

Dielectric constant of silver-thermosetting polyester composites

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The dielectric constant of a conductor-insulator composite is measured and no percolation threshold is observed up to $V = 45\%$, where V is the volume fraction of conducting filler. The composite is fabricated by dispersing silver-coated glass spheres in unsaturated polyester. It is found that the dielectric constant varies smoothly as $(1 - V)^{-3}$ within the experimental range and that this relationship may be satisfactorily interpreted on the basis of classical electromagnetic theory.

1. Introduction

In a previous paper [1] studies on the d.c. electrical conduction of composites fabricated from unsaturated polyester with silver powder (SP) and silver-coated glass spheres (SCGS) as fillers were reported. It was found that SCGS samples have more stable current characteristics than SP samples. It was also pointed out there that the d.c. electrical behaviour of these composites is history dependent which suggests that some permanent changes begin to occur in the composite, e.g. the formation of conducting filaments, once a current starts to flow after the switch-on voltage is reached.

This investigation extends the study to the dielectric constant at audio frequencies of freshly prepared SCGS samples free from the effects of conditioning. A prerequisite for avoiding conditioning of the sample is to keep the applied voltage below its threshold value, hence a small a.c. voltage is used in our measurements.

Studies of the dielectric constant of a heterogeneous system having a conducting phase dispersed in an insulating phase appear to have drawn quite some attention in the literature recently. The main interest seems to arise from the work of Fortuin and Kasteleyn [2] who point out the similarity between percolation and second-order phase transitions, and the works of Kirkpatrick [3, 4] who advocates a scaling hypothesis according to which certain transport properties, e.g. electrical conductivity and dielectric constant,

of a percolating system should obey a power-law relationship. Experimentally and by computer simulation, the scaling theory is verified in many systems as far as electrical conductivity is concerned. It appears that the first experimental observation of a dielectric singularity at percolation threshold is that of Grannan *et al.* [5], who also affirm the validity of the scaling law.

The results of dielectric constant measurements in our present work on freshly prepared SCGS-polymer samples with a volume concentration of the conducting phase ranging from 0% to 45% do not, however, exhibit any percolation threshold within the range, and the dielectric constant increases smoothly from 0% volume concentration to about six-fold at 45%. As typical percolation thresholds from percolation calculations lie far below 45% volume fraction, we believe that percolation effects, if any, are unimportant in our unconditioned samples. Traditional expressions such as Maxwell's formula cannot account for the measured values of dielectric constant towards the high concentration end. We have, however, in this paper, demonstrated that a theory based on classical electromagnetism may be constructed for a two-phase heterogeneous system which gives satisfactory agreement with the experimental data.

2. Experimental results

The materials used in this investigation as well as the sample preparation procedure are the same as in the previous study [1], except that for the

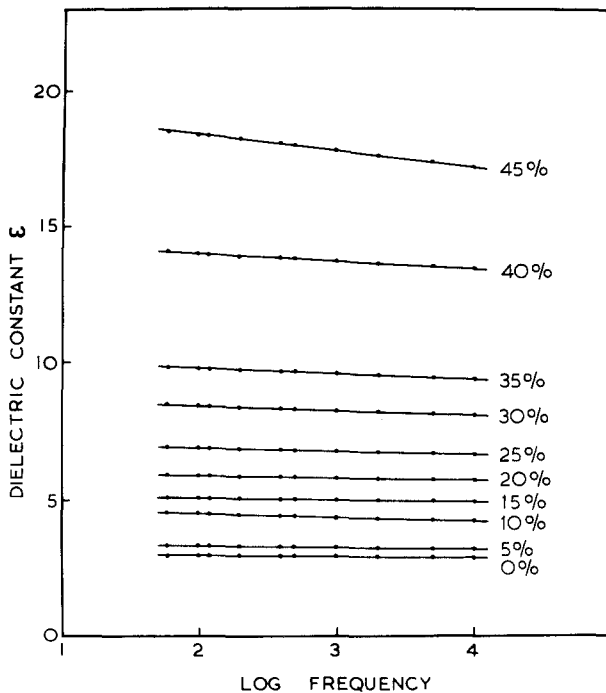


Figure 1 Dielectric constant as a function of log frequency for various volume concentrations of SCGS filler. The data points represent average values.

present purpose of dielectric measurement, silver epoxy was not pasted on to the samples. Samples with volume concentrations of silver-coated glass spheres up to 45% were prepared, each being 8 cm diameter and 1.8 mm thick, and for each volume concentration measured, there belonged at least two samples.

The dielectric constant of each sample at room temperature was measured using a General Radio capacitance bridge at audio frequencies (60 to 10^4 Hz) with a peak-to-peak voltage of about 1 V, a voltage below the threshold voltage of all samples.

The results of the dielectric constant measurements on samples of various SCGS concentrations at audio frequencies are plotted in Fig. 1. Here the data points represent average values and, although not indicated, the experimental spread tends to be larger for higher concentrations of filler. (This is apparent in subsequent figures where experimental spreads are drawn in.) It is noted that:

1. the dielectric constant for a given concentration of filler has a measurable frequency dependence and it bears a fairly linear relationship with log frequency, and
2. the slope of these lines increases (in absolute value) with concentration and is more marked for higher concentrations.

To compare with recent experimental results

reported in [5], the dielectric constant at 1 kHz is plotted against filler volume concentration in Fig. 2. The absence of a "singularity" at some (critical) concentration within our range may be interpreted to mean that percolation effects in our freshly prepared samples are insignificant. Of course, one cannot exclude the possibility that a concentration threshold existed somewhere beyond 45%; if this were the case, then these SCGS-polyester composites had a percolation threshold higher than any reported, typical values of which are in the 15% to 25% range.

Perhaps it is relevant to remark here that our inability to produce samples with concentrations higher than 45% was mainly due to the high viscosity and poor flow characteristics of the resulting mix which render moulding of the sample very difficult. Indeed for the same reason the experimental spread for the dielectric constant of the 45%-samples is appreciably larger than for samples of lower concentrations.

Coming back to Fig. 2, it was found that a power law of the form

$$\epsilon(V) = \epsilon_p(1 - V)^{-3} \quad (1)$$

gives a good fit to the experimental data. Here $\epsilon(V)$ is the dielectric constant of the composite at volume concentration V , and $\epsilon_p \equiv \epsilon(0)$ is the dielectric constant of the unsaturated polyester and has an average value of 2.946 at 1 kHz. If

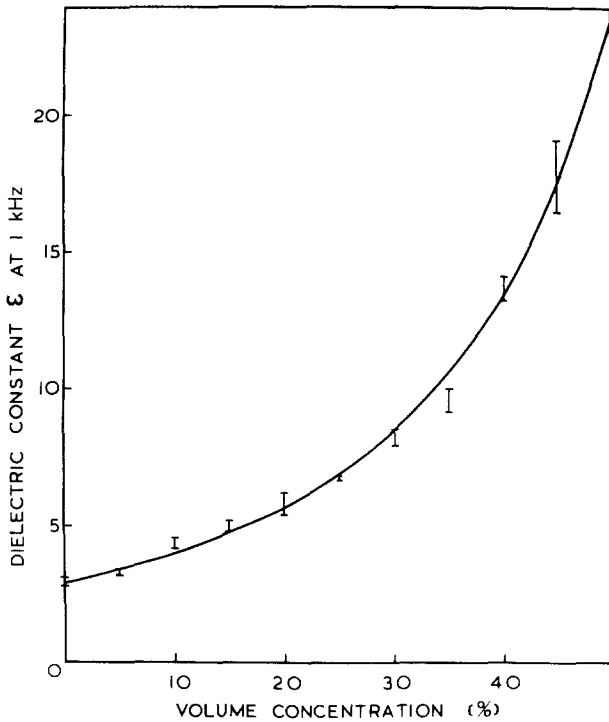


Figure 2 Dielectric constant at 1 kHz for various concentrations. The solid line depicts the fitting given by Equation 1, where $\epsilon_p = 2.946$, the average experimental value at 1 kHz, is used.

Equation 1 is interpreted as a scaling law, then the percolation threshold is at $V = 100\%$.

3. Theoretical interpretation

Variation of dielectric constant with volume concentration of conducting filler such as that given by Equation 1 suggests that percolation effects are unimportant in the SCGS-polyester composites investigated.

It should be noted that our samples are not fabricated under pressure and the freshly prepared samples have negligible conductance if the applied voltage is less than their respective threshold voltages [1]. This suggests that the surfaces of the silver-coated glass spheres may have been well wetted by the resin during mixing, resulting in a final composite with "separate particles", to use a terminology of Scarisbrick [6], and without the application of a large enough field to aid the formation of a labyrinth of "conducting paths", the particles remain quite unconnected electrically. These circumstances, therefore, do not favour the occurrence of percolation phenomena. Hence we attempt to seek for a theoretical understanding of Equation 1 in classical electromagnetic theory.

Classical expressions for the calculation of the effective dielectric constant for a two-phase heterogeneous system with a conducting phase include Maxwell's formula

$$\epsilon(V) = \frac{1 + 2V}{1 - V} \epsilon_p \quad (2)$$

and its modifications [7, 8]. These formulae invariably predict values of dielectric constant much too low in comparison with our data; for example, $\epsilon(40\%) = 3\epsilon_p$ from Equation 2, whereas our experimental value is $\sim 4.6\epsilon_p$. For low concentrations, however, Equation 2 is satisfactory.

The theory proposed here for the calculation of dielectric constant to higher concentrations of conducting filler is built on the validity of Equation 2 for low concentrations. We follow a common practice in the literature, for example, in [9], by considering the corresponding electrostatic problem.

Consider a spherical conductor of radius a sitting in an infinite matrix of an insulator of dielectric constant ϵ_p in the presence of an electric field of strength E_0 far away from the conductor. Take the origin to be the centre of the sphere and the polar axis $\theta = 0$ parallel to the field direction. Then the potential ϕ at a point (r, θ) outside the conductor is given by

$$\phi(r, \theta) = -E_0 \left(1 - \frac{a^3}{r^3} \right) r \cos \theta \quad (3)$$

Now consider a composite sphere of radius R ($R > a$) consisting of a conducting sphere of

radius a at its centre surrounded by an insulator of dielectric constant ϵ_p . Supposing that its effective dielectric constant is ϵ_1 , then $\phi(r, \theta)$ outside the composite sphere may be written as

$$\phi(r, \theta) = -E_0 \left(1 - \frac{R^3}{r^3} \frac{\epsilon_1 - \epsilon_p}{\epsilon_1 + 2\epsilon_p} \right) r \cos \theta \quad (4)$$

On comparing Equations 3 and 4, we get

$$\frac{\epsilon_1 - \epsilon_p}{\epsilon_1 + 2\epsilon_p} = \frac{a^3}{R^3} = V_1 \quad (5)$$

= volume concentration of filler in this case

or, after rearrangement,

$$\epsilon_1 = \frac{1 + 2V_1}{1 - V_1} \epsilon_p \quad (6)$$

which is the usual expression, Equation 2.

Now we shall repeat the same calculation as outlined above with the original insulator replaced by one of dielectric constant ϵ_1 . If ϵ_2 stands for the effective dielectric constant of the composite sphere, then the expression corresponding to Equation 5 is

$$\frac{\epsilon_2 - \epsilon_1}{\epsilon_2 + 2\epsilon_1} = \frac{a^3}{R^3} = V_1 \quad (7)$$

which, after rearrangement, gives

$$\epsilon_2 = \frac{1 + 2V_1}{1 - V_1} \epsilon_1 = \left(\frac{1 + 2V_1}{1 - V_1} \right)^2 \epsilon_p \quad (8)$$

where Equation 6 has been used to arrive at the last equality. To calculate the volume concentration, V_2 , of conducting filler in this composite sphere of radius R , we note that the volume of the conductor situated at its centre is $\frac{4}{3}\pi a^3$ and that the remaining volume of the sphere, of dielectric constant ϵ_1 , has effectively the following composition: a conductor content of $\frac{4}{3}\pi(R^3 - a^3)V_1$ in an insulator of dielectric constant ϵ_p . Thus

$$V_2 = \frac{\frac{4}{3}\pi a^3 + \frac{4}{3}\pi(R^3 - a^3)V_1}{\frac{4}{3}\pi R^3} \\ = V_1 + (1 - V_1)V_1 = 1 - (1 - V_1)^2 \quad (9)$$

By repeating the above procedure of replacing the dielectric medium successively for n times, we finally have

$$\epsilon_n = \left(\frac{1 + 2V_1}{1 - V_1} \right)^n \epsilon_p \quad (10)$$

$$V_n = 1 - (1 - V_1)^n \quad (11)$$

Equations 10 and 11 may be combined to give

$$\epsilon_n = \frac{[3 - 2(1 - V_n)^{1/n}]^n}{1 - V_n} \epsilon_p \quad (12)$$

after elimination of the parameter V_1 . Equation 12 gives the effective dielectric constant, ϵ_n , of a composite sphere having a volume fraction, V_n , of conducting filler. When n becomes sufficiently large, i.e. when the composite contains a sufficiently large number of conducting particles, ϵ_n approaches the limit $[1/(1 - V_n)^3] \epsilon_p$. (The mathematical details involved in the calculation of this limit are given in the Appendix.) Bearing in mind the meaning of the symbols, this last result is identical to the experimental result of Equation 1.

To recapitulate on the method of approach of this theory for the calculation of the effective dielectric constant, $\epsilon(V)$, of a composite containing a volume fraction, V , of conducting particles, we first start with a medium of dielectric constant $\epsilon(0)$. Then particles are added to it one by one until the desired volume concentration of particles, V , is reached. As each particle is added, the effective dielectric constant is altered, and the next particle interacts with the "new" medium. In so doing, we have avoided the necessity of considering the very difficult problem of mutual interactions amongst particles.

4. Discussion and conclusions

We have investigated unconditioned SCGS-polymer samples in a small a.c. voltage and findings on the variation of dielectric constant as a function of both the SCGS volume fraction and frequency are reported in this paper. When compared with recent work [5], our experimental results, shown in Fig. 2, of dielectric constant as a function of volume fraction of conducting filler for a fixed frequency (1 kHz) does not show an expected threshold concentration within the range investigated (0% to 45%). Whereas Grannan *et al.*'s samples are press-moulded [5] and hence the silver particles are capable of making direct contact with one another, each silver particle in our samples is likely to be encased by a film of polyester because of the wetting property of the resin. We believe the lack of direct contact between the conducting particles renders our heterogeneous system a non-percolative one.

Our experimental dielectric constant values are notably higher than the theoretical values of Meredith and Tobias [8] for volume fractions beyond, say, 30%. Their prediction is, of course,

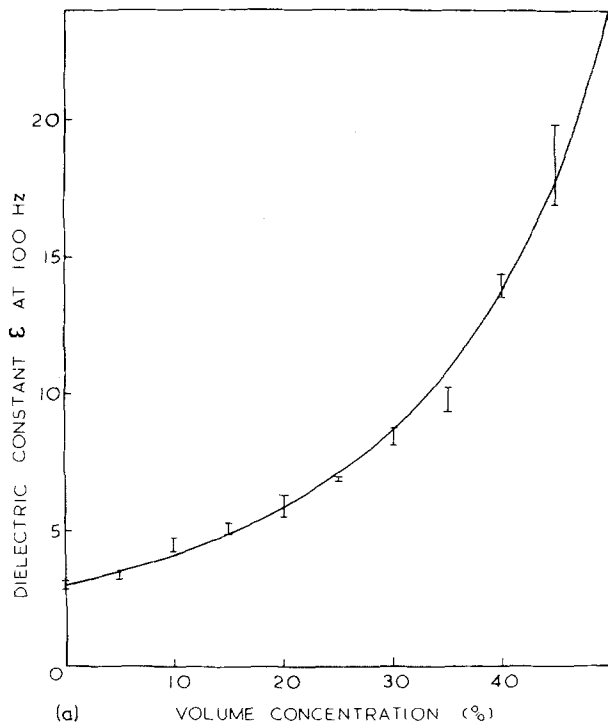


Figure 3a Dielectric constant at 100 Hz plotted against volume concentration. The solid line depicts the theoretical curve in which the average experimental value $\epsilon_p = 3.007$ at 100 Hz is used.

based on a cubic array of spherical conductors whereas our system may be considered as having a randomly distributed conducting phase. Therefore, it appears that a random distribution gives higher values of dielectric constant, or other conduction properties for that matter, than a regular array of conductors.

The theoretical calculation of dielectric constant given in the previous section is essentially based on the accuracy of Equation 2 for low volume concentration of conducting filler together with an iteration procedure which allows the dielectric constant to be calculated for higher concentrations. The simple final expression, identical to Equation 1, fits our data at 1 kHz well. The fact that we have used Equation 1 to fit dielectric constant/volume fraction data at a fixed frequency (1 kHz), implies that we have implicitly assumed the relation

$$\epsilon(\omega) = \frac{\epsilon_p(\omega)}{(1 - V)^3} \quad (13)$$

to hold, at least approximately, for the frequency range investigated. Similar remarks should also apply to those works in the literature where theoretical results arising from electrostatic calculations are compared to measurements at fixed frequencies (usually 1 kHz). Such a comparison is justifiable provided that the loss peak is suffi-

ciently far away from the experimental frequency/frequencies.

That Equation 13 is a satisfactory description of our data is further illustrated in Figs. 3a and b for 100 Hz and 10 kHz, where the average experimental values $\epsilon_p(100 \text{ Hz}) = 3.007$ and $\epsilon_p(10 \text{ kHz}) = 2.901$ are used, respectively. In fact, according to Equation 13, the slopes in Fig. 1 are proportional to $1/(1 - V)^3$, which therefore tend to increase with volume concentration, as noted earlier in Section 2.

The deficiency of the theory, however, lies in its inability to predict anomalous effects when the packing of conductors reaches a close-pack situation at $V \approx 74\%$. In principle, the volume fraction of any sample cannot go beyond this limit if the spherical particles are identical in size. Our formula fails to give any clue to an upper limit of this kind. Perhaps it is relevant to remark here that the Rayleigh formula and the formula of Meridith and Tobias are also deficient in this regard.

Appendix

We shall evaluate the limit of ϵ_n in Equation 12 as n tends to infinity.

Taking the logarithm of Equation 12, we obtain

$$\ln \frac{\epsilon_n}{\epsilon_p} = n \ln [3 - 2(1 - V_n)^{1/n}] - \ln (1 - V_n) \quad (14)$$

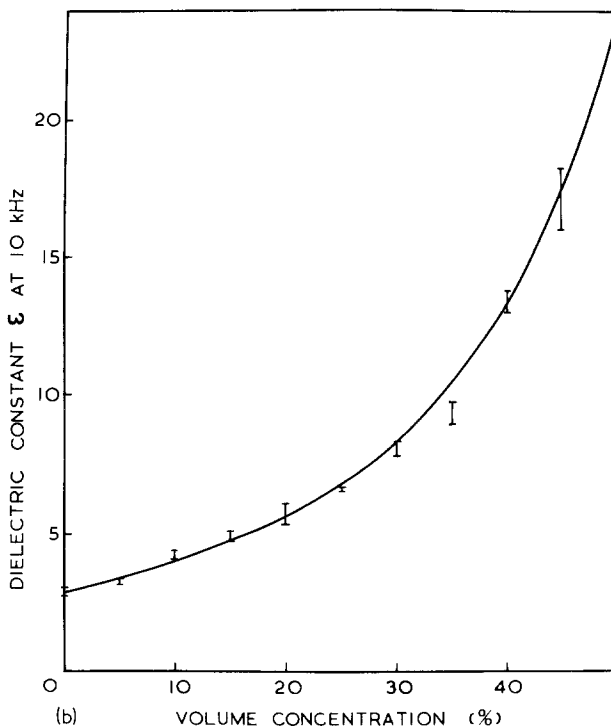


Figure 3b Dielectric constant at 10 kHz plotted against volume concentration. The solid line depicts the theoretical curve in which the average experimental value $\epsilon_p = 2.901$ at 10 kHz is used.

As $n \rightarrow \infty$, the left-hand side becomes $\ln(\epsilon/\epsilon_p)$ and the second term on the right-hand side is $\ln(1-V)$; however, the first term on the right is indeterminate, of the form $\infty \cdot 0$, and may be evaluated by L'Hospital's rule. Thus

$$\begin{aligned} \lim_{n \rightarrow \infty} n \ln [3 - 2(1-V)^{1/n}] \\ &= \lim_{m \rightarrow 0} \frac{\ln [3 - 2(1-V)^m]}{m} \\ &= \lim_{m \rightarrow 0} \frac{-2(1-V)^m \ln(1-V)}{[3 - 2(1-V)^m]} \Big/ 1 \\ &= -2 \ln(1-V) \end{aligned}$$

where $m = 1/n$.

Putting this limit into Equation 14 yields

$$\ln \frac{\epsilon}{\epsilon_p} = -3 \ln(1-V)$$

or $\epsilon = \epsilon_p/(1-V)^3$ which is the desired result.

Table I gives an idea of how fast ϵ/ϵ_p approaches $1/(1-V)^3$.

TABLE I

V	ϵ/ϵ_p for $n =$				
	10	20	50	100	∞
10%	1.367 26	1.369 48	1.370 83	1.371 29	1.371 74
20%	1.925 19	1.938 86	1.947 34	1.950 22	1.953 13
30%	2.812 26	2.861 92	2.893 54	2.903 84	2.915 45
40%	4.307 9	4.459 01	4.558 90	4.593 83	4.629 63
45%	5.451 63	5.711 21	5.885 46	5.947 04	6.010 52

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Received 16 August 1983

and accepted 13 March 1984