press: Oxford, 1998; pp 767–774.
22. Stark, E. B.; Seferis, J. C.; Apicella, A.; Nicolais, L. Thermochim Act 1988, 77, 19.