

Cement Hydrate Catalyzed Hydrolysis of Polyimide Lightweight Materials

T. SUGAMA, L. E. KUKACKA, and N. CARCIELLO, *Process Sciences Division, Department of Applied Science, Brookhaven National Laboratory, Upton, New York 11973*

Synopsis

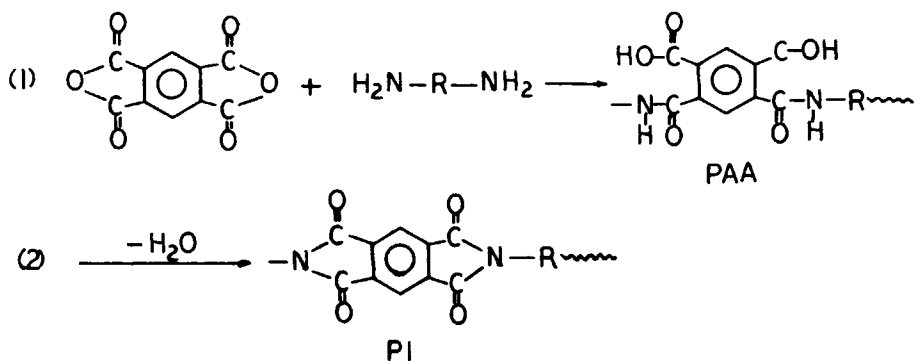
Polyimide (PI) resins which are produced by an in situ imidization condensation reaction of polyamic acid (PAA) precursors were evaluated for use as binders in high-temperature performance lightweight cement-filled material systems. Unfortunately, the presence of partially hydrated cement in the system led to strength retrogression at room temperature. Significant mechanical failure was observed upon exposure of the specimens to steam at $> 150^{\circ}\text{C}$. This was found to be due mainly to alkali catalyzed hydrolysis of the functionaries of unreacted PAA adjacent to the cement surfaces and the imide rings of PI matrices. The formation of Ca-complexed carboxylate salts derived from the hydrolysis resulted in chain scission of the polymer, thereby decreasing the mechanical strength, and making the composites unsuitable for use in aqueous environments.

INTRODUCTION

Since polyimide (PI) polymers have high temperature stability, high radiation and chemical resistance, and good mechanical and dielectric properties,¹ they are the subject of ever increasing interest for use in microelectronic^{2,3} and aerospace applications.⁴ Based upon this information, work was performed at Brookhaven National Laboratory (BNL) to evaluate the potential for the use of PI polymers as a thermally stable matrix in lightweight cementitious material systems which could be used in hydrothermal environments at temperatures up to 200°C .

The PIs are generally formed by a typical two-stage synthesis^{5,6} as shown in eqs. (1) and (2) below. In this synthesis, solution condensation reactions between carboxylic dianhydride compounds such as benzophenonetetracarboxylic dianhydride, benzenetetracarboxylic dianhydride, or 3,3',4,4'-benzophenonetetracarboxylic dianhydride, and aromatic diamines such as 1,4-phenylenediamine, 1,3-phenylenediamine, or 4,4'-diaminodiphenyl ether et al., are initiated at ambient temperature in organic solvents such as N-methylpyrrolidone, bis (2-methoxyethyl) ether, or dimethyl acetamide. These yield a soluble polyamic acid (PAA) precursor (see eq. (1)). The PI polymer is then formed through in situ imidization condensation reactions by means of thermal or chemical dehydration of the PAA polymer (see eq. (2)).

This work was performed under the auspices of the U.S. Department of Energy, Washington, D.C. under Contract No. DE-AC02-76CH00016, and supported by the U.S. Army Research Office Program MIPR-ARO-102-89.



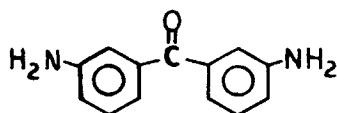
When considering this unique curing process for the formation of cementitious systems, it was realized that the reactions would have to take place in a slurry consisting of the solvent-based PAA precursor and the lightweight fillers. It was, therefore, predictable that when moisture was incorporated into the composite slurry, the carboxylic acid, COOH , groups within the PAA might be converted into cation-accepting carboxylate anions, COO^- , before transforming the COOH into the imide ring structure of PI. These functional COO^- groups will preferentially react with counterion species such as Na, Ca, Mg, Cu, et al.⁷

Hydrated portland cement is a Ca counterion-releasable material. Therefore, it was decided to investigate the effects of the addition of hydrated cement particles to the PAA composite slurries on the interactions at interfaces between the cement hydrate and PAA. The strength developed by the material system as a function of temperature was also determined. Accordingly, our approach to evaluating the applicability of PI polymer-based lightweight materials for use in hydrothermal environments was focused on the following three subjects: (1) the rate of the in situ imidization reaction of PAA when the system constituents are in slurry form under hydrothermal environments, (2) hydrothermal stability and degradation of the cured PI systems, and (3) influence of hydrated cement on the mechanical properties of the systems.

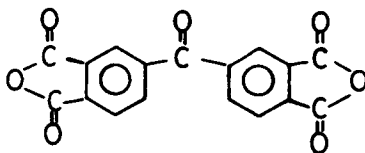
EXPERIMENTAL

Materials

A commercially available PAA varnish product, supplied by Mitsui Toatsu Chemical Inc. of Japan, was used in this study. This PAA precursor was derived from a solution condensation between 3,3'-diaminobenzophenone,



and 3,3',4,4'-benzophenonetetracarboxylic dianhydride,



in a bis (2-methoxyethyl) ether (BME) solvent. Since the viscosity of this varnish was too high to fully wet the surface of the lightweight fillers, additional BME solvent was added to the varnish. After adjusting to the appropriate viscosity, the resultant PAA component was composed of 40 wt % varnish and 60 wt % BME solvent.

The lightweight filler used was composed of pressure-resistant hollow alumina silica microspheres having an average particle size of approximately $\sim 125 \mu\text{m}$ and a bulk density of 0.4 g/cc. They were supplied by Fillite U.S.A., Inc. The chemical components in the microspheres were 55 to 60% SiO_2 , 30 to 37% Al_2O_3 , and 4% Fe_2O_3 .

Type I portland cement which is known as an ordinary cement consisting of 64 wt % CaO , 20.1 wt % SiO_2 , 6.1 wt % Al_2O_3 , 3.0 wt % MgO , 2.4 wt % Fe_2O_3 , and 2.8 wt % SO_3 , was used to produce the partially hydrated cement grains for use as Ca counterion-releasable materials. The cement was exposed to an atmosphere of 80% relative humidity at 24°C for 1 h before mixing with the PAA solution.

A lightweight material slurry consisting of 65 wt % PAA solution and 35 wt % microspheres was used to prepare control specimens. Hydrated cement particles in concentrations of 2, 5, and 8% by weight of the total slurry mass were then added to the PAA-microsphere mixed slurries, which were then cast into glass test tubes, 3.5 cm diam by 7.0 cm long, for subsequent determinations of the compressive strength. The test tubes were stored in air or steam for 24 h at temperatures up to 400°C before the compressive strength tests were conducted. The densities of the slurries containing 0, 2, 5, and 8 wt % hydrated cement were 0.81, 0.83, 0.87, and 0.91 g/cc, respectively, and the bulk densities for the 300°C -air cured specimens containing 0, 2, 5, and 8 wt % cement were 0.35, 0.39, 0.44, and 0.47 g/cc, respectively.

Measurements

Thermogravimetric analysis (TGA) and infrared (IR) spectroscopy were used to follow the PAA solution \rightarrow PI solid transition resulting from the in situ imidization condensation of PAA and for determining the onset temperature of thermal decomposition of PI polymers. TGA measurements were made at a heating rate of $10^\circ\text{C}/\text{min}$ in flowing N_2 using a DuPont Model 951.

The chemical states and possible interactions at the interfaces between the PI and the hydrated cement or microsphere surfaces were explored using the combined techniques of x-ray photoelectron spectroscopy (XPS) and IR. The samples for IR analyses were prepared by placing the materials onto NaCl plates and by preparing KBr discs made by mixing 200 mg KBr and 3 to 5 mg

materials which had been crushed to <0.104 mm. X-ray photoelectron spectroscopy (XPS) provided by an aluminum $K\alpha$ X-ray source operated at a constant power of 200 W (10 kV, 20 mA). The vacuum in the analyzer chamber of the instrument was maintained at 10^{-9} Torr throughout the experiments. For the XPS studies, discs, 12 mm in diameter and 0.5 to 1 mm thick, of the hydrated cement were made by pressing the cement powders at 100 MPa. The discs were then dipped for 20 sec into 5 wt %, 1 wt %, and 0.5 wt % PAA solutions. After wetting the disc surfaces with the PAA, the samples were dried in an oven at 300°C for 5 h to convert the PAA solution into solid PI films.

An Instron TIMB testing machine, which advanced at 0.1 cm/min, was used to determine the compressive strength of the specimens 2.2 cm in diameter and 4.4 cm long.

RESULTS AND DISCUSSION

A TGA curve for a PAA solution consisting of 40 wt % varnish and 60 wt % BME solvent is given in Figure 1. Over the temperature range 25° to 650°C , three distinct regions are indicated. The first occurs at temperatures between 25° and 280°C and is characterized by a weight loss of approximately 70%. This significant weight reduction is probably due to volatilization and vaporization of the BME solvent and the water by-product yielded by the in situ imidization reaction of the PAA precursor upon heating. The magnitude of the weight loss indicates that the as-received PAA varnish product contained approximately 10% BME solvent, since the remaining 60% is associated with the additional BME used to dilute the varnish. In the second region, between 280° and 510°C , the curve levels off, thereby suggesting that the PI polymers have

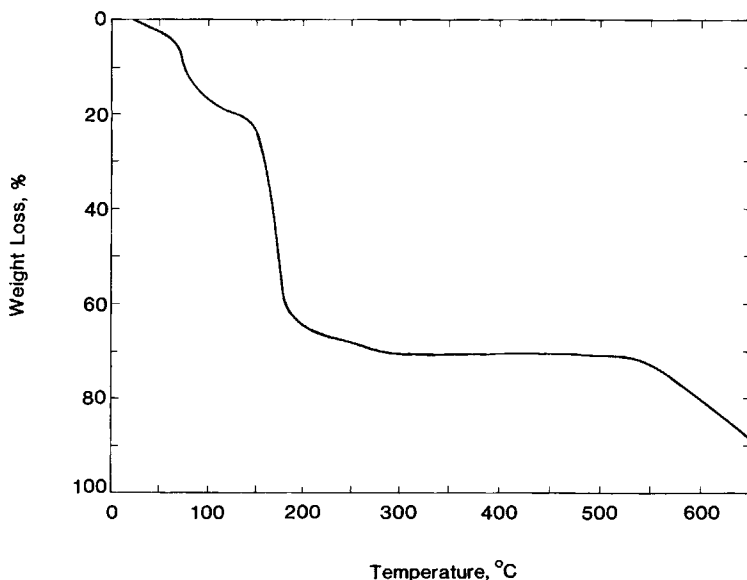


Fig. 1. TGA curve for PAA solution.

excellent thermal stability in N_2 gas. Beyond $510^\circ C$, thermal decomposition of the PI seems to occur.

The above data are supported by the results from IR analyses which are given in Figure 2. For use in this examination, thin film samples were prepared by placing the PAA solution onto NaCl plates and then spinning at 1000 RPM for 10 sec. This was followed by curing for 2 h in air at temperatures of $100^\circ C$, $200^\circ C$, or $280^\circ C$. Compared to that for the BME solvent (Fig. 2a), the assignments of the main IR absorption bands for the PAA solution (b) are as follows; the vibrations of amide amine and amide carbonyl within PAA at 3450 , 1660 , 1550 , and 1300 cm^{-1} , the CH vibrations of the methylene and methyl in BME at 2890 and 1450 cm^{-1} , the C—O—C ether vibrations in BME at 1200 and 1100 cm^{-1} , the aromatic C=C stretching vibrations in PAA at 1600 , 1585 , and 1490 cm^{-1} , and the carbonyl stretching in COOH of PAA at 1730 cm^{-1} . The spectrum for the $100^\circ C$ -treated samples (curve c) is characterized by the appearance of new bands at 1770 , 1360 , and 710 cm^{-1} , a shift of the C=O peak from 1730 to 1710 cm^{-1} , and the marked decrease in peak intensities at 3450 , 1660 , 1550 , and 1300 cm^{-1} which reveals the amide groups in PAA. The reason for the decreased amide peak intensities is the progression of the imidization reaction between the amide and the carboxylic acid groups within PAA. Thus, the new peaks and the shifted peak appear to be ascribed with the C—N and C=O stretching in the imide rings as a result of PI formation.⁸⁻¹¹ However, the strong peaks at 2890 , 1450 , and 1100 cm^{-1} indicate that a large amount of

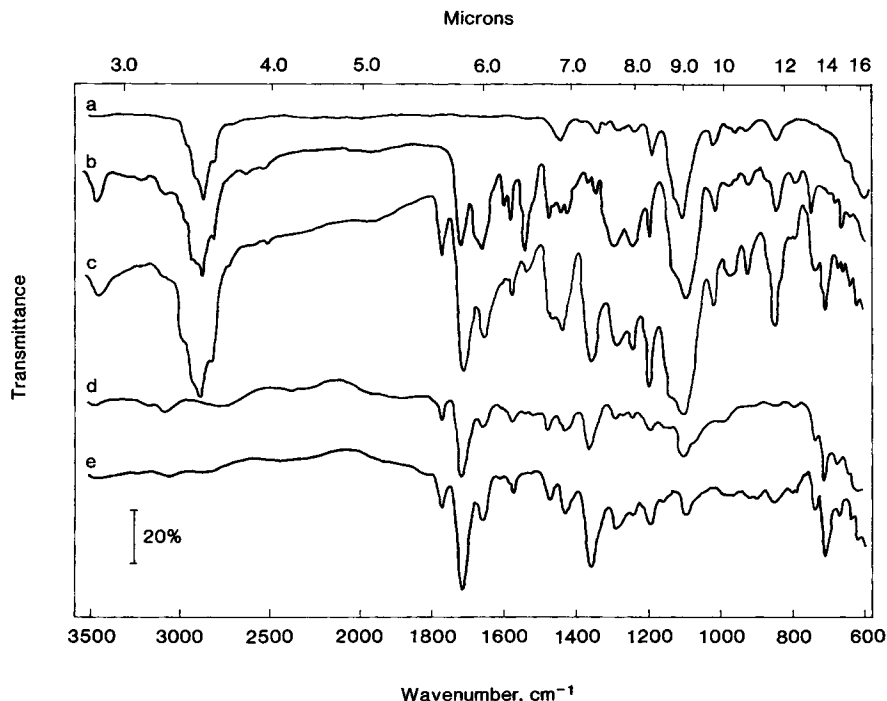


Fig. 2. Infrared spectra for (a) BME solvent, (b) PAA solution, (c) $100^\circ C$ -heated, (d) $200^\circ C$ -heated, and (e) $280^\circ C$ -heated films.

BME solvent was still present within the film. Almost all of the solvent remaining in the film seemed to be decomposed or volatilized at a temperature of 200°C. This is indicated by the disappearance and significant diminution of these bands on absorption spectrum (d). This spectrum also indicates the further decay of amide peak intensities, suggesting that the rate of the imidization reaction significantly increased at 200°C. For the film treated at a temperature of 280°C, the presence of weak amide peaks on spectrum (e) indicates that a small fraction of unreacted PAA still remained within the cured PI film. This is reflected on the band at 1710 cm^{-1} which reveals the imide carbonyl and the carboxylic acid carbonyl in the residual PAA.

At 510°C which was determined by TGA to be the onset temperature for the thermal degradation of PI, the spectrum (not shown) exhibited a slight reduction in the intensities of the imide bands at 1770, 1360, and 710 cm^{-1} . On the basis of the fundamental knowledge obtained regarding the thermal imidization process and thermal degradation of PI polymer, the curing characteristics for microsphere-filled lightweight PI cementitious specimens upon exposure to hot air and steam environments, were then investigated. In this work, the PI specimens were precured in air at 80°C for 10 h and then exposed for 24 h in either air or steam at temperatures up to 400°C. Compressive strength measurements were then made.

Figure 3 shows the compressive strength of the specimens as a function of post-heating temperature. As expected, the strength of specimens exposed to hot air increases with temperature between 80° and 300°C. At 300°C, the

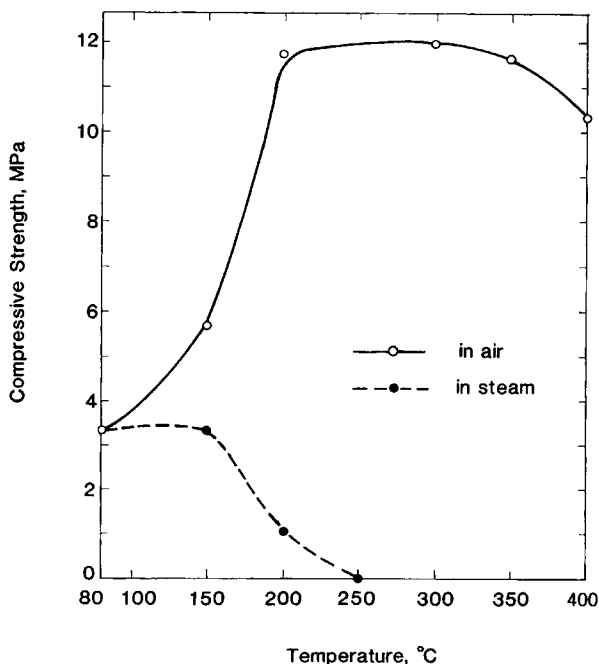


Fig. 3. Changes in compressive strength of 80°C air-precured PI specimens after exposure to air or steam at temperatures up to 400°C.

strength was more than three times that of 80°C-precured specimens. Beyond 300°, the strength decreased slowly. In contrast, no strength improvement was obtained for the steam-cured specimens. Beyond 150°C, the steam-exposed specimens exhibited significant strength reductions, as compared to that of the 80°C-precured one. Further increases in steam temperature to 250°C resulted in severe hydrothermal disintegration of the specimens and the strengths were too low to be measured.

Experiments were also performed in which the PI cementitious materials were cured and post-heated in air prior to exposure to hydrothermal environments. For use in these tests, PI specimens, with and without partially hydrated cement grains, were prepared and oven heated in the following sequence: 24 h at 80°C → 10 h at 150°C → and 24 h at 300°C. After curing, the specimens were exposed for 24 h to steam at temperatures of 150°, 200°, 250°, and 300°C. Compressive strength measurements were then made to evaluate the hydrothermal stability and to investigate the influence of the inclusion of hydrated cement on the mechanical properties of the materials. These test results are shown in Figure 4. As is evident from the figure, the compressive strengths for the unexposed specimens at 25°C varied with the concentration of cement hydrate added to the PAA slurry; namely, the strength decreased with increased cement hydrate content.

In an attempt to determine the cause of this effect, the interfaces between the hydrated cement and the PI polymer were explored using XPS. Preliminary

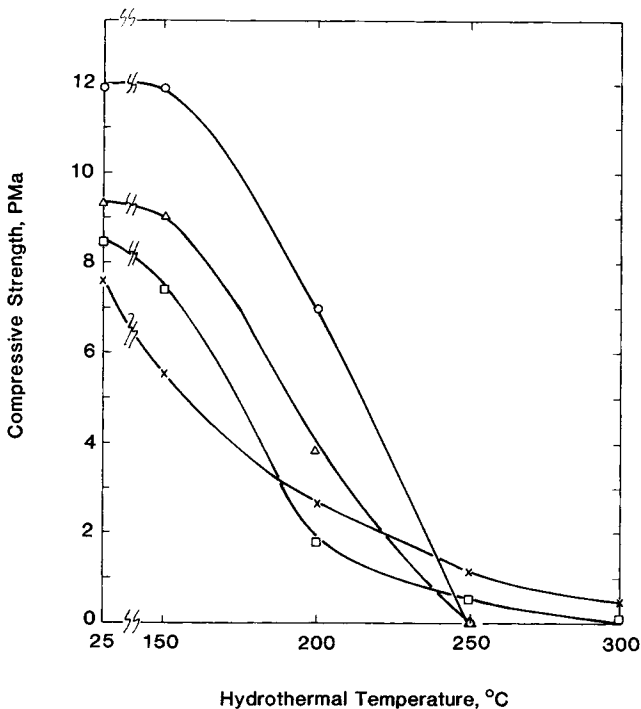


Fig. 4. Compressive strength vs hydrothermal temperature for PI specimens containing 0% (○), 2% (△), 5% (□) and 8% (×) cement.

examinations of wide scan XPS spectra for the cement discs coated with ≤ 1.0 wt % PI which corresponds to ≤ 1.0 wt % PAA, revealed the presence of a doublet Ca2p peak of substantial intensity. This suggests that certain areas of the cement surfaces were covered with a thin layer of PI polymer, no thicker than 5 nm, which associates the escape depth of aluminum photoelectrons. For all samples, the binding energy (BE) scale in the XPS spectra was calibrated with the C_{1s} of the principal hydrocarbon-type carbon peak fixed at 285.0 eV as an internal reference standard.

The C_{1s} core level photoemission spectra for bulk PI and the 5 wt %, 1 wt %, and 0.5 wt % PI-covered cement surfaces and interfaces are shown in Figure 5. The C_{1s} region for the bulk PI polymer (Fig. 5a) contains three resolvable peaks situated at 285.0, 286.1, and 288.8 eV. According to the literature,¹² the major carbon peak at 285.0 eV includes contributions from the aromatic carbon, the component at 286.1 eV can be assigned to phenylic carbons joined to N, and that at 288.8 eV to carbonyl, C=O, carbons. As evidenced by the lack of a component at 289.4 eV in the C_{1s} region, no free carboxylic acid, COOH, groups which relate directly to the presence of the PAA precursor, were observed

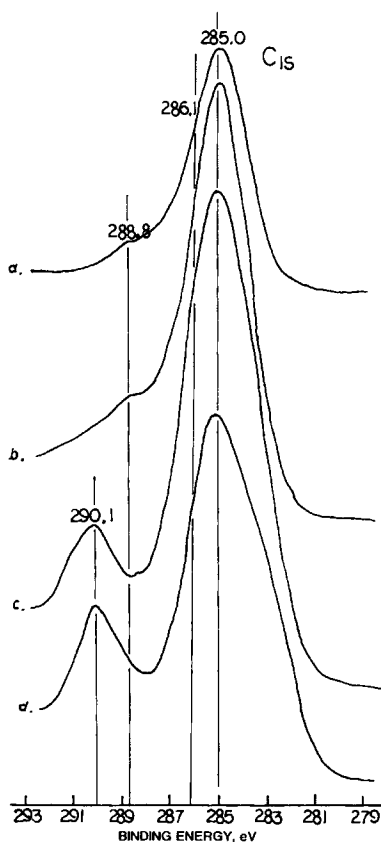


Fig. 5. XPS C_{1s} regions for (a) bulk PI, (b) 5% PI-, (c) 1% PI- and, (d) 0.5% PI-covered cement samples. Integrated intensity ratio of C (COO) and C ($-\text{C}(\text{O})-\text{C}-$): (c) 0.22; (d) 0.35.

on the bulk PI polymer surfaces. In Fig. 5b, the features of the spectrum for a cement pellet surface covered with 5 wt % PI polymer which is recognized as a thick coating, are similar to those of the bulk PI surface. An interesting spectral feature was observed when a thin 1.0% PI film was deposited on the hydrated cement substrate. As seen in Fig. 5c, this spectrum is characterized by the presence of a prominent peak at 290.1 eV and a considerably decayed intensity for the carbonyl carbon peak at 288.8 eV. At a lower coverage of 0.5% PI, the peak intensity of BE at 290.1 eV was increased further (see Fig. 5d). Since the latter is assigned to the carboxyl, COO, carbon components,¹³ it is believed that a large number of COO groups are present in the interfacial regions. This becomes more readily apparent from a consideration of the integrated intensity ratio between the C (COO) peak at 290.1 eV and C (—⊙—) at 285.0 eV. The resultant (C (COO)/C (—⊙—)) intensity ratio for the 0.5% PI/cement interface was higher than for the 1.0% PI-covered cement (Fig. 5). Figure 6 shows the Ca2p_{3/2} regions for the hydrated cement substrate surface and the 0.5% PI/cement interface. The BE value for the main Ca2p_{3/2} peak for the cement surfaces (Fig. 6e) was 347.3 eV, which can be ascribed to calcium silicate hydrate species. When the cement substrate was covered with a thin film of 0.5% PI, the Ca2p_{3/2} region for the PI/cement interface exhibited a new peak at 347.7 eV. This is at a BE 0.4 eV higher than that for the cement peak. This new peak is indicative of the formation of a COO—Ca complex¹⁴ produced at the interface. In contrast, no specific changes in the spectral features were observed in the Si2p regions (Figure 7). Thus, it is reasonable to assume

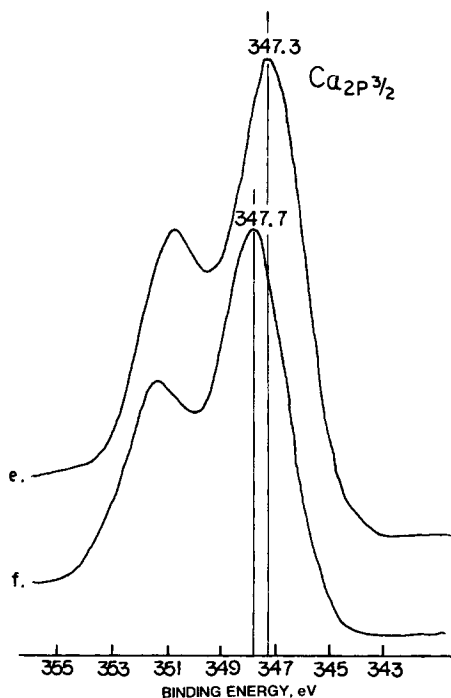


Fig. 6. Ca_{2p_{3/2}} spectra for (e) hydrated cement and (f) 0.5% PI/cement samples.

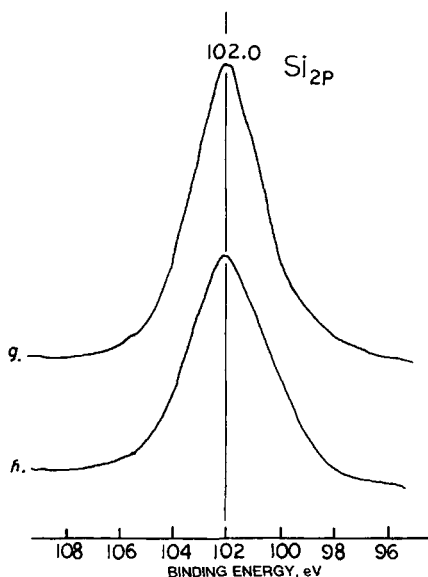


Fig. 7. Si_{2p} spectra for (g) hydrated cement and (h) 0.5% PI/cement samples.

that the carboxylic acid and amide functionalities in the PAA adjacent to the hydrated cement, preferentially react with the transitional Ca ions liberated from the cement and not with the Si. The hydrated cement surfaces have a strong alkaline nature, and it is well known¹⁵ that when carboxylic acid comes in contact with hydroxide anions, OH⁻, the reduction of the hydrogen-oxygen bond in the COOH forms the carboxylate anion, COO⁻. After loss of the proton, the remaining COO⁻ group becomes a counterion acceptor which reacts with transitional Ca²⁺ ions. On the other hand, information regarding the amide-cement interaction mode was gained by examination of the N_{1s} core level regions (see Figure 8). The high resolution N_{1s} signal (Fig. 8i) for the bulk PI polymer surface indicates a single peak at 400.4 eV which is due to the imide nitrogen

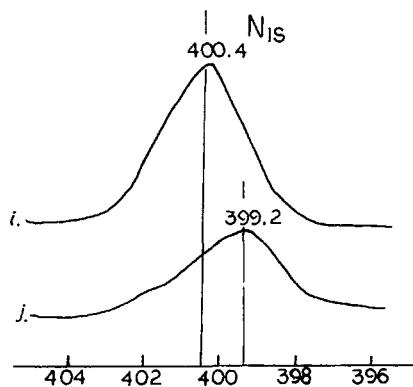
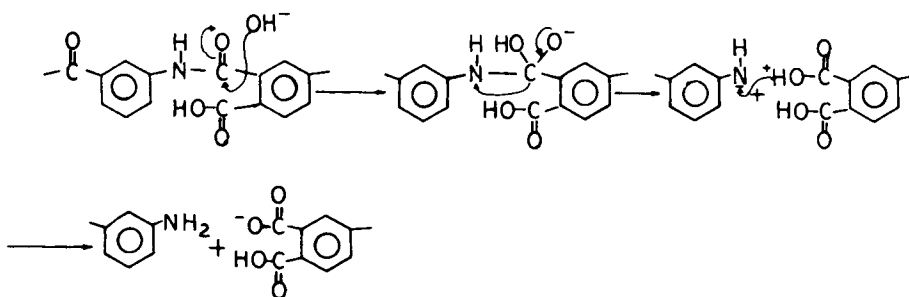
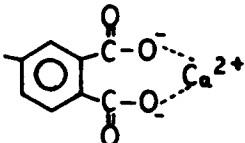


Fig. 8. N_{1s} spectra for (i) bulk PI and (j) 0.5% PI/cement samples.

in the PI. In comparison, the spectrum (Fig. 8j) at the PI/cement interface exhibits a predominant peak at 399.2 eV in addition to the weak peak of the imide at 400.4 eV. Since the BE of the amide nitrogen in PAA is commonly located at 401.4 eV,¹⁶ this principal peak is more likely to be associated with the amino, $-\text{NH}_2$, nitrogen joined to the phenyls¹⁷ rather than that of the unreacted amide in the PAA. The results suggest that when the amide groups in the PAA are contacted with hydrated cement, they are transformed into carboxylate anions, COO^- , through the alkalicycatalyzed hydrolysis mechanism of amides which are susceptible to reaction with hydroxide anions. This mechanism can be addressed as follows:



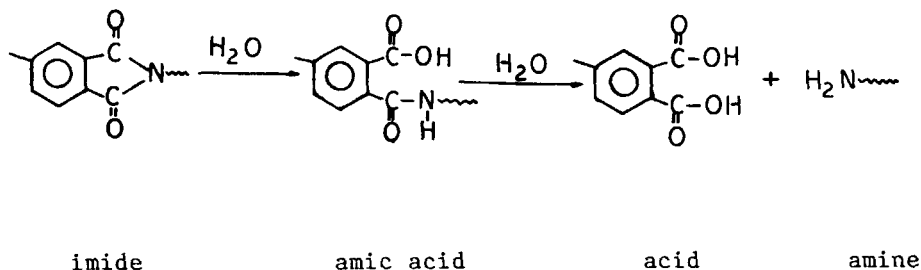
As seen above, the PAAs undergo bond breakages of the amide linkage caused by nucleophilic attack of the OH^- ion on the amide carbon. This breakage leads to the formation of a base soluble intermediate compound containing a carboxylate anion and a base insoluble amine compound. As mentioned previously, the carboxylic acid groups which are one of the other functionalities in the PAA are readily converted into carboxylate anions in alkali environments. Therefore, these carboxylate anions quickly react with the calcium cations from

the cement and then form Ca-bridged  carboxylate com-

plexes. The formation of Ca-carboxylate complexes not only disturbs the intermolecule imidization reaction of PAA, but also leads to scission of the linear polymer chains, resulting in lower molecular weight species. This results in the formation of a gel at the interfaces, thereby leading to a weak PI-cement boundary layer. From the above information, it can be conclusively drawn that when the PAA precursor comes in contact with alkaline substrates, the alkalicycatalyzed hydrolysis of PAA acts to promote mechanical failure at the interfaces in PI systems. Hence, the poor strength development in the PI specimens is not surprising, and it becomes less as the proportion of hydrated cement is increased.

Let us return to the compressive strength-hydrothermal temperature relations summarized in Fig. 4. As predicted, the extent of strength reduction after exposure of specimens to steam at 150°C increases as the amount of cement in the composites is increased. Although the PI specimens prepared without the inclusion of the cement filler exhibited very little strength loss upon exposure

at 150°C, considerable decrease was observed at 200°C. At 250°C, the strength of the cement-free specimens was too low to be measured. Since a certain amount of unreacted PAA is likely to be present in the specimens, the cause for the hydrothermal degradation of the cement-free PI composites can be explained on the basis of the hydrolysis of the imide rings in the PI polymer structures and of amide linkages in the PAA, as reported previously by several investigators.¹⁸⁻²⁰ This mechanism is as follows:



For the cement-filled PI specimens at $\geq 250^\circ\text{C}$, the extent of retrogression seems to decrease with increased cement content. In fact, the 8 wt % cement-filled specimens at 300°C displayed a compressive strength of 0.5 MPa, compared with the no measurable strength for the cement-free specimens at $\geq 250^\circ\text{C}$.

Figure 9 compares the IR spectra for 8.0 wt % cement-filled PI composite samples before and after exposure to steam at 300°C. Severe alkali-catalyzed

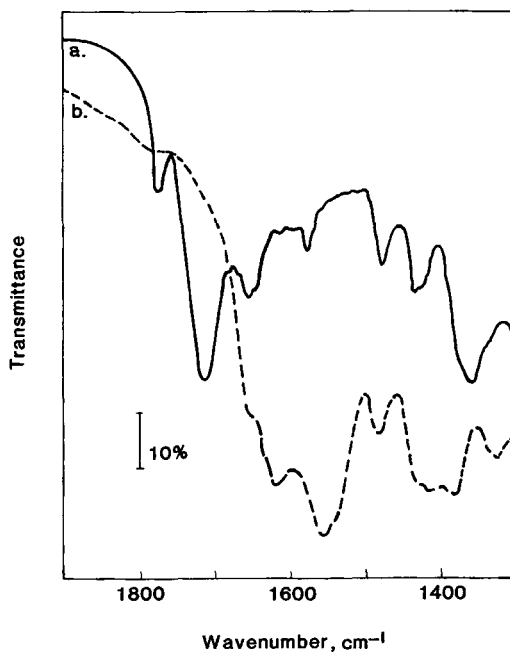
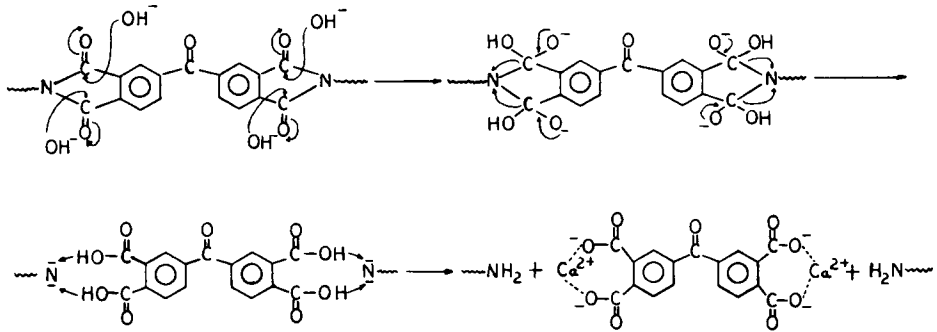


Fig. 9. Infrared spectra for cement-filled PI specimens before (a) and after (b) exposure to steam at 300°C.

hydrolysis of the imide rings in the PI, is revealed by the appearance of the carboxylate anion peaks at 1560 and 1420 cm^{-1} in conjunction with the disappearance of the imide ring and carboxylic acid vibrations at 1770, 1710, and 1360 cm^{-1} (Fig. 9b).

On the basis of the open literature to date,^{21,22} the alkali-induced hydrolysis of PI may occur through the following modified mechanism:



As is clear from the above proposed hydrolysis processes, it appears that the eventual formation of Ca-complexed carboxylate salts result in the disintegration of the composite brought about by the chain scission of a linear PI macromolecule.

CONCLUSIONS

Microsphere-filled PI lightweight materials having a slurry density of 0.81 g/cc and a bulk density of 0.35 g/cc, displayed a compressive strength of 12 MPa after exposure to hot air at 300°C. Unfortunately, the PI polymer matrix undergoes hydrolysis in hydrothermal environments at temperatures of > 150°C. Base-catalyzed hydrolysis of the functional groups in the unreacted PAA and the PI imide groups significantly promoted as partially hydrated cement fillers were incorporated in the PAA slurry. Hydrolysis of the former occurs principally in the interfacial regions between the PAA and the alkaline cement hydrate at room temperature, and the latter is initiated by the attack of hydroxide anions on the imide carbon in steam at $\geq 150^\circ\text{C}$. In these mechanisms, the bond breakage and cleavage of the amide linkages in PAA and the imide rings in PI, brought about by the nucleophilic attack of OH^- , lead to the formation of transitory intermediate compounds containing carboxylate anions and amine compounds. The anionic intermediate organic compounds immediately react with the Ca counterions liberated from the cement surfaces and then form Ca-complexed carboxylate salts. These salt formations not only act to promote the scission of polymer chains, but also result in considerable strength decrease of the PI materials. Therefore, it is concluded that PI lightweight materials not containing any alkaline fillers may be suitable for use in hot air environments at temperatures up to 300°C, but are questionable for use in high pH hydrothermal environments.

References

1. C. E. Sroog, *J. Polym. Sci., Macromol. Rev.*, **11**, 161 (1976).
2. L. B. Rothman, *J. Electrochem. Soc.*, **127**, 2216 (1980).
3. A. M. Wilson, *Thin Solid Films*, **83**, 145 (1981).
4. A. K. St. Clair and T. L. St. Clair, in *Polyimide: Synthesis, Characterization and Applications*, K. L. Mittal, Ed., Vol. 2, Plenum Press, New York (1984).
5. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience, New York, (1968).
6. R. J. Cotter and M. Matzner, *Ring-Forming Polymerization*, Vol. B-2, Academic Press, New York, (1972).
7. T. Sugama, L. E. Kukacka, C. R. Clayton, and H. C. Hua, *J. Adhesion Sci. Tech.*, **1**, 265 (1987).
8. J. Sykee and T. Hoar, *J. Polym. Sci., Part A-1*, **7**, 1385 (1969).
9. G. F. L. Ehters, K. R. Fisch, and W. R. Powell, *J. Polym. Sci., part A-1*, **8**, 3511 (1970).
10. H. Ishida, S. Wellingshoff, E. Baer, and J. L. Koenig, *Macromolecules*, **13**, 826 (1980).
11. J. R. Salem, F. O. Sequeda, J. Duran, and W. Y. Lee, *J. Vac. Sci. Technol.*, **A4**, 369 (1986).
12. P. L. Buckwalter and A. I. Baise, *Polyimides, Synthesis, Characterization, and Applications*, K. L. Mittal, Ed., Vol. 1, Plenum Press, New York (1984).
13. D. Briggs and M. P. Seah, *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, John Wiley & Sons, Ltd., New York (1983).
14. T. Sugama, L. E. Kukacka, N. Carciello, and N. Hoeker, *Cem. Concr. Res.*, **19**, 857 (1989).
15. T. Sugama, L. E. Kukacka, and N. Carciello, *J. Mater. Sci.*, **19**, 4045 (1984).
16. A. Toth, et al., *Surf. Interface Anal.*, **8**, 261 (1986).
17. R. Nondberg, et al., *Arkiv Kemi*, **28**, 257 (1968).
18. R. Delasi and J. Russell, *J. Appl. Polym. Sci.*, **15**, 2965 (1971).
19. J. O. Punderson and J. F. Heacock, International Wire and Cable Symposium Proceedings, pp. 44-50 (1985).
20. C. A. Pryde, Proceedings of ACS Division of Polymeric Materials Science and Engineering, **59**, 219 (1988).
21. J. A. Kreuz and C. M. Hawkins, Proc. Tech. Program—Annual International Electron Package Conf. 2nd, 653 (1982).
22. W. P. Pawlowski and D. D. Coolbaugh, Proceeding of ACS Division of Polymeric Materials Science and Engineering, **59**, 68 (1988).

Received September 12, 1989

Accepted November 6, 1989