

Thermal Stability and Deformation of Poly(acrylic acid)–Metal Oxides

HO-SHING WU, HEAY-CHAIN JONE, SHANG-SHIN MENG

Department of Chemical Engineering, Yuan-Ze University, #135, Far-East Road, ChungLi, Taoyuan, 32026, Taiwan, Republic of China

Received 5 December 1996; accepted 15 May 1997

ABSTRACT: In this work, we investigated the thermal stability and deformation of the compound of poly(acrylic acid) (PAA) and metal oxides (ZnO, CaO, CuO, Al₂O₃, and Cr₂O₃). The kinetic parameters of the desorption of water from PAA–metal oxide were calculated. The activation energies of the water desorption of PAA–metal oxide were less than 5 kcal/mol. The order of bonding capability of oxygen (PAA–O–metal) and water was PAA–CaO > PAA–ZnO > PAA–CuO > PAA–Cr₂O₃ > PAA–Al₂O₃. The reaction types of the composites were clarified. Incorporating metal oxide into PAA increased the thermal stability. The factors which influence the mechanical properties of the composites, e.g., the chemical compositions, curing environment, and curing time, were also studied. The various curing environments (pure water, 0.1N HCl, 0.1N NaOH, and methanol) decreased the compressive strength of PAA–metal oxide. Moreover, the thermal stability and compressive strength of PAA–ZnO and PAA–CuO reached an optimum because of their crosslinking nature. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2021–2027, 1997

INTRODUCTION

Some polyelectrolyte cements are formed by certain powdered metal oxides or ion-leachable silicates reacting with concentrated aqueous solutions of poly(alkenoic acids). Such materials are characterized by an extremely rapid rate of hardening compared to hydraulic cements, excellent mechanical properties, low-temperature processing, and good adhesion to many engineering materials. They are found in dentistry and other applications.^{1–3}

Many investigators in recent years have characterized the chemical and physical nature of dental zinc polyacrylate cements by infrared spectroscopy.^{4–10} Saniger et al.¹¹ described the dehydra-

tion of PAA–metal oxide and the water content of the materials. Padilla and Vázquez,¹ Field and Nielsen,¹² and Hu et al.^{8,13} examined the role of the relation of metal oxide to PAA, the curing time, and the strain rate on the final properties of the composites. Their discussion focused on the PAA–ZnO composite. Other composites were little studied. Moreover, this class of composites may have considerable potential for other applications. Hence, we study the thermal stability and deformation of PAA–divalent and –trivalent metal oxides. The results of thermal deformation in this study are compared with those of previous infrared spectroscopic studies to clarify the bonding capability between PAA and metal oxide. We measured the damage of the PAA–metal oxide composite by a tensile tester when the composite was utilized for various operating environments. The factors influencing the mechanical properties of the composites, for instance, the chemical composition, curing environment, and curing time, were examined as well.

Correspondence to: H. S. Wu.

Contract grant sponsor: National Science Council of the Republic of China.

Journal of Applied Polymer Science, Vol. 66, 2021–2027 (1997)

© 1997 John Wiley & Sons, Inc.

CCC 0021-8995/97/102021-07

EXPERIMENTAL

Materials

Aqueous poly(acrylic acid) (Aldrich, 25% by weight of solid PAA, average molecular weight of 90,000), metal oxides (Strem), and other reagents were all reagent-grade chemicals.

Procedure

Materials were prepared by mixing a PAA solution and metal oxide powder in a glass beaker (50 mL) under the required temperature. The magnetic stirrer's agitation rate was 400 rpm. The agitation was stopped to withdraw the sample at a selected time (30 min). The solution was filled by an aspirator, washing with distilled water several times. Next, the solid was dried in an oven for 24 h at 30°C and then for 3 h at 120°C.

Thermal analysis was done at (1) 10°C/min, 100 mL of N₂/min, between 20 and 800°C, and (2) isothermally at 50, 100, and 150°C for a thermogravimetric system (TGA; DuPont 910). The compressive tests (ST-6022) were performed under room temperature and at a deformation rate of 1 mm/min. A typical specimen made at 40°C was 40 cm² and 0.2 mm in thickness.

RESULTS AND DISCUSSION

We performed a kinetic study of the reaction of PAA and metal oxides (ZnO, CaO, CuO, Al₂O₃, and Cr₂O₃) using infrared spectroscopic techniques.⁹ The reactions of PAA and metal oxides were rapid, with a conversion of some COOH groups to COO⁻ groups. The order of reactivity was CaO > ZnO > CuO > Al₂O₃ > Cr₂O₃.

Saniger et al.¹¹ observed that the mechanical properties of the materials were influenced by its water content. They discussed the bond between the water molecules and the polyelectrolyte cement through kinetic studies of the dehydration process. They reported that the water molecules were attached to the compound by formation of hydrogen bonds based on the activation energy. However, their results were unclear. The activation energy was calculated from a plot of ln Δ*W* versus 1/*T*. The concept was erroneous. Hence, we correct such an error in this study.

If we assume that the adsorption of water on PAA–metal oxide follows the Langmuir isotherm,

the rate of adsorption and the rate of desorption were expressed as

$$r_a = k_a C_w (\bar{C}_m - \bar{C}) \quad (1)$$

and

$$r_d = k_d \bar{C} \quad (2)$$

where *k_a* and *k_d* represent the rate constants of adsorption and desorption, respectively, for PAA–metal oxide, *C_m* denotes the molar concentration of total sites, and *C_w* is the concentration of the adsorbable component (H₂O) in the gas. From eqs. (1) and (2), the net rate of desorption for H₂O is

$$r_n = k_d \bar{C} - k_a C_w (\bar{C}_m - \bar{C}) \quad (3)$$

We assume that the diffusion resistance can be neglected because water molecules diffuse with the vapor type in the interparticle. The *C_w* was equal to the concentration of water in the bulk phase and remained constant. The solution of eq. (3) is

$$\frac{\bar{C} - \frac{A}{h}}{\bar{C}_m - \frac{A}{h}} = e^{-ht} \quad (4)$$

in which

$$A = k_a C_w \bar{C}_m \quad (5)$$

and

$$h = k_d + k_a C_w \quad (6)$$

Equation (4) can be rewritten as

$$\begin{aligned} \frac{\Delta W}{W} &= \frac{(\bar{C}_m - \bar{C})}{W} \\ &= \frac{\bar{C}_m}{W} \left(1 - \frac{k_a C_w}{h} \right) (1 - e^{-ht}) \quad (7) \end{aligned}$$

where Δ*W* and *W* denote the weight loss and total weight of PAA–metal oxide, respectively. According to the experimental results, the maximum weight percentages of water in PAA–metal oxide for ZnO, CaO, CuO, Al₂O₃, and Cr₂O₃ were 8.4,

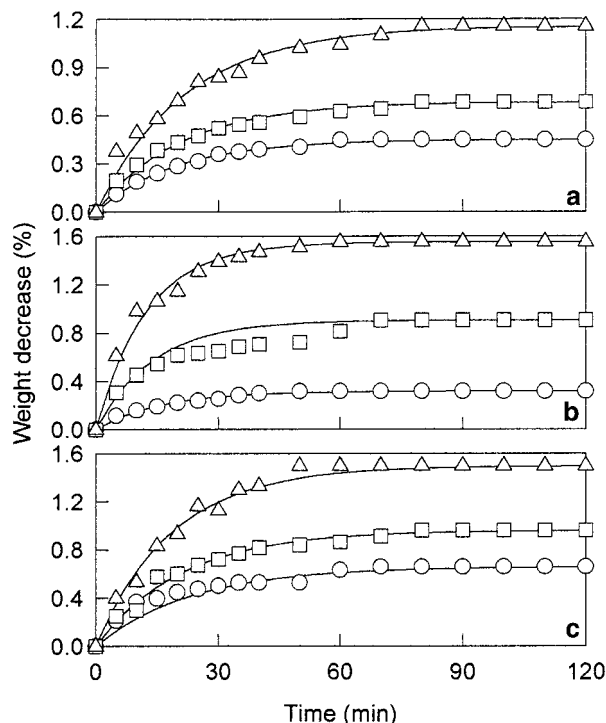


Figure 1 Effect of weight decrease on the thermogravimetric time for the dehydration: (a) PAA-ZnO; (b) PAA-CaO; (c) PAA-CuO; (○) 50°C; (□) 100°C; (△) 150°C. The solid lines are the simulated results by eq. (7).

13.5, 6.5, 10, and 10%, respectively. Figures 1 and 2 plot the weight decrease of water vs. operating time that were isothermally analyzed at 50, 100, and 150°C by the thermogravimetric analyzer. The solid lines are the simulated results by eq. (7). The standard deviations between experimental results and simulated results were less than 0.05. The kinetic parameters were estimated as listed in Table I. The k_d values of PAA-divalent metal oxides were less than those of PAA-trivalent metal oxides, whereas the $k_a C_W$ values of PAA-divalent metal oxides were more than those of PAA-trivalent metal oxides. The Arrhenius law was applied to calculate the capability of the desorption of water:

$$\text{Log}(k) = \text{Log}(k_0) + \left(\frac{E_a}{2.303R} \right) \frac{1}{T} \quad (8)$$

Figure 3 plots the kinetic parameters versus $1/T$ by the Arrhenius law. Because the concentrations of water in air (C_W) on various temperatures

in the thermogravimetric chamber were unknown, the k_a value could not be directly calculated. The order of the slope value of $\text{Log}(k_a C_W)$ versus $1/T$ is PAA-ZnO (118) > PAA-CuO (-28.7) > PAA-Cr₂O₃ (-52) > PAA-CaO (-81) > PAA-Al₂O₃ (-128). The PAA-ZnO's slope was peculiar and positive. As demonstrated, the varied range of k_a was small for various temperatures. The concentration of C_W varied the $k_a C_W$ value. However, the values were small. Restated, the capability of the adsorption of water from air was high. The apparent activation energies of the desorption of water for PAA-ZnO, PAA-CaO, PAA-CuO, Al₂O₃, and Cr₂O₃ were 2.25, 4.97, 2.71, 4.52, and 3.83 kcal/mol, respectively.

According to Table I and Figure 3, the capabilities of desorption of PAA-trivalent metal oxide were larger than those of PAA-divalent metal oxide. The deformations of water in PAA-ZnO and PAA-CuO were large. The report of Saniger et al.¹³ indicated that the apparent activation energies of water desorption of PAA-metal oxide were about 5 kcal/mol. Their experimental results differed from the results in this study. Such differences could be related to the calculated method, the different sizes, and the cations' coordination numbers. According to the activation energy and

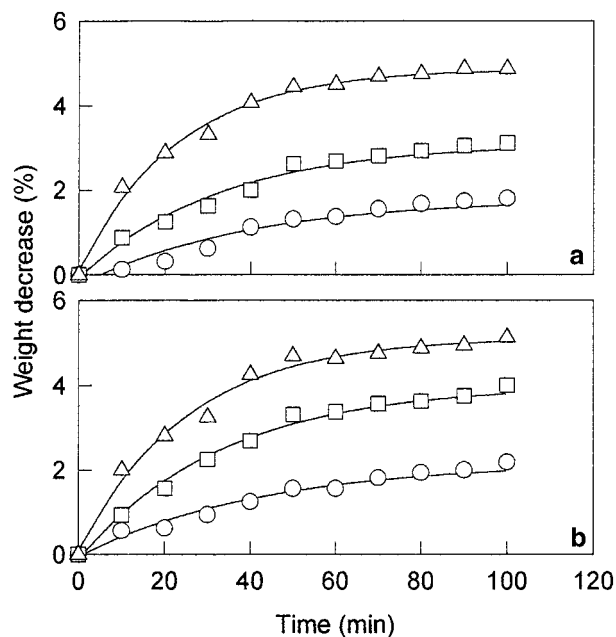


Figure 2 Effect of weight decrease on the thermogravimetric time for the dehydration: (a) PAA-Al₂O₃; (b) PAA-Cr₂O₃; (○) 50°C; (□) 100°C; (△) 150°C. The solid lines are the simulated results by eq. (7).

Table I Kinetic Parameters Based on Figures 1 and 2 and Eq. (7)

Composite	50°C			100°C			150°C		
	h $\times 10^2$	k_d $\times 10^3$	$k_a C_w$ $\times 10^2$	h $\times 10^2$	k_d $\times 10^3$	$k_a C_w$ $\times 10^2$	h $\times 10^2$	k_d $\times 10^3$	$k_a C_w$ $\times 10^2$
PAA-ZnO	5.18	2.76	4.90	4.91	3.99	4.51	4.64	6.39	4.00
PAA-CaO	6.39	1.51	6.23	7.00	4.70	6.52	8.10	9.34	7.17
PAA-CuO	5.46	4.46	3.95	4.79	7.08	4.09	5.38	12.4	4.14
PAA-Al ₂ O ₃	2.26	4.11	1.85	3.00	9.34	2.05	4.49	21.9	2.30
PAA-Cr ₂ O ₃	2.31	5.06	1.81	2.94	11.7	1.77	4.08	20.9	1.99

the incorporation of metal oxide in PAA, we believe that (1) the water molecules are attached to COOH in PAA-metal oxide by forming hydrogen bonds and (2) the water molecules are attached to the composite by a van der Waals' force or an electrostatic force unless the electronic density of metal is high.

Thermal deformations of the PAA-ZnO and PAA-CaO could be viewed as a one-stage process; that of PAA-CuO was a two-stage process; and those of the PAA-trivalent metal oxide approached a three-stage process (Fig. 4). We can conclude that the reaction type of PAA-ZnO and PAA-CaO were monodentate and that of PAA-CuO was bidentate chelating.⁹ From Figure 4, the conclusion in the previous work is clarified. Their structures are different. The formations of PAA-

ZnO and CaO produced the crosslinking of carboxyl groups through a metal. The thermal stability is high. Table II lists the data for thermal decomposition of the PAA-metal oxide. The order of weight loss for first stage is PAA-CaO > PAA-Cr₂O₃ > PAA-Al₂O₃ > PAA-ZnO > PAA-CuO.

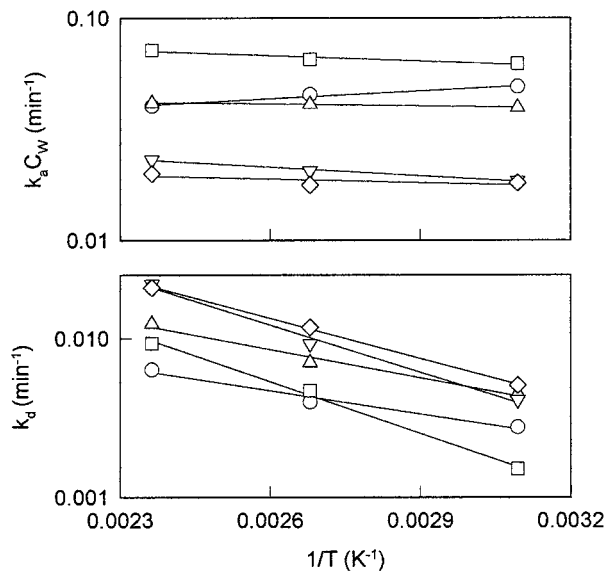


Figure 3 Plot of the Arrhenius equation for the dehydration of water: (○) PAA-ZnO; (□) PAA-CaO; (△) PAA-CuO; (▽) PAA-Al₂O₃; (◇) PAA-Cr₂O₃.

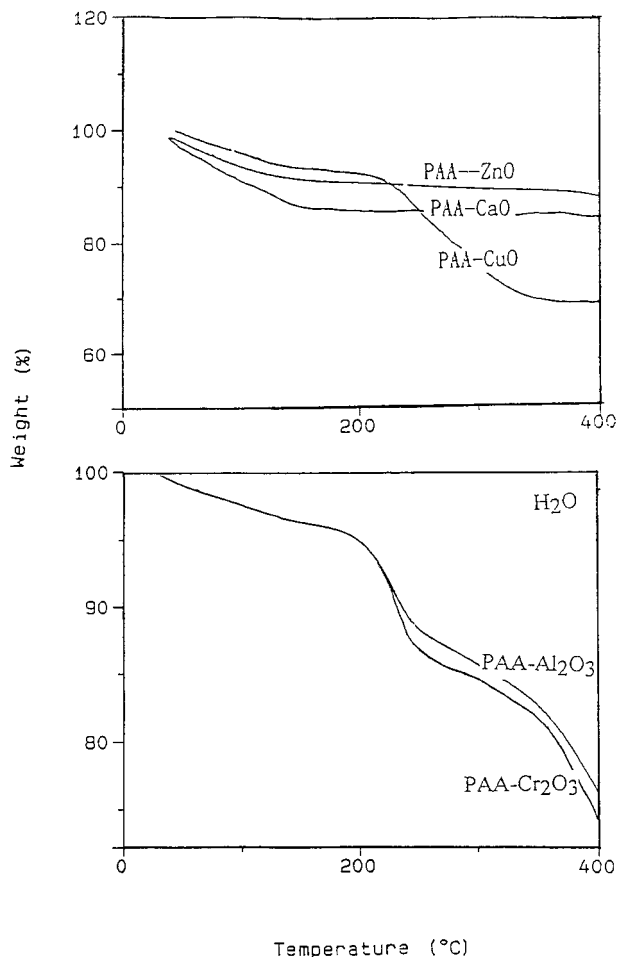


Figure 4 Thermogravimetric curve of weight loss versus operating temperature.

Table II Thermal Analysis Data for PAA-Metal Oxide

Compound	MO (g)	Weight Loss at 100°C (%)	$T_{1/2}$ (°C)	T_p (°C)	Weight Loss at T_p (%)
ZnO	0.05	1.56	385	386	38
	0.28	1.50	636	460	30
	0.40	1.46	638	483	20
CaO	0.05	5.56	370	380	38
	0.20	4.65	601	466	30
	0.40	4.63	608	469	20
CuO	0.05	2	353	290	30
	0.28	2	366	300	30
	0.40	2	370	311	20
Al ₂ O ₃	0.1	3.0	209	339	22
	0.35	3.0	210	340	18
	0.60	2.5	212	342	10
Cr ₂ O ₃	0.2	3	230	360	19
	0.53	3	231	362	15
	0.70	3	231	362	14

Reaction conditions: 30°C; 400 rpm; 30 min; PAA, 1 mL.

A previous work⁹ studied the reactivity of the reaction of PAA and metal oxides. The order of reactivity for PAA with metal oxides was CaO > ZnO > CuO > Al₂O₃ > Cr₂O₃. The equal amounts of ZnO, CaO, CuO, Cr₂O₃ and Al₂O₃ for 1 mL of PAA aqueous solution are 0.28, 0.2, 0.28, 0.35, and 0.53 g, respectively, since the number of moles of acrylic acid (MW = 72) monomer units in the PAA was 1250 (= 90,000/72). When the amount of metal oxide reacting with PAA increased, the weight loss at 100°C decreased. The increasing bonding number of PAA and metal oxide decreases that of COOH and H₂O. The incorporating content of trivalent metal oxide in PAA-trivalent metal oxide was small because the order of the degree of PAA reacting with metal oxide was CaO > ZnO > CuO > Al₂O₃ > Cr₂O₃. Hence, the order of the bonding capability of oxygen (PAA-O-metal) and water is PAA-CaO > PAA-ZnO > PAA-CuO > PAA-Cr₂O₃ > PAA-Al₂O₃.

$T_{1/2}$ and T_p represent the temperatures of 50% weight loss and the fastest rate of weight loss of the PAA-metal oxide, respectively. The incorporation of metal oxide into PAA increased the thermal stability. The $T_{1/2}$ and T_p values increased with increasing the incorporated amount of metal oxide. The order of thermal stability is PAA-ZnO > PAA-CaO > PAA-Cr₂O₃ > PAA-Al₂O₃ > PAA-CuO.

The compressive strengths of PAA-metal ox-

ides, cured for 36, 48, 72, 96, and 120 h in each case, are depicted in Figures 5 and 6. The curing time, for forming the films of PAA-CuO, PAA-Al₂O₃, and PAA-Cr₂O₃, must be more than 48 h. The compressive strength increased when the curing time increased. The compressive strengths were more than 80 MPa. The compressive strength must generally be larger than 6 MPa in dentistry. Hence, the compressive strengths of five materials are sufficient. The order of the compressive strength was PAA-ZnO ≈ PAA-CaO > PAA-CuO > PAA-Cr₂O₃ ≈ PAA-Al₂O₃ in air. When the specimen was immersed in the solution of pure water, 0.1N hydrogen chloride, 0.1N sodium hydroxide, and methanol in each case after 24 h, the compressive strength decreased. The capability of ion bonding between PAA and metal oxide was reduced with the solvation of the solution. PAA-ZnO and PAA-CaO are the optimum materials. The compressive strength was changed from 120 to 96 MPa. The compressive strength of PAA-CuO (22 MPa) became less than one-fourth of the original value (99 MPa). The compressive strengths of PAA-Cr₂O₃ and PAA-Al₂O₃ approached zero. The specimen was cured in air 24 h after being immersed in solution. The compressive strengths of PAA-ZnO and PAA-CaO could recover nearly the original values. The compressive strengths of PAA-CuO could recover nearly half of the original value. The compressive strengths of PAA-Cr₂O₃ and PAA-Al₂O₃ could

not be recovered. Their structures were destroyed and dissolved in the solution. PAA and Al_2O_3 (or Cr_2O_3) were separated in a dilute solution. The bonding capability of PAA and Al_2O_3 (or Cr_2O_3) was extremely low. Therefore, two composites could not be used in a solution environment. The effect on various solvents for PAA-metal oxides was different. The optimum solutions of the recovery compressive strengths for PAA-ZnO, CaO, and CuO were 0.1N HCl, pure water, and methanol, respectively.

CONCLUSION

According to the experimental results, the activation energies of deformation of water were small. Water molecules were attached to the composite with two positions: (1) $\text{H}_2\text{O}-\text{COOH}$ and (2) $\text{H}_2\text{O}-\text{PAA}-\text{metal oxide}$. Hence, we believe that (1) the water molecules are attached to COOH in PAA-metal oxide by formation of hydrogen bonds and

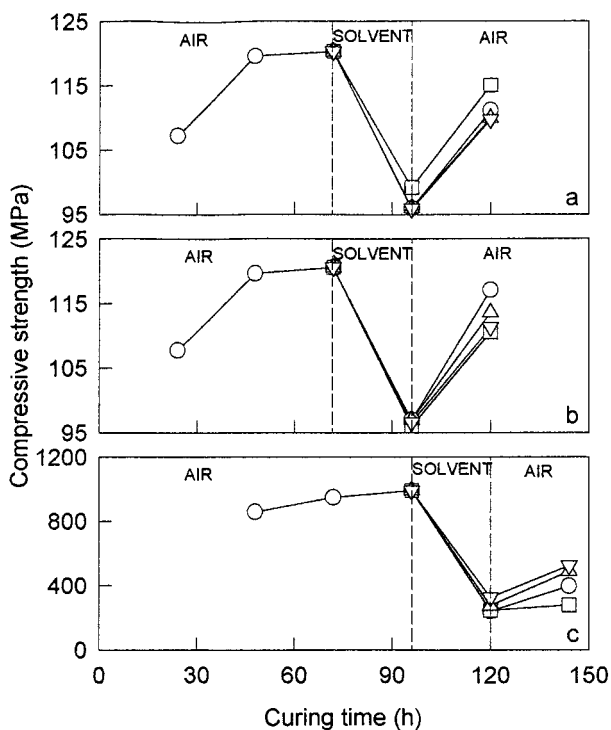


Figure 5 Effect of compressive strength on curing time: PAA = 20 mL; (a) ZnO = 5.6 g; (b) CaO = 4 g; (c) CuO = 5.6 g; (O) pure water; (□) 0.1N HCl; (Δ) 0.1N NaOH; (∇) CH_3OH .

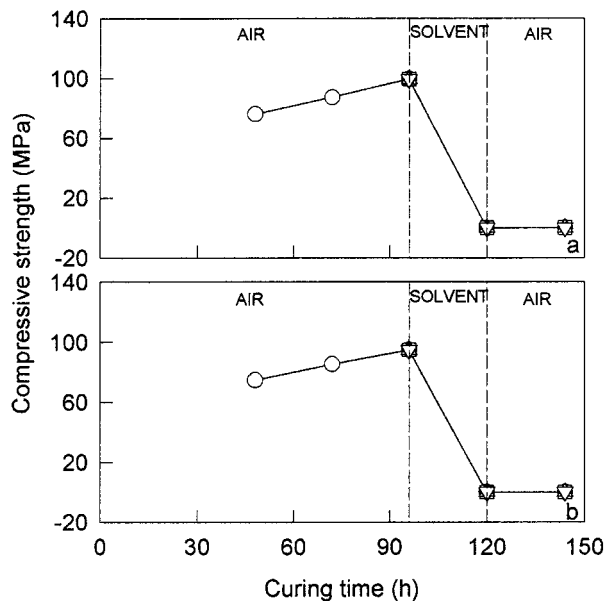


Figure 6 Effect of compressive strength on curing time: PAA = 20 mL; (a) Al_2O_3 = 7 g; (b) Cr_2O_3 = 10.54 g; (c) CuO = 0.28 g; (O) pure water; (□) 0.1N HCl; (Δ) 0.1N NaOH; (∇) CH_3OH .

(2) the water molecules are attached to the composite by a van der Waals' force or an electrostatic force unless the electronic density of the metal was high. Therefore, the increasing amount of metal oxide in the reaction could decrease the composite's water content. The mechanical properties of PAA-ZnO and PAA-CaO were the best because their structures were of a crosslinking nature. The bond strength is not so highly affected when the meal salt has a high ionicity. PAA- Al_2O_3 and PAA- Cr_2O_3 had good mechanical properties, whereas if they are used in a solution environment, they are bad. In addition, the incorporated amount of Al_2O_3 (or Cr_2O_3) was small.

The authors would like to thank the National Science Council of the Republic of China for financially supporting this study.

REFERENCES

1. A. Padilla and A. Vázquez, *J. Mater. Res.*, **6**(11), 2452 (1991).
2. D. C. Smith, *Br. Dent. J.*, **125**, 381 (1968).
3. A. D. Wilson and B. E. Kent, *J. Appl. Chem. Biochem. technol.*, **21**, 313 (1971).

4. S. Crisp, H. J. Prosser, and A. D. Wilson, *J. Mater. Sci.*, **11**, 36 (1976).
5. M. A. Moharram and N. Abdel-Hakeen, *J. Mater. Sci.*, **21**, 1681 (1986).
6. S. M. Rabie, A. Sawaby, M. A. Moharam, and A. M. Nassar, *J. Appl. Polym. Sci.*, **41**, 445 (1990).
7. H. Hu, J. Saniger, J. Garcia-Alejandre, and V. M. Castaño, *Mater. Lett.*, **12**, 281 (1991).
8. H. Hu, J. Saniger, and V. M. Castaño, *Mater. Lett.*, **16**, 200 (1993).
9. H. S. Wu, H. C. Jone, and J. W. Hwang, *J. Appl. Polym. Sci.*, **63**, 89 (1997).
10. B. Crescenzi, A. De Chirico, and A. Ripamonti, *Chem. Abstr.*, **54**, 4109 (1960).
11. J. Saniger, H. Hu, and V. M. Castaño, *Mater. Lett.*, **15**, 113 (1993).
12. J. E. Field and L. E. Nielsen, *J. Appl. Polym. Sci.*, **12**, 1041 (1968).
13. H. Hu, J. Saniger, and V. M. Castaño, *Mater. Lett.*, **14**, 83 (1992).