Chapter 5
Dielectric Breakdown in Polymer Nanocomposites

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5.1 Introduction

This article treats with short- and long-time breakdown in nanodielectrics. Short-time breakdown is theoretically established. This is related to more or less intrinsic breakdown of thin insulating films. Such types of breakdown include intrinsic breakdown, electron avalanche breakdown, thermal breakdown, and electromechanical breakdown. Data are collected for pure polymers [2] and polymer nanocomposites [6]. Nanofillers are considered to become carrier traps and play an important role in dielectric breakdown processes. But no breakdown phenomena have been adequately correlated with any of the theoretical models yet, because of their complexity. Long-time breakdown is observed in thick polymer insulations and appears in the shape of electrical treeing. This treeing is especially important from the engineering point of view. Treeing phenomena in nanocomposites can be analyzed from a certain theoretical point of view. Tree initiation takes place in chemical or electronic degradation. Trees grow by partial discharges taking place inside of tree channels and retarded by nanofillers. Under a certain condition such as extremely high electric field, electrons can be accelerated by the field formed by nanofillers.

5.2 Theories of Dielectric Breakdown

Solids are governed by two basic elements, i.e., electrons and phonons (quantum modes of lattice vibration) in electronic conduction. In the case of semiconductors, electrons are available in the conduction band from electron donors and from the

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valence band. On the other hand, in the case of dielectrics, i.e., electrical insulating materials, electrons are in the conduction band and are usually considered to be supplied form from outside (actually electrodes). Therefore, charge that electrons hold is easily accumulated inside the dielectrics. It is called space charge. Usually electrons are trapped in trapping centers or trap to for such space charge.

Electrons gain energy from electric field and transfer their energy to phonons by collision to reach a steady state. Electronic conduction takes place in this energy balance. This energy balance will collapse if electrons gain more energy than energy loss (energy transferred to phonons). This is an electronic breakdown in solids. This is called dielectric breakdown in solid dielectrics. Dielectric breakdown includes:

1. Intrinsic breakdown
2. Electron avalanche breakdown
3. Thermal breakdown (impulse and steady state)
4. Electromechanical breakdown

5.2.1 Intrinsic Breakdown

Electrons are accelerated by the electric field and lose their energy to the lattice (or phonons) by collision, as shown in Fig. 5.1 [7]. Energy balance in an ensemble of electrons is represented by the formula 5.1

$$A\left(F_c, T_0, E\right) = B\left(T_0, E\right) \tag{5.1}$$

The critical field E, i.e., breakdown strength, is determined by energy balance between the energy gain per unit time from the field and the energy transfer per unit time to phonons. Energy transfer means energy loss of electrons by collisions with phonons or lattice vibrations. Electrons are newly available by impact ionization. Energy transfer B is determined by collision cross sections.

There are several criteria according to mechanisms of energy transfer from the conducting electrons to phonons: there are two categories, i.e., (1) single-electron approximation and (2) collective electron approximation [1]:

1. Single-electron approximation

    • High-energy criterion proposed by Fröhlich
      All electrons fulfill the criterion: Formula 5.1:
    • Low-energy criterion proposed by von Hippel and Callen

All electrons in the conduction band fulfill the criterion:

$$E_H = \frac{hv}{e\lambda} \tag{5.2}$$

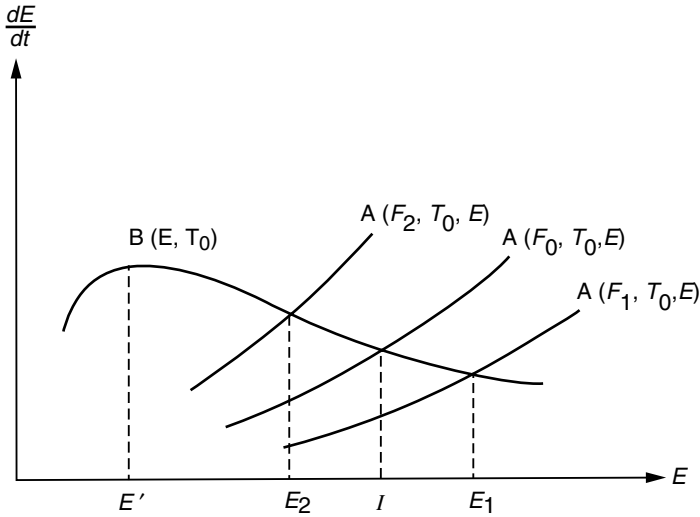This is called von Hippel electric field for dielectric breakdown.

Fig. 5.1 The average rate of energy gain A (F, T_0, E) from an applied field for various field strengths, and the average rate of energy loss to the phonon B (E, T_0) (O'Dwyer [7], p. 21, Fig. 3)

2. Collective electron approximation

- Collective electron criterion: This is proposed by Franz and Stratton. Electrons have an energy distribution. Averaged electrons over energy distribution fulfill the criterion (i) the low density approximation: avalanche theory and (ii) the high-density approximation.
- Electronic thermal breakdown: This is proposed by Fröhlich.

  Electro–electron interaction is larger than electron–phonon interaction.

If electron–electron interactions are strong, electronic thermal breakdown is likely to take place. Electrons can be hot. Such electrons are called hot electrons. This type of breakdown will take place in amorphous or noncrystalline dielectrics when interactions of electrons with impurity levels (donors and/or traps) exceed those with phonons. These results in electron temperature will increase rapidly. This was calculated by Fröhlich. It is considered that this will explain well the high-temperature breakdown characteristics.

5.2.2 Electron Avalanche Breakdown

Successive electron multiplication like avalanche takes place due to the ionization by collision process as shown in Fig. 5.2. This avalanche gives large energy to phonons to cause dielectric breakdown. There are two ways to calculate the critical field, i.e., single-electron approximation and collective electron approximation.

Fig. 5.2 Schematics of
electron avalanche process
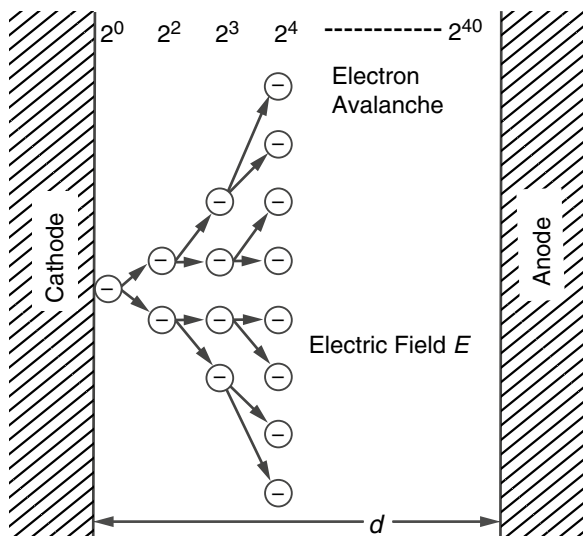
Here is the simplest case with the single-electron approximation. As electron ava-
lanche in solid dielectrics has no feedback mechanisms including photoionization,
the critical field cannot be determined automatically. Therefore, we need some
assumption. A condition for 40 generations was given by Seitz [9]:

$$E_c = \frac{H}{\ln\left(\dfrac{d}{40 E_c \mu \tau}\right)} \tag{5.3}$$

H: constant, d: insulation thickness, μ: electron mobility, τ: average collision time of
electrons

5.2.3 Thermal Breakdown (Impulse and Steady State) (Fig. 5.3)

Temperature rise due to Joule heating and heating by dielectric dissipation loss will
melt insulation to cause dielectric failure. Intrinsic breakdown is material specific,
but this type of breakdown is affected not only by materials but also by heat radia-
tion conditions like electrode sizes and structures. Energy balance in this case is as
follows:

$$\underbrace{C_v \frac{dT}{dt}}_{\text{Heat Absorption}} - \underbrace{div\left(k\, grad\, T\right)}_{\text{Diffusion}} = \underbrace{\sigma E^2}_{\text{Joule Hear or Dielectric Heat}} \tag{5.4}$$

Fig. 5.3 Temperature rise associated with thermal breakdown
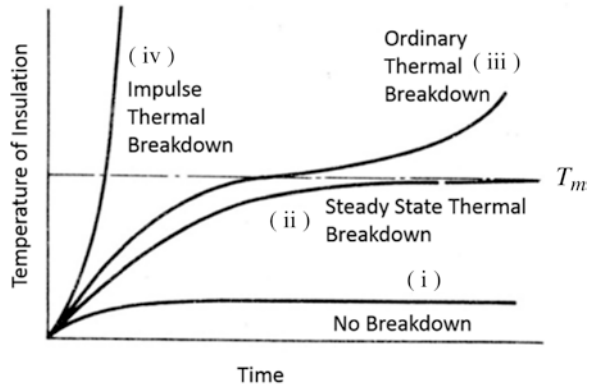
C_v, is specific heat at constant volume; T, absolute temperature; t, time; κ, thermal conductivity; σ, electrical conductivity; and E, electric field strength.

In that meaning, thermal breakdown can be called extrinsic breakdown. It takes place at relatively high temperatures. Thermal breakdown strength tends to decrease with the increase of temperature. Thermal breakdown is divided into categories, i.e., steady-state and impulse breakdown modes. Steady-state thermal breakdown, as time dependence can be neglected, is governed by the formula

$$-div\left(k\,grad\,T\right)=\sigma E^2 \tag{5.5}$$

In a plane-parallel electrode system, steady-state thermal breakdown strength is given by

$$V_c = \left(\frac{8\kappa kT}{\sigma_0\phi}\right)^{\frac{1}{2}} \exp\left(\frac{\phi}{2kT}\right) \tag{5.6}$$

where κ is thermal conductivity and $\sigma = \sigma_0\exp(-\phi/kT)$.

Impulse thermal breakdown is determined by the formula 5.7 as the diffusion term can be neglected:

$$C_v\frac{dT}{dt}=\sigma E^2 \tag{5.7}$$

Breakdown takes place in impulse thermal BD before generated heat is dissipated through insulation to outside. All of the generated heat will thermally damage materials directly. If the electrical conductivity is of thermally activated type independent of applied voltage, impulse breakdown strength is given by

$$E_c = \left\{\frac{3C_vkT}{\sigma_0\phi}\cdot\frac{1}{t_c}\right\}\exp\left(\frac{\phi}{2kT}\right) \tag{5.8}$$

$\sigma = \sigma_0 \exp(-\phi/kT)$ is electrical conductivity; k, Boltzmann's constant; ϕ, activation energy for electrical conductivity; and t_c, voltage application time.

Impulse breakdown strength will be lowered, as specific heat becomes smaller, electrical conductivity becomes larger, and temperature becomes higher. The strength is independent of melting point. Time lag for breakdown is relatively long and is in the range of several minutes to several seconds. Ionic conduction, Schottky conduction, and Poole–Frenkel conduction can be taken into consideration.

5.2.4 Electromechanical Breakdown

Soft insulating materials can be reduced in thickness due to Maxwell stress when they are subjected to voltage. In that case, the electric stress is enhanced and then the thickness is further reduced. This causes a positive feedback process to lead to the insulation to electric failure. This is called electromechanical breakdown. Since ordinary solid insulating materials have large Young modulus, they will breakdown via other mechanisms at the lower voltage than the voltage at which they breakdown by the electromechanical breakdown. At high temperatures near softening temperatures, thermoplastic polymers are subject to thermal flow and become thinner due to Maxwell stress and thereby suffer from breakdown:

$$\frac{\varepsilon}{2}\left(\frac{V}{d}\right)^2 = Y \ln\left(\frac{d_0}{d}\right) \quad \text{i.e. } E_c = 0.607\left(\frac{Y}{\varepsilon}\right)^{\frac{1}{2}} \tag{5.9}$$

5.3 Treeing Breakdown Phenomena

5.3.1 Electrical Trees Electrode Systems for Performance Evaluation

Treeing is a phenomenon whereby partial breakdown or dendritic paths progressively grow and branch into hollow channels in a solid dielectric, as clearly shown in Fig. 5.4. They have the appearance of trees; therefore such breakdown paths are called electrical trees or simply trees. They can occur at rather low applied voltage but possibly at very high electric field. Treelike discharge patterns, sometimes leading to total breakdown of the insulation used, have been observed for many years in oil-impregnated pressboard and oil-impregnated laminate paper cables. They propagate preferentially in a direction parallel to the internal paper interfaces and only occasionally break through layers. Treeing is presently more serious in solid dielectrics such as polyolefinic polymers, rubbers, and epoxy resins, which appear to be

Fig. 5.4 Profile of electrical trees in PMMA

susceptible to treeing. Once a tree starts, it is likely to cause breakdown sooner or later. They have been observed in cables, but rubbers and resins are often pigmented or mineral filled; the existence of treelike channel phenomena may go unnoticed in these materials.

Treeing is observed in thick insulation. It is experimentally evaluated using some electrode systems as shown in Fig. 5.5. Electrical trees are classified into two types, i.e., tree-type trees and bush-type trees, as shown in Fig. 5.6.

Breakdown takes place step by step. Some of the dielectric breakdown processes that are described in subsection 5.2 are involved in each step. Intrinsic breakdown, electron avalanche, or thermal breakdown is taken into consideration. First electrons to be accelerated are supplied from the electrodes. Treeing phenomena in polymer insulating materials were intensively investigated for a long time in the past on mechanisms and well documented [2]. They include two or three stages, i.e., tree initiation, growth, and final breakdown [11, 12, 14, 15]. It should be noted that a tip of trees reaching the opposite electrode does not necessarily mean final breakdown. A certain gaseous discharge process is necessary prior to breakdown. Under these processes, a thin and long tree formed in the beginning is expanded laterally in its radius into a thick tree to be led to the final breakdown.

Treeing takes place in the four stages as indicated below:

Stage 1: Incubation period
Stage 2: Initiation
Stage 3: Growth or propagation
Stage 4: Total breakdown

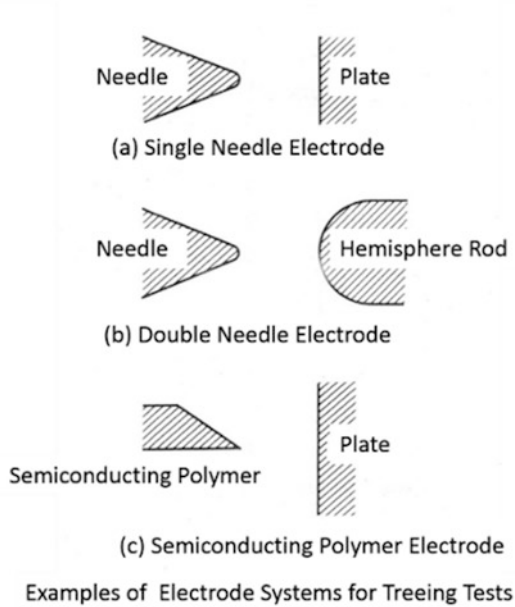Needle of 3 mmφ in diameter and 3 μmR in its tip radius for example

Needle   Plate

(a) Single Needle Electrode

Needle   Hemisphere Rod

(b) Double Needle Electrode

Semiconducting Polymer   Plate

(c) Semiconducting Polymer Electrode

Examples of Electrode Systems for Treeing Tests

Fig. 5.5 Several types of treeing test electrode systems

5.3.2   Three Possible Processes in Incubation Period

There are two distinct time periods in treeing (stage 1 and stage 2): the first is an incubation period during which nothing appears to happen, and the second is a propagation period during which treelike figures grow in the insulation. A tree appears immediately after the incubation period. Up to the visual appearance of a tree figure and the start of significant measurable partial discharges, no obvious effects may occur. The initiation of electrical trees from sharp point of high electric stress in resins, as contrasted to the propagation, is surely the least understood aspect of electrical tree development. It may be inferred from experimental results obtained thus far that at low stress levels where trees are not immediately observed, cumulative processes are proceeding which eventually foster conditions which initiate a tree channel. Several explanations may be offered for the initiation of an electrical tree:

1. Possible process 1 – Tree initiation by mechanical fatigue
   High Maxwell compressive forces in the dielectric, caused by high electric fields at local areas when ac voltage is applied, produce a mechanical fatigue cracking in the polymer.
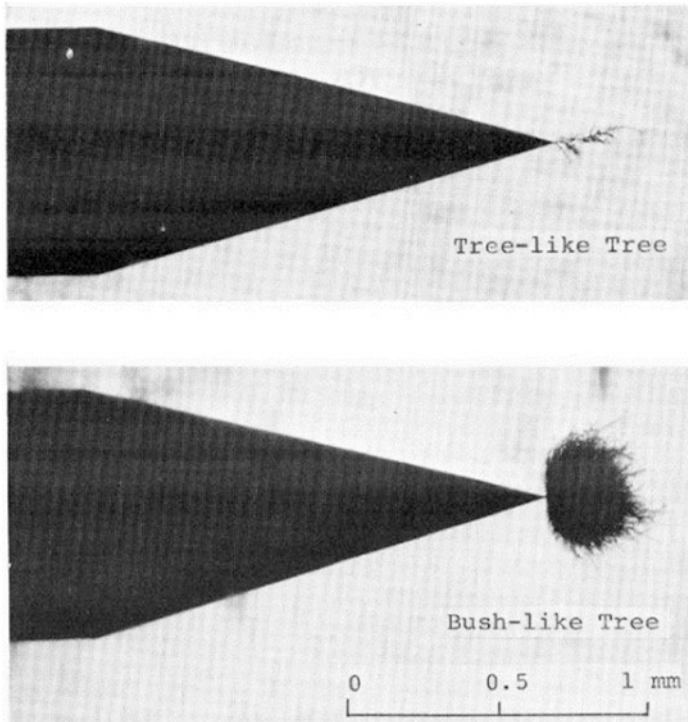
Fig. 5.6 Two types of trees generated in polyethylene

2. Possible process 2 – Tree initiation by partial discharges
   This phenomenon is based on that belief that small cavities exist at tips of foreign particles, asperities, or needles due to different thermal expansion of the resin and the metal or as a consequence of adsorbed or accumulated gas on the surface. It is supported by evidence. Another probable cause is bombardment of the surface of the insulation by high-speed electrons, the source of the electrons being high-intensity ionization in a void or field emission from the surface of a metal point with very small radius of curvature.
3. Possible process 3 – Tree initiation by charge injection and extraction
   Under ac voltage conditions, some electrons will be emitted or injected for a short distance into the dielectric during the negative half cycle, the distance being limited by the declining stress away from the emitting points. If they are not trapped, they will be drawn back into the point on the positive half cycle and re-injected in the following cycle. In each cycle some of the electrons will

gain sufficient energy to cause some resin decomposition to lower molecular weight products and gases.

As an alternative or addition to electrons injected from the electrode, it has been suggested that free electrons within the dielectric may acquire enough energy to cause inelastic collisions with lattices, leading to a molecular degradation and, finally, the initiation of a tree. Electrons may be supplied from deep donors (or trap levels) via the Poole–Frenkel effect and then be accelerated in the conduction level by the external field to become hot electrons.

5.3.3   *Charge Injection and Extraction in Tree Incubation Period*

Electrons are supplied from inside bulk (the valence band and donors), from the electron reservoir thermodynamically formed in contact, and/or from the outside electrodes via the Schottky and field emission. High-energy electrons working for tree initiation must be injected from the electrode via the field emission [10, 15]. Injected electrons transport in the quasi-conduction band and even in the conduction band with a short distance. They are also trapped in traps, i.e., localized states with trapping capability. Electrons, once injected, travel for a distance called schubweg. It is generally defined as the mean distance traveled by a charge carrier before it is trapped, as shown in Fig. 5.7. This terminology derives from photoconduction in ionic crystals.

Treeing is now a target of interest under ac divergent field condition. After electrons are injected from one electrode via the field emission at extremely high electric filed in a half or quarter cycle of applied ac voltage, they transport in the quasi-conduction band to acquire energy within their schubweg. If it is high enough, a partial breakdown will take place. It is a treeing bud formation process. This can be also called tree initiation. It is generally considered that treeing is a kind of fatigue. Therefore, a repeated electron injection and extraction model was proposed [15], as shown in Fig. 5.7. This model consists of material degradation and charge buildup for tree initiation. Material degradation is caused by polymer chain scission and oxidation under the condition of repeated injection and extraction, and it will lower dielectric breakdown strength. Charge buildup will take place in a distance of schubweg from the tip of the electrode used, as a result of the same repeated process, as shown in Fig. 5.8. Therefore, the length of a tree bud or an initial tree is considered to be around schubweg. Furthermore, it should be noted that a built-up charge will generate higher electric field under opposite cycle of ac voltage, as shown in Fig. 5.9. This will also possibly cause breakdown in some time after voltage application.
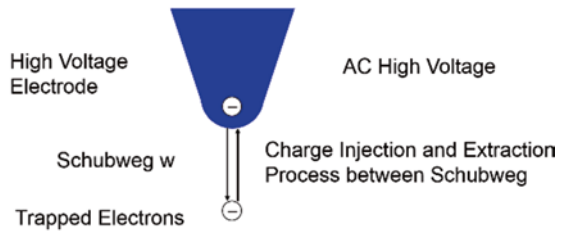
Schubweg

$$\mathcal{W} = \mu E \tau_t = (e\tau_c / m)E\tau_t$$
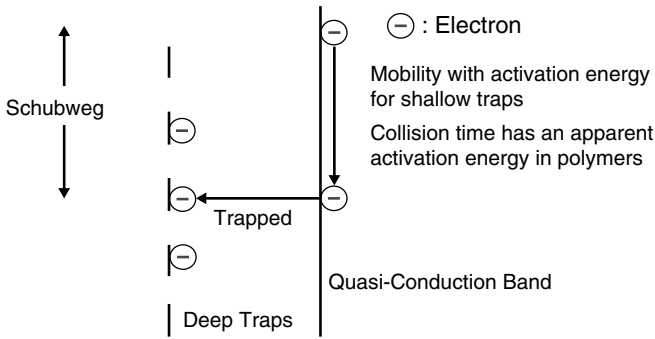
w: Schubweg, μ: electron mobility, E:electric field, τ_t:mean trapping time,
e: electronic charge, τ_c : mean collision time, m: electron mass

Fig. 5.7 Schubweg associated with electron trapping

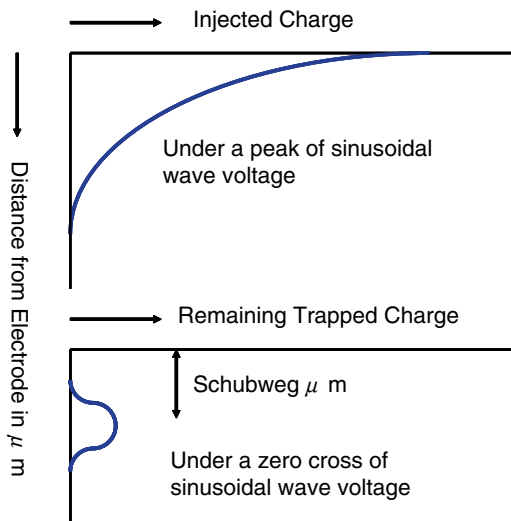**Fig. 5.8** Electron injection and extraction process for tree initiation

Phenomena in the Range of Schubweg

(i) Repeated Back and Forth Movement of High Energy Electron to Provide Material Degradation such as Polymer Chain Scission and Oxidation

(ii) Electrons Trapped in Deep Traps to Cause Added Electric Field in Opposite Polarity Cycle of Voltage

5.3.4   Processes from Tree Initiation to Growth

A treeing breakdown process includes a budding process and a growing process. This budding process can be discussed using the basic understanding of electron behaviors at high electric field. Electron transport mechanisms are described for polymer dielectrics on the basis of a modified energy band model where a quasi-conduction band and localized states in the band gap. Electron injection and extraction processes via the metal electrodes would cause tree initiation, i.e., the formation and growth of tree buds. It is a local dielectric breakdown near the tip of a needle electrode. It must be determined by

Fig. 5.9 Spatial distribution of electrons produced by their injection and extraction process under ac voltage application

Injected Charge

Under a peak of sinusoidal wave voltage

Distance from Electrode in μ m

Remaining Trapped Charge

Schubweg μ m

Under a zero cross of sinusoidal wave voltage

the fact that electrons are injected into a dielectric and extracted back to the electrode via some potential barrier such as the Schottky barrier [15]. Injected electrons transport up to their schubweg to be effectively trapped. This must be a length of a tree bud or an initial tree. SEM observation of the buds of schubweg length must clarify how they will interact with nanofillers in epoxy resins. Buds for treeing are possibly affected by trapping by localized states and the local electric field induced by nanofillers [14].

In the growing process, a tree is extended through the following two major processes:

1. Successive local breakdown
2. Continuous PD attack

Treeing must be a fractal process, because the aforementioned budding process and the above two processes are alternatively and/or successively taking place. A sharp tip of the tree will act as the metal electrode, if the inside of the tip is electrically conductive enough by sufficient energy supply from the electrode, i.e., the outer circuit. This is a budding process in the tree growing process. This results in local breakdown to cause an initial tree. Such a tree will be expanded laterally by partial discharges.

Thus a repeated process of BD-originated tree initiation and PD-originated tree extension will produce tree propagation with a certain speed. Such speed can be measured by a certain technique. Comparison in this speed between neat epoxy and nanocomposites will give us in-depth insight into nanofiller effects on tree propagation.

5.4 Short-Time Dielectric Breakdown of Nanocomposites

Much data are available on short-time dielectric breakdown of nanocomposites. Improvement by nanofiller addition in this type of breakdown is controversial at present. Comprehensive phenomenological review was made (Li Shengtao 2010).

But obtained data are apparently contradictory in many cases, no appropriate con-
clusion has been reached yet, and furthermore no reasonable mechanistic analysis
has been given. This is probably due to that fact that breakdown strength is structure
sensitive. It is likely to be influenced by inclusion of unwanted defects. It was con-
firmed that there is an optimum nanofiller loading content to improve breakdown
performances of polymer resin insulation. The degree of nanofiller agglomeration
greatly affects breakdown strength, which is closely related to nanofiller mixing
techniques.

Figure 5.10 shows a trend of breakdown strength depending on voltage shape
under some optimum conditions. When nanofillers are loaded in a certain loading
level, there is a tendency that breakdown strength shows an increase for DC, no
change for AC, and a decrease for impulse voltage. Increase in DC breakdown
strength may be closely related to the formation of barrier and space charge. In the
analysis of treeing, electrons can be accelerated by nanofillers under AC high elec-
tric field conditions. Similar phenomenon might take place under AC and impulse
voltage application. In the case of AC, improved performances are also confirmed.
Therefore, if unwanted defects can be removed, it is also possible to increase AC or
impulse breakdown strength by the addition of nanofillers.

It is possible to increase even AC breakdown strength if interfaces between
nanofillers and surrounding polymer matrices are improved, as polyethylene–silica
nanocomposites are observed. In the case of polyethylene–MgO nanocomposites,
thermal breakdown is considered to be probable. Nanofiller inclusion will increase
electrical resistivity, resulting in the increase of DC breakdown strength. It is also
interesting that nanofillers interact with applied electric field. Nanofillers are electri-
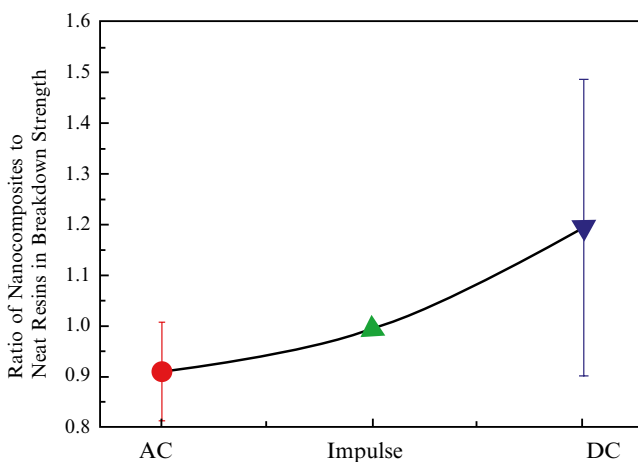cally charged in the range of Debye shielding distance and induce the electric field.

Fig. 5.10 Relative change of breakdown strength due to nanofiller addition as a function of volt-
age shape [6] p. 1527, Fig. 6)

This field may accelerate or decelerate propagating charge carriers (electrons and holes). This kind of interaction is discussed in Sect. 5.5.

5.5 Long-Term Breakdown Characteristics of Nanocomposites

Long-term breakdown, i.e., treeing in this case, is one of the most important performances from engineering point of view. Treeing characteristics for nanocomposites have been recently investigated to lead to the very interesting conclusion that treeing breakdown time is enormously extended for polymers when they are doped with nanofillers [3–5, 8, 13]. It means that long-term breakdown strength increases due to the inclusion of nanofillers in polymer such as epoxy, polyethylene, and polypropylene. However short-time breakdown strength increases in some cases but decreases in other cases. The short-time breakdown strength is considered to be sensitive to processes for nanocomposite preparation; in other words, it might be influenced by not only possible positive effects of nanofiller loading but also negative effect of accidental or in-process inclusion of impurities. This section deals with long-term breakdown by treeing processes.

Usually final breakdown time is measured and evaluated to compare neat polymers with their nanocomposites, as was done for different kinds of materials in the past. Time for breakdown by treeing can be converted into tree propagation speed by dividing material thickness of interest by breakdown time. In this research, time to three propagation distances, i.e., 10, 100, and 3000 μm, was measured, resulting in obtaining three kinds of speeds that depend on applied voltage. Such speeds are influenced by nanofiller addition, as speculated from *V-t* characteristics. Results obtained from this analysis of three kinds of speeds will give us the deep insight of tree growth in nanocomposites, which is explained in this chapter.

5.5.1 V-t *Characteristics*

Three sets of data are presented by a conventional *V-t* characteristics scheme as shown in Fig. 5.11. This shows a positive effect of nanosilica filler addition on suppression of tree propagation. Actually, values of *n* increases by the addition of nanofiller. The time of tree propagation to a certain length is increased with the decrease of applied voltage. This tendency is beneficial from the engineering point of view. Inversely, if two curves for a specified tree length are selected, the two curves tend to merge into the same values, and even crossover, as applied voltage is increased. This means that short-time breakdown voltage might be reduced by the addition of nanofillers.
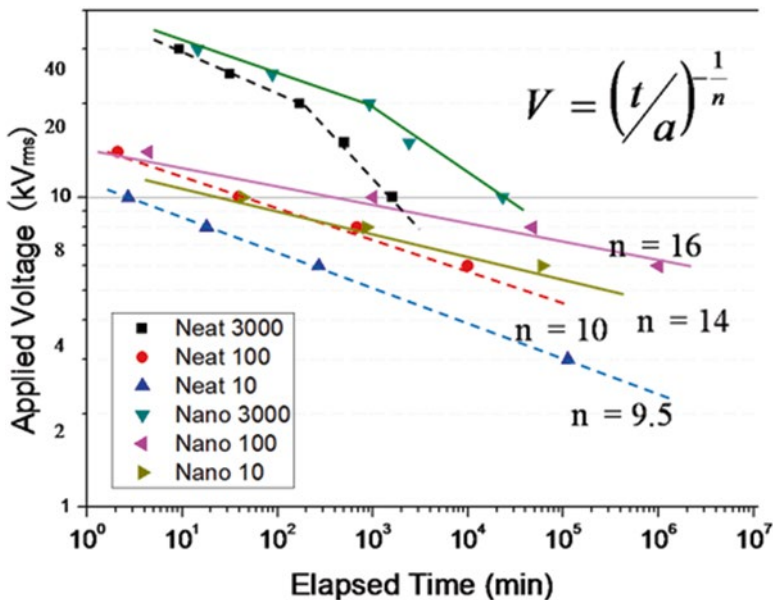
Fig. 5.11 *V-t* characteristics for trees growing up to 10, 100, and 3000 μm in length. Remark: 3000 μm (3 mm) length means breakdown

5.5.2   Derivation of Tree Growth Speed

A small-PD measurement system was developed so that a high voltage source might be shut down by detection of a certain partial discharge magnitude. PD magnitude is considered to be proportional or at least to increase with the increase of tree length. Three kinds of tree lengths, i.e., 10, 100, and 3000 μm (3 mm: sample thickness), can be detected by 10 pC, 100 pC, and breakdown, as shown in Fig. 5.12. Usually conventional *V-t* characteristics can be obtained:

$$V^n t = a \, (\text{constant}) \tag{5.10}$$

where *V*, *t*, *n*, and *a* are applied voltage, time, *n*-value, and constant, respectively. In order to find out other characteristics of tree growth, a new representation is introduced, i.e., average tree growth speed vs. applied voltage characteristics (S-V characteristics). This representation becomes possible since the time of tree growth up to several lengths is enabled to be measured since the developed small-PD measurement system can shut down a power source when a tree grows up to a specified length. If time and length of a tree are given at a certain applied voltage, S-V characteristics can be represented by the following formula:
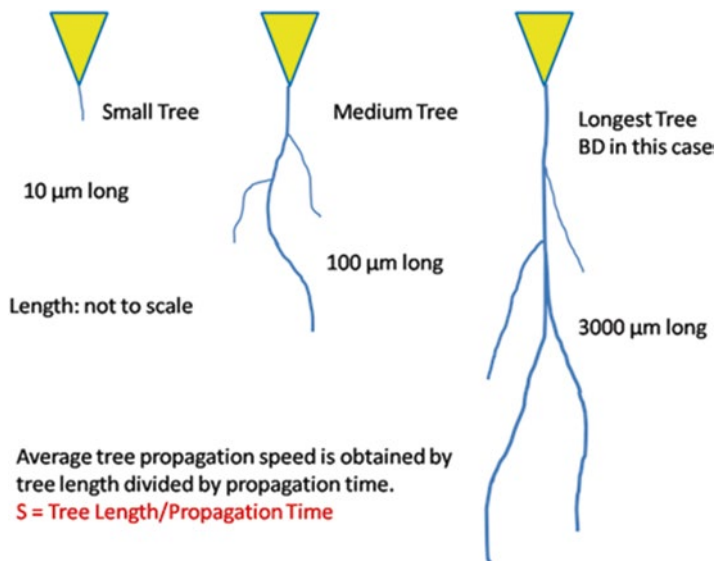
$$S = bV^n \tag{5.11}$$

Fig. 5.12 Schematics of tree lengths dependent on applied voltage

where *S* and *b* are the average tree growth speed and a constant (tree length/a), respectively. Formula shows the dependence of tree growth speed on applied voltage. It means that the speed is proportional to V^n. Such characteristics experimentally obtained are shown in Fig. 5.2 for trees growing up to 10 μm, 100 μm, and 3 mm. The above relation applies for trees up to 10 and 100 μm length but not for 3 mm length (BD).

5.5.3   S-V *Characteristics*

In order to analyze these characteristics, it would be helpful to look into different aspects such as *S-V* characteristics as described in the formula (2). Figure 5.13 shows tree growth speed vs. applied voltage characteristics (*S-V* characteristics) for trees growing up to 10, 100 and 3 mm. These characteristics can be obtained by the transformation from *V-t* characteristics as shown in Fig. 5.11. It is clearly observed that tree growth speed is a strong positive function of voltage in general. The speed is proportional to the nth power of applied voltage especially for tree length up to 100 μm. It should be pointed out that there are five kinds of cross points found at which tree growth speeds become the same, as indicated as X_1, X_2, X_3, X_4, and X_5 as shown in Fig. 5.13 and in Table 5.1.
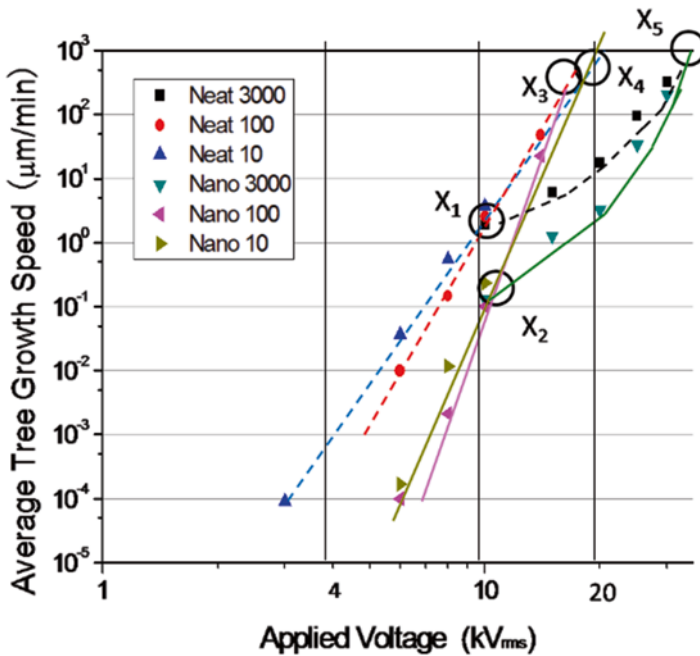
Fig. 5.13 Tree growth speed vs. applied voltage characteristics (S-V characteristics) for trees growing up to 10, 100, and 3 mm

Table 5.1 Four kinds of cross points in *S-V* characteristics

Cross point	Interpretation of cross point at the same speed	Voltage kV$_{rms}$	Speed µm/min
X_1	Epoxy–epoxy 10, 100 and 3000 µm	10	3×10^0
X_2	Nano–nano 10, 100 and 3000 µm	11	3×10^{-1}
X_3	Epoxy–nano 100 µm	15	3×10^2
X_4	Epoxy–nano 10 µm	18	4×10^2
X_5	Epoxy–nano 3 mm BD	>30	$\simeq 10^3$

5.5.4   Explanation of Cross Points X_1, X_2, X_3, X_4, and X_5

Triple cross points found as X_1 and X_2 in two groups of three curves as shown in Fig. 5.13 are related to behaviors of trees of 10, 100, and 3000 µm in length within the same material, either neat epoxy or nanocomposite. It is also possible to compare the neat epoxy with the nanocomposite based on the difference in a tree propagation speed and a certain critical voltage at points X_1 and X_2.

Let us take a triple point X1 for neat epoxy at 10 kV_{rms}. There are three kinds of speeds recognized for a 10-μm tree, a 100-μm tree, and a 3000-μm tree, respectively. They are merged into the same speed at 10 kV_{rms}. It is interesting to note that a tree grows at a constant (same) speed (3 μm/min) from the beginning to the end at applied voltage 10 kV_{rms} finally to cause dielectric breakdown. It means that a tree length is proportional to elapsed time, i.e., a linear curve in tree length vs. time characteristics. Below this critical voltage, no breakdown would take place, although a tree grows. A 100-μm (long) tree is slower in speed than a 10-μm (short) tree. This means that a tree grows more slowly as it grows from 10 to 100 nm, resulting in a saturation curve in tree length vs. time characteristics. On the contrary, above the critical voltage 10 kV_{rms}, a tree grows more quickly as it grows from 10 to 100 nm but later drastically slowly as it is reaching to the opposite electrode. This might be a logistic curve in tree length vs. time characteristics.

Then, let us look at another triple point X_2 at 11 kV_{rms} for nanocomposite as indicated in Fig. 5.13. A tree grows at a constant (same) speed (0.3 μm/min) from the beginning to the end at applied voltage 11 kV_{rms} finally to cause dielectric breakdown. The qualitatively same thing with the discovery made to neat epoxy can be said to nanocomposite in regard to a linear curve, a saturation curve, and a logistic curve depending on applied voltage, as observed in the lower three curves in Fig. 5.13. It is thus interesting to propose that a relation between neat epoxy and nanocomposite must be fractal in tree length vs. time characteristics.

It should be pointed out that the speed for tree growth is much reduced by almost one order of magnitude from 3 to 0.3 μm/min by the addition of nanofiller. Furthermore, a critical voltage is shifted a little bit from 10 to 11 kV_{rms}. These findings mean that a tree grows very much slowly in nanocomposite than in neat epoxy and that higher voltage (11 kV_{rms}) is needed for nanocomposite than voltage (10 kV_{rms}) for neat epoxy as for long-term breakdown.

Three kinds of double cross points referred to as X_3, X_4, and X_5 are representative of a relationship between two different materials, i.e., neat epoxy and nanocomposite, under the same condition of tree length, either 10 nm, 100 nm, or 3000 nm in length, respectively. The double cross point X_3 is marked as applied voltage 15 kV_{rms} and tree propagation speed 300 μm/min. Below the critical voltage 15 kV_{rms}, a 100-μm length tree grows more slowly in nanocomposite than in neat epoxy. It is easy to understand. On the contrary, above this critical voltage, a 100-μm length tree gains higher speed in nanocomposite than in neat epoxy.

The double cross point X_4 is marked as applied voltage 18 kV_{rms} and tree propagation speed 400 μm/min. It should be noted that the cross point X_4 (10-μm tree) is smaller the cross point X_3 (10-μm tree) in both the critical voltage and the tree propagation speed. Below the critical voltage 18 kV_{rms}, a 100-μm length tree grows more slowly in nanocomposite than in neat epoxy. On the contrary, above this critical voltage, a 10-μm length tree gains higher speed in nanocomposite than in neat epoxy.

The double cross point X_5 for a 3000-μm tree is designated as a little bit higher voltage than 30 kV_{rms} and 1000 μm/min. Below this critical voltage around 30 kV_{rms}, longer time is needed in nanocomposite for the 3000-μm tree growth than in neat
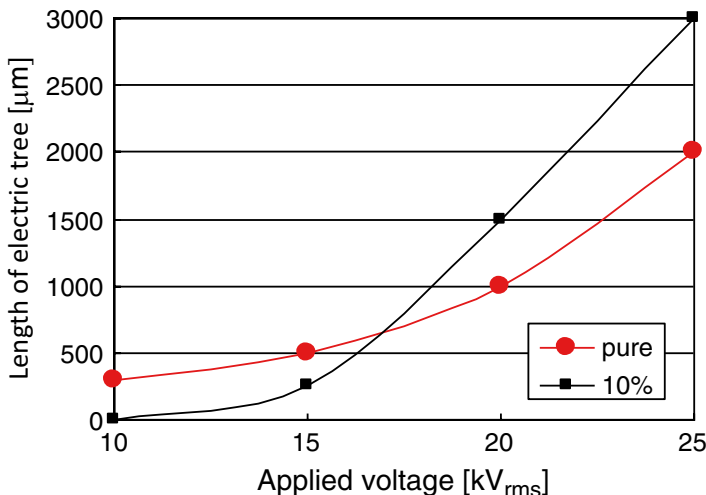
Fig. 5.14 Crossover phenomenon in tree length vs. applied voltage characteristics

epoxy. It is easy to accept this performance. On the contrary, above the critical voltage, it is anticipated that shorter time is needed in nanocomposite for the 3000-μm tree growth than in neat epoxy. In other words, a tree reaches the opposite electrode faster in nanocomposite than in neat epoxy. This might suggest that ac breakdown voltage becomes lower if nanofiller particles are added into epoxy. This is opposite to our expectation.

A similar phenomenon was already observed in short-time breakdown experiments based on a voltage increasing method at a constant speed of 500 V_{rms}/s [5]. Namely, a tree length is smaller in nanocomposite at low voltage than in neat epoxy but becomes larger in nanocomposite above a certain critical 17 kV_{rms} than in neat epoxy, as shown in Fig. 5.14. This was called a crossover phenomenon. This critical voltage 17 kV_{rms} is lower than the other critical voltage around 30 kV_{rms}, because the former was obtained by short-time breakdown tests, while the latter was obtained in long-time breakdown tests (*V-t* characteristics).

A tree reaches the opposite electrode in a needle-plane electrode system in the above discussion. But it does not necessarily mean dielectric breakdown of a whole sample. The tree is too thin in its diameter in the beginning to cause dielectric breakdown. Partial discharges (PDs) are considered to be involved to expand the diameter. PDs erode the inner surface of the tree to expand the diameter of the tree. This increases PDs in turn, which is a positive feedback process for PDs. Finally ac breakdown takes place when a trunk of the tree is spacious enough to form a sufficiently conducting path. Nanocomposite is more resistant to PDs than neat epoxy. Thus short-time ac breakdown voltage can be higher for nanocomposite than for neat epoxy. This is usually obtained experimentally.

5.5.5   Consideration of X_3 and X_4

As indicated in Table 5.1, a cross point X_3 appears at a coordinate (15 kV$_{rms}$, 300 µm/min) for a 100-µm tree, while X_4 is recognized at 18 kV$_{rms}$, 400 µm/min for a 10 µm tree. Thus, it is concluded that 1.5 s is needed to form a 10-µm tree, while it takes 20 s to form a 100-µm tree. It seems that a 100-µm tree grows faster than a 10-nm tree under this condition of applied voltage. As already observed, voltage at which tree propagation speed in nanocomposite exceeds that in neat epoxy is higher for the 10-µm tree than for the 100-µm tree. Time to be needed to form a 10-µm tree must include tree incubation time to form a tree bud. If this point is taken into consideration, a tree grows more quickly in nanocomposite than in neat epoxy under such a high electric field.

5.5.6   Initial Tree Length and Tree Buds

Lengths of initial trees or tree buds are estimated from a relation between tree length and elapsed time at several voltages. This is derived for neat epoxy and epoxy–silica nanocomposite from data obtained for *V-t* characteristics (Fig. 5.11), for tree initiation, and for treeing breakdown. Results are shown in Table 5.2. Then, it is concluded that initial trees possess the following characteristics:

(i)   Initial tree length seems to be independent of applied voltage at least up to 10 kV$_{rms}$.
(ii) Initial tree length seems to be irrespective of presence or absence of nanofiller.
(iii) Average value of initial tree length is 6 µm.

This initial tree is considered to represent the first burst local breakdown in the range of schubweg for charge injection. It should be noted that this value is for relatively low electric field. At high field, it might be modified because it is known that a tree becomes long at high field once it is generated. A somewhat different mechanism will appear under this condition. Furthermore, it is of interest to note that this value for epoxy is shorter than 20 µm for polyethylene presented in the past [15], which suggests some difference in schubweg by different materials.

Table 5.2 Estimated initial tree length for epoxy and nanocomposite

	Estimated initial tree length (µm)		
Applied voltage	6 kV$_{rms}$	8 kV$_{rms}$	10 kV$_{rms}$
Neat epoxy	7.6	7.5	2.3
Nanocomposite	4.3	8.3	6.0
Average	6.0		

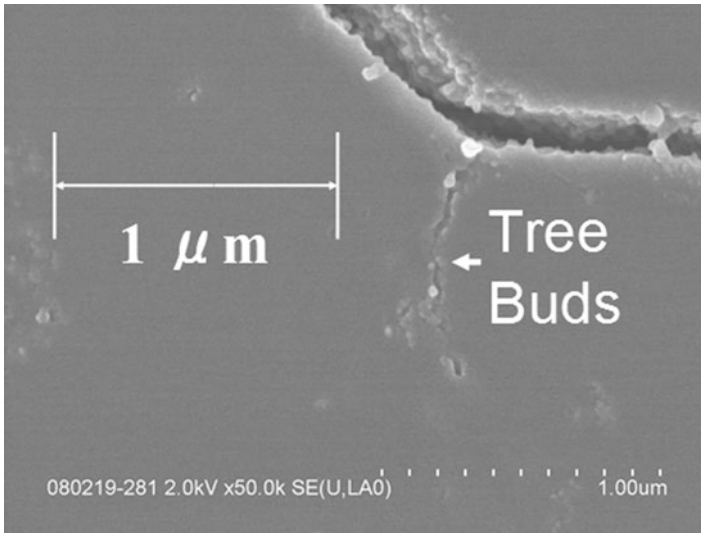Estimated from the dependence of tree length on time

Fig. 5.15 Photo of a tiny thin branch tree from a thick tree trunk that shows some interaction with nanofiller particles

An initial tree or a tree bud generated from an electrode tip has not been directly observed yet. Figure 5.15 shows some tree traces in epoxy–silica nanocomposites including a tree trunk and a tiny tree branch. The tree trunk must be formed due to erosion created by repeated PDs after tree formation, and the tiny tree must be formed by a single shot of voltage. If the latter represents a tree bud, it is 800–900 nm in length, which is smaller than 1 μm. It has further branches in 500 nm apart.

It is to be noted that there is a discrepancy between estimated extrapolated length (6 μm) of an initial tree and the length (1 μm) of a small branched tree. If a tree is fractal, they should be the same. Much ambiguity must remain by the extrapolation method. Therefore, an absolute value of the initial tree length is not conclusive.

5.5.7 Suppression of Treeing by Nanofillers

There is a marked difference in tree growth below and above a critical voltage. Different mechanisms seem to be operative below and above such a voltage. This critical voltage is about 10 kV_{rms} for epoxy and its nanocomposite tested in a specified treeing electrode system used in this research. Maximum electric field in the tip of a needle electrode before a tree starts is 520 kV_{rms}/mm (MV/m) in this case. The following knowledge can be drawn:

1. A tree grows at a constant speed at the critical voltage.
2. A tree starts but stops below the critical voltage.
3. A tree grows up to the opposite electrode above the critical voltage.

Figure 5.16 illustrates the above three characteristics. A tree grows at a constant speed at 10 kV$_{rms}$ for neat epoxy and nanocomposite. Below this voltage, a tree grows at its initial stage but slows down and finally stops growing. In these two cases at least, nanofillers act to suppress tree growth. Above 10 kV$_{rms}$, a tree grows up to the opposite electrode. At a certain voltage above this voltage, a tree grows slower first and faster later in nanocomposite than in neat epoxy. This performance is described in Fig. 5.16 as two logistic curves. Nanofillers decelerate tree growth in the beginning but accelerate it in the end as described as a crossover point beyond which tree propagation is faster in nanocomposite than in neat epoxy. It means that a tree reaches the opposite electrode in nanocomposite faster than in neat epoxy. This finding must correspond to a crossover phenomenon discovered in tree length vs. applied voltage characteristics (Fig. 5.15).

Figure 5.17 illustrates what are happening in tree growth in the two voltage ranges. At low voltage below 10 kV$_{rms}$, a tree starts to grow to a certain length such as 100 μm and slows down if nanofiller particles are present. Therefore it will take longer time in nanocomposite than in neat epoxy. Tree shapes with the same length are shown for epoxy and nanocomposite. In epoxy, a tree is easy to grow to have thin channels. In nanocomposite, it is blocked by nanofillers and then subjected to PDs for longer time, resulting in forming thick channels. These characteristics are illustrated in Fig. 5.17(1). The formation tree is governed at low voltage by such a PD dominant mechanism.

At high voltage, a tree is extended fast both in epoxy and nanocomposite by successive local breakdown and then is slowly widened by PD activity. From the experimental results, it grows faster in nanocomposite than in epoxy. A tree is considered to grow in epoxy matrix region between neighboring nanoparticles by successive local breakdown. Thin channels extend rapidly and progressively. This performance is illustrated in Fig. 5.17(2). The formation tree is governed at high voltage by such a treeing dominant mechanism.
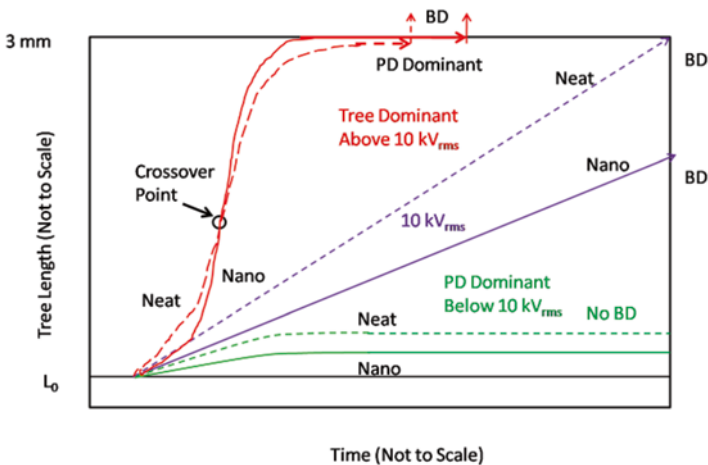

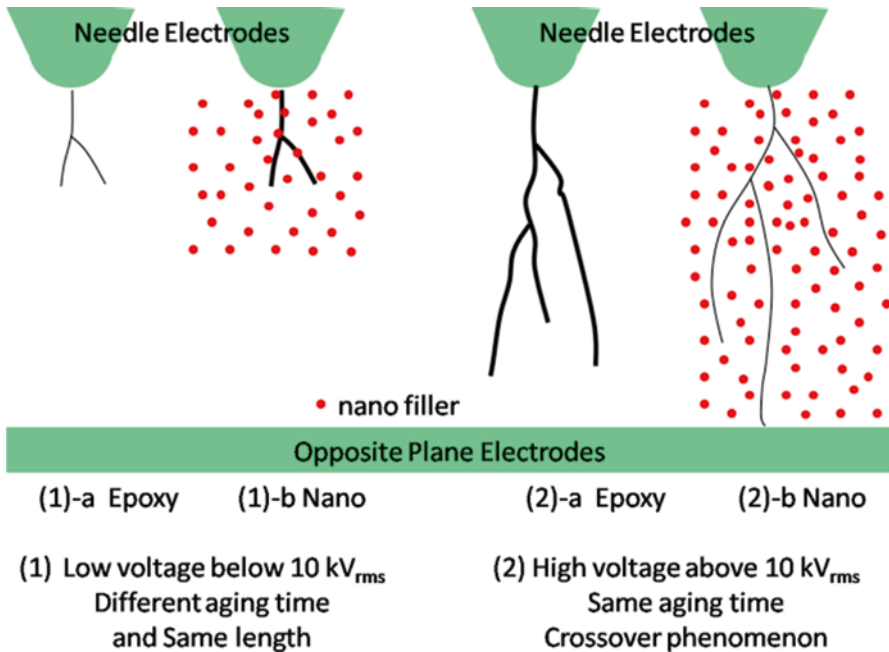**Fig. 5.16** Image of tree growth with time depending on applied voltage

Fig. 5.17 Possible mechanisms for high and low voltage tree growth

An infancy tree at low voltage is estimated to have a 6-μm length that must be equivalent to schubweg. Considering that the incubation period until this growth is prolonged by nanofiller, the following mechanisms are responsible for this:

1. Charge injection is suppressed by nanofiller.
2. Material degradation, especially oxidation, is retarded due to the existence of nanofiller.
3. Schubweg is reduced by nanofiller.

However, as the measured time to be required for 10-μm tree extension includes incubation time or budding time, and the initial tree length 6 μm seems to be independent of applied voltage, there is some contradiction in explanation to be clarified further.

5.5.8 Roles of Nanofillers in Tree Growth Processes

One of the most striking findings is that the existence of nanofillers in epoxy retards tree propagation at low electric field but expedites it at high electric field. Thus a crossover phenomenon is recognized. A tip of thin tree channels reaches the opposite electrode in nanocomposite earlier than in neat epoxy. But it does not mean that

ac breakdown voltage is reduced by the addition of nanofillers. To fulfill the final breakdown, some more time is needed to expand the trunk of a formed tree sufficiently to accommodate gaseous discharges inside the tree channel.

Some other results are obtained as follows:

1. Initial tree lengths are around 6 μm seemingly irrespective of neat epoxy or nanocomposite. But there is an evidence for the fact that filler plays a role to retard the birth of a tree bud.
2. The addition of nanofillers would extend tree initiation time as well as BD time and increase n values as the slope of the curves in log–log plot of *V-t* characteristics.
3. At 10 kV$_{rms}$, the tree growth speed becomes the same for trees of 10, 100, and 3000 μm (BD) in length. Under this condition, a tree grows at a constant speed of 3 μm/min and 0.3 μm/min for neat epoxy and nanocomposite, respectively.
4. Below 10 kV$_{rms}$, a tree starts to grow at first but tends to stop growing afterward. It is presumed that PD is predominant to extend a tree but expand in the direction of its diameter at the same time, resulting in forming thick channels. A tree seems to attract nanofillers on its inner surface. Nanofiller is much effective to suppress its growth, because nanofillers are considered to play a significant role against PD attack.
5. Above 10 kV$_{rms,}$ a tree grows rapidly forming thin channels. Tree channels are considered to be extending in matrices by being exerted by some force like Coulombic repulsion force.
6. From *V-t* and *S-V* characteristics, it can be said that nanofiller addition seems to be ineffective to increase short-time breakdown strength at high electric field.

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