Absorption current behaviour of polyethylene/silica nanocomposites

K Y Lau1,3,4, A S Vaughan1, G Chen1, I L Hosier1 and A F Holt2

1 School of Electronics and Computer Science, University of Southampton, Southampton SO17 1BJ, United Kingdom
2 School of Chemistry, University of Southampton, Southampton SO17 1BJ, United Kingdom
3 Faculty of Electrical Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia

E-mail: kyl1g10@ecs.soton.ac.uk

Abstract. Absorption current is an important characteristic of polymers with regard to their time-domain response to a direct current (DC) poling field. This is because the results of absorption current measurements can be used to gain understanding of the relationship between space charge accumulation and movement. In semicrystalline polyethylene, for example, charge accumulation is likely to be influenced by the presence of charge trapping sites, which are associated with interfaces between the crystalline and amorphous phases. With the addition of a nanofiller, the charge transport mechanism will become more complicated than in the unfilled polymer, as the inclusion of the nanofiller will introduce nanofiller/polymer interfaces. The presence of such interfaces will affect the current flow due to the introduction or modification of the distribution of trapping sites within the system. In this paper, we report on an investigation into the absorption current behaviour of polyethylene nanocomposites containing 0 wt%, 2 wt%, 5 wt% and 10 wt% of silica nanofiller, either untreated or treated using trimethoxy(propyl)silane coupling agent. Our results indicate that the absorption current behaviour of the polyethylene was affected by the presence of the nanosilica. While the current behaviour through the unfilled polymer decreases with time in a conventional manner, all nanocomposites reveal an initial decrease followed by a period in which the current increases with increasing time of DC field application.

1. Introduction

When an electric field is applied to a non-ideal dielectric material between two plane parallel electrodes, the applied field interacts with charges, causing their motion, which manifests itself as a current flow in the external circuit [1]. The current flow can mainly be categorized into three types, as follows: the initial current that flows through the material is the capacitive charging current, which causes a dramatic rise at the very beginning of the voltage application. This is followed by a gradual decrease of current, known as the absorption current or the anomalous current. Conventionally, the absorption current decreases slowly until it reaches a quasi-steady state, providing a conduction current which is often used to compare the conductivity of different dielectric materials.

4 To whom any correspondence should be addressed.
The slowly decaying current, i.e. the absorption current, is considered to be an important characteristic of polymers with regard to their time-domain response to a DC poling field. This is because results from absorption current measurements can be related to space charge measurements to gain a better understanding of relationship between space charge accumulation and movement, as well as the resulting effects in the external circuit [2]. In general, factors affecting the absorption current include electrode polarization, dipole orientation, charge accumulation, tunnelling of charge carriers from the electrodes to empty traps and hopping of charge carriers through localized states [3].

The determination of charge transport mechanisms in polymeric insulation is, however, complicated in comparison with conducting and semiconducting materials. In semicrystalline polyethylene, for example, the crystallites are surrounded by amorphous regions, and there are likely to be high concentrations of traps at the crystalline/amorphous interfaces. With the addition of a filler, the charge transport mechanism is likely to become more complicated than in the unfilled polymer. In nanocomposites, for example, the inclusion of nanoparticles will introduce additional interfaces between the nanofiller and the polymer, as has been emphasized by many researchers [4-7]. The presence of such nanofiller/polymer interfaces will affect the current flow due to the introduction of additional nanofiller/polymer trapping sites and/or through the modification of the original crystalline/amorphous trapping sites. Therefore, investigations into absorption current behaviour would contribute to a better understanding of filler/polymer interactions in nanocomposites, in particular, in relation to charge transport mechanisms.

2. Experimental

2.1. Materials and Preparation

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

Surface treatment of the nanosilica was performed using trimethoxy(propyl)silane via an anhydrous route, while the nanocomposites were prepared using a solution blending method; these systems are subsequently described as C3-treated. Details of the nanosilica surface treatment and the nanocomposite sample preparation procedure can be found elsewhere [8]. The required test samples (~200 µm thick) were melt pressed at 150 ºC, followed by isothermal crystallization in an oil bath at 115 ºC for 1 h. The samples were sputtered coated with gold to ensure good electrical contact between the electrodes and the samples.

2.2. Characterization

Absorption current measurements were performed using a Keithley 6487 picoammeter / voltage source and a sample holder with two opposing 20 mm diameter electrodes. A step voltage equating to an applied field of 40 kV/mm (DC) was applied and the absorption current was recorded. Prior to measurement, each sample was grounded at 60 ºC in a vacuum for at least 72 h so that excess charge would dissipate.

3. Results

3.1. Absorption Current Measurements at 40 kV mm$^{-1}$ DC Field

Figure 1 shows the plot of the time dependence absorption current for all investigated samples at a constant DC field of 40 kV mm$^{-1}$ over 1 h at room temperature. It is obvious that all the nanocomposites exhibit a current-time characteristic that is different from that of the unfilled polyethylene. At the beginning of the test, it can be noticed that the rate of decrease of current for all the nanocomposites is significantly greater than for the unfilled polyethylene (see the fitted lines).
It is noteworthy that, although the absorption current values differ for each sample at the beginning of the test, these variations fall within experimental uncertainties; repeated experimental runs showed that data variations within a factor of 3 are typical, and can occasionally be up to a factor of 5, which causes the exact quantitative analysis of such behaviour to become questionable. The poor reproducibility of test data is, however, a common issue with absorption current measurements [1]. Quantitative analysis of this facet of the data is therefore not the main interest of this study.

After the initial relatively rapid decrease of current, all the nanocomposites exhibit a characteristic reduction in slope (at ~200 s). The precise time at which this occurs varies from sample to sample, even if the same type of sample were used. No comparable change of slope occurs in the unfilled polyethylene.

Finally, at long times, the current flowing through the nanocomposites begins to rise (at ~1000 s). Such behaviour is, again, not found in the unfilled polyethylene. To aid with data interpretation, Figure 2 was plotted to show the current-time characteristics of all the investigated samples, obtained over a longer time scale (~3 h). From this, the current behaviour of the nanocomposites can be interpreted based on three phases: the region corresponding to the initial decrease of current (Phase I), the region immediately following the initial reduction in slope (Phase II) and the region where the current rises (Phase III).

3.2. Data Analysis

The current-time characteristic of the absorption current is often found to follow the power law relationship:

\[ I = At^{-b} \]  \hspace{1cm} (1)

where \( I \) is the current, \( t \) is the time after the application or removal of the external voltage, \( A \) is a temperature dependent factor and \( b \) is a constant representing the slope of the log-log current-time plot. It should be noted that simple interpretation of the exponent \( b \) is complicated by the fact that polymers exhibit a distribution of relaxation times and that these times may not be easily determined in polyethylene at normal temperatures [2].

In Phase I, although the absolute magnitude of the absorption current was found to vary from sample to sample, repeated experimental runs showed the rate of decrease of current with time to be

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**Figure 1.** Plot of absorption current against time up to 1 h for all investigated samples at an applied field of 40 kV mm\(^{-1}\). Two lines are fitted for nanocomposites to indicate a change in slope prior to a current rise.

**Figure 2.** Plot of absorption current against time up to \( 10^4 \) s for all investigated samples at an applied field of 40 kV mm\(^{-1}\). The data were divided into three phases for the ease of interpretation.
reproducible in all the investigated nanocomposites. Significantly, the rate at which the current decreased was found to be significantly greater at the beginning of the test in comparison with the unfilled polyethylene; the variation of current with poling time at the beginning of the test (0 s to 200 s) is summarized in Table 1.

Table 1. Exponent calculated from the absorption current data at the beginning of the test (0 s to 200 s) at an applied DC field of 40 kV mm\(^{-1}\). The symbol \(b_1\) was used specifically to refer to exponent \(b\) in Phase I.

| Sample          | \(b_1 \times 10^{-2}\) |
|-----------------|-------------------------|
| Unfilled        | 17.5 ± 0.3              |
| 2 wt% untreated | 52.7 ± 0.6              |
| 5 wt% untreated | 67.3 ± 0.4              |
| 10 wt% untreated| 59.6 ± 1.3              |
| 2 wt% C3-treated| 53.9 ± 1.0              |
| 5 wt% C3-treated| 64.4 ± 0.9              |
| 10 wt% C3-treated| 66.7 ± 0.6             |

Generally, all the nanocomposites possess a higher value of the exponent \(b_1\) in Phase I, when compared with the unfilled polyethylene. Also, this parameter increases with increasing amount of the nanosilica, although any influence of nanosilica surface treatment appears to be comparable to experimental uncertainties. Figure 3 shows a plot of exponent \(b_1\) against nanosilica content; the indicated \(b_1\) values of the nanocomposites were obtained from the average values of the untreated and C3-treated systems.

Using the data in Figure 1, the charge carrier mobility can be estimated in each system using the formula [9]:

\[
\mu = \frac{0.786d^2}{t_pV}
\] (2)

where \(\mu\) is the mobility of charge carriers, \(d\) is the sample thickness, \(t_p\) is the time at which the absorption current is at its maximum (or the time at which a slope change occurs) and \(V\) is the applied voltage. The resulting charge carrier mobility is shown in Figure 4; the change of slope for the unfilled polyethylene was assumed to occur at 10000 s. It can be noticed that all the nanocomposites are characterized by a higher charge carrier mobility than the unfilled polyethylene; the charge carrier mobility estimated for the unfilled polyethylene falls within the measurement range of a series of polyethylenes reported by Montanari et al. [10], suggesting that our analysis is reasonable.

In Phase II, the exact quantitative determination of the exponent \(b\) was complicated somewhat by the difficulty in establishing the appropriate time range. Despite this, the same fitting procedure described above was, nevertheless, employed and the resulting estimated \(b_2\) values are shown in Table 2. Comparing the data presented in Table 1 and Table 2, it is evident that the rate at which the current decreases for all the nanocomposites in Phase II is much lower than in Phase I; this does not apply to the unfilled polyethylene. While the quantitative value of exponent \(b_2\) in Phase II is not crucial for our argument, we believe it is important to note that the values become comparable to that which characterizes the unfilled polyethylene. It is noteworthy that a comparable quantitative analysis was not attempted for Phase III since the observation of current rise is not common in the context of absorption current measurements.
**Figure 3.** Plot showing the variation of the exponent $b_1$ as a function of nanosilica content. The $b_1$ values of the nanocomposites were obtained from the average values of the untreated and C3-treated systems.

**Figure 4.** Charge carrier mobility of unfilled polyethylene and nanocomposites containing different types and amounts of nanosilica.

**Table 2.** Exponent calculated from the absorption current data in Phase II. The symbol $b_2$ was used specifically to refer to exponent $b$ in Phase II.

| Sample                  | $b_2 \times 10^{-2}$ |
|-------------------------|-----------------------|
| Unfilled                | 17.5 ± 0.3            |
| 2 wt% untreated         | 17.3 ± 2.0            |
| 5 wt% untreated         | 16.5 ± 2.4            |
| 10 wt% untreated        | 14.6 ± 1.3            |
| 2 wt% C3-treated        | 19.6 ± 0.9            |
| 5 wt% C3-treated        | 24.7 ± 0.8            |
| 10 wt% C3-treated       | 30.2 ± 0.8            |

**4. Discussion**

In Phase I, the current decreases more rapidly in the nanocomposites than in the unfilled polyethylene. This implies that the incorporation of nanosilica into polyethylene has increased the mobility of charge carriers in the nanocomposites, so leading to faster decay of the current as the carriers take a shorter time to reach the electrodes. It is noteworthy that $0 \leq b \leq 2$ is consistent with dipole orientation, carrier tunnelling and carrier hopping while $0 \leq b \leq 1$ is consistent with charge injection forming trapped space charge [11]. While nanoparticles with their large surface areas may act as additional electron traps, they may also reduce the average hopping distance relative to that of the polymer matrix and thus increase the mobility [12]. As the nanofiller content increases, charge mobility may increase due to increased nanofiller/polymer interfaces. This is consistent with the analysis of $b_1$ in Phase I, where this parameter increases with the nanofiller content.

The mobility of charge carriers is highly dependent upon the release of charges from deep traps in addition to the underlying current caused by the large number of shallower traps introduced by the nanoparticles [2]. Analysis of charge carrier mobility shows that all the nanocomposites possess higher charge mobility in comparison with the unfilled polyethylene. Although it remains difficult to judge the effect of nanofiller type and amount on the charge carrier mobility, it is reasonable to deduce that, the incorporation of nanosilica into polyethylene results in the presence of shallower traps that are
related to the nanofiller/polymer interfaces in addition to the original trap distribution that characterizes the crystalline/amorphous interfaces; the former serves to assist in charge transport. 

The change in the $b$ exponent seen in all the nanocomposites, on entering Phase II, could indicate a change in dominant mechanism of the absorption current. This could be attributed to interfacial polarization, as explained elsewhere in the literature [13-14]. The change of slope could also be interpreted in the following way: electronic transport is effectively controlled by trapping, i.e., an electron may travel rapidly through the system for a short time, but its effective or average mobility is greatly reduced as a result of being immobilized for much longer period in localized states (traps) [11]. Alternatively, the change in slope could indicate that the absorption current in Phase II is dominated by the matrix rather than the nanofiller (which we believe dominates in Phase I), since the decay in absorption current within this phase occurs at a rate that is: i) very different from Phase I and ii) comparable to that seen in the unfilled polyethylene.

Although the increasing absorption current with poling time seen in Phase III is extremely unusual, such observations are not without precedent. A comparable increase of current was also discovered by Smith [2] for microcomposites and was thought to be caused by interfacial polarization related to the interfaces between the filler and the matrix. However, no convincing explanation has been proposed in relation to this phenomenon.

5. Conclusions

While the current behaviour through the unfilled polyethylene decreases with time in a conventional manner, all nanocomposites reveal an initial decrease followed by a period in which the current increases with increasing time of DC field application. In addition, the inclusion of nanosilica into polyethylene causes the decay of the absorption current initially to occur more rapidly than in the unfilled PE, highlighting the possibility of increased charge mobility in the nanocomposites. Presently, the literature concerning such current-time characteristics of absorption current is scarce and more work is necessary fully to explain the underlying charge transport mechanisms in nanocomposites.

6. References

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