

The trapping characteristic of low density polyethylene in the presence of crosslinking by-products

Nuriziani Hussin and George Chen

School of Electronics and Computer Science
University Of Southampton, SO16 1BJ, United Kingdom

Email: nh07r@ecs.soton.ac.uk

Abstract. The by-products of dicumyl peroxide (DCP) from the crosslinking process such as acetophenone, cumyl alcohol and α -methylstyrene are said to be the sources of space charge formation in XLPE cable due to deep traps in the chemicals. However, by using space-charge-experimental approach, it appeared that these chemicals show a different trapping nature. This paper is intended to present this approach. Additive-free low density polyethylene (LDPE) was used as base material so that each chemical can be tested individually. Space charge measurement was done using the pulse electroacoustic (PEA) method. All results were compared to the clean LDPE to identify the contribution of the chemicals to the trapping characteristic. The data collected supported that although the chemicals introduce charge in the insulator, the charge decay is extremely fast especially in the presence of α -methylstyrene. It is believed that the chemicals modify the trapping characteristic of LDPE so that more shallow traps are formed in the insulator.

1. Introduction

Crosslinked Polyethylene (XLPE) has been applied in low and high voltage cables due to its good insulating properties. These properties are low dielectric loss, thermal and chemical resistance, resistance to deformation and stress-cracking as well as improved tensile strength and modulus. Nevertheless, the deposition of by-products in the PE structure formed during the crosslinking process is said to be a drawback of this insulating polymer. Space charge accumulation that is found in XLPE has always been associated with the by-products that act as deep traps in the insulator [1,2]. With the space charge existing in the insulator, premature dielectric breakdown might happen due to local field enhancement, ionization and electromechanical energy storage [3,4]. The real effects of the by-product chemicals on the trapping characteristic of insulator will be revealed in this paper.

2. Experiment

All samples used in this project were supplied by GoodFellow Cambridge Ltd. The samples with a thickness of 180 μm were cut into circular film. For the space charge measurement, sample diameter used was 36 mm. In this project, LDPE was chosen over XLPE to eliminate any possibility of having more than two by-products in the sample, allowing for easy identification of the role of each individual by-product in the dynamics of space charge.

2.1. Part I

The sample was soaked in α -methylstyrene and acetophenone for 2 h at room temperature and in cumyl alcohol at 80 °C since the melting temperature for cumyl alcohol is 23 °C. For space charge measurement, PEA technique was employed with semiconductor (Sc) and aluminium (Al) as anode and cathode, respectively. A pulse voltage of 600 V with time duration of 5 ns was applied to the sample to generate an acoustic signal wave. 8 kV DC voltage was applied to the samples at room temperature for one hour. In this research, measurements during short circuit were conducted to capture the slow moving charges in the sample. Every 10 min, the samples were short-circuited and the volts off measurements were conducted 5 s after voltage removal. As soon as the readings were recorded, the samples were recharged again until the next 10 min. This procedure was repeated until one hour of total charging time. Afterwards, the decay of the accumulated space charge in specimen was observed for another extended hour.

2.2. Part II

Another three samples were soaked into chemicals that consisted of two by-products. There are three different combinations of by-products, which has been simplified in the Table 1. Similar procedure as mentioned in *Part I* was conducted to these samples.

Table 1. The mixture of by-product chemicals

Sample	Chemicals
A	LDPE in acetophenone plus α -methylstyrene
B	LDPE in acetophenone plus cumyl alcohol
C	LDPE in α -methylstyrene plus cumyl alcohol

3. Results

3.1. Part I- Single by-product chemical

A clean LDPE sample is used as reference to distinguish the trapping characteristic that is caused by the by-products chemical and the polymer structure. The volt off result can be observed in figure 1.

In a clean LDPE sample, both positive and negative charges are injected into the sample and trapped in the vicinity of electrodes. After 20 min of charging, more positive charges are observed in the sample bulk. At the same time, more negative charges are trapped near the electrode and increase the peaks height. When the by-products are introduced into the LDPE, the charge density profiles are altered. In acetophenone soaked LDPE sample (figure 1(b)), the domination of negative charges in the sample can be observed. In the vicinity of the positive electrode, the amount of positive charge decreases by time, indicating the amount of negative charges overcoming the numbers of positive charges. As the aging time increases, more negative charges drifted towards the anode and at the same time, positive charge is suppressed. As a result, the amount of positive charge gets lesser by time.

In cumyl alcohol soaked LDPE sample, heterocharges are observed during the first 10 min of charging. As more negative and positive charges are injected from the cathode and anode respectively, the heterocharges can no longer be seen and are replaced by the homocharges. Over one hour of charging, both positive and negative peaks grow equally although one could roughly see that negative charge is accumulated in the centre of the sample.

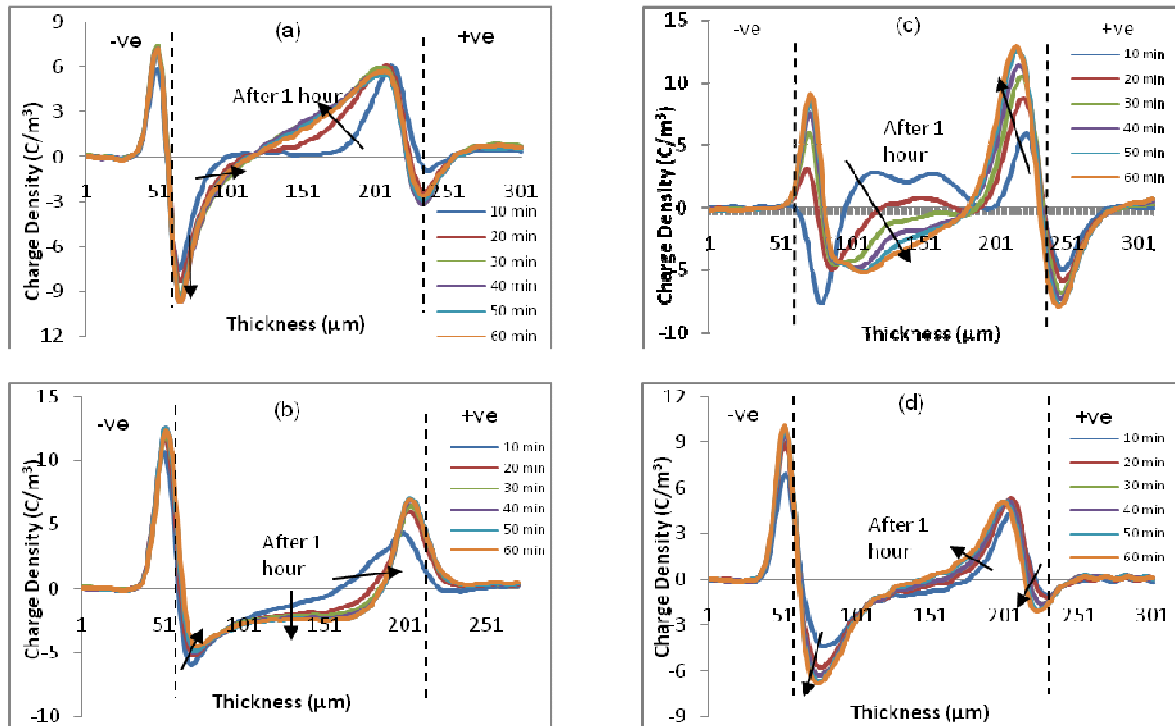


Figure 1. Charge Density of 180 μm a) clean LDPE b) acetophenone, c) cumyl alcohol and d) α -methylstyrene soaked LDPE stressed at 8 kV, during Volt OFF condition. Arrow shows the charge movement during one hour charging.

Unlike the former two by-products, α -methylstyrene has less effect on the charge density profile of LDPE in term of charge pattern. The space charge profile in figure 1(c) is almost similar to the charge profile in figure 1(a). However, lesser positive charge injection is seen in α -methylstyrene soaked LDPE thus equal amount of positive and negative charges are observed.

It is agreed that some of the results obtained in this paper are not similar to the results reported before. For instance, Maeno in his paper [5] found heterocharge in the presence of acetophenone and only homocharges are observed in cumyl alcohol soaked LDPE. These differences might be due to different electrodes system that was used during measurement. This factor is very vital in determining the charge injection profile in the dielectric sample. The electrode effects on space charge formation are reported elsewhere [6, 7].

3.2. Part II- Two by-products in sample

The charge density of Samples A, B and C for Volt Off measurement are presented in figure 2. For Sample A, the Volts Off measurement shows the domination of negative charges in the sample bulk similar to the charge density pattern of acetophenone soaked LDPE. Acetophenone is more prominent than α -methylstyrene in terms of controlling the charge build up. The positive charges are suppressed and as a result, a small positive peak is formed at the interface of the LDPE and anode. Similar characteristic is observed in figure 1(b).

The domination of acetophenone over the other by-product is also shown in Sample B. Although negative peak is only observed near to the cathode, the decreasing amount of positive charges by charging time and the movement of the positive peak towards the anode showed that the charges are suppressed. This observation is believed to be associated with the existence of acetophenone in the sample.

In the bulk of Sample C, no heterocharges appeared although cumyl alcohol subsisted in the sample. Positive charges are trapped at the vicinity of the anode and at the same time, the negative charges migrate from cathode to the sample bulk. As a result, more negative charge is seen in the sample. In Sample C, it is hard to tell which by-product is more dominant since the space charge dynamics does not show any distinctive pattern that can be associated to any of the individual by-products.

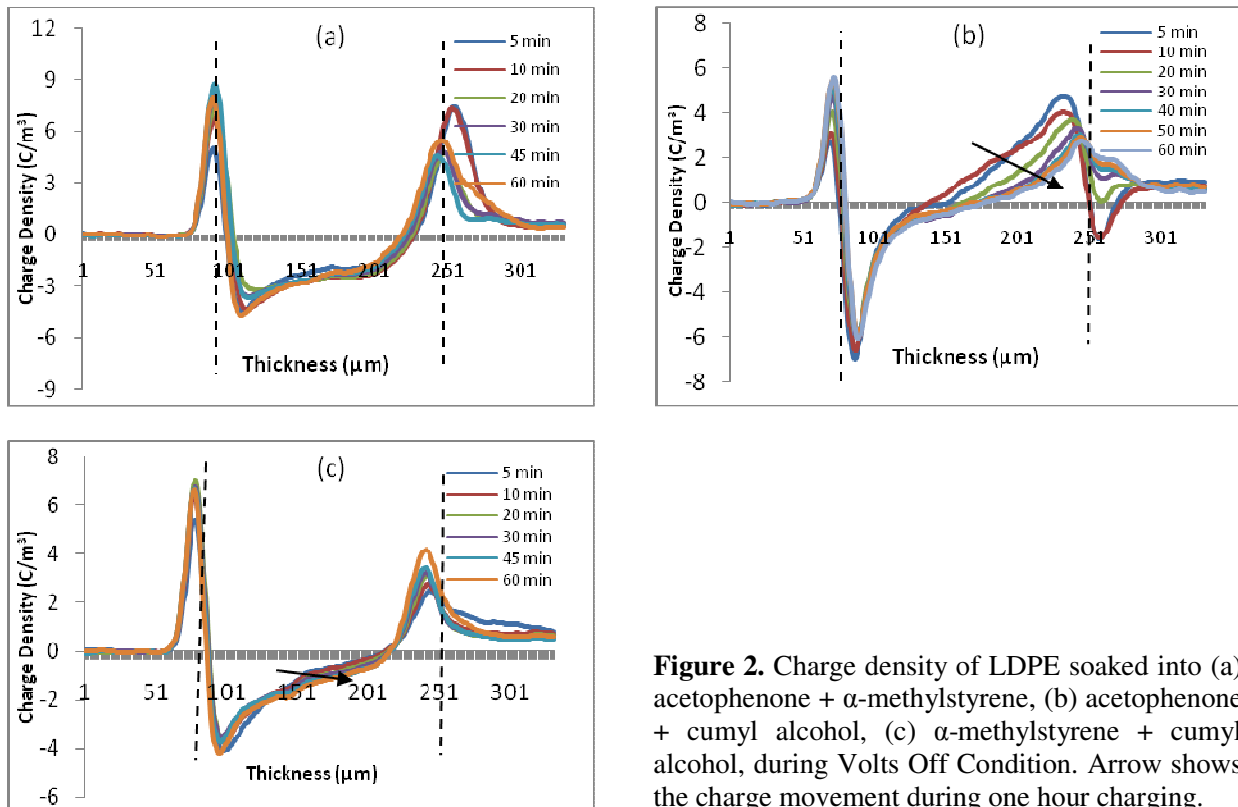


Figure 2. Charge density of LDPE soaked into (a) acetophenone + α -methylstyrene, (b) acetophenone + cumyl alcohol, (c) α -methylstyrene + cumyl alcohol, during Volts Off Condition. Arrow shows the charge movement during one hour charging.

4. Discussion

The total amount of charge in the sample, $q(x, t; E_a)$ that is relevant to the applied field E_a , is obtained by integrating the space charge density over the insulation thickness x , at a certain time t , [8].

$$q(t; E_1 \alpha) = 1/L \int_0^L \rho(x, t; E_1 \alpha) dx \quad (1)$$

where 0 and L denote the positions of the electrode excluding the charges at the electrodes. The charge density profile of the samples in figures 1 and 2 could be analysed to obtain the total charge value during charging and decay process. The results of this calculation are presented in figure 3. Figure 3(a) demonstrates the total charge build up during charging process. The drop in the total charge that accumulated in cumyl alcohol soaked LDPE for 20 min of charging is due to the height reduction of heterocharges peaks by the injected charges. Nevertheless, as shown in the same figure, after 35 min of charging, cumyl alcohol soaked LDPE has more charges in the sample compared to the other samples. On the other hand, acetophenone and α -methylstyrene reduce the total charge injection and accumulation in the LDPE film. α -methylstyrene soaked LDPE has the least amount of charges in the sample.

Observation of the rate of decay in figure 3(b) can be used to investigate the trapping behaviour in insulator. Generally, the by-products gear up the decay process particularly in the first 15 to 20 min. Afterward, the charge decays gradually reduce to a rate that is similar to the rate of decay of the clean sample. Acetophenone and α -methylstyrene reduce the number of total charge trapped into deep trap. Although the total charge in cumyl alcohol soaked LDPE is greater than that of the clean LDPE, but the overall rate of decay for that sample is quite high.

Similar observation can be seen in Samples A, B and C. The total charge decay result indicated that any sample that contains α -methylstyrene will show a fast charge decay, compared to the one that does not contain the by-product, which is Sample B. Hence it can be said that α -methylstyrene is dominant in the charge decay mechanism although it does not give much effect in the space charge formation.

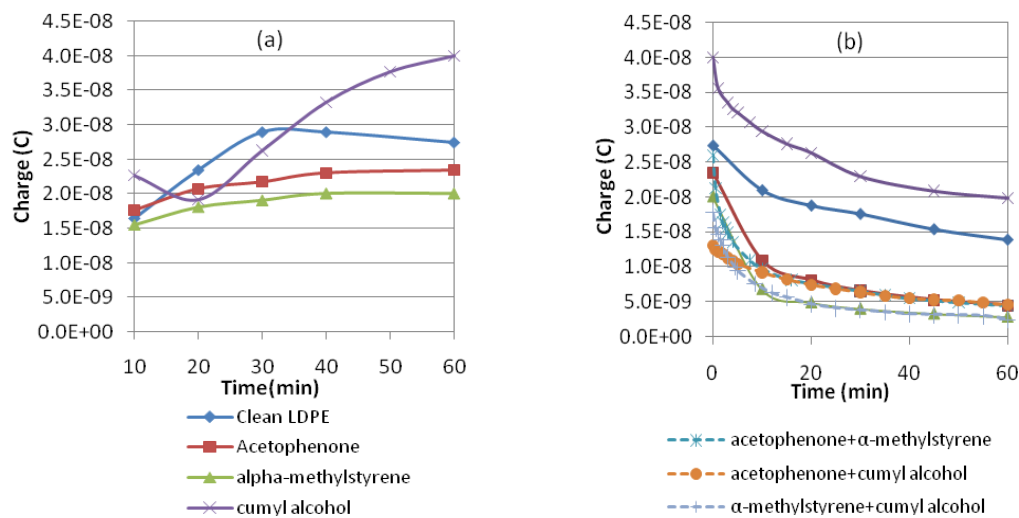


Figure 3. a) Total charge accumulated in sample during charging. b) Total charge decay in samples.

Based on the results, the by-products modify the trapping characteristic of LDPE in two possible ways which are, 1) by increasing the population of the shallow traps, and 2) by reducing the number of deep traps in the LDPE, replacing them with the shallow traps.

Voids and small spaces between the crystal structures that exist in the insulator will be filled by the byproducts. Originally, the regions of reduced density such as sub-microvoids with surrounding polymer chain will become deep electron traps [9]. Since the typical features of the chemical structures of these crosslinking by-products compared to LDPE are benzene ring, carbonyl group, double bond, and hydroxyl group, it is necessary to associate the changes in trapping behaviour with the existence of the chemical group [10].

The above argument comes with an assumption that during charging process, the charges have a higher tendency to fill in the shallow traps rather than the deep traps. The validity of this assumption has been confirmed via a short experiment involving LDPE sample that is charged at the same voltage, but for various charging periods. Samples that are charged for a shorter period of time will have faster charge decay. The result is presented in figure 4. Based on this assumption, it is proposed that the similar rate of decay observed in figure 3(b), during 20 to 60 minutes after short circuit in all samples is due to the original deep traps in LDPE.

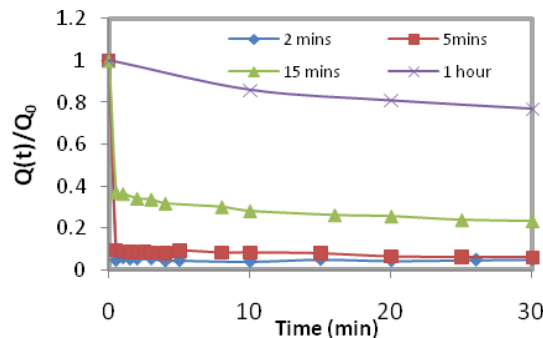


Figure 4. Plot of $Q(t)$ in relative value with respect to $Q_0=Q(0)$ against the decay time.

5. Conclusion

Our investigation upon the by-products showed that instead of introducing deep traps, the by-products increase the number of shallow traps in the insulator. This is due to the faster decay of the total charge in the presence to the crosslinking by-products.

α -methylstyrene has less effect on the charge density profile of LDPE but plays the main role in speeding up the decay process. Meanwhile cumyl alcohol is dominant in causing charge injection into the sample.

6. References

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