Multiple Threshold Percolation in Polymer/Filler Composites

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Summary: Local variations in filler particle concentration and/or shape and orientation in static filler/polymer composites are modelled as distributions of percolation thresholds. The concentration variations can be due to insufficient mixing, formation of semicrystalline voids during cooling from the melt, shrinkage during polymer curing, flow during physical compression or the like. Irregular filler shapes, especially elongated shapes, reduce the percolation threshold; thus natural variations in the shapes and orientations of filler particle aggregates lead to locally varying percolation thresholds. A distribution of percolation thresholds leads to an apparent percolation threshold based on the conductivity below the mean percolation threshold. For filler concentrations above the apparent percolation threshold the dielectric constant continues to increase before reaching a lowered peak value at the mean percolation threshold and then decreasing. Own experimental results on EBA /carbon black composites support the theory.

Keywords: carbon black; dielectric constant; percolation; polymer composite

Introduction

When electrically conductive filler particles are added to an insulating polymer matrix at first the conductivity of the composite rises only slowly. When the concentration of the filler particles is high enough they form a continuous but tortuous network across the whole composite, leading to a dramatic increase of the conductivity beginning from the percolation threshold. Also the dielectric permittivity of the composite increases up to the percolation threshold, where it peaks and then decreases in exactly the same way as it increased. This behaviour in both two and three dimensions is well understood and modelled in percolation theory (Efros and Shklovskii[1] Bergman and Imry[2], Stauffer[3, 4]) as confirmed in numerous experiments.

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However, in some less than ideal solid systems experimental results show that the permittivity continues to increase even above the percolation threshold. This has been observed by several investigators, among them McLachlan and Heaney[5] for carbon black in PE (polyethylene), McLachlan et al.[6] for powders on insulating grains, McLachlan et al.[7] for colloidal graphite coated polystyrene balls, Tchmutin et al.[8] for carbon black in epoxy resin, Jäger et al.[9] for carbon black in EBA (ethylene butylacrylate copolymer), Jäger, McQueen and Vilčáková [10] for carbon black in PMMA (polymethyl methacrylate) and Flandin et al.[11] for carbon black in epoxy. Characteristic of these static systems is that the polymers have either been cooled through a structural transition, allowed to cure after mixing the filler and polymer or physically compressed.

The question arises whether there is a problem with the experimental technique (for instance with the sample preparation) or with the theory (is percolation theory correct or is something lacking in the model?). Much effort has been expended in checking on and extending percolation theories and their associated scaling functions (Sarychev and Brouers[12], Balberg[13], McLachlan et al.[6], McLachlan et al.[7], Balberg[14]). Of especial interest is an exploration of the effects of allowing variations in the electrical characteristics of the gaps between conducting filler particles (Sarychev and Brouers [12], Balberg [13] 1998, Rubin et al. [15], Balberg [14], Jäger et al. [9], Jäger et al.[10]). To date no completely satisfactory quantitative explanation for “anomalous” results concerning the dielectric constant above the percolation threshold has been worked out in detail. Thus there may be a problem with the experimental technique (mixing).

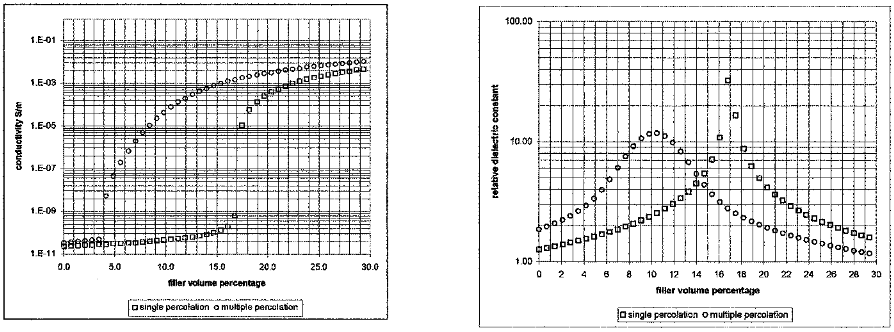
As these experimental results are in fundamental disagreement with theory, it is important to sort out this problem.

In the following we show that a viable explanation of the discrepancy between theory and experiment is that the dielectric properties of the finite size solid composites are not homogeneous, but rather vary locally. This can be due to insufficient mixing, formation of semi-crystalline volumes during cooling from the melt, shrinkage during polymer curing, flow during physical compression, variations in the shape and orientation of the filler particles and their aggregates, etc. This is modelled as a distribution of percolation thresholds such that the dielectric properties of the whole finite composite sample are the sum of the properties of many small volumes in parallel with percolation thresholds distributed around an average percolation threshold. The results of the model provide an explanation of the experimental results.

Theory

The individual percolation curves were calculated using the most common formulae for the conductivity and the dielectric permittivity. The exact nature of the distribution (shape, width) of the percolation threshold distribution is not important for the purposes of the arguments put forward here. It is reasonable to assume a smooth percolation threshold distribution over a range of concentrations. Here a Gaussian distribution has been chosen with mean at 10.5% vol % and standard deviation 3.5 vol %. Twenty percolation curves as shown in Fig. 1 ("single percolation") spaced at filler concentration intervals of 0.7% were summed with the Gaussian weighting to give the left hand curves in Fig. 1 ("multiple percolation"). The lowest percolation threshold was then 3.5% and the highest one was 17.5%.

It is clear from the left hand curve for the conductivity in Fig. 1a that the apparent percolation threshold is about 5% rather than at 10.5% filler volume concentration. This shift from the "average" percolation threshold is related to the fact that the conductivity curve is asymmetrical around the percolation threshold. On the other hand, the left hand curve for the permittivity in Fig. 1b is symmetrical around 10.5%. The height of the permittivity against concentration curve decreases as the width of the percolation threshold distribution increases.

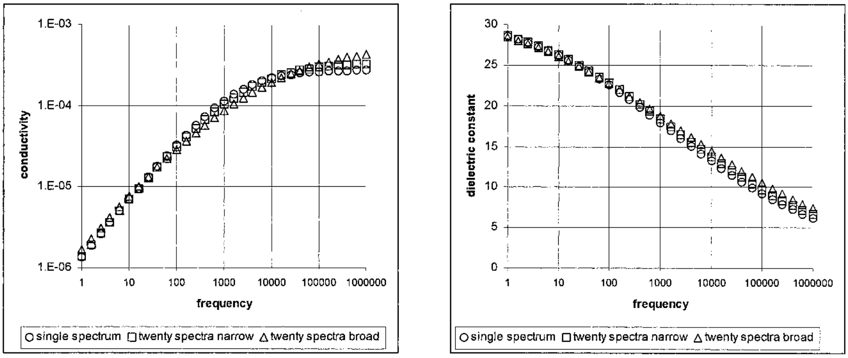


a) b)

Figure 1. The filler concentration dependence of a) the electrical conductivity and b) the relative dielectric constant for the case of (i) a single percolation threshold at 17% and (ii) multiple percolation thresholds between 3.5% and 17.5% by volume.

Figure 1 makes it clear that this distribution of percolation thresholds corresponding to parallel samples can produce results where the permittivity continues to increase at filler concentrations far above the apparent percolation threshold. The apparent critical exponent increases roughly according to t = 1.9 + 0.75 (std dev) with "std dev" the standard deviation of the Gaussian distribution in volume percentage. Below the percolation threshold the concentration dependence changes from a power law to exponential [12].

The above discussion has been concerned with filler concentration dependencies. For practical reasons it would be good to be able to extract information on the homogeneity of a composite from a single measurement on a sample. In principle such a procedure may be possible using frequency analyses.



a) b)

Figure 2. The frequency dependencies of a) the conductivity and b) the relative dielectric constant for a single relaxation time, a narrow Gaussian distribution of relaxation times with a standard deviation corresponding to 100 and a broad Gaussian distribution of relaxation times with a standard deviation corresponding to 10^4 or four orders of magnitude.

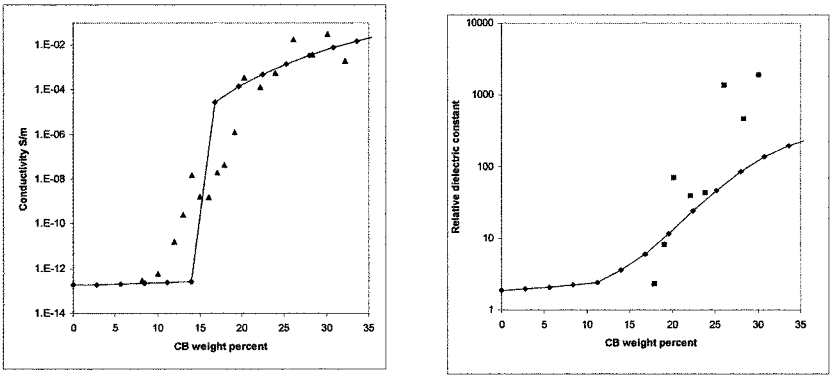
For a given relaxation time τ the frequency dependencies of the conductivity and relative dielectric permittivities were modelled according to standard formulae. Figure 2 shows single characteristic relaxation time spectra compared to two multiple characteristic relaxation time spectra with Gaussian distributions of the logarithm of the relaxation times. The narrower distribution has a mean of - 4 (log 0.0001) with a standard deviation of 1 corresponding to a factor of ten and the broader distribution has the same mean and a standard deviation of 2 corresponding to a factor of one hundred. (Both distributions extend from minus two standard deviations to plus two standard deviations.) Thus in the latter case the variation in the characteristic relaxation time is over a factor of 10^4 from minus one standard deviation to plus one while the whole characteristic time spectrum starts from minus two standard deviations to plus two, corresponding to a factor of 10^8.

In spite of this broad variation in characteristic relaxation times especially the low frequency side of the spectra shown in Figure 2a for the conductivity are almost unchanged in shape. Only in the region of the transition to the high frequency plateau does the distribution have a significant effect. Figure 2b shows that the effect of the characteristic relaxation time distribution on the permittivity is also minimal. Essentially this is because even when there is a single characteristic relaxation time the spectrum already includes a broad distribution of Debye-type relaxation spectra, here covering something like four orders of magnitude. An important or perhaps irritating effect of the characteristic relaxation time distribution is to lower the slopes of the curves in Figures 2a and 2b, thus producing lower apparent critical exponents. This does not seem to be a good way of evaluation the homogeneity of the sample.

Experimental results for EBA and acetylene black

The pelletised thermoplastic samples consisted of an EBA matrix (similar to LDPE but with 4.3 mol% butylester side groups, density 925 kg/m^3) with varying amounts of acetylene black (carbon black) filler (density 1800 kg/m^3). They were press-moulded at 180 °C for thirty minutes. Then the two millimetre thick samples were cut to 15 millimetre diameter round discs and the flat sides covered with conductive paint. The dc conductivities of the samples were measured with a sensitive ohmmeter (Keithley 595 Quasistatic CV Meter). Finally, their capacitances and resistances were measured perpendicular to the flat faces as functions of the frequency with a Hewlet Packard 4284 A Precision LCR Meter in the range 20 Hz to 1 MHz.

Figure 3a shows the conductivity of the composites as a function of the filler concentration in weight percent (about double the concentration in volume percent). Each data point is the average of measurements on three samples. The apparent percolation threshold is between about 11 and 12 weight percent or about 6 vol %. The connected symbols are a theoretical fit to the data using a wide distribution of percolation thresholds (average percolation threshold 21 vol % corresponding to about 42 weight %) similar to that in figures 1 and 2.



a) b)

Figure 3. Experimental results: a) the dc electrical conductivity versus the carbon black weight percent and b) the relative dielectric constant for 20 Hz versus the carbon black weight percent in thermoplastic EBA at room temperature as well as theoretical fits (connected symbols) to the data.

Figure 3b for the relative dielectric constant as a function of the filler concentration (again the average of three samples) shows that the dielectric constant continues to increase long after the apparent percolation threshold around 11 or 12 weight percent or about 6 vol % has been passed. The theoretical "fits" in figures 3a and 3b are only fair. A next step might be to vary the percolation threshold distribution to better fit the data. This potentially rather complicated task has not been attempted. A further step would be to relate the percolation threshold distribution to the filler particle distribution, as measured by some appropriate means.

Figure 4 show the frequency dependence of the conductivity with five representative spectra for filler concentrations from 8.14 weight percent to 30.16 weight percent. The slope of the low frequency part of the 8.14 weight percent curve is about 1.58, and the two spectra for the other samples have corresponding slopes of 1.95 and 1.64. As the concentration is significantly lower than the apparent percolation threshold, slopes approaching 2.0 are expected. The slope of the next curve (filler concentration 14.07 weight percent), still below the apparent percolation threshold, is about 0.88 (other sample spectra having slopes of 0.48 and 1.01). The following spectrum is for a concentration quite near the percolation threshold (17.07 weight percent) and the slope in the lower part of the curve is 0.44 (other curves having slopes of 0.34 and 0.81). The slope of the 22.17 weight percent curve is 0.45 (other curves having slopes of 0.42 and 0.53) in the high frequency segment. These slopes around 0.50 are a little lower than that predicted by the theory for single percolation thresholds (about 0.65) and are thus in better agreement with the multiple threshold slope prediction (about 0.55). Finally, the curve for 30.16 weight percent is almost flat, as expected.

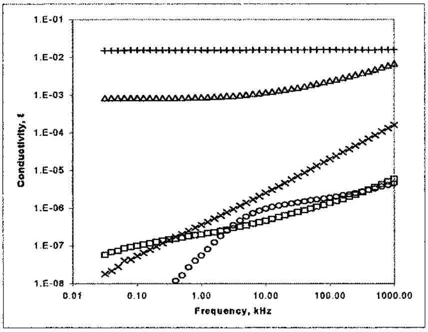


Figure 4. The frequency dependence of the electrical conductivity for different carbon black weight percentages in thermoplastic EBA at room temperature: (o) 8.14 w%, (x) 14.07 w%, (□) 17.07 w%, (Δ) 22.17 w% and (+) 30.16 w%.

These data show considerable scatter. Some of the imperfections may be due to measurement difficulties such as problems with measuring the dielectric permittivity of high conductivity samples, noise problems especially for samples with low conductivity, difficulty in achieving intimate electrical contact with the sample, etc. Other imperfections are due to real variations between samples that give rise to variations in the measurement results. This is intimately connected with the sample inhomogeneity and thus unavoidable.

Discussion and Conclusions

We propose that the static samples that show dielectric constants that increase with increasing concentration above the apparent percolation threshold are inhomogeneous on a scale of the thickness of the sample. The measurement results are interpreted as an average of the characteristics of a large number of small sample volumes measured in parallel. The different volumes have different filler concentrations, for instance due to formation of semicrystalline voids, stress fields or plastic flow during compression. When the filler particles are not spherical their shapes and orientation distributions reduce the percolation threshold. Thus irregularly shaped filler particles and filler particle aggregates lead to varying local percolation thresholds. This is often the case with intermediate structure or high structure carbon blacks. The ratio of the local filler concentration to the local percolation threshold can vary greatly on a laboratory scale. This leads to a concentration difference between the apparent percolation threshold and the peak in the concentration dependence of the dielectric constant, which can be at a much higher filler concentration.

The ideal case is a sample with the same statistical distribution of filler particles on all relevant scales throughout the whole sample. This is naturally very difficult to achieve in static (solid) samples, especially those in which the carbon black structures have a “high structure”.[14, 15] Here we should like to emphasise that not only does the carbon black structure affect the percolation characteristics of the composites, but also the matrix polymer has a strong influence on the experimental results.[16] It is easier to achieve a “good” filler particle distribution in microemulsions[17, 18] or in two-dimensional samples prepared for instance by sputtering or etching.

A weakness of the present approach is that the distribution of percolation thresholds used to model the inhomogeneity of the composite can vary within wide limits as to shape and width. There are few physical restrictions on what can be possible. It is therefore difficult to test the model in detail. This does not mean that this sort of modelling is simply “sweeping the problem under the rug” since it is really possible, if not probable, that real samples often are inhomogeneous on the relevant scale. Outside the laboratory, in natural formations and structures, for instance rocks, one should surely expect that filler concentrations are variable within rather wide limits.

A disproof of the present multiple threshold model could be provided by a composite with homogeneous matrix and spherical, non-interacting filler particles randomly distributed throughout. If experimental results showing that the dielectric constant continues to increase significantly above a percolation threshold in the neighbourhood of 17% by volume were to be obtained, then the present multiple threshold model would be disproved. We know of no such example.

We conclude that a reasonable distribution of percolation thresholds in a sample can lead to a peak in the capacitance versus filler concentration curve at a higher concentration than that of the percolation threshold as determined from the conductivity versus filler concentration curve. The critical exponent t increases as the distribution of percolation thresholds broadens. Further, in the frequency plane the percolation threshold distribution can lead to a slight reduction of the apparent critical exponents x and y.

[1] A L Efros, B I Shklovskii, Physica Status Solidi b **1976**, *76*, 475
[2] D J Bergman, Y Imry, Phys. Rev. Let. **1977**, *39(19*), 1222
[3] D Stauffer, Phys. Reports **1979,** *54(1),* 1
[4] D Stauffer, "*Introduction to Percolation Theory*", Taylor and Francis, London 1985
[5] D S McLachlan, M B Heaney, Phys. Rev. B **1999**, *60*, 12746
[6] D S McLachlan, W D Heiss, C Chiteme, J Wu, Phys. Rev. B **1998**, *58*, 13 558
[7] D S McLachlan, Kefeng Cai, C Chiteme, W D Heiss, Physica B **2000**, *279*, 66
[8] I A Tchmutin, A T Ponomarenko, V G Shevchenko, N G Ryvkina, C Klason, D H McQueen, J. Polymer Sci. B: Polymer Phys., **1998**, *36*, 1847
[9] K-M Jäger, D H McQueen, I A Tchmutin, N G Ryvkina, M Klüppel, J. Phys. D: Appl. Phys. **2001**, *34*, 2699
[10] K-M Jäger, D H McQueen, J Vilčáková, J. Phys.D: Appl. Phys. **2002**, *35*, 1068
[11] L Flandin, T Prasse, R Schueker, K Schulte, W Bauhofer, J-Y Cavaille, Phys. Rev. B **1999**, *59(22)*, 14349
[12] A K Sarychev, F Brouers, Phys. Rev. Lett. **1994,** *73*, 2895
[13] I Balberg, Phys. Rev. B **1998**, *57*, 13 351
[14] I Balberg, Carbon **2002**, *40*, 139
[15] Z Rubin, S A Sunshine, M B Heaney, I Bloom, I Balberg, Phys. Rev. B **1999**, *59*, 12 196
[16] O Breuer, R Tchoudakov, M Narkis, A Siegmann, J. Appl. Polymer Sci. **1999**, *73*, 1655
[17] M T Clarkson, S I Smedley, Phys. Rev. A **1988**, *37*, 2070
[18] M T Clarkson, Phys. Rev. A **1988**, *37*, 2079