

# Electrical Properties of Silane Crosslinked Polyethylene in Comparison with DCP Crosslinked Polyethylene

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## ABSTRACT

The electrical properties such as water tree length, electrical conduction, ac breakdown strength and space charge of silane crosslinked polyethylene (SXLPE) were investigated, with a purpose to compare this material with ordinary dicumyl peroxide (DCP) crosslinked polyethylene (XLPE). Experimental results show that SXLPE has a smaller water tree length, much lower conduction current density, a little bit higher ac breakdown strength than XLPE, and on SXLPE only a very small homocharge is seen. The better behavior of SXLPE under electric stress is attributed to the absence of residual curing byproducts present in XLPE and the change of chemical structure by grafting and curing reactions.

## 1 INTRODUCTION

DICUMYLPEROXIDE crosslinked polyethylene (XLPE) has been playing a main role in solid dielectric insulated power cables, which has much merit such as high electrical strength, easy handling in laying and jointing, simple maintenance, *etc.* and a dry curing process has been developed to substitute steam curing, in order to reduce microvoids. However, the curing process today becomes very complicated, strict and expensive. During the 40 years since 1953 when General Electric first established the application of chemical crosslinking, people kept looking for other crosslinking methods in addition to dicumyl peroxide (DCP) curing. In the late 1960's Dow Corning introduced technology that allowed crosslinking polyethylene (PE) using organofunctional silanes. Since the early 1970's silane crosslinking technology has been applied to manufacturing crosslinked PE pipe and power cables.

Crosslinking PE using organo-functional silanes involves three reactions: grafting the silane onto the PE, hydrolysis of the silane groups, and condensation to form Si-O-Si links between the PE molecules. The combination of the hydrolysis and condensation reactions is generally termed 'crosslinking'. An organic peroxide initiator is used in the grafting reaction and a tin catalyst is used in crosslinking. Correspondingly silane crosslinked polyethylene (SXLPE) cable production also has 3 steps: grafting, cable fabrication, and crosslinking. Crosslinking can be accomplished after extrusion in hot water or steam.

SXLPE has a hard quality due to the introduction of silicone, and can be used for abrasion-resistant cables. Another advantage of SXLPE is the much simpler curing process than that required by DCP curing, thus the manufacturing cost could be lower. Moreover, the off-line curing yields higher productivity than XLPE in continuous vulcanization (CV)

lines. Although in many countries SXLPE currently is applied mainly in low voltage cables, European cable producers use it for medium voltage cable insulation. It is necessary to compare the electrical properties of silane crosslinked and DCP crosslinked PE and find out the theoretical feasibilities of using SXLPE material in HV power cables.

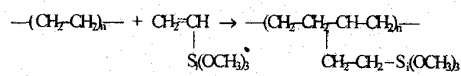
The electrical properties investigated in this report are water tree length, electrical conduction, ac breakdown strength and space charge. Electrical conductivity and ac breakdown strength are two of the most important parameters of dielectrics. Water treeing shows the aging of the materials in a given environment. And space charge accumulation in insulating material is known to affect the material behavior in electric fields. In this work the four types of electrical properties of SXLPE and XLPE are studied, in an attempt to compare the two materials.

## 2 DETAILED DESCRIPTION OF SXLPE

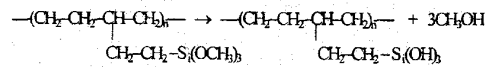
The reactions forming SXLPE contain 3 steps as shown in Figure 1. Crosslinked PE bridges from condensed silanol groups are formed in the last step.

According to the method of combining these chemical processes, there are different techniques for SXLPE cable production. Regardless of manufacturing techniques, the final process *i.e.* crosslinking the cable, can be accomplished by placing reels of cable in a hot water bath, steam chamber, or humid storage area.

(1) Grafting: PE + silane + peroxide



(2) Hydrolysis: catalyst, H<sub>2</sub>O



(3) Condensation: catalyst

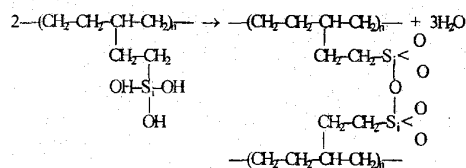


Figure 1. Chemical reactions forming SXLPE.

### 3 EXPERIMENTAL ON ELECTRICAL PROPERTY MEASUREMENTS

#### 3.1 SAMPLE PREPARATION

XLPE and SXLPE materials are both supplied by LG Chemical Corp., Korea. The XLPE is made of low-density polyethylene (LDPE) containing DCP and antioxidants. The concentration of DCP is 2.0 parts per hundred (phr) resin. The LDPE has a density of 0.920 g/cm<sup>3</sup> and a melt index of 2.0 g/10 min. Its number and weight average molecular weight are 25800 g/mol and 178600 g/mol, respectively. Its molecular weight distribution is 6.92. The SXLPE is Sioplas material, a mixture of LDPE with grafting components and master batch, ready for crosslinking. The graft reaction takes place while all components are extruded by a so-called reaction extrusion method. Basically the same type of LDPE used for the XLPE was used for the preparation of graft copolymer.

XLPE samples were prepared by melting at 120°C for 10 min and crosslinking at 180°C under pressure for 20 min. SXLPE samples were first compression molded at 120°C for 20 min, and then boiled in 90°C distilled water for 4 h with a water bath.

#### 3.2 MEASUREMENTS

Water tree length measurements were conducted in a test cell shown in Figure 2. Slab samples which have 8 cone-shaped indentations were prepared by compression molding, using a specific mold with 8 needles on it, with tip radius 5 μm. As also shown in Figure 2 is the 2 mm distance in the sample from the tip of the inner cone to the ground side. 0.1 M AgNO<sub>3</sub> aqueous solution was used as electrolyte, which is known to produce silver trees [1]. Water trees were grown in samples with 10 kV voltage after a certain time (10 to 200 h) at room temperature. The averaged value from 8 measured water tree length data, observed under a microscope, for each sample was taken as the water tree length.

Electrical conduction characteristics were investigated on 100 μm thick film samples by using a measuring system composed of a dc power

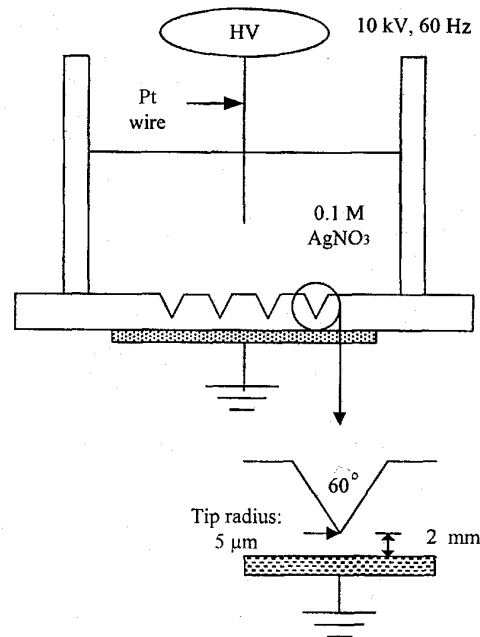


Figure 2. Water tree length test cell scheme.

supply (Keithley 247), an electrometer (Keithley 617) connected through GPIB to a computer, and a three-electrode system test cell set in an oven. Tests were carried out at temperatures from 30°C to 90°C and applied electrical stresses were adjusted in the range from 0 to 40 MV/m. The current at 40 min after voltage application was taken as the conduction current [2].

The ac breakdown strength (ACBD) of 100 μm thick samples were obtained using a Hypotronics ac breakdown tester. The electrode is spherical, and breakdown happened at the center of the sample. All tests were carried out at 1 kV/s in an insulating oil.

Space charge distributions were measured by a pulsed electroacoustic (PEA) method, which is very sensitive and has been applied very successfully in many worldwide research units. The principles and techniques can be found elsewhere [3, 4]. A dc voltage is applied to the sheet sample for 30 min and then short circuited, after which an electric pulse is applied and charge distribution is measured using an oscilloscope. The charge distribution is the profile of the charge remaining after the short circuit. Amplitude and width of the electric pulse were 2 kV and 10 ns, respectively. Sample thickness was typically 0.7 mm.

In the measurements of conduction and space charge, semiconductive electrodes were used, considering their practical application for shield in power cables. These electrodes were prepared by curing at 180°C for 20 min, and before use they were vacuum degassed at 80°C for 100 h in order to eliminate the volatile impurities which may affect the carrier behavior in the material to be measured [5].

## 4 RESULTS AND DISCUSSION

### 4.1 WATER TREE PROPERTIES

Figure 3 shows the grown water tree lengths of SXLPE and XLPE with the time that the samples were under stress. It can be seen from Figure 3 that the water tree length of SXLPE samples is smaller than that of XLPE, within the time from 10 to 200 h. People tend to think that SXLPE might have worse water tree degradation properties because its crosslinking process is accomplished in water (or steam). The result in this report disproves this. It seems more difficult for water trees to develop in SXLPE, probably because of the grafted silane. The condensed silanol groups among PE molecules may act as obstruction to water tree growth. Secondly, the morphology of SXLPE may become very different from XLPE as a result of grafting.

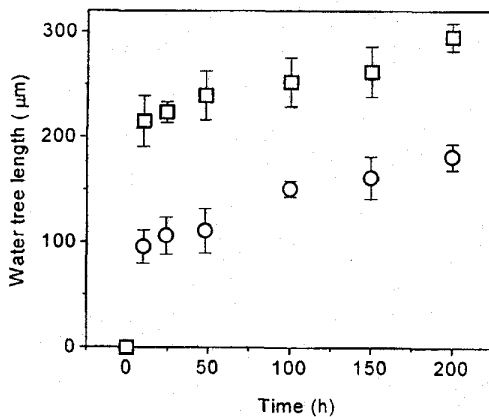


Figure 3. Water tree length of SXLPE and XLPE; open circle: SXLPE, open square: XLPE.

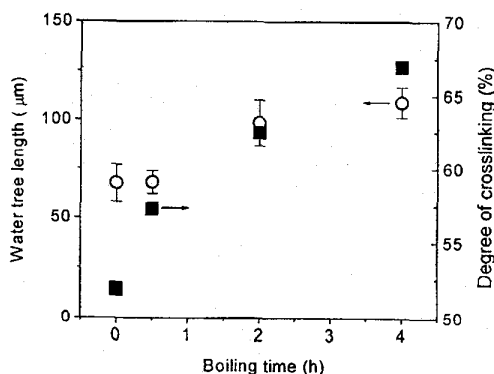


Figure 4. Water tree length and crosslinking density of SXLPE as functions of boiling time: crosslinking method: boil in 90°C distilled water; water tree growth time: 100 h; open square: water tree length, closed square: crosslinking density.

Figure 4 shows the relationship of water tree lengths of SXLPE with SXLPE sample crosslinking time, at tree growth time of 100 h. The samples were boiled with different time of up to 4 h. With the increment of crosslinking time, water trees in SXLPE became bigger, this might be due to more voids or water drops in SXLPE samples with longer crosslinking time. In Figure 4 the crosslinking density at different crosslinking

time is also shown. Figure 5 shows the relationship of water tree length of XLPE with degree of crosslinking. Water tree lengths get smaller with the increase of crosslinking density. As degree of crosslinking increases, PE chains crosslink more effectively, resulting in an increased resistance to the propagation of micro-cracks.

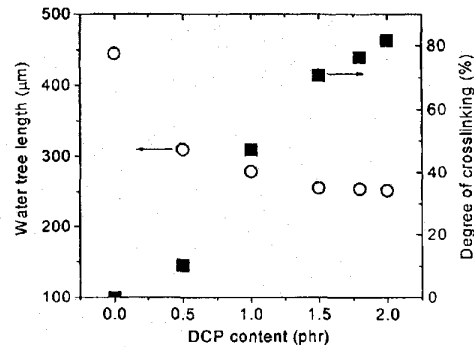


Figure 5. Water tree length and crosslinking density of XLPE as a function of DCP content.

One interesting fact is that, with the increment of crosslinking density, water tree length of SXLPE gets larger while that of XLPE gets smaller. XLPE with various crosslinking density was obtained by curing at identical condition (180°C for 20 min) using pellets containing different DCP content. On the other hand, SXLPE with various crosslinking density was obtained by steaming for different times. It suggests that heat treatment after crosslinking reaction could increase water tree length. To prove this, water treeing tests were carried out for the XLPE vacuum degassed at 80°C for 100 h. The result at the condition of 10 kV for 100 h was the increase of water tree length from 240 to 600 μm. These results indicate that heat treatment after crosslinking enhances the water tree growth in both SXLPE and XLPE. The effect of heat treatment on the water tree growth is under investigation and the results will be reported later.

### 4.2 ELECTRICAL CONDUCTION CHARACTERISTICS

Figure 6 shows the conduction current density  $J$  vs. electric field  $E$  of SXLPE and XLPE measured at 30 and 70°C. The conduction current density of SXLPE is lower (0.5 to 1 order of magnitude) than that of XLPE under same electric field and with same sample thickness. The possible reason is that there are fewer charge carriers in SXLPE, or that charge trapping is more efficient in SXLPE. A significant source of carriers forming the higher conduction current of XLPE is supposed to be the residual byproducts after crosslinking, and the authors hold that these byproducts are not present in SXLPE in which the DCP content is one tenth of that in XLPE. XLPE and SXLPE are also different in their chemical structures and morphologies.

To prove this, conduction currents of vacuum degassed XLPE sample were measured. In Figure 7, comparison of  $\log J$  vs.  $\log E$  curves of SXLPE, XLPE and vacuum treated XLPE is shown. After vacuum treatment (100 h), conduction currents of XLPE decrease markedly (0.5 to 1

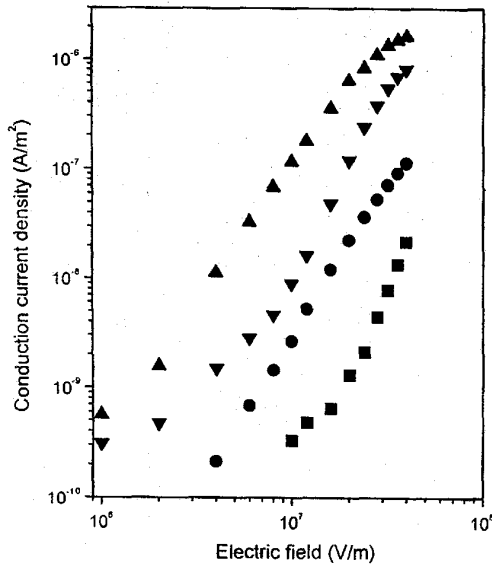


Figure 6. Comparison of conduction current density of SXLPE and XLPE at 30°C and 70°C: closed square: SXLPE, 30°C closed down triangle: SXLPE, 70°C, closed circle: XLPE, 30°C, closed up triangle: XLPE, 70°C.

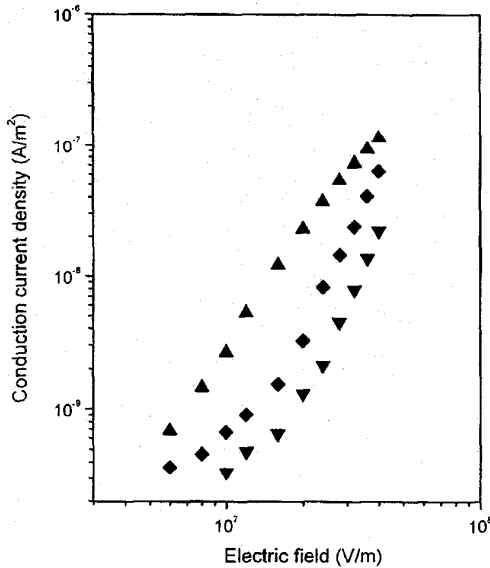


Figure 7. Comparison of conduction current density of SXLPE, XLPE and vacuum treated XLPE at 70°C: closed up triangle: XLPE, closed diamond: vacuum treated XLPE, closed down triangle: SXLPE.

order of magnitude). Moreover, the variation trend in the  $J-E$  characteristic curve of vacuum treated XLPE is very close to that of SXLPE. However, the conduction currents of SXLPE are still lower than those of vacuum degassed XLPE. Lower current densities could be due to silanol groups formed by grafting and curing reactions. These silanol groups may act as charge trapping sites.

The slopes of  $J-E$  curves are indicated in Table 1. For XLPE, the slope decreases at higher electric fields, typically 2.7 to 2.0 in value. However,

Table 1. Slopes in  $\log J-\log E$  curves of SXLPE, XLPE and vacuum treated XLPE at 30°C.

Sample	SXLPE	XLPE	vac. XLPE
slope (low field)	1.4	2.7	1.7
slope (high field)	4.6	2.0	4.2

Table 2. Mobility and activation energy of SXLPE, XLPE and vacuum treated XLPE: mobility at 70°C,  $2.8 \times 10^7$  V/m; activation energy at  $2.8 \times 10^7$  V/m.

Sample	SXLPE	XLPE	vac. XLPE	Unit
Mobility	$7.94 \times 10^{-14}$	$1.27 \times 10^{-13}$	$1.23 \times 10^{-13}$	$m^2/Vs$
Activation energy	0.95	0.71	0.83	eV

for both vacuum treated XLPE and SXLPE, the slopes increase with increased electric field, and the values are 1.7 to 4.2 for vacuum treated XLPE, 1.4 to 4.6 for SXLPE. The closeness of slopes between SXLPE and vacuum treated XLPE implies that after vacuum treatment the conduction process in XLPE is similar to that in SXLPE, i.e. the conduction mechanism and carrier type might be similar.

Based on the agreement that the conduction currents in SXLPE and XLPE are attributed to space charge limited current (SCLC), the carrier mobilities of SXLPE, XLPE and vacuum treated XLPE were calculated by using Child's Law and finding the transient peak time on current vs. time curves, as listed in Table 2 [6]. The activation energy obtained from  $J/E$  vs. temperature  $T$  curves also are shown in Table 2. It is seen that the mobility of SXLPE is lower than that of XLPE, and its activation energy is higher.

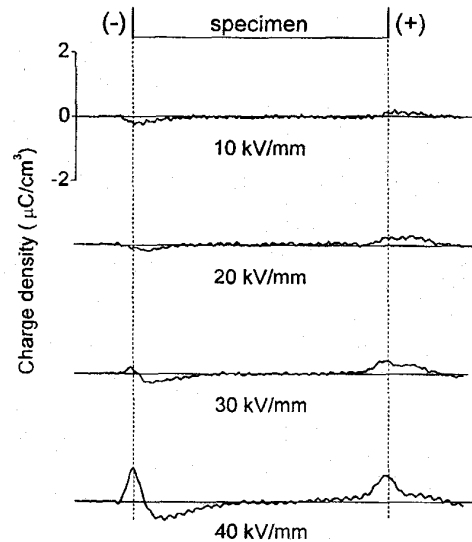


Figure 8. Space charge distribution of SXLPE.

To summarize the results on electrical conduction, SXLPE shows better property as insulating material due to its different production method which eliminates the presence of DCP curing byproducts and changes the chemical structure as well as physical properties. These byproducts increase conduction current in XLPE, as pointed out previously [2].

Table 3. ac breakdown strength of SXLPE and XLPE with Weibull statistical analysis results

Sample	SXLPE	XLPE	Unit
Average strength	1.55	1.29	MV/cm
Weibull characteristic strength	1.59	1.43	MV/cm
Weibull minimum strength	1.26	0.53	MV/cm
Weibull shape parameter	2.53	1.86	

#### 4.3 ac BREAKDOWN STRENGTH

ACBD of SXLPE and XLPE are shown in Table 3, together with Weibull Statistical analyzing results. The strength of SXLPE is a little bit higher than that of XLPE. Breakdown is a very complicated process and the breakdown strength depends on many factors. The results indicate that although SXLPE may contain more water than XLPE, its breakdown strength keeps in the high level. The reason of the higher ACBD of SXLPE is not clear at this moment.

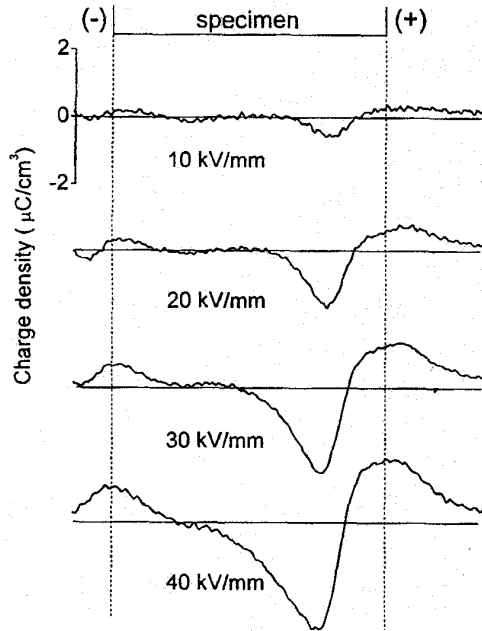


Figure 9. Space charge distribution of XLPE.

#### 4.4 SPACE CHARGE PROFILES

On SXLPE samples, a very small homocharge is observed as shown in Figure 8, while on XLPE a large heterocharge peak appears, Figure 9, which is probably produced by small molecules, such as crosslinking byproducts and additives *etc.* The big heterocharge in XLPE is detrimental to the insulating property, and it can cause breakdown under lower voltages. With vacuum treatment the heterocharge could be reduced [4]. In SXLPE, the small homocharge comes from injection, and the harmful effect of it is of much less concern than the big heterocharge in XLPE.

#### 5 CONCLUSIONS

EXPERIMENTAL results show that the water tree lengths of SXLPE samples are smaller than those of XLPE, the conduction current density of SXLPE is much lower than that of XLPE, the ac breakdown strength of SXLPE is somewhat higher than that of XLPE, and on SXLPE samples only a very small homocharge is seen.

All these indicate that SXLPE has better behavior under electrical stress as an insulating material than XLPE. This is attributed to the change of chemical structure by grafting reaction and the absence of effects of residual curing byproducts present in XLPE. The results are very useful to today's development on SXLPE product for higher voltage power cable insulation.

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