On sample preparation and dielectric breakdown in nanostructured epoxy resins

M Reading, Z Xu, A S Vaughan and P L Lewin
The Tony Davies High Voltage Laboratory, University of Southampton, UK

E-mail: asv@ecs.soton.ac.uk

Abstract. There are many methods available to achieve a good dispersion of fillers within a polymeric matrix. This investigation considered several methods of dispersing three chosen fillers within an epoxy resin; the same processes were also performed on unfilled materials to investigate any effects they may have on the host material. For this investigation, the epoxy system (EP) was combined with sodium montmorillonite (MMT), micrometric silicon dioxide (SD) or nanometric silicon dioxide (NSD) as fillers. The effect of the different sample preparation routes on breakdown behaviour was then evaluated. While more thorough mixing protocols were found to lead to improved breakdown behaviour in the case of the various filled systems, surprisingly, an entirely equivalent form of behaviour was also seen in the unfilled epoxy. The influence of changes in sample geometry on the breakdown strength was established.

1. Introduction
There has been much interest in creating composite dielectrics over recent years, many involving a polymer matrix with a filler or additive present to increase one or more specific properties of the overall material. Fillers were originally, and can still be, used as cheap diluents to reduce costs and improve material production and processing, this being the origin of the term filler [1]. However in recent years, more focus has been given to fillers that actively improve the final-material properties. By dispersing such fillers into a host material, such as a polymer, it has been seen that properties such as electrical breakdown strength, crystallisation kinetics, fire retardancy and more, can be altered to create superior materials for chosen purposes [2]. When creating a polymer composite using a particulate filler, many issues must be addressed, including the compatibility of the filler with the polymer, the size of the filler particulates, the agglomeration of the filler, the filler loading and the dispersion of the filler within the polymer [3]. It is commonly known that a poor dispersion of filler will result in a material with non-uniform properties, often a particularly undesirable attribute [4, 5]. Therefore, the aim for most of these composite systems is for the filler to be as well dispersed as possible, giving uniform behaviour across the whole material. Much work has been performed on fillers for polymers and Rothon [1] provides a good review on the use of such particulate fillers, including those with nanoscopic dimensions.

This study was undertaken with three objectives. The first of these was to investigate methods of dispersing fillers with varying geometries and particle sizes within an epoxy matrix; the second, which
was directly related to the first, involved determining the influence of dispersion on electrical breakdown behaviour. The subsequent data and its analysis will reveal the effectiveness of the dispersion methods for the varying systems and whether the dispersion achieved varies due to the particle geometry and size. The third objective relates to the effect of sample thickness on the measured breakdown strength. It is well known that the apparent breakdown strength is influenced by volume effects (sample thickness and area tested) and, therefore, fluctuations in sample thickness will influence the scatter seen in breakdown data [6]. Also, since our interest in the epoxy-based systems studied here concerns their potential use in full scale plant, it is important to evaluate the extent to which conclusions drawn from thin films can reliably be extrapolated to thicker, technologically relevant geometries.

2. Sample Details and Production

DER 332 epoxy resin was chosen for this investigation, due to its simple chemistry and appropriate viscosity, allowing easy mixing. Jeffamine D-230 was chosen as the hardener based upon previous experience in this laboratory [7]. The standard stoichiometric ratio calculation leads to a resin:hardener ratio of 1000:344. The fillers used for this investigation were a sodium montmorillonite (MMT) formed of platelets nanometric in one dimension and two sizes of nominally spherical particulate silicon dioxide, a micro filler 1-5 µm in size (indicated SD) and a nano filler containing particles 5-15 nm in diameter (indicated NSD). All fillers were obtained from Sigma Aldrich and were used as received.

For electrical breakdown measurements, film specimens of the required thickness (50 – 1000 µm) were produced using a gravity-fed moulding technique. Figures 1 and 2 show one of the moulds used to produce these films. A QZ13 release agent was applied to the moulds prior to assembly since this has previously been effective at aiding release of DER 332 epoxy systems [8]. All epoxy samples, including the filled systems, were given the same curing treatment, with the fillers being added and dispersion methods performed at the de-gassed resin stage.

![Figure 1. One of the pre-made sample moulds](image1)

![Figure 2. The spacer and sample inside the pre-made mould from figure 1](image2)

Figure 3 shows a flowchart of the procedure followed in producing the various samples and Table 1 lists the sample types generated during this investigation and the mixing regime performed on each sample. The five sample preparation regimes were employed to produce samples exhibiting dispersion states ranging from poorly dispersed through to a highly dispersed state. Regime NM leads to a poor dispersion state, as the sample is completely unmixed. Regime HM gives a low state of dispersion with only basic hand mixing being used. Regime MS provides an intermediate level of dispersion, with magnetic stirring being performed using a standard heated stirrer plate held at ~50 °C. Regimes US and SON represent attempts at achieving a higher state of dispersion using an ultrasound bath and a sonicator respectively. In regime US an UltraWave DP201 Precision Ultrasonic bath was used at 50 °C while, in regime SON a Hielscher UP200S Ultrasonic processor was used at 50% amplitude.
These two techniques rely on the same fundamental technique to break-up aggregations of fillers and improve the dispersion with the polymer, although the delivery method is slightly different since the ultrasound bath exposes the outside of the flask whereas the sonicator is a point source located in the middle of the specimen. Table 2 contains further details of the procedures used.

To examine the effect of specimen thickness, the unfilled epoxy was used in conjunction with mixing regime MS and different spacers were used during sample preparation. For samples between 50 \( \mu \)m and 500 \( \mu \)m, Melinex films (DuPont) were used; 1 mm thick specimens were produced using an aluminium spacer.

### 3. Experimental

For the study of mixing effects, electrical breakdown data were obtained using an AC ramp testing rig developed in-house [9]. In line with the ASTM D149 standard (AC ramp, 50 Hz, 50 V/s), tests were performed on typically 15 sites per sample. The test cell contained silicone oil, which covered the sample.

#### Table 1. Samples generated and their corresponding mixing regime

| Sample | Filler %wt | Mixing Regime |
|--------|------------|---------------|
| EP NM  | -          | NM            |
| EP HM  | -          | HM            |
| EP MS  | -          | MS            |
| EP US  | -          | US            |
| EP SON | -          | SON           |
| MMT NM | 5% MMT    | NM            |
| MMT HM | 5% MMT    | HM            |
| MMT MS | 5% MMT    | MS            |
| MMT US | 5% MMT    | US            |
| MMT SON| 5% MMT    | SON           |
| SD NM  | 5% SD     | NM            |
| SD HM  | 5% SD     | HM            |
| SD MS  | 5% SD     | MS            |
| SD US  | 5% SD     | US            |
| SD SON | 5% SD     | SON           |
| NSD NM | 5% NSD    | NM            |
| NSD HM | 5% NSD    | HM            |
| NSD MS | 5% NSD    | MS            |
| NSD US | 5% NSD    | US            |
| NSD SON| 5% NSD    | SON           |

![Figure 3. A flowchart showing sample production](image_url)
sample to prevent flashover, and 6.3 mm steel ball bearing electrodes were used. The electrodes were changed after every other sample to avoid pitting and the linearity of the AC ramp rate was also checked. The resulting data were analysed using a two parameter Weibull expression with 90% maximum likelihood confidence bounds. Since the maximum reliable operating voltage of the above breakdown rig is limited to about 15 kV, it was incapable of breaking down 1 mm thick specimens. Consequently, the study of thickness effects used, in its place, a Phenix Type 600C AC dielectric test set and an equivalent test protocol to that described above.

4. Results

4.1. Mixing Regime

Figures 4 to 7 present electrical breakdown data obtained from the unfilled and filled composite specimens 100 µm in thickness. Figure 4 shows that even in the absence of any nanofiller, the extent of mixing has a dramatic effect on the data; the scale parameter, \( \alpha \), increases progressively from

| Regime | Details |
|--------|---------|
| NM     | Resin, hardener and filler combined with no mixing |
| HM     | Hand mixing for 20 minutes |
| MS     | Hand mixing for 20 minutes followed by magnetic stirring for 20 minutes |
| US     | Hand mixing for 20 minutes, magnetically stirred for 20 minutes and ultrasound for 20 minutes |
| SON    | Hand mixing for 20 minutes, magnetically stirred for 20 minutes and sonicated for 20 minutes |

Table 2. Details of the five mixing regimes

Figure 4. Weibull plots of breakdown data for differently processed unfilled samples

Figure 5. Weibull plots of breakdown data for differently processed MMT-filled samples
~135 kV mm⁻¹ to a value in excess of 150 kV mm⁻¹ and the shape parameter, \( \beta \), increases from ~9 to more than 20; the best breakdown performance is obtained from the sonicated system. Although such procedures have been advocated in connection with nanofilled epoxy, we are not aware of any previous accounts showing such a marked effect in the unfilled resin.

Qualitatively equivalent behaviour is also seen in the various filled systems; as more thorough mixing regimes are used, the spread in the data drops and the breakdown strength progressively increases. However, quantitatively, these results are not what we would expect. In filled systems, the

| Sample  | Weibull Parameter | Sample  | Weibull Parameter |
|---------|-------------------|---------|-------------------|
|         | \( \alpha \)     |         | \( \beta \)      |
| EP NM   | 135.8             | SD NM   | 129.8             |
| EP HM   | 141.3             | SD HM   | 127               |
| EP MS   | 143.8             | SD MS   | 132.5             |
| EP US   | 147.5             | SD US   | 138.3             |
| EP SON  | 152               | SD SON  | 141.5             |
| MMT NM  | 128.9             | NSD NM  | 129.2             |
| MMT HM  | 137.8             | NSD HM  | 135.3             |
| MMT MS  | 139.2             | NSD MS  | 139.5             |
| MMT US  | 138.5             | NSD US  | 145.9             |
| MMT SON | 141.8             | NSD SON | 138.5             |

Figure 6. Weibull plots of breakdown data for differently processed SD-filled samples

Figure 7. Weibull plots of breakdown data for differently processed NSD-filled samples

Table 3. The Weibull parameters obtained from the plots shown in figures 4-7
reduced filler agglomeration that should result from more intensive mixing should augment any benefits seen in the unfilled analogue. This is not seen here. In all three systems, the NM materials exhibit breakdown strengths values close to 129 kV mm\(^{-1}\) (c.f. \(\sim 136\) kV mm\(^{-1}\) for the unfilled resin), which subsequently rises for the sonicated samples to \(\sim 142 \pm 4\) kV mm\(^{-1}\) (c.f. \(\sim 150 \pm 2\) kV mm\(^{-1}\) for the unfilled resin). While more intensive mixing is beneficial in enhancing the breakdown behaviour of nanocomposites, the fact that equivalent behaviour is also seen in the same, unfilled resin, makes it very difficult to argue that this effect is related to improved dispersion of the filler, as is widely claimed in the literature [10, 11].

4.2. Specimen Thickness

For studying new or filled/altered materials, the use of thin films has several benefits; in that the volume of material required is low, as is the voltage range required to cause breakdown. However, even small variations in sample thickness can then have a disproportionate effect on the apparent breakdown strength, leading to increased scatter in the resulting Weibull plots. Figure 8 shows the thickness dependence of breakdown data obtained from unfilled epoxy specimens prepared using mixing regime MS. At a thickness of 50 \(\mu\)m, all samples breakdown at applied fields close to 180 kV mm\(^{-1}\) (applied voltage 9 kV) whereas, when the thickness is increased to 1 mm, this falls to \(\sim 40\) kV mm\(^{-1}\) (applied voltage 40 kV). Plotting the derived location parameter as a function of sample thickness yields the graph shown in figure 9. For this system, the thickness dependence of the breakdown strength, \(E_b\), conforms closely to an equation of the form:

\[
E_b = E_0 \exp(-kx) + E_{\infty}
\]

where \(x\) represents the specimen thickness and \(E_0\) and \(E_{\infty}\) represents the limiting breakdown strength as \(x \Rightarrow 0\) and \(\infty\) respectively. Here, \(E_0 = 172 \pm 6\) kV mm\(^{-1}\) and \(E_{\infty} = 32 \pm 5\) kV mm\(^{-1}\). Since the Weibull distribution is essentially a weak link theory, it is tempting to ascribe the breakdown value in the limit
that $x \Rightarrow 0$ as corresponding to a defect-free specimen, such that $E_o$ will represent some form of intrinsic breakdown strength; the value of $E_o = 172 \pm 6$ kV mm$^{-1}$ derived from figure 9 is, however, significantly lower than “intrinsic breakdown strength” values in the literature [11].

5. Conclusions
It is evident that the mixing protocol used to prepare epoxy-based specimens can have a major effect on breakdown performance. In the case of nanodielectrics, this has traditionally been ascribed to nanofiller dispersion effects. The fact that comparable effects are seen here in unfilled epoxy systems is unexpected; evidently, good mixing of the resin and hardener is also critical and, it would appear that this can also benefit from sonication. Regimes A and B result in materials which exhibit reduced Weibull parameter values in all cases; sonication results in materials which exhibit enhanced Weibull parameter values in all cases. The thickness dependence of the breakdown strength conforms well to a simple exponential function, which enables the zero-thickness breakdown strength to be evaluated. The conventional interpretation given for the decrease in experimental breakdown strength with sample thickness is related to the probability that the tested volume contains an appropriate defect. The relatively low value of $E_o$ determined here suggests that, while the Weibull distribution may be an adequate description of breakdown data, its mechanistic validity is questionable.

6. References
[1] Rothon R N 2002 Smithers Rapra Publisher, volume 12, no. 9
[2] Huang X, Lewis S and Brittain W J 2000 Macromolecule, 33 2000
[3] Tee D I, Mariatti M, Azizan A, See C H and Chong K F 2007 Compos. Sci. Tech. 67 2584
[4] Chiang C L, Ma C C M, Wang F Y and Kuan H C 2003 Euro. Poly. J. 39 825
[5] Jawahar P and Balasubramanian M 2006 J. Nanomaterials 1 4
[6] Dissado L A and Fothergill JC 1992 Electrical Degradation and Breakdown in Polymers, ed G C Stevens (London: Peter Peregrinus)
[7] Reading M, Xu Z, Vaughan A S and Lewin P L 2011 EIC Conf. Proc. to be published
[8] Singhal R G Thesis at Graduate Faculty of North Carolina State University
[9] Reading M Thesis at University of Southampton
[10] Vaughan A S, Swingler S G and Zhang Y 2006 Trans. Instit. Elec. Engin. Jpn 126 1057
[11] Herzig R and Baker W E 1993 J. Mater. Sci. 28 6531
[12] Heylen A E D and Postoyalko V 2003 IEEE Trans. Diele. Electr. Insul. 10 708