On the effect of nanosilica on a polyethylene system

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On the effect of nanosilica on a polyethylene system

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Abstract. The topic of polymer nanocomposites remains an active area of research in terms of its potential applications in dielectric and electrical insulation applications. Although more than a decade has passed since Lewis first considered these systems as dielectric materials, the precise effects of incorporating nanofillers into different polymers are yet to be confirmed. While this strategy is generally regarded as a promising means for tailoring insulation performance, the consequences of adding a nanofiller to an insulating matrix are not always positive; for example, where dispersion is poor the breakdown strength can be adversely affected. This paper reports on an investigation into a nanofilled polyethylene system prepared via a solution blending route. Specifically, in this study, the effect of processing and nanofiller dispersion on the structure and physical properties of the nanocomposites that forms was considered. The crystallization behaviour and morphology of the differently processed materials have been evaluated by differential scanning calorimetry (DSC) and polarised optical microscopy (POM). The influence of nanofiller dispersion on breakdown behaviour is also described.

1. Introduction
Polymer nanocomposites, defined as polymers in which nanometre-sized fillers are homogeneously dispersed at just a few weight percentage (wt%), remains as an interesting topic of discussion in the context of dielectrics and electrical insulation. Since Lewis [1] first considered these systems as dielectric materials, numerous publications have emerged, exploring the dielectric properties of various polymers combined with different inorganic nanofillers [2-7]. While there were numerous results supporting the dielectric enhancement brought about by nanostructuration in electrical insulation systems, such results were not always positive. Furthermore, lots of uncertainties concerning nanocomposite applications in dielectric systems remain unanswered and are yet to be confirmed.

This paper reports on an investigation into a nanofilled polyethylene system prepared via a solution blending route. This involves the initial dissolution of the polyethylene in nonpolar xylene and the dispersion of the nanosilica in relatively polar methanol – a non-solvent for polyethylene. Mixing together the two components results in the rapid precipitation of the polymer, including the nanoparticles. The use of solution blending method is not new in nanodielectrics research and has been

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explored by some researchers [8-11]. This preparation method enables many different formulations to be produced with ease and, as such, is ideal for a scoping survey, providing a different perspective on the understanding of nanodielectrics.

2. Experimental

2.1. Materials and Preparation

The polymers used in this research were low density polyethylene (LDPE) grade LD100BW obtained from ExxonMobil Chemicals and high density polyethylene (HDPE) grade Rigidex HD5813EA obtained from BP Chemicals. The nanofiller used was silicon dioxide (SiO$_2$) nanopowder (i.e. nanosilica) obtained from Sigma-Aldrich, with a quoted particle size range from 10 nm to 20 nm.

The desired amount of nanosilica was added into polar methanol – a non-solvent for polyethylene and dispersed through sonication. Concurrently, the proper amount of HDPE and LDPE were dissolved in xylene under heating and stirring. The hot xylene/polyethylene mixture was then poured into the methanol/nanosilica mixture quickly with vigorous stirring, resulting in the rapid precipitation of the nanocomposite as a white mass. Upon filtering and drying, the resulting nanocomposite was melt pressed at 150 ºC and vacuum dried at 100 ºC. Samples for different tests were subsequently prepared by melt pressing at a temperature of 150 ºC, followed by direct quenching into water or isothermal crystallisation. For comparison purpose, the unfilled polyethylene system was prepared in the same way.

For convenience, all materials were denoted using the following general notation: P/F/T. In this, P signifies the polymer used, F represents the filler used and T defines the thermal treatment used. Examples of designations are summarised as in Table 1.

| Designation    | Polymer (wt%) | Filler (wt%) | Description                                                                 |
|----------------|---------------|--------------|-----------------------------------------------------------------------------|
| PEA/0/Q        | 80            | 20           | 0 Polyethylene system type A (i.e. the one with 20 wt% of HDPE and 80 wt% of LDPE), not added with nanofiller, and being quenched directly into water. |
| PEA/5S1M/Q     | 80            | 20           | 5 Polyethylene system type A (i.e. the one with 20 wt% of HDPE and 80 wt% of LDPE), added with 5 wt% of nanosilica being sonicated for 1 hour in methanol, and being quenched directly into water. |
| PEA/0/115      | 80            | 20           | 0 Polyethylene system type A (i.e. the one with 20 wt% of HDPE and 80 wt% of LDPE), not added with nanofiller, and being isothermally crystallised at 115 ºC. |
| PEA/5S1M/115   | 80            | 20           | 5 Polyethylene system type A (i.e. the one with 20 wt% of HDPE and 80 wt% of LDPE), added with 5 wt% of nanosilica being sonicated for 1 hour in methanol, and being isothermally crystallised at 115 ºC. |

2.2. Characterisation

A Perkin Elmer DSC7 with Perkin Elmer Pyris software was used to characterise the thermal behaviour of the materials being investigated. For each differential scanning calorimeter (DSC) measurement, a sample of ~5 mg in weight was used, placed in a sealed aluminium pan. The experiment was performed in a nitrogen atmosphere at a scan rate of 10 ºC/min. Polarised optical microscopy (POM) was used to evaluate the morphology of the materials.
Dielectric breakdown tests were conducted based upon the general consideration laid down in the ASTM Standard D149-87. The test sample, with a thickness of about 85 µm, was placed between two 6.3 mm diameter steel ball bearings immersed in Dow Corning 200/20cs silicone fluid, with an applied AC voltage of 50 Hz and a ramp rate of 50 V/s until failure. 20 breakdown tests were performed on each type of sample. The breakdown data were statistically analysed using the two-parameter Weibull distribution analysis.

3. Results and Discussion

3.1. Thermal Analysis
The DSC melting behaviour for the materials investigated is shown in Figure 1. In the case of unfilled polyethylene, at least two melting peaks can be observed in both the quenched and isothermally crystallised materials. The lower melting peaks are associated with the LDPE-rich phase, while the upper melting peak is associated with the HDPE component of the blend. Such observation is not unusual and has been reported in other studies [12, 13].

Comparing both the quenched, nanofilled and quenched, unfilled polyethylene systems, the melting behaviour of PEA/5S1M/Q is similar to PEA/0/Q, with a lower peak at ~114 ºC and an upper peak at ~125 ºC. For the case of the isothermally crystallised systems, the lower and upper melting peaks of the nanofilled material, PEA/5S1M/115 were ~106 ºC and ~125 ºC, respectively, with no significant difference from the unfilled material, PEA/0/115. Consequently, the DSC thermal traces indicated that there were no thermal changes caused by nanosilica inclusion.

![Figure 1. DSC melting traces.](image_url)

3.2. Morphological Analysis
Figure 2 illustrates the dependence of morphology on thermal treatment and material composition. In the unfilled polyethylene system that had been isothermally crystallised at 115 ºC (Figure 2(a)), spherulites can be clearly observed by POM. Isothermal crystallisation at 113 ºC (Figure 2(b)) and 117 ºC (Figure 2(c)) also show clear evidence of spherulites in this material. However, as shown in Figure 2(d), the nano-inclusion appears dramatically to suppress spherulitic development. In the case of both the unfilled and nanofilled polyethylene systems that had been quenched, no spherulites can be observed by POM, as shown in Figure 2(e) and Figure 2(f), respectively.
3.3. Breakdown Strength Analysis

Figure 3(a) and Figure 3(b) show Weibull plots that compare the breakdown strength of the quenched and isothermally crystallised materials, respectively. It can be noticed that the breakdown strength of PEA/5S1M/Q and PEA/5S1M/115 were significantly lower than that of PEA/0/Q and PEA/0/115, respectively. In the case of unfilled polyethylene systems, the breakdown fields of PEA/0/Q and PEA/0/115 were about 148 kV/mm and 152 kV/mm, respectively. The addition of nanosilica caused the breakdown field to reduce to about 132 kV/mm and 138 kV/mm for PEA/5S1M/Q and PEA/5S1M/115, respectively. Therefore, in this preparation route, the addition of nanosilica caused a reduced breakdown strength in both quenched and isothermally crystallised polyethylene systems.

![Weibull plots for (a) PEA/5S1M/Q vs. PEA/0/Q, (b) PEA/5S1M/115 vs. PEA/0/115.](image)
The effect of nanoparticle sonication on the breakdown strength was also studied, as shown in Figure 4. For PEA/5S1M/Q and PEA/5S1M/115, the nanosilica was sonicated in methanol for 1 hour prior to precipitation with the polyethylene/xylene mixture. Increasing the sonication duration to 2 hours, with materials denoted as PEA/5S2M/Q and PEA/5S2M/115 for the quenched and crystallised nanofilled polyethylene blends, respectively, did not help in improving the breakdown strength. Table 2 summarises the Weibull parameters obtained through a two-parameter Weibull distribution analysis.

![Figure 4. Weibull plots for (a) PEA/5S1M/Q vs. PEA/5S2M/Q, (b) PEA/5S1M/115 vs. PEA/5S2M/115.](image-url)

**Table 2.** Weibull parameters.

| Material       | Scale parameter (kV/mm) | Shape parameter |
|----------------|-------------------------|-----------------|
| PEA/0/Q        | 148 ± 4                 | 16 ± 5          |
| PEA/5S1M/Q     | 132 ± 4                 | 13 ± 4          |
| PEA/5S2M/Q     | 128 ± 5                 | 10 ± 3          |
| PEA/0/115      | 152 ± 3                 | 19 ± 6          |
| PEA/5S1M/115   | 138 ± 6                 | 9 ± 3           |
| PEA/5S2M/115   | 140 ± 5                 | 12 ± 4          |

**4. Conclusions**

Nanofilled and unfilled polyethylene systems were prepared by a solution blending route. Considering both the quenched and isothermally crystallised polyethylene systems, the DSC melting behaviour was not altered by nano-inclusion. In the isothermally crystallised polyethylene systems, the dispersion of nanosilica caused less pronounced spherulitic development, as determined by POM. The breakdown strength was significantly reduced due to nano-inclusion, regardless of the nanoparticle sonication duration in methanol. The lowered breakdown strength could be related to the preparation and/or morphology of the materials, but more detailed analysis, such as the use of scanning electron microscopy, is required for such understanding.
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