JOURNAL OF MATERIALS SCIENCE 24 (1989) 3353–3355

Polymer impregnation of macro-defect-free cements

G. V. CHANDRASHEKHAR, M. W. SHAFER
I. B. M. Watson Research Center, Yorktown Heights, New York 10598, USA

Impregnation of MDF cements based on Secar-71 with high-strength heat-resistant polymers, like the novolac epoxies, produces composites with vastly improved properties. Some typical properties are: (1) at 1 MHz and 0% relative humidity, dielectric constant of 8 to 9, dissipation factor of 0.005 to 0.008, and d.c. resistivity of about $10^{13}\,\Omega\,\mathrm{cm}$; (2) less than 5% increase in dielectric constant after exposure to 90% humidity for extended periods of time; (3) flexural strengths of 150 to 200 MPa; and (4) thermal stability up to 350° C.

1. Introduction

In a previous paper [1], we reported the preparation and properties of macro-defect-free (MDF) cements based on Secar-71. While the electrical properties of these cements were adequate in low humidities for consideration as potential low-cost substrates, they deteriorated rapidly in higher humidities. We also found that while impregnation and *in situ* polymerization with a hydrophobic monomer like dimethylsiloxane (silanol terminated) very significantly inhibited the effect of higher humidities, the strengths of the impregnated cements were very poor. This is probably because the impregnation process requires heating to 225° C for extended periods of time which softens the original polymer.

Polymer impregnation of concrete and cementitious materials has long been known [2, 3]. The process involves heating to drive off water, open up and even modify the pore structure and refilling the pores with an organic monomer which is then polymerized to form a composite of an organic polymer network interpenetrating an inorganic cementitious network. Usually, the more porous the sample, the better the impregnation, and such cements have been found to have high tensile and compressive strengths [2]. We have explored the possibility of adapting this technique to the macro-defect-free cements, because in addition to durability and high strength, good thermal stability is also necessary. For impregnation, we have used methyl methacrylate and some high-strength, heat-resistant novolac epoxies. These cements, as-made, have very little open porosities and the viscosities of the resins are high; therefore they were preheated to completely remove the water and the original polymer, thus making them reasonably porous and facilitate maximum impregnation. In this paper, we report these impregnation studies and the properties of the resulting materials.

2. Experimental details

For the impregnation studies, a cement-based on Secar-71 and with a composition 11.5 (water)/7 (polyvinyl acetate)/0.7 (glycerol)/100 (Secar-71) was used. Cement discs of 1 in. (2.54 cm) diameter and 2 to 3 mm thick were made using a high shear mixer and a roller mill as described previously [1]. Some of the discs were hot pressed at 70° C and 7000 p.s.i. ($\sim 48.23\,\mathrm{N\,mm^{-2}}$), while others were air cured for a couple of days. Both types of sample were used in the impregnation studies and subsequent measurements.

The cement discs were heated in air at 500° C for 5 to 6 h to completely remove the water and the original polymer (polyvinyl acetate) and then stored in vacuum at 150° C to prevent reabsorption of moisture. In a typical impregnation experiment, these discs were dipped in a molten mixture of the epoxy and hardener for a period long enough to result in complete impregnation. Then they were removed, and after removal of the excess adhering resin, cured. After cooling, the residual resin was removed from the surfaces by sanding. The details are as follows: (a) a mixture of methyl methacrylate (70%) and trimethylolpropanetrimethacrylate (30%) with benzoyl peroxide as catalyst was used as the impregnating agent in a manner similar to dimethylsiloxane [1]. The schedule was 75° C for 2 h followed by curing at 125° C for 24 h; (b) Dow epoxy novolacs (DEN 438 and 431) were used with diaminodiphenylsulphone (DADPS) as hardener. The novolacs and DADPS were heated separately at 150° C for 1 h. DADPS (36 or 22% by weight for DEN 438 or 431, respectively) was stirred in and allowed to dissolve (about 10 min). The cement samples were introduced and impregnation carried at 150° C for 1 h. Curing was done at 150° C for 1 h followed by 3 h at 225° C; (c) DEN431 was also used with a mixture of nadic methyl anhydride (NMA) and benzyldimethylamine (BDMA) as hardeners. The novolac was preheated to 90° C for 1 h, 87.5% by weight NMA was added and the mixture heated for 0.5 h; 1.5% by weight BDMA was stirred in and the cement samples introduced. Impregnation was done at 90° C for 1.5 h and curing was at 90° C for 1.5 h followed by 4 h at 165° C and finally 16 h at 200° C; (d) a Ciba-Geigy Ecobond novolac, ECN 1235 was used with HT 976 (Ciba-Geigy) as hardener. 27% by weight HT 976 was melted by heating to 180° C and dissolved in the novolac

0022-2461/89 $03.00 + .12

TABLE I Electrical properties of impregnated cements

Sample	$\varepsilon_{1\,\mathrm{MHz}}$		$\tan\delta_{1\,\mathrm{MHz}}$		$\varrho_{\mathrm{d.c.}}$ (Ωcm)	
	0% r.h.	90% r.h.	0% r.h.	90%r.h.	0% r.h.	90% r.h.
Unimpregnated cement sample	11.10	16.5	0.0235	0.20	2×10^{13}	2×10^{7}
Cement + dimethylsiloxane	8.4	9.3	0.016	0.03	5×10^{12}	$\sim 10^{12}$
Cement + MMA + benzoyl peroxide	9.1	10.7	0.008	0.018	$> 10^{13}$	$\sim 10^{13}$
Cement + DEN 438 NMA + BDMA	9.3	9.8	0.008	0.023	$> 10^{14}$	$\sim 10^{13}$
Cement + DEN 438 + DADPS	8.7	10.0	0.007	0.018	$> 10^{14}$	$\sim 10^{13}$
Cement + DEN 431 + DADPS	9.1	9.5	0.01	0.017	$> 10^{14}$	$\sim 10^{13}$
Cement (R.T. cured) + ECN 1235 + HT 976	9.1	9.8	0.009	0.014	$> 10^{14}$	$\sim 10^{13}$
Cement (hot pressed) + ECN 1235 + HT 976	8.9	9.3	0.009	0.015	$> 10^{14}$	$\sim 10^{13}$

at 84° C. The cement samples were introduced and impregnation was carried out for 5 h. Curing was at 120° C for 4 h followed by 16 h at 200° C.

The electrical properties of the impregnated cements were measured in both 0 and 90% relative humidities as described earlier [1]. The strength measurements were made on a MKS testing instrument using a four-point bending technique. At least six discs were used for each measurement. The temperature range of stabilities of some of the samples was determined by measuring the thermal expansion coefficient to 150° C and repeating the experiment with the upper temperature limit 50 degrees higher in each subsequent reheating, until the data were no longer reversible.

3. Results and discussion

Table I lists the electrical properties of the impregnated samples. For comparison, data for an as-made cement as well as a sample impregnated with dimethylsiloxane are also included.

From examination of the table, the following observations can be made. (a) The 1 MHz dielectric constant and loss factor values as well as the d.c. resistivities in 0% relative humidity are nearly the same for all the impregnated samples. The decrease in the dielectric constant (from about 11 to about 9) and the loss factor (from about 0.025 to less than 0.01) after impregnation are due to removal of water and refilling of the pores with the polymer. (b) Preheating followed by impregnation and *in situ* polymerization with the novolac epoxies and methyl methacrylate inhibit the effect of higher humidities in much the same way as dimethylsiloxane – by filling the pores. The table shows that in the best cases (for example with ECN 1235 + HT 976), the dielectric constant increases by as little as 5% even after exposure to 90% relative humidity for extended periods of time as opposed to an increase of 50% or more for the as-made sample. Similarly, the d.c. resistivities decrease by just about an order of magnitude compared to six orders of magnitude for an as-made sample. (c) The inhibition effect at higher humidities on the electrical properties is the same for the dimethylsiloxane and the novolac epoxies. (d) Similarly, there is no significant difference between cement samples which were hot pressed and those that were cured at room temperature.

Table II lists the flexural strengths and thermal stability ranges for the impregnated samples. The strength measurements shown are the average of six samples. Again, for comparison, data for an as-made cement and one impregnated with dimethylsiloxane are included. The superiority of the novolac epoxies is obvious. Cement samples impregnated with DEN 431 or ECN 1235 have flexural strengths of 150 to 200 MPa, much higher than samples impregnated with dimethylsiloxane (about 30 MPa). Even DEN 438 and methyl methacrylate seem better than dimethylsiloxane though not as good as DEN 431 or ECN 1235. Also, the fact that in quite a few cases, the maximum

TABLE II Thermal stability and strengths of impregnated cements

Sample	Max. temp. of stability (° C)	Flexural strength (MPa)	
		Average	Maximum
1. Unimpregnated cement	~ 175	120	135
2. Cement + dimethylsiloxane	~ 175	~ 30	–
3. Cement + MMA + benzoyl peroxide	150–175	69	70
4. Cement + DEN 438 + NMA + BDMA	–	78	86
5. Cement + DEN 438 + DADPS	–	96	110
6. Cement + DEN 431 + DADPS	350	173	183
7. Cement (R.T. cured) + ECN 1235 + HT 976	350	145	183
8. Cement (hot pressed) + ECN1235 + HT 976	350	156	230

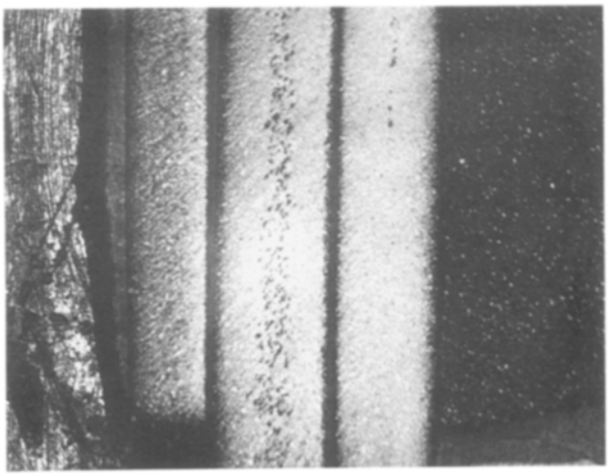

Figure 1 Microscopic cross-sections along the thickness for three representative polymer impregnated and cured cement samples. × ~ 17

value of the flexural strength is much higher than the average values, makes it likely that the strength values can be further improved by optimizing the impregnation and curing schedules. Further, cements impregnated with the novolacs are thermally stable and can be cycled up to 350° C, while the as-made cements and those impregnated with dimethylsiloxane or methylmethacrylate could not withstand temperatures higher than 150 to 175° C. In fact, with both ECN 1235 and DEN 431 impregnation, the post-cure strengths are very much comparable to the as-made MDF cements, while at the same time, the temperature range of stability and durability of the electrical properties in higher humidities is vastly improved. Though the as-made cements have good strengths and very little open porosity, the polymer used to facilitate the processing (polyvinyl acetate) is water soluble. Hence water can permeate the cement network resulting in the deterioration of the electrical properties. By removing this polymer and water while retaining the basic MDF structure and refilling with a high-strength heat-resistant polymer, the improvement in properties is attained.

The improved properties of the impregnated cements also depend on the decrease in the porosity achieved which depends on the depth and uniformity of penetration of the structure. While there is no direct relation between the solid fraction of the cement paste and the monomer and the mechanical strength of the impregnated composite for a cement of given porosity, the strength and durability properties increase with monomer loading [2]. Fig. 1 shows, for three of the impregnated samples, cross-sections along the thickness (× 17). An as-made but preheated sample could not be included, because it was too weak to be polished. It is seen from the figure that the polymer penetration is quite uniform across the entire thickness of the sample. Samples heated to 500° C showed a volume porosity of about 20% by mercury porosimetry. A calculation using the Maxwell equation for dielectric constant of a random mixture

$$\varepsilon = \frac{v_1\varepsilon_1\left(\frac{2}{3} + \frac{\varepsilon_2}{3\varepsilon_1}\right) + v_2\varepsilon_2}{v_1\left(\frac{2}{3} + \frac{\varepsilon_2}{3\varepsilon_1}\right) + v_2} \qquad (1)$$

where ε is the dielectric constant of the composite, ε_1 and ε_2 are dielectric constants of the two phases, and v_1 and v_2 are the volume fractions of the two phases, shows a polymer uptake of 18 to 19% which indicates almost complete filling. Also the impregnated cements do not show any open porosity.

Data for polymer-impregnated concretes [4] show that improvements in strength cannot be predicted by the pore-filling concept alone, but should also be related to improvements in interfacial bonding. This may explain the differences in strength among the various impregnated cements, though all of them seem to be equally resistant to high humidities. Data [5] also show that the sealing of pores, in addition to improving the strength and elastic properties of the composite, increases its resistance to crack propagation.

4. Conclusion

By preheating the MDF cements to about 500° C to remove most of the water and the hydrophilic polymer used in processing, and then impregnating them with high-strength heat-resistant novolac epoxies, we have been able vastly to improve their properties. The resulting composites have (a) low dielectric constant and high resistivity, (b) very small changes in electrical properties after extended exposure to high humidities, (c) good flexural strengths, and (d) good temperature range of stability. By optimizing the choice of the epoxies and the impregnating and curing schedules, it may be possible to make further improvements. These properties make them attractive candidates for consideration as low-cost substrates in electronic packaging.

Acknowledgements

The authors thank R. A Figat and C. F. Guerci for help in sample preparation and J. Kim for use of the MKS testing apparatus.

References

1. G. V. CHANDRASHEKHAR, E. I. COOPER and M. W. SHAFER, *J. Mater. Sci.* **24** (1989) 3356.
2. R. NARAYANASWAMY, *ibid.* **14** (1979) 1521 and references therein.
3. R. P. BRIGHT, S. WISE and M. L. MACKENZIE, *Mater. Res. Symp. Proc.* **42** (1985) 287.
4. D. G. MANNING and B. B. HOPE, *Cem. Concr. Res.* **1** (1971) 631.
5. R. NARAYANASWAMY, *J. Mater. Sci.* **14** (1979) 1547.

Received 23 August
and accepted 11 November 1988