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Dielectric properties of macro-defect-free (MDF) cements

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Macro-defect-free cements, based mostly on Secar-71 and using polyvinyl acetate as a plasticizer, have been prepared. Dielectric constant and loss factor at 1 MHz and d.c. resistivity of these cements have been measured as a function of their composition, processing conditions and humidity. For some of the samples, flexural strengths have been measured in order to correlate with their electrical properties. Results of efforts to inhibit the effects of higher humidities on the electrical properties are also reported.

1. Introduction

The recently developed macro-defect-free (MDF) cements [1–3], based on ordinary Portland cement or calcium aluminate clinkers but using polymer additives and special processing methods, have much higher tensile strength, toughness and lower permeability than ordinary cements. Compared to ceramics in particular, cements have the advantage of low-temperature processing and easy forming. Compared to most plastics, they have much higher strength. Much consideration is therefore being given to cements for uses which are normally reserved for plastics, metals or ceramics [3].

One such possible application being considered for MDF cements is as large-area low-cost substrates in electronic packaging. Because the hardening rates can be controlled, complex patterns and vias can be produced with little shrinkage during processing. For such an application, desirable properties in addition to good mechanical integrity are (a) low dielectric constant and loss (present materials have values ranging from 5.8 for cordierite to 9.8 for the most commonly used alumina), (b) good insulating properties (high d.c. resistivity), (c) temperature stability and (d) stability of electrical and mechanical properties in humid atmospheres.

There have been few measurements of the electrical properties of these materials [4–7]. The composition dependence (of both the cementitious material and the polymer additive) as well as the effect of frequency on the electrical properties of these cements have been studied but the effect of humidity has been largely overlooked. The combined effect of composition change and humidity on the mechanical properties has not been studied either. Some effort has been made [8, 9] to reduce the dielectric constants to lower values – to below the weighted average of the values for their cementitious constituents – by loading them with low dielectric constant materials like crushed borosilicate glass or hollow microspheres of silica. No strength measurements have been reported, but because these additives increase the porosity, it is very likely that the lower dielectric constants will be accompanied by lower strengths.

We have prepared these MDF cements based mostly on La Farge Secar-71 and have measured their electrical properties as a function of the composition, processing conditions and humidity. We have measured flexural strengths for some of the samples with a view to correlate them with their electrical properties. We also report on the results of efforts to inhibit the effect of higher humidities on the electrical properties.

2. Experimental details

2.1. Sample preparation

The starting materials used were: (1) Secar-71 (calcium aluminate cement, Lone Star LaFarge), (2) commercial white Portland cement, (3) Ludox (colloidal suspension of silica, Dupont), (4) 88% hydrolysed polyvinyl acetate (PVA, mol. wt 10 000, Aldrich), (5) polydimethyl siloxane (silanol terminated, P.S.340, 50 cP, Petrarch). Test samples were made using two somewhat different methods of preparation. In one method (A), the cement powder was mixed with the water/polymer/glycerol solution in a planetary type of mixer and the resulting mix was fabricated into discs which were cured under a pressure of $\simeq 5000$ p.s.i. ($\sim 34.45\,\mathrm{N\,mm^{-2}}$). The other method (B) also used a planetary mixer for the pre-mix, which was followed by twin roll milling and formation of sheets ranging between 1 and 2 mm thick. Test discs were punched from the sheets and cured in four ways: (a) room temperature and ambient relative humidity, (b) 65° C and ambient relative humidity, (c) 70° C and 80 to 90% relative humidity, and (d) 65° C and 5000 p.s.i. ($\sim 34.45\,\mathrm{N\,mm^{-2}}$) pressure. Discs made by method (A) needed higher amounts of water to process than discs made by method (B). The discs made by both methods were then studied by measuring their electrical and mechanical properties and the results were compared.

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2.2. Electrical measurements

For the electrical measurements, we used cylindrical samples either 15 or 25 mm diameter and up to 2 mm thick, on which $\simeq 200$ nm thick gold electrodes of 1 cm diameter were sputter deposited. Both two and three electrode configurations were employed. Dielectric constant and loss factor in the 10^3 to 10^7 Hz range were measured with a Hewlett-Packard 4192-A low-frequency impedance analyser. D.c. resistivities of the same samples were measured using a Hewlett-Packard 4392-A high resistivity meter. To ensure reproducibility, four to five samples of each batch were measured.

The samples after electrode deposition were held between spring-loaded electrodes inside constant humidity chambers. Four different relative humidities, (a) 0% (calcium chloride + calcium oxide), (b) $\simeq 33\%$ (saturated solution of sodium acetate), (c) $\simeq 57\%$ (saturated solution of sodium bromide), and (d) $\simeq 90\%$ (saturated solution of sodium metaborate) were employed. The samples were first introduced into the 0% relative humidity chamber and measurements made as a function of time up to equilibration and then transferred to a higher humidity chamber and the procedure repeated. The time taken for equilibration varied from 3 to 5 wk. In some cases, after equilibration at the highest humidity, the sample was transferred back to the 0% humidity chamber to check the reversibility of humidity effects.

2.3. Mechanical properties

The strength measurements were made on an MKS testing instrument using a four-point bending technique. At least six discs were used for each measurement.

3. Results and discussion

The sample compositions are generally represented as $A/B/C/D$ where A, B, C and D are the proportions by weight of water, polymer, glycerol and clinker, respectively.

The dielectric properties of several representative cement samples were measured as a function of frequency in the 10^2 to 10^7 Hz range in low humidity. The dielectric constant values showed slight dispersion in the 10^2 to 10^5 Hz range, with the values decreasing with increasing frequency. In the 10^5 to 10^7 Hz frequency range, they were almost frequency independent. The higher values in the low-frequency range are probably due to unbound water or water–PVA network present in the sample. All the results reported below pertain to a fixed frequency of 1 MHz.

In Table I, we show comparative data for the various cements studied. The 1 MHz values of the dielectric constant and loss factor as well as the d.c. resistivities in both 0 and 90% relative humidities are listed. All the cements listed in Table I were processed by method A – by mechanical mixing and cold pressing. These are not strictly MDF cements and they require more water for processing than those made by method B. However, their behaviour is quite similar to those made by method B, as will be shown later. Several observations can be made by an examination of Table I. (a) Without any addition of polymer, both Secar and white Portland cements have higher dielectric constant and loss factor values compared to the most commonly used substrate material, alumina (9.8 at 1 MHz), even at 0% humidity. At higher humidities, these properties and particularly the d.c. resistivities deteriorate very badly. Cements based on Secar-71 tend to fare better than those based on white Portland cement at higher humidities. (b) The addition of polymer (polyvinyl acetate – 88% hydrolysed) while improving the electrical properties at 0% humidity, does not have any effect at higher humidities, presumably because it is water soluble. (c) The addition of Ludox – which supplies fine-grained silica ($\varepsilon \simeq 3.8$) and part of the water for mixing and thereby reduces the overall amount of water available – does not have any beneficial effect on the electrical properties. (d) The addition of aluminium fluoride to the cement mixture in the expectation that F substitution for OH^- may lead to lower dielectric constant and better thermal stability (many F^- containing minerals are thermally more stable than OH^- containing analogues) did not result in any improvement.

In Fig. 1a, the 1 MHz values of the dielectric constant and loss factor for the Secar-71 cements are plotted as a function of the polymer concentration. It is seen that with the addition of 1% PVA (88% hydrolysed), both the dielectric constant and loss decrease significantly ($\varepsilon_{1\,\mathrm{MHz}}$ from $\simeq 13$ to $\simeq 8$ and $\tan\delta$ from $\simeq 0.1$ to $\simeq 0.015$) in 0% humidity but further polymer addition does not have any effect. The reduction with 1% polymer may be due to the reduction of volume fraction of water-filled closed pores, which probably does not change with further increase in polymer concentration. This also explains the fact that the addition of polymer has no effect in high humidities, indicating that the deterioration in electrical properties is due to water reacting with the water-soluble polymer and filling up the open porosity in the sample.

TABLE I Comparative physical properties of MDF cements made by method A

	Sample	$\varepsilon_{1\,\mathrm{MHz}}$		$\tan\delta_{1\,\mathrm{MHz}}$		$\varrho_{\mathrm{d.c.}}$ (Ω cm)		Flexural strength (MPa)
		0% r.h.	90% r.h.	0% r.h.	90% r.h.	0% r.h.	90% r.h.	
1	Secar 25/0/100	13.65	19.1	0.1	0.3	8×10^{10}	1×10^6	16
	White Portland cement 30/0/100	11.8	41.0	0.06	1.26	1×10^{10}	1×10^6	11
2	Secar 25/1/0.7/100	8.0	18.7	0.015	0.27	4×10^{12}	5×10^6	20
	White 25/6/0.7/100	9.0	22.0	0.04	0.9	1×10^{11}	1×10^7	–
3	Secar 25/6/0.7/100 → pressed	9.0	19.8	0.03	0.26	1×10^{12}	7×10^6	58
	Secar 11.5/7/0.7/100 → roller mill	9.0	16.0	0.016	0.21	2×10^{13}	2×10^7	108
4	Secar + Ludox (15 + 15)/3/0.7/100	9.3	18.0	0.03	0.3	2×10^{10}	2×10^6	46
5	Secar + AlF_3 (25 + 10)/1/0.7/100	11.9	19.0	0.1	0.4	5×10^{10}	1.3×10^6	–

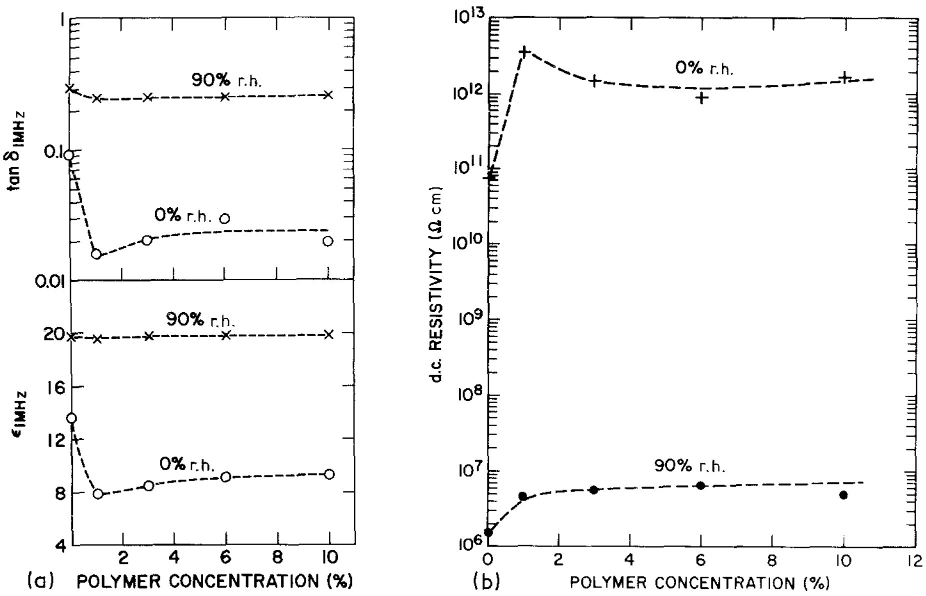

Figure 1 Electrical properties of Secar-71 based cements as a function of polymer composition. (a) Dielectric constant and loss factor at 1 MHz, (b) d.c. resistivity.

The d.c. resistivity data in Fig. 1b show a similar behaviour.

Fig. 2a shows the ε and tan δ values at 1 MHz for a Secar 25/6/0.7/100 sample as a function of the relative humidity. The pronounced deleterious effects of high humidity are evident with $\varepsilon_{1\,\mathrm{MHz}}$ increasing from $\simeq 8$ to $\simeq 20$ and tan δ increasing by more than an order of magnitude. The effect is dramatic in Fig. 2b, where the d.c. resistivity decreases by almost six orders of magnitude when exposed to 90% humidity.

In Table II, we compare the electrical properties of Secar-71 cements processed and cured under different conditions. It can be seen that at lower humidities, samples made by using roller mill (method B) have slightly higher values of dielectric constants and lower losses than samples made by method A – mixing and cold pressing. This is due to the lower porosity of samples made by method B and strength values listed in Table II confirm this. The main components of these cements, the anhydrous mono- and tri-calcium aluminates, when fully sintered have dielectric constants between 8 and 9 at 1 MHz and any lower values should be due to porosity. This lower porosity of the samples made by method B also explains their lower dielectric constant ($\simeq 16$) and loss values in 90% humidity as compared to values of 20 and above for samples made by method A. The d.c. resistivities show a similar trend. The almost identical values at higher humidities for ε, tan δ and $\varrho_{\mathrm{d.c.}}$ listed in the table for the cements made by method B indicate that the different curing conditions have a minimal effect at least on the electrical properties.

In Fig. 3, the changing values in $\varepsilon_{1\,\mathrm{MHz}}$ at 90% humidity for several of the samples – cured under different conditions – are plotted as a function of time. Similar results have been obtained for samples made by method A and seem to indicate two stages of hydration. One possible explanation for this is that the initial gradual increase is due to water and water-filled expanding polymer filling up the micropores present in the as-made samples (open porosity) and to the increasing water concentration in the polymer. As time progresses, this concentration eventually reaches a value enabling the water with the aid of capillary tension to condense into the small "closed" pores (closed in part by polymer), which probably make up a significant portion of the volume [10, 11]. This results in additional water uptake at a stage when diffusion through the softened polymer is much faster; hence the second, sharp increase in ε. However, the

TABLE II Effect of processing and curing conditions on the physical properties of Secar-71 based MDF cements

	Sample	$\varepsilon_{1\mathrm{MHz}}$		tan $\delta_{1\mathrm{MHz}}$		$\varrho_{\mathrm{d.c.}}$ (Ω cm)		Flexural strength (Mpa)
		0% r.h.	90% r.h.	0% r.h.	90% r.h.	0% r.h.	90% r.h.	
1	25/6/0.7/100 → mixed and pressed	9.0	19.8	0.03	0.26	1×10^{12}	7×10^{6}	58
2	11.5/7/0.7/100 → roller mill cured at room temperature	9.15	16.0	0.016	0.21	2×10^{13}	2×10^{7}	108
3	11.5/7/0.7/100 → roller mill cured at 80° C in air for 65 h	8.8	16.3	0.013	0.18	2×10^{13}	3×10^{7}	118
4	11.5/7/0.7/100 → roller mill cured at 80° C and 80% r.h. for 30 h	9.3	16.6	0.035	0.20	2×10^{12}	2×10^{7}	97
5	11.5/7/0.7/100 → hot pressed at 45° C and 7000 p.s.i. ($\sim 48.23\,\mathrm{N\,mm^{-2}}$) and microwaved	11.1	16.5	0.024	0.20	2×10^{13}	2×10^{7}	84

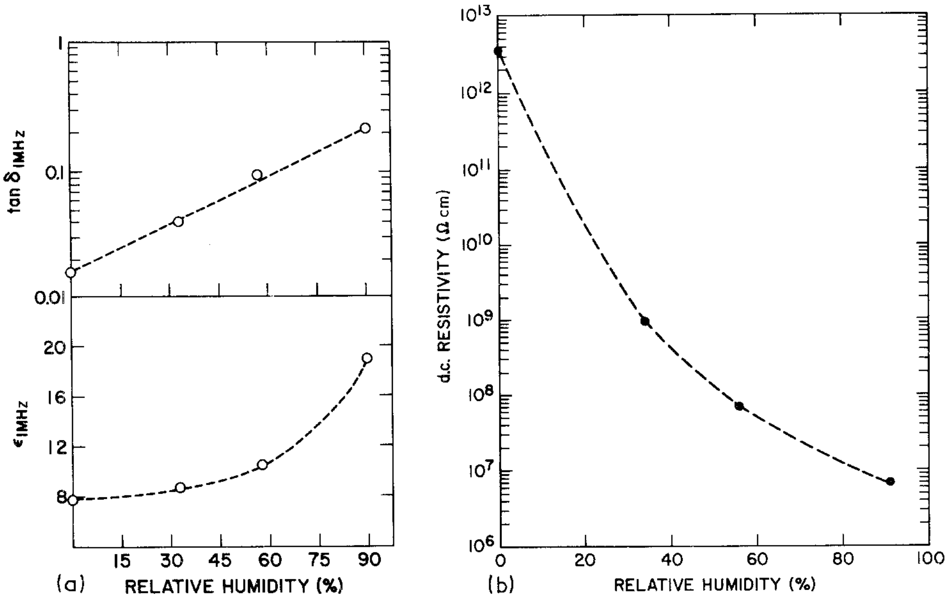

Figure 2 Electrical properties of Secar-71 based cements as a function of relative humidity. (a) Dielectric constant and loss factor at 1 MHz, (b) d.c. resistivity.

transition-like phenomenon may just reflect the passage of the dielectric relaxation rate of PVA-dissolved water through the range of the a.c. frequency of measurement (10^6 sec^{-1}). This is possible in view of the very pronounced softening (i.e. increased mechanical relaxation rate) of partially hyrolysed PVA at high humidity. More data would be needed to decide on the correct explanation. Chemistry is probably not involved, however: when cement samples after equilibration at 90% humidity are transferred back to 0% ambience, ε values decrease to almost the original post-cure values, indicating the reversibility of these hydration effects and the absence of significant post-cure reaction with water.

From the preceding results it appears that when fully densified, in terms of the generally accepted MDF cement terminology, dielectric constants around 9 and d.c. resistivities of $> 10^{12}$ Ω cm can be expected in dry atmospheres. At higher humidities, it is clear that much poorer values are obtained making these materials unsuitable for conventional packaging considerations. One option for eliminating or at least greatly reducing the effect of humidity is to coat the entire surface of the dried sample with a hydrophobic polymer. However, damage such as cracking or chipping of the coating over even a small area will lead to a diffusion of humid air and water absorption throughout the sample through the interconnected capillary network in the cement. The hydrophilic polymer (PVA) originally mixed into cement reduces but does not eliminate water mobility, because of its high solubility in water and its softening effect on the polymer. In order to practically eliminate water diffusion through the sample and the accompanying deterioration in electrical properties, we have opted to impregnate the dried cement with a hydrophobic monomer which is then polymerized *in situ* to permanently fill the open porosity of the cement. The choice of the polymerizable liquid is restricted by the high basicity of the cement and the thermal stability requirements of the product. One such liquid we used was a low-viscosity polydimethylsiloxane (silanol terminated, P.S.340, 50 cP, Petrarch).

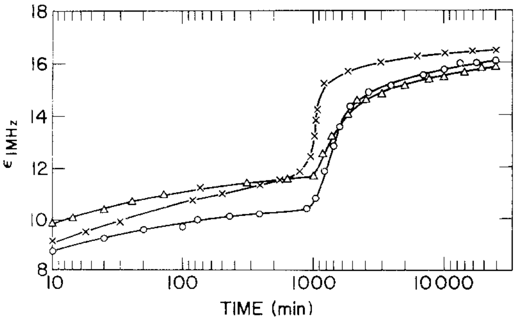

Figure 3 Dielectric constant at 1 MHz for a 11.5/0.7/7/100 cement sample cured under three different conditions as a function of time when exposed to 90% relative humidity: (x) cured at room temperature; (○) heated at 80° C in air for 65 h;(△) heated at 80° C and 80% relative humidity for 40 h.

In a typical impregnation experiment ("siliconization"), the cement sample is vacuum dried at room temperature to remove capillary water and then immersed in the hydrophobic liquid at room temperature under vacuum for up to 4 h. The liquid is drawn into the open capillary network of the sample by surface tension. The sample is then heated in an excess of liquid to 225° C and held there for up to 10 h. The excess silicon gum is removed from the sample surface and direct contact between uncoated cement particles and ambient air is re-established. In Figs 4a and 4b, the effects of high humidity on the electrical properties of such a sample are shown. The results shown are for a Secar 25/1/0.7/100 cement made by method A, but similar results have been obtained for other compositions as well as samples made by method B. The effects of the *in situ* impregnation treatment are obvious from the results shown, with only very small changes in electrical properties even after prolonged exposure to 90% humidity. The very small increase in ε and tan δ in 0% humidity after impregnation and *in situ* polymerization is due to the replacement of air in the cement pores by the polymerized

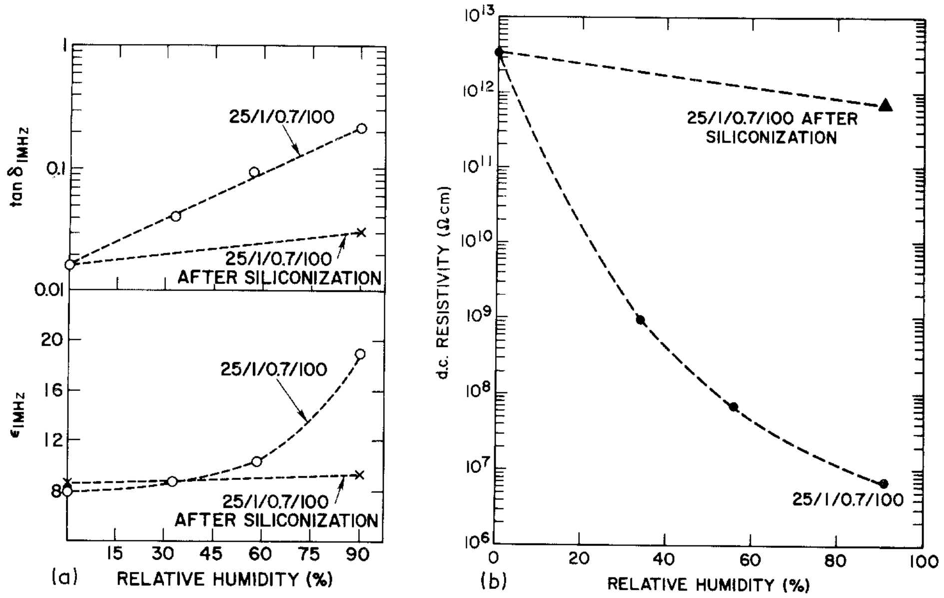

Figure 4 Effect of siliconization on the electrical properties of a 25/1/0.7/100 cement as a function of relative humidity. (a) Dielectric constant and loss factor at 1 MHz, (b) d.c. resistivity.

dimethylsiloxane with a higher dielectric constant (slightly > 2). But by closing up most of the porosity and preventing diffusion of humid air, the impregnation treatment is highly effective in preventing deterioration of the electrical properties.

4. Conclusion

From the preceding results, it is seen that: (1) MDF cements, when fully densified, have dielectric constants comparable to their major constituents, mono- and tri-calcium aluminates ($\simeq 8$ to 9 at 1 MHz); (2) high humidities have a very deleterious effect on their electrical properties; (3) the humidity effects are reversible and may be due to filling up of the microporosity with water; (4) samples made by roller mill processing have lower porosity and higher dielectric constants in dry ambients and are affected less by higher humidities than samples made by mixing and cold pressing; (5) curing conditions have minimal effect on the electrical properties at high humidities; (6) impregnation and *in situ* polymerization with hydrophobic monomer fills up the pores and greatly reduces the effect of humidity.

Thus it can be seen that while the electrical properties of Secar-71 based MDF cements are adequate in dry atmospheres for consideration in packaging applications, they are unsuitable in moderate and high humidities. Impregnation with a hyrophobic monomer and *in situ* polymerization appears to hold promise if the mechanical integrity after such a treatment is adequate. The results of mechanical and electrical measurements on these and samples impregnated with other monomers are presented in a further paper [12].

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