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Effect of carbon addition on the ferroelectric hysteresis properties of lead zirconate–titanate ceramic–cement composites

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Abstract

Piezoelectric composites made from lead zirconate–titanate ceramic and cement have recently been developed as sensors in smart concrete structures due to their compatibility with the host concrete structure. However there is difficulty in poling the composite due to the insulating nature of the cement phase. In this work, carbon powder was used as a conducting phase in the composites at up to 2.0% by volume. The ferroelectric properties of the composites were investigated. For the same electric field, composites with added carbon were found to have higher polarization values. Therefore, this suggests that carbon could be added as a conducting phase to lead zirconate–titanate ceramic–cement composites in order to improve their polarization.

Keywords: Lead zirconate–titanate; Cement; Composite; Carbon; Ferroelectric hysteresis

1. Introduction

Cement-based piezoelectric composites consisting of piezoelectric lead zirconate–titanate ($(Pb(Zr_{0.52}Ti_{0.48})O_3$ or PZT) ceramic [1–19] play an important role in the development of structural health monitoring of concrete structures, where they can be used as sensors–thus making the structures, so-called, ‘‘smart’’ or ‘‘intelligent’’ [7]. The use of such composites would provide an advantage in the matching of structural concrete [1]. Li et al. [1] showed that 0–3 white Portland cement–lead zirconate–titanate (PZT) piezoelectric composites can overcome the matching problem, and that for ≈40–50% PZT by volume, the acoustic impedance is close to that of concrete, i.e. 8.95×10^6 kg m^{-2} s^{-1} as compared to PZT (≈21.2×10^6 kg m^{-2} s^{-1}).

It is difficult to obtain good piezoelectric properties for 0–3 connectivity composites due to the poling difficulty of ceramic particles. One way to effectively improve their poling, is to create a continuous electric network between piezoelectric particles, by the introduction of a small volume fraction of a third phase, such as graphite (C), germanium (Ge) or silicon (Si) [20–23]. An increase in the piezoelectric coefficient has been found when carbon, in the form of graphite, was used at 1.5% by volume in PZT–polymer composites, where the piezoelectric coefficient values for PZT–polymer composites, with and without carbon, are 35 pC/N and 15 pC/N, respectively [23]. Furthermore, for 0–3 connectivity cement-based composites (0 represent disperse phase of PZT piezoelectric ceramic and 3 represent matrix phase of cement), it has been reported that the dielectric and piezoelectric properties can be improved through the addition of carbon black as a conductive phase [24,25].

No studies have yet been reported on ferroelectric hysteresis (which is an important behavior for materials with ferroelectric properties [15,16], that can be used to indicate the difficulty of the poling process involved) of piezoelectric–cement composites with carbon particles added as the third phase. It is thus the aim of the current work to investigate the ferroelectric hysteresis behavior of piezoelectric–cement composites with carbon particles added as the third phase.

2. Experimental procedure

In this work, composites consisting of Portland cement (PC) matrix and lead zirconate–titanate (PZT) ceramic, with carbon

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particles, were prepared using the pressed and cured method in which the samples were first pressed together before curing. PZT ceramic particles (median size 450 μm) of composition $Pb(Zr_{0.52}Ti_{0.48})O_3$ were produced from PZT pellets sintered at 1,250 °C for 3 h. The PZT ceramic particles were then mixed with Portland cement (PC) to produce 0–3 connectivity using 1:1 PZT ratio to Portland cement (ASTM type I) by volume. Carbon was also added as the third phase in the composite at 0, 0.5, 1.0 and 2% by volume. The composites were then cured at 60 °C and 98% relative humidity for 3 days before measurement [7]. Ferroelectric hysteresis (*P–E*) loops were determined at room temperature using a computer-controlled modified Sawyer–Tower circuit [26]. An electric field was applied to a sample, from a signal generator, by a high-voltage AC amplifier, with an input sinusoidal signal and a frequency of 50 Hz.

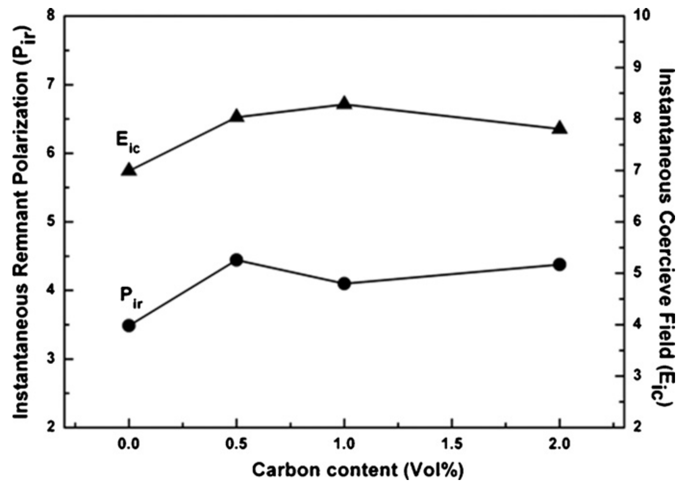

Fig. 2. Effect of carbon phase on the instantaneous remanent polarization (P_{ir}) and coercive field (E_{ic}) of PZT–cement composites.

3. Results and discussion

The polarization–electric field (*P–E*) loops of PZT ceramic–Portland cement composites, with added carbon, are shown in Fig. 1. It should be noted that all ferroelectric hysteresis loops (*P–E* loops) of the PZT ceramic–cement composites show a ''lossy'' feature, with round tips as a result of cement matrix in the composites. This is believed to be due to weak conducting ions such as Ca^{2+}, OH^- and Al^{3+} in the cement matrix. The ions begin to migrate in alignment with the polarization of the PZT ceramic – hence a lossy feature is then observed in all the *P–E* loops obtained. Since it is impossible to achieve fully saturated loops with a lossy behavior, for comparison purposes we defined the *y*-axis intercept at a given applied field as the ''instantaneous'' remanent polarization (P_{ir}), and the *x*-axis intercept as the ''instantaneous'' coercive field (E_{ic}) [15]. It is clear from these hysteresis measurements, that the carbon phase has an effect on the polarization–electric field loop, where composites with added carbon phase are found to show higher polarization, and where the P_{ir} value of all composites with carbon phase can be seen to increase (Fig. 2). The highest P_{ir} value is at $\approx 4.5 \times 10^4$ μC/m^2 when using carbon, as the third phase at 0.5% by volume. This is $\approx 1.0 \times 10^4$ μC/m^2 (a 30% increase) higher than the composites with no added carbon (3.5×10^4 μC/m^2). There appears to be a significant and noticeable increase when the carbon phase is added at 0.5%. Thereafter P_{ir} values remain approximately the same, with no further increase observed. Therefore it would appear that the optimum is reached in this range of 0.5–2% by volume. Nonetheless, these values are all noticeably higher than for composites with no carbon phase.

Furthermore, E_{ic} is seen to increase from $\approx 7.0 \times 10^2$ kV/m to $\approx 8.0 \times 10^2$ kV/m when comparing the E_{ic} values of composites, with no carbon, and with added carbon, as the third phase. Similarly, with the increase in the P_{ir} value, the E_{ic} value is increased most significantly when carbon is added at 0.5% v/v, and remains fairly constant at $\approx 8.0 \times 10^2$ kV/m when carbon is further added up to 2% v/v. This, therefore, would suggest, that the composite would benefit from the

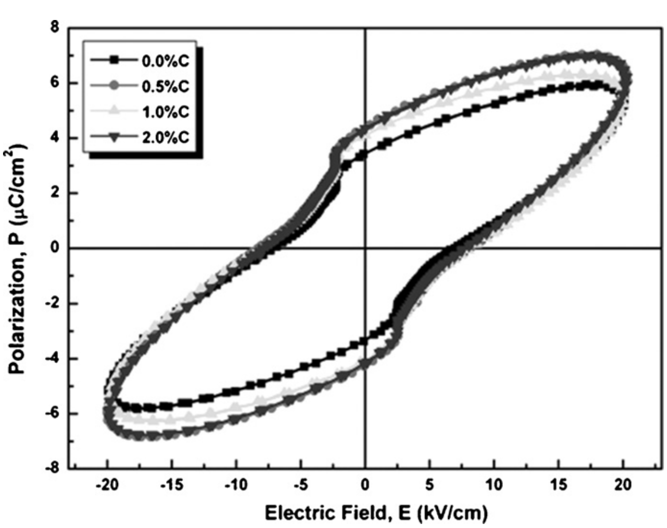

Fig. 1. Effect of carbon phase on the ferroelectric (*P–E*) hysteresis loops of PZT–cement composites.

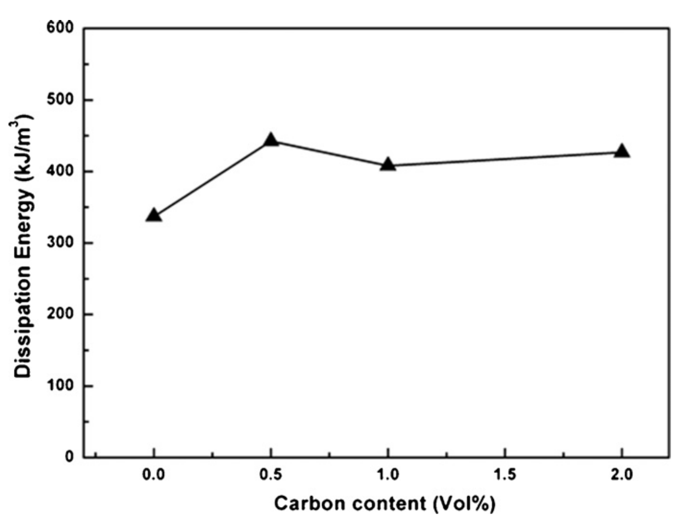

Fig. 3. Effect of carbon content on the dissipation energy determined from the P-E hysteresis loop area of PZT–cement composites.

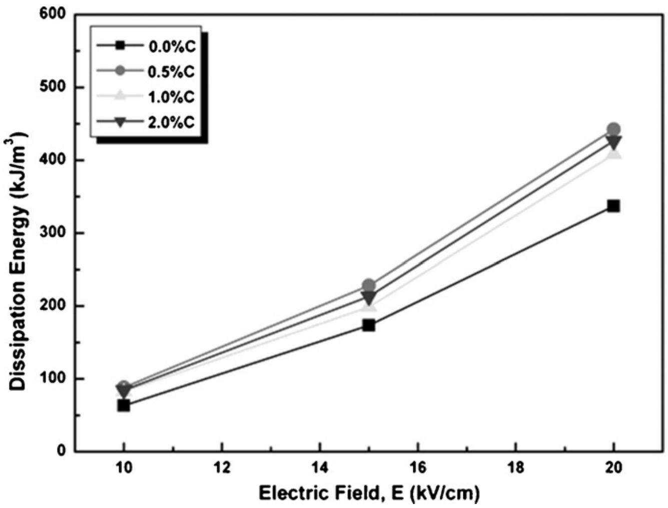

Fig. 4. Variation with electric field of the dissipation energy of PZT–cement composites at various carbon contents.

carbon phase – since the applied electric field is the same at 20×10^2 kV/m, more electric field would be applied at zero polarization. The carbon phase thereby acts as a conducting phase and also as a connecting network between the cement matrix and PZT ceramic particles.

Although all composites were found to resemble typical ferroelectric hysteresis loops, the loss is still observed. The lossy characteristic is noticed from the round tips of the *P–E* loops and also by the loop area. Thus, when plotting the dissipation energy (determined from the *P–E* hysteresis area) against the carbon content, as shown in Fig. 3, it is observed, that the area, increases with increased carbon phase content. The trend is also similar to that for the P_{ir}. Furthermore, it should be noted that the increasing trend of the dissipation energy, with the carbon content, is generally the same in an applied electric field in a range of $10–20 \times 10^2$ kV/m and a frequency of 20–100 Hz, as shown in Figs. 4 and 5, respectively. It is understandable that the loss would increase

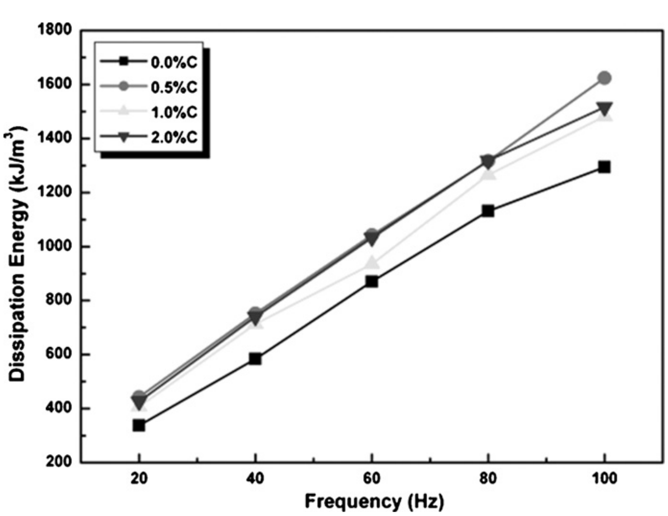

Fig. 5. Variation with frequency of the dissipation energy of PZT–cement composites at various carbon contents.

due to the increase in conducting material. This would agree with the reported results on the dielectric loss (tan δ) in previous investigations [24,25] with the use of up to 1.4% v/v carbon black. It is even more interesting to observe (Figs. 4 and 5) that at a given carbon content the dissipation energy is seen to increase with both the electric field amplitude and frequency. An increase of the loop area with electric field amplitude is intuitively expected, as has also been reported in several previous investigations [27–30]. The nearly linear increase of the loop area with the frequency is, on the other hand, unexpected. Generally, in ferroelectric ceramics, the observation, which the loop area decreases with increasing frequency, is ascribed to the delayed response of the polarization reversal to the varying external field [27–30]. However, the increase of the loop area, with increasing frequency, observed in the present study, is not fully understood, but could be attributed to the presence of the conducting carbon phase in the composites.

4. Conclusions

This work showed an increase in the polarization in PZT–Portland cement composites when carbon is added as the third phase, which supports the results reported recently for improved dielectric constant and piezoelectric coefficients of PZT–cement composites with added carbon black. Therefore, this would suggest, that adding the carbon phase to the composite system, would improve the network within the cement matrix (the three-dimensional matrix) and that poling can be enhanced, giving better piezoelectric properties.

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