Space Charge and Aging in Polyethylene Cables

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Abstract: Aging of the polyethylene (PE) insulation in high voltage power cables is explained by the suppression of electromagnetic (EM) radiation released by the breaking of van der Waals (vdW) bonds in the interstice between PE molecules. The interstices are treated as quantum electrodynamics (QED) cavities having EM resonances beyond the ultraviolet (UV). Since the suppressed EM radiation may only be conserved at the EM resonant frequency of the QED cavity, a burst of at least UV radiation is produced that scissions the PE molecules forming its surfaces leaving both a space charge of CH+ radicals and a submicron cavity. Aging typified by microscopic cavities and reduced electrical breakdown is therefore reduced by adding UV blockers to the PE during processing.

1 INTRODUCTION

Space charge in polyethylene (PE) insulation of high voltage power cables is generally [1] thought caused by the trapping of field induced injection of charge from electrodes by microscopic cavities. However, it was recently disclosed [2] space charge of CH+ radicals is produced without electric fields by scission of PE molecules at the instant submicron cavities form at low stress levels. But what causes PE to scission at low stress levels?

The PE molecule is usually considered to scission only under high tensile stress. Computer simulations [3] suggest the tensile scission of PE molecules to occur ~ 4 eV, but experiments show 5-10 times lower ultimate strength. Indeed, the CH+ radical signatures found by electron paramagnetic resonance (EPR) during tensile tests [4] at stress levels less than 50 % of ultimate suggest another mechanism is operating at low stress levels to scission the PE molecules.

The PE molecule may scission at zero applied stress if irradiated [5] with ultraviolet (UV) radiation, and therefore a plausible explanation for the low ultimate found in experiments is photolysis from *internal* UV sources. UV blockers are used to protect PE against *external* UV sources, but the literature is silent the use of blockers to protect PE against *internal* UV sources.

In tensile tests, exposing the specimens to *external* UV sources is representative of *internal* UV sources. Indeed, 1 % of the UV stabilizer Tinuvin® 327 added to LDPE powder prior to compression moulding showed [6] significant improvement in mechanical properties after exposure to *external* sources of UV radiation.

Similarly, the scission of PE molecules from *internal* UV sources was simulated [4] by exposing bundles of micron-sized diameter PE filaments to an *external* UV source. Here the EPR spin-trap - Tinuvin®770 - was applied as a coating to the filaments by soaking the bundles in 1% wt dichloromethane solution. Although CH+ radicals were detected during tensile testing, no EPR signal was observed after washing the filaments. This suggests the Tinuvin®770 blocked the *external* UV from the filaments, thereby supporting the argument that adding Tinuvin®, or the like, to the PE in the extrusion process will tend to block any *internal* UV produced during the life of the PE.

In this paper, PE scission is caused by photolytic scission under UV radiation, the UV produced as van der Waals (vdW) bonds break in submicron quantum electrodynamics (QED) cavities. The process producing the UV is called cavity QED induced EM radiation applicable where photons and electrons are found at ambient temperature including: flow electrification [7], Casimir effect [8], and ultrasonic ionization [9].

2 BACKGROUND

Photolytic scission of PE molecules is proposed initiated by the breaking of vdW bonds in submicron QED cavities having EM resonances beyond the UV, and therefore is suppressed only to be conserved by a gain at the resonant VUV frequency of the QED cavity. In this way, *internal* UV radiation is produced to scission the PE molecules.

2.1. QED Cavities

Cavity QED induced EM radiation in the interstice between PE molecules is depicted in Fig. 1.

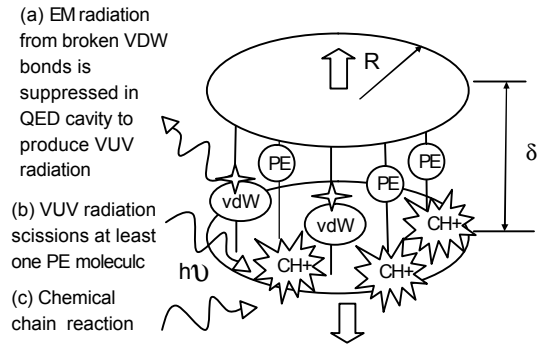

Fig. 1 Space Charge by QED induced EM radiation

The QED cavity is taken as a "penny" crack having thin cylindrical shape of radius R and height d. The load is transferred across the crack faces by vdW bonds in parallel with PE molecules. The process comprises: (a) suppression of EM radiation released by the breaking of vdW bonds that is conserved at the EM resonant frequency of the QED cavity to induce a burst of *internal* UV radiation, (b) By photolysis, the VUV radiation scissions at least one PE molecule to form a CH+ fragment. (c) The CH+ fragment [2] having highly reactive primary end radicals (-CH_2 - C*H_2) scissions neighboring PE molecules by chemical chain reaction [10] leaving a space charge of CH+ fragments in a submicron cavity.

Although the PE molecule scissions under high tensile stress, scission in a QED cavity occurs by photolysis as vdW bonds break at low stress levels.

3 THEORY

The total EM energy U suppressed from the breaking of vdW bonds is,

$$U = NE_{vdW} \tag{1}$$

where, N is the number of vdW bonds in the QED cavity, and E_{vdW} is the EM energy released in breaking a single bond. For PE, $E_{vdW} \sim 0.1$ eV [11]. Since the QED cavities are VUV resonant, the conservation of EM energy is,

$$U = N_{VUV} E_{VUV} = NE_{vdW} \tag{2}$$

where, E_{VUV} is the Planck energy of the VUV photons and N_{VUV} is their number,

$$E_{VUV} = \frac{hc}{2(d + 2e_p)} \quad \text{and} \quad N_{VUV} = \frac{NE_{vdW}}{E_{VUV}} \tag{3}$$

where, h is Planck's constant, c is the speed of light, and e_p is the penetration depth of VUV radiation, say $e_p \sim 10$ nm.

Assuming a close packing of PE molecules in the surfaces of the "penny" crack, the number N of vdW bonds depends on the C-C spacing D along the PE molecule chain, $D = 0.154$ nm.

$$N = p\left(\frac{R}{D}\right)^2 \tag{4}$$

Combining,

$$N_{VUV} = p\left(\frac{R}{D}\right)^2 \frac{E_{VDW}}{E_{VUV}} \tag{5}$$

The conditions for initiating the chemical chain reaction in the QED cavity of radius R and gap d is related to the number N_{VUV} of VUV photons having Planck energy E_{VUV} shown in Fig. 2.

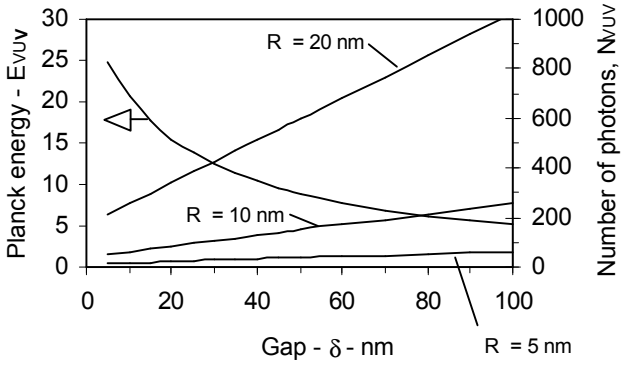

Fig. 2 Planck energy E_{VUV} and number N_{VUV}

The number N_{CH+} of CH+ charged fragments depends on the scission quantum yield Y of PE, i.e., $N_{CH+} = Y N_{VUV}$. The PE yield in the UV is not known, but taking the yield [12] of poly methyl methacrylate (PMMA) as representative of PE, $Y \sim 0.03$ to 0.04 for UV from 214 to 229 nm, or $E_{VUV} \sim 5$ eV. Fig. 3 shows $E_{VUV} > 5$ eV for all $d < 100$ nm. For $R = 5$, 10, and 20 nm, $N_{VUV} \sim 64$, 256, and 1023, and therefore $N_{CH+} \sim 2$, 9, and 36. Thus, to produce at least one CH+ fragment to initiate the chemical chain reaction, $R > 5$ nm.

4 DISCUSSION

Generally, space charges are thought [13] to occur after physical defects are formed,

> "It is our contention that space charges are a consequence of aging, i.e., charges are injected only when physical defects (such as microcavities) have been formed by the field-induced strain…space charges are related to the formation of submicrocavities, and therefore, are a consequence, not a cause of high field aging."

But space charges are produced in PE before defects form under field-induced strain, e.g., the 0.25 Cm^{-3} residual charges [13] always observed in PE. To explain this anomaly absent fields, QED theory [2] was proposed that asserts space charges are produced at the instant the submicron cavities form.

4.1. Molecular and QED Theory

The Molecular theory [14] relies on a double energy barrier for submicron cavity formation and molecular deformation to explain PE lifetime t given by,

$$t = (h/kT)\exp\left\{\left(DG - \left[1/2e(DV/2)F^2\right]\right)/kT\right\} \tag{6}$$

where, DG is Gibb's free energy representing the barrier height, k is Boltzmann's constant, T is absolute temperature, F is the field, and e is the permittiviy. The

strained volume DV is the slope of the F^2 vs. log t curve that for typical PE data [1] abruptly changes between Regions I and II as shown in Fig. 3.

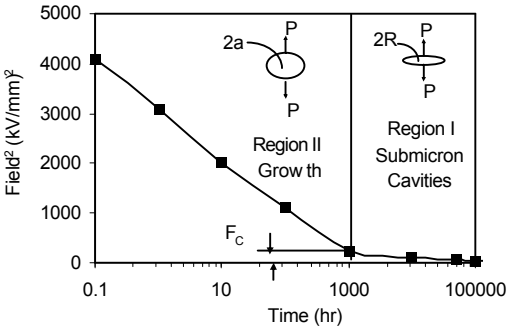

Fig. 3. Plot of F^2 vs. log t for PE

The QED theory treats Region I as the formation of submicron cavities while Region II comprises cavity growth. The major difference between the Molecular and QED theories is in Region I. The QED theory provides a physical mechanism to produce space charge in the formation of submicron cavities; whereas, the Molecular theory makes no claim of space charge production, instead relying on the general view that space charges are produced by charge injection after the submicron cavities are formed.

The QED theory is based on PE morphology. In Region I, vdW bonds break to form submicron cavities of width 2R and height d; while in Region II, the submicron cavities grow to form larger cavities of width 2a and height 2b. Region I is described by QED theory, but Region II may be described by cavity growth using conventional crack growth formalism This does not mean the breaking of vdW bonds and formation of CH+ fragments only occurs in Region I, as vdW bonds are broken in the crack tip during cavity growth in Region II.

In Region II, conventional crack growth [15] formalism in PE gives the cavity growth rate da/dt by the power law,

$$\frac{da}{dt} = B' K_1^4 \left(1 + R_L\right)^{-6} \tag{7}$$

where, B' = 0.4 for HDPE at ambient temperature, and R_L is the ratio of minimum to maximum load. For creep, R_L = 1, and for fatigue $R_L = 0$.

The stress intensity factor K_1 depends on the cavity geometry. For a central loaded microcavities of width 2a shown in Region II of Fig. 3.

$$K_1 = P\sqrt{pa} \tag{8}$$

where, P is the Maxwell pressure,

$$P = 1/2e_o eF^2 \tag{9}$$

For fatigue with $R_L = 0$, PE follows the Paris relation,

$$\frac{da}{dt} = ADK^{4\pm0.5} \tag{10}$$

where, DK_1 is the range in stress intensity, and $A = B$' is the material constant.

Features of the QED cavity theory in explaining other anomalies in the aging of PE are discussed as follows.

4.2. Space charge models

The space charge models [1] claim PE aging is caused by charges, but have difficulty in explaining [13] why breakdown under AC fields occurs at lower fields than under DC, although the charges remaining in the dielectric under the AC field are 100 x less than under the DC field.

In the QED theory, space charge is produced by different mechanisms. In Region I, CH+ fragments are produced as the PE molecules scission by chemical chain reaction initiated by UV radiation produced in the formation of submicron cavities. In Region II, the CH+ fragments form as the PE scission under during the growth of the submicron cavities.

Because of the cyclic Maxwell pressure in PE under AC fields, Region II is marked by rapid growth of submicron cavities beyond micron sizes compared to that for the slower growth under DC fields. In PE, fatigue growth [15] to reach creep growth levels similar to steady DC fields required 3 orders of magnitude less time. Thus, breakdown under AC fields occurs far faster than under DC fields.

Moreover, the residual charge under AC fields should also be less than for DC fields. Both Regions I and II produce space charge, but space charge and breakdown are not the same. Irrespective of whether the field is AC or DC, breakdown occurs because of the micron cavities produced during Region II. Since Region I cavity growth under AC fields may be 3 orders of magnitude shorter than under DC, the charge remaining in the dielectric under AC fields may be expected to be 100x lower than for DC fields.

4.3. Sample Size

The size of PE test samples is known [14] to have a significant effect on electrical breakdown, but no model takes this parameter into account. Indeed, the observation that the electrical breakdown [17] of dielectrics may increase as with a decrease in sample thickness is not surprising if viewed from the standpoint of fracture mechanics embodied in the QED theory where smaller specimens are invariably tougher in fracture than larger ones.

4.4. Photo Aging

Photo aging of polymers has long been known [18] to correlate with increased free radical density and

decreased dielectric strength. Because of the difficulties in performing field aging of polymers, aging by *external* UV sources is used to simulate aging under electrical fields. Since QED theory claims *internal* UV radiation is produced by the breaking of vdW bonds under field induced strain, UV radiation to simulate field aging is supports the QED theory.

4.5. Carbon Black as UV Blocker

Similar to Tinuvin®327, or the like, carbon black is an excellent UV blocker. Support of the QED theory is found [19] by the improved mechanical properties of ultra high molecular weight (UHMW) PE found by the addition of 5 wt% carbon nano tubes (CNT) shown in Fig. 4. Tests are ongoing to determine if Tinuvin®327 provides a similar improvement in the properties of UHMWPE.

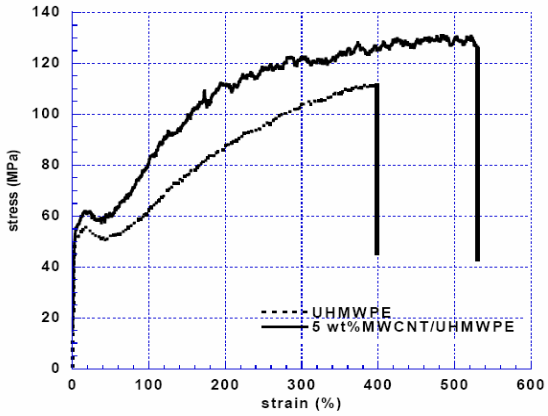

Fig. 4. CNT improvement of UHMWPE

5 CONCLUSION

The scission of PE molecules by photolysis from UV radiation produced as vdW bonds break in submicron QED cavities suggests cable life may be extended by the addition of UV blockers to PE during processing.

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