Study of the Factors Affecting the Electrical Conductivity of Zinc–Polycarboxylate Cement

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Synopsis

The behavior of the electrical conductivity of polycarboxylate cement with temperature was studied from room temperature up to 160°C. The effects of powder/liquid ratio, mixing temperature, percentage of MgO in the powder, and aging on this behavior were also investigated. The results obtained revealed that the electrical conductivity decreases with increasing the powder/liquid ratio and with decreasing mixing temperature and the amount of MgO in the powder. The reason for the changes of the conductivity due to the mentioned factors were discussed.

INTRODUCTION

Until recently little has been known about the specific conductivities of various restorative materials. It has long been recognized that the electrical conductivity of the materials used to replace tooth constitutes is a serious problem in restorative dentistry. However, the effectiveness of insulating bases of cements and other nonmetallic materials is not yet completely established.

The composition and several properties of polycarboxylate cement developed for cementing full crown restorations and bridges on teeth with vital pulps have been investigated by a number of workers.[1-5] The conductivity properties of dental cements are of interest because good information can be obtained about the setting reaction[6,7] as well as conduction behavior of the cement.

The aim of the present investigation is to study the effect of some parameters such as aging, mixing temperature, powder/liquid ratio and replacing ZnO by MgO on the electrical conductivity of polyacrylate cement.

EXPERIMENTAL

The commercial polycarboxylate cement used in the present study was Lumien (Bayer). The liquid is an aqueous solution of polyacrylic acid 45% (w/w) and the powder is zinc oxide 90 and 10% (w/w) MgO. The powder was mixed with the liquid with different ratios ranging from 0.5 : 1 to 2 : 1.

Spec pure MgO was mixed with spec pure ZnO to different concentrations namely, 2, 5, 10, 13, and 25%. The resultant mixtures were then added to the above liquid with the ratio recommended by the manufacturer which is 3.5 : 2.

For the electrical conductivity measurements, equal weights of the sample in powder form were placed in special die. The die is placed in hydraulic press for 15 min under 10,000 kg in a vacuum press (Beckman 00-25, Glenrothes Fife, Scotland) to form a disc of about 1.5 mm thickness and 13 mm in diameter. The disc sample was sandwiched between two copper electrodes (similar connection results were obtained with other metal electrodes, such as silver electrodes) using special designed holder where the specimen could be handled and introduced quite easily between these two electrodes. One of these two electrodes connected to the power supply (dry battery) and the other connected in series with suitable standard resistance (10^5–10^{11} Ω). The voltage drop on the specimen or on the standard resistance was measured using a high impedence electrometer of type (VA-J52, Dresden, DDR) and the dc resistance of the sample could be calculated from the relation

$$\frac{V_{\text{sample}}}{V_{\text{standard}}} = \frac{R_{\text{sample}}}{R_{\text{standard}}}.$$

Variation of temperature was carried out using a well-calibrated electric furnace and all the measurements were made in open air. A Beckman 4250 spectrophotometer was used for IR spectra.

RESULTS AND DISCUSSION

Our previous paper[8] about the electrical conductivity of polycarboxylate cement revealed that during the heating of the samples from room temperature up to 160°C an anomalous behavior was observed at 130°C showing a peak at 130°C. Below 130°C, the temperature dependence of the electrical conductivity followed the relation

$$\sigma = \sigma_0 \exp(-\Delta E/kT)$$

with $\Delta E = 1.78$ eV. The mechanism of the conduction in this range is thought to be associated with metal ion migration. The decay of the conductivity above the transition temperature was attributed to unidirectional reaction between the unreacted polyacid and unreacted metal ions. Our previous studies[8] indicated that the processes responsible for the observed decay in the conductivity either by an annealing process below 130°C or by direct heating above that temperature are of the same nature (i.e., further reaction between polyacrylic acid and metal ions). This reaction was found to have an activation energy of 0.22 eV and obey a chemical rate equation with order of reaction $\gamma = 1.2$.

In the present paper similar electrical conductivity behavior was observed as shown in Figure 1, which represents the aging effect on the conductivity values of polycarboxylate cement. However, it was noticed that the electrical conductivity of polycarboxylate cement decreases with increasing the aging of the prepared samples as shown in Figure 1. Curve A refers to the first day measurements (measured after 24 h), curve B was plotted after 3 days, and curve C after 10 days. Curve C remains practically stable in time.

It has been reported that the conductivity of the polycarboxylate cement decreases continuously until the setting reaction, which takes about 1 h,[9] is
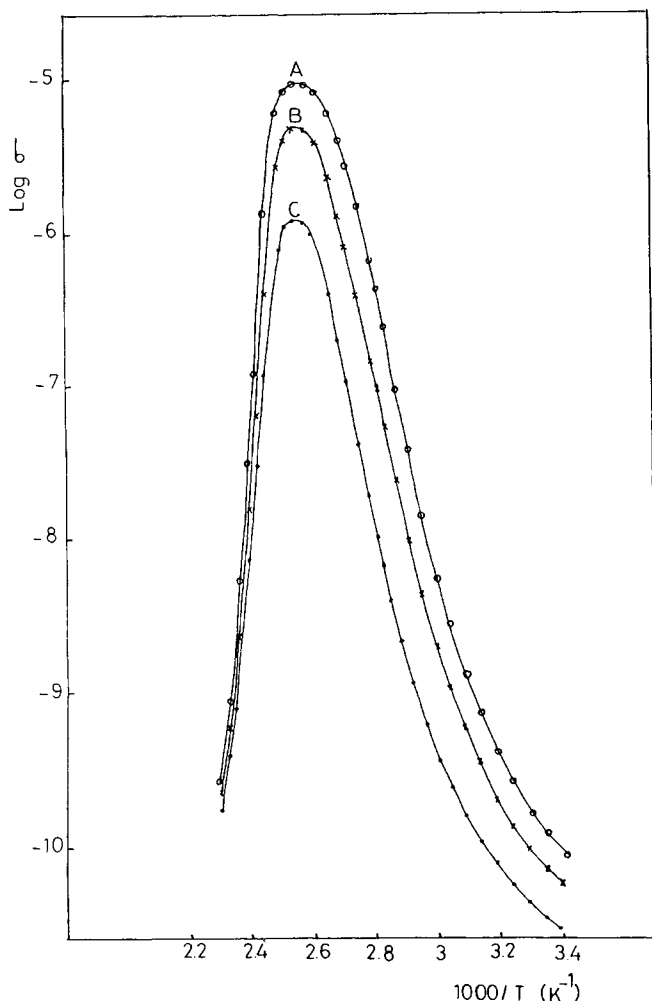
Fig. 1. Relation between $\log \sigma$ and $1/T$ for polycarboxylate cement after aging for different times: (A) 1 day; (B) 3 days; (C) 10 days.

complete. Therefore, it can be concluded from the present results that the concentration process can be continued due to a slow reaction which takes many days at room temperature. This reaction is so slow that it cannot be observed short time after completion of the fast setting reaction. However, by increasing the aging of the prepared cements, further reaction as well as molecular rearrangement may slowly occur, leading to a decrease in the electrical conductivity of the cement. However, 2 days was taken as the standard age for all the test samples in order to avoid unjustified comparisons of values of the conductivity.

Effect of Mixing Temperature upon the Electrical Conductivity

The effect of mixing temperature on the reaction between the polyacrylic acid and metal oxide was previously studied by an IR technique.[10] However, it seemed appropriate to study this effect by the electrical conductivity method.
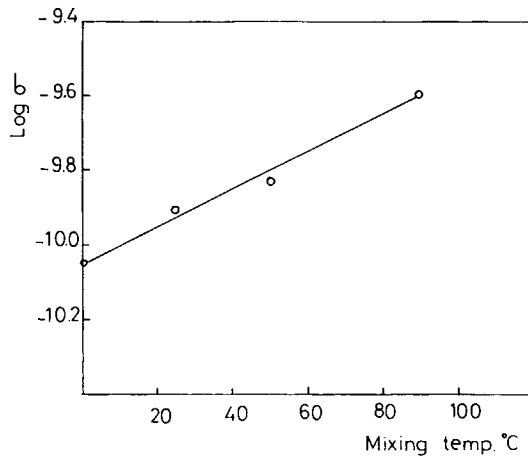
Fig. 2.   Effect of mixing temperature on the electrical conductivity of polycarboxylate cement.

Therefore, the measurements were carried out at different selected mixing temperatures such as 0, 25, 50, and 90°C. These temperatures were used during the setting of the cement for 30 min. Our measurements were carried out at room temperature 2 days after preparation.

Figure 2 shows the relation between the mixing temperature of reaction and the values of log σ at room temperature. It is evident that, the value of log σ decreases with decreasing the mixing temperature. The lowest value of the electrical conductivity of the cement is at 0°C. It was previously concluded thta the metal oxide–polyacrylic acid reaction is an exothermic reaction.[11] Thus one would expect that raising the mixing temperature would result in inhibiting the salt formation. On the other hand, the electrical conductivity decreases with increasing the reaction between the polyacid and metal oxide.[8] Therefore, the present conductivity results were in agreement with these conclusions, since the electrical conductivity was found to be gradually increased by increasing the mixing temperature as a result of incomplete reaction, i.e., the increase in the unreacted free acid by increasing the mixing temperature; this result was also found to agree with IR results.[10]

Effect of Powder / Liquid Ratio

The electrical conductivity of Zn–polycarboxylate cement with different ratios of P/L ranging from 0.5 : 1 to 2 : 1 was also studied. Figure 3 reveals that the P/L ratio has a noticeable effect upon the slope of log σ vs. $1/T$ relation especially in the temperature range 20–160°C.

It can be seen from this figure that increasing the values of P/L ratio leads to decreasing the conductivity. This behavior can be discussed on the bases of the reaction between the polyacid and metal oxide.

At low P/L ratio such as 0.5 : 1, the concentration of the polyacrylic acid with respect to the powder was high. Therefore, strong reaction between the acid and metal oxide was expected where the polyacid plays an important role in this reaction. It can be noticed that the increasing and the decreasing of log σ with $1/T$ were not sharp on the both sides of the transition point (glass
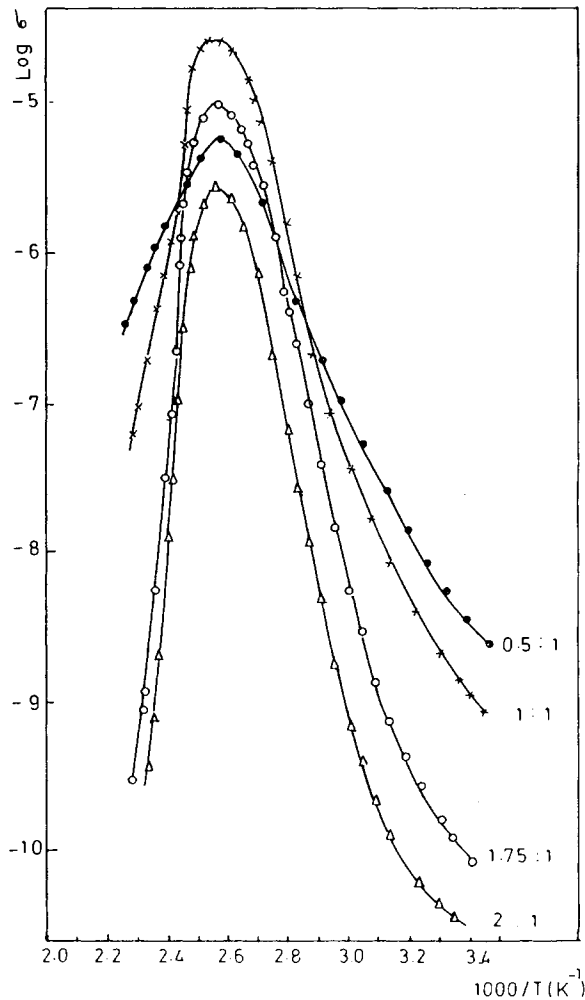
Fig. 3. Relation between log σ and $1/T$ for different powder/liquid ratios (P/L).

transition) at 130°C. This behavior is similar to the conductivity behavior of the polyacrylic acid around the glass transition and therefore can be taken as an evidence to the presence of excess of polyacrylic acid and the absence of metal oxide. By increasing the ratio of P/L up to 1.2 : 1, the product cement was expected to have unreacted polyacrylic acid and unreacted metal oxide. Around the transition point, it can be seen from this that sharp increase in the value of the conductivity was observed to reach maximum at about 130°C. Above this temperature, sharp decay in the conductivity was also observed. This conductivity behavior was attributed to the strong reaction which takes place at the transition point between unreacted polyacid and unreacted metal oxide.

The observed effect of P/L ratio upon conductivity is in good agreement with the previous suggestion of ionic conduction[8] for polycarboxylate cement materials. Thus, for low powder content, it is expected that all the metal oxides are consumed in the reaction. As the powder content was increased, the

unreacted metal oxide concentration consequently took the role in conduction irrespective of the acid radical.

The observed decay in conduction for all P/L ratios beyond the transition temperature and their sharp decrease for P/L ratio more than $1.2:1$ may be attributed to the following. The reaction between polyacrylic acid and metal oxides is known as a partial reaction system[11] which leads to the formation of dangling (i.e.; unsatisfied) bonds which arise from the disordered structure of the amorphous materials as suggested by Mott[12] (polycarboxylate cement is an amorphous material). The presence of these bonds leads to an increase in conductivity. However, for polycarboxylate cement a number of these dangling bonds may have disappeared as a result of heating above the transition temperature ($130°C$), where molecular rearrangement as well as further reaction between unreacted polyacrylic acid and unreacted metal oxide can occur. Consequently, electrical conduction is expected to decrease as a result of the disappearance of some of these dangling bonds which was experimentally observed, on the other hand. The excess metal oxide in the case of high P/L ratio may be incorporated as filler in interstices, which are rigid, thus lowering their mobilities.

The presence of unreacted acid and unreacted metal oxides was also previously confirmed by IR studies.[5]

Effect of Replacing ZnO by MgO

In the present study, magnesium oxide (MgO) was mixed with pure ZnO at different concentrations, namely, 2, 5, 10, 15, and 25%. These mixtures were then mixed with the polycarboxylate liquid with powder to liquid ratio suggested by the manufacturer, namely $3.5:2$. Figure 4 represents the spectra of polycarboxylate cements with different MgO concentration. It can be seen from this figure that the shoulder appearing at about 1700 cm^{-1} in the spectrum of the pure Zn polycarboxylate cement disappeared after adding 10% MgO. It can also be seen that, by increasing MgO over 10%, the COO^- band splits into two peaks, at about 1540 and 1575 cm^{-1} corresponding to COO–Mg and COO–Zn bands, respectively. In the spectrum of the sample containing 25% MgO, the characteristic features of COO–Mg band predominates those of the COO–Zn band. However, the values of the ratios of absorbances ($A(1575$ $cm^{-1})/A(2950$ $cm^{-1})$) were measured and are given in Table I.

The relationship between these ratios and concentration of MgO is represented graphically in Figure 5. It appears from this figure that the value $[A(1575)/A(2950)]$ decreases sharply with the addition of 2% MgO and then increases linearly with increasing the concentration up to 15%. Continued increase in the concentration results in a decrease in the values of this ratio.

The initial decrease in the $[A(1575$ $cm^{-1})/A(2950$ $cm^{-1})]$ can be attributed to the reaction of MgO with the acid groups which may give rise to the COO–MgO band overlapping the COO–Zn band. At lower concentration the COO–Mg band is weak and results in the broadening of the COO–Zn band and in lowering its height. By increasing the concentration up to 15%, the intensity of the COO–Mg band increases and this consequently increases the height of the COO–Zn band. Above 15% the COO–Mg and COO–Zn bands
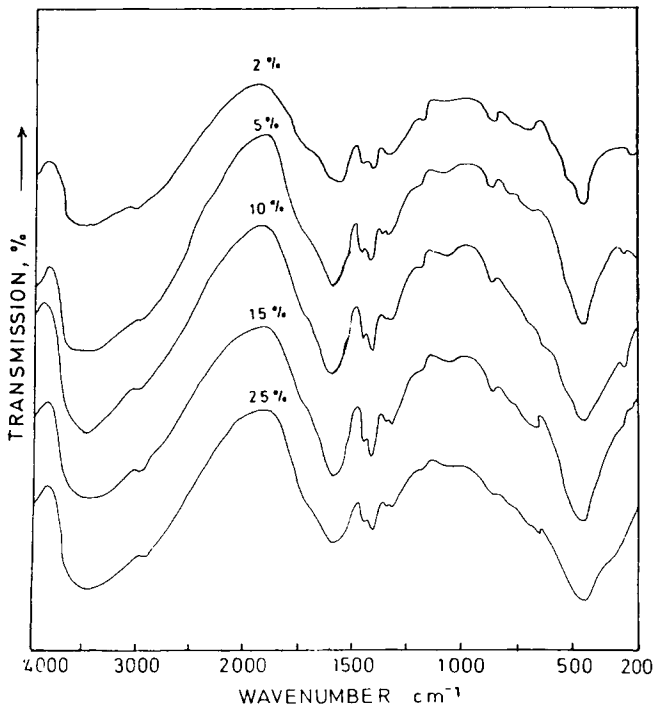
Fig. 4. IR spectra of polycarboxylate cement with varying concentrations of MgO in replacement of ZnO.

begin to appear as two separate bands at 1540 and 1575 cm^{-1}, respectively. It should be borne in mind that the ratio $[A(1575$ cm$^{-1})/A(2950$ cm$^{-1})]$ is a measure of the height of the band and not of its integrated intensity.

On the other hand, electrical conductivity was also studied for the same condition of ZnO/MgO. It was noticed that the value of electrical conductivity decreases with increasing the amount of MgO in the powder as shown in Figure 6. As mentioned before an increase in the reaction between the powder (metal oxide) and the liquid (polyacrylic acid) usually leads to decrease the conductivity of the product cement. Therefore, the present electrical conductivity indicates that increasing the amount of the MgO in the powder until 25% led to increase the reaction between the powder and the liquid of

TABLE I

Data Calculated for Different Concentrations of MgO for P/L Ratio of 3.5 : 2

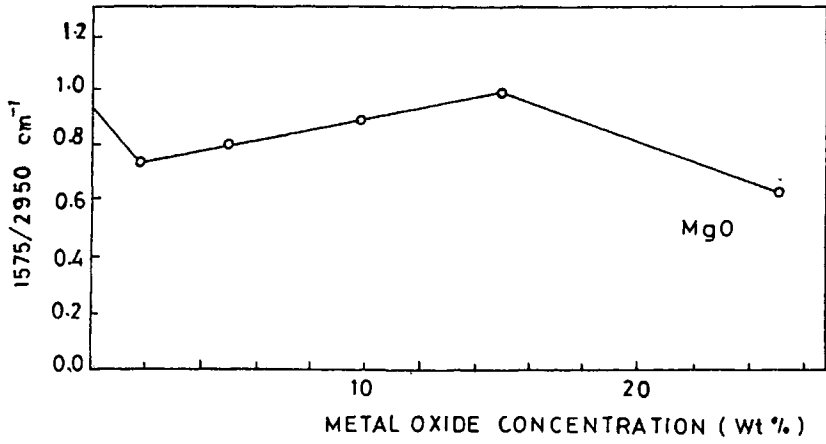| MgO concentration (wt %)	$A(1575$ cm$^{-1})/A(2950$ cm$^{-1})$
0	0.932
2	0.740
5	0.802
10	0.899
15	0.984
25	0.634

Fig. 5. Effect of metal oxide concentration on the ratio for the absorption band intensity at 1575 and 2950 cm^{-1}.
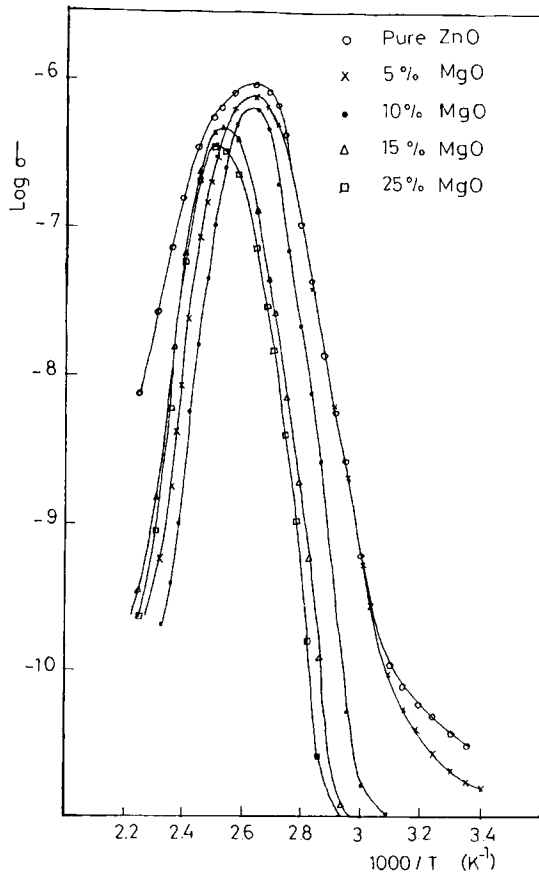

Fig. 6. Relation between $\log \sigma$ and $1/T$ for polycarboxylate cement containing varying concentrations of MgO in replacement of ZnO.

TABLE II
Weight and Mole Ratios of Powder Composition

Sample no.	Wt ratio		Mole ratio		Total moles of metal oxide relative to sample no. 1
	ZnO	MgO	ZnO	MgO	
1	100	—	100	—	100
2	95	5	94.97	10.04	105
3	90	10	90.03	20.09	110.12
4	85	15	85.00	30.15	115.14
5	75	25	74.95	50.24	125.19

polycarboxylate cement. However, the IR and conductivity results on the effect of MgO on the reaction between the metal and polyacid can give evidence about the role that MgO plays in the reaction.

The observed decrease in conductivity upon replacing ZnO by MgO is not in contradiction with the results reported before.[7] Most of these studies concerned the replacement upon weight ratios without consideration for the differences in the molecular weight of the two oxides.

Referring to Table II, it is clear that the total metal oxide concentration in moles increases progressively upon replacing equal weight parts of ZnO by MgO. This is due to the large difference in their molecular weights. Thus one may expect more salt formation upon this replacement; consequently, the electrical conductivity would decrease progressively upon replacing ZnO by MgO.

The effect of replacing ZnO by MgO may also be explained by recalling the fact that the ionic radius of Mg^{2+} is less than that of Zn^{2+} (0.65–0.74), respectively. The lower ionic radius of Mg^{2+} may lead to more compact products with small interstices which decrease the defects or missing atoms thus decrease the conductivity of the product cement.

The progressive increase of the transition temperature with increasing MgO concentration in the powder may be easily explained by considering the difference in the bond strength of the MgOH in comparison with that of ZnOH. Thus by suggesting the pendant half salt as an intermediate stage before the final glass formation which is mainly[11] disalt, one would expect higher glass transition temperature for the Mg disalt than that of Zn disalt.

These results and conclusions are in good agreement with the previous suggestions reached by Fields and Nielsen,[11] who found that the complete reaction of ZnO to give disalt increases the glass transition temperature.

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