On Polymers Nanocomposites: Electrical Treeing, Breakdown models and Related Simulations

G. Melissinos
Democritus University of Thrace
Department of Electrical and Computer Engineering
Power Systems Laboratory, Xanthi, Greece
melissinosgeorg@gmail.com

M. G. Danikas
Democritus University of Thrace
Department of Electrical and Computer Engineering
Power Systems Laboratory, Xanthi, Greece
mdanikas@ee.duth.gr

Abstract—This paper deals with polymer nanocomposites and their related breakdown mechanisms. Polymer nanocomposites seem to be a very promising alternative to conventional polymers regarding high voltage applications. Some developed breakdown models are discussed as well as the mechanism of treeing in such materials. Treeing simulation results are presented.

Keywords—polymer; nanocomposites; insulation; treeing; breakdown.

I. INTRODUCTION

Polymeric materials have been used for a long time in high voltage engineering [1]. Polymer nanocomposites were proposed more than twenty years ago as a plausible alternative to traditional polymeric materials [2] but their full potential was realized more recently [3]. It was realized that the unique properties of polymer nanocomposites were due to the interfacial region and the base polymer was crucial for the development of new insulating materials [4-6]. In polymer nanocomposites, the nanoparticles are homogenously dispersed in the matrix in concentrations <10 wt%, the size of particles being smaller than 100 nm.

The interfacial region in the nanocomposites is significantly increased in comparison to microcomposites, due to the nanometric scale of the particles, which means that the augmentation of the interfacial region gives to nanocomposites different and unique properties compared to microcomposites. Nanoparticles can improve or adjust significantly different properties, such as electrical, mechanical, thermal, and optical but with the condition to be homogenously dispersed in the polymer matrix. A very good dispersion of the nanoparticles into the polymer matrix can be achieved by using different methods and preparation techniques among them mechanical dispersion methods, including ultrasonic vibration or special sol-gel techniques, high shear energy dispersion mixing and/or through a tailored surface modification of the nanoparticles [7]. Lack of compatibility between the polymer matrix and the nanoparticles may cause the formation of agglomerations [8].

II. BREAKDOWN AND DEGRADATION IN POLYMER NANOCOMPOSITES

At breakdown, the electric field frees bound electrons. If the applied electric field is sufficiently high, free electrons from background radiation may become accelerated to velocities that can liberate additional electrons during collisions with neutral atoms or molecules in a process called avalanche breakdown. Breakdown occurs quite abruptly, resulting in the formation of an electrically conductive path, thus destroying the insulating capability of the material. The first approach, an effort made so that the breakdown strength be explained on quantum mechanics level, was proposed in [9] that suggested the low energy criterion, which says that fast avalanche breakdown can only occur if the average energy gained of electrons are larger than the average energy losses of electrons. Von Hippel’s theory was the basis for the density functional perturbation theory (DFPT), for estimating the breakdown of new insulating materials [10] and also for the determination of the depths of impurity states created by common chemical impurities [11].

In 2005, Ma and others showed in experiments with LDPE/TiO2 nanocomposite, that the breakdown strength improved after the treatment of nanoparticles surface with silanes, which promoted deep trapping of charges [12]. Han and others, in their experiments with LDPE/NaY nanocomposite with 3 wt% zeolite nanoparticles, concluded that deep traps that create homo space charges can suppress the injection of charges from the electrodes, decrease the mobility.
of charge carriers resulting in improved breakdown strength [13]. Classical theories of breakdown may apply to polymer nanocomposites, such as the electrical avalanche breakdown [14], the water treeing breakdown theory [15], the electrical treeing breakdown theory [16], the thermal breakdown theory [17] and the electromechanical breakdown theory [18]. It happens, however, that in certain cases, the above mentioned models can be intermingled, as is the case of [19], where it was pointed out that, for PE and EVA polymer samples, thermal breakdown happens along with dominating fast avalanche mechanism at low temperatures and a dominating electromechanical mechanism at higher temperatures, depending on the temperature level.

It is to be remembered that besides such classical models of breakdown, in the case of polymer nanocomposites, a crucial role plays the interface between the polymer matrix and the nanoparticles. The improved nanodielectric properties seem to stem from the immensely enlarged interface region around the nanoparticles, in usually low concentrations (1-10 wt%) in comparison of the interface regions of microcomposites with the same concentrations. In a simple example, Kickelbick [20] demonstrated the importance of the interface in nanoscale level, as almost every nanoparticle in the nanocomposite, has surface that interacts with the polymer matrix. Generally speaking, nanocomposites seem to have higher breakdown strength than their conventional counterparts. In the following chapter, interface models and related problems and interpretations will be studied.

III. INTERFACES IN NANO COMPOSITES

Apparently the degrading mechanisms of the polymers, such as partial discharges (PD) and electrical and/or water treeing, can also lead polymer nanocomposites to destructive failure [21]. In [22], authors suggested that the advantageous nanocomposite properties have their origins in the behavior of the interfacial interaction zone surrounding the nanoparticles. In this regard, two main features would appear to be dominant a) the mobility ascribed to the physical and chemical bonding occurring at the interface, and b) the formation of a double layer in the interfacial region which can influence local conductivity. The mobility and the type and degree of crystallinity changes with nanoparticle addition in the polymers [23]. Moreover the polymeric chain mobility in the interface zone is affected by many factors, such as the polymeric chain length [21], the morphology of the nanoparticle surface and the polymer-particle interactions (repulsive or attractive) [24], the kind of polymer-particle chemical bonds [25] and the wt% nanoparticle concentrations [26, 27]. In [28], authors observed in nanocomposite with silica nanoparticles, two glass transition temperatures (GTT), and they proposed for the explanation of these morphological and structural anomalies a model according to which the lower GTT was attributed to the usual polymeric regions, while the higher to the interface zone with the reduced mobility. For concentrations of nanoparticles more than 10 wt% the mobility is considerably decreased, while for above 20 wt% the polymeric chains are almost immobilized. In [29], authors suggested that in order for the voltage endurance to be increased in a nanocomposite, internal charges should be decreased through interfacial effects and if the interaction zone is the primary agency in determining the electrical behavior, then clearly the engineering of nanodielectrics should be centered on chemical modifications of the interface.

In [12], the authors presented the results of the influence of surface modification of TiO2 nanoparticles on the short-breakdown strength and space charge distribution of LDPE. They concluded that the improved dielectric breakdown strength was directly due to beneficial effects related to the variation of the electrical features at the particle surface due to introduction of polar groups. For the same reason, with the use of surface modified nanoparticles, the formation of space charge was suppressed. In [30], it was reported that the deep traps for electron carriers which are formed by additives in polymers, reduced the energy of space charges, while the created homocharges hindered further charge injection from the electrodes, which improved the breakdown strength. In a later work [31], the authors presented a hypothesis for the mechanisms that lead to the improved AC, DC and impulse breakdown strength of composite XLPE with nanoparticles SiO2. They suggested that 'the inclusion of nanoparticles provides myriad scattering obstacles and trap sites in the charge carriers’ paths, effectively reducing carrier mobility and thus carrier energy. The result is homocharge buildup at the electrodes, which increases the voltage required for further charge injection due to blocking by the homocharge'. Scattering, caused by both particle/polymer interfaces and possibly disrupted crystalline structure, contributes to the better electrical behavior of nanocomposites besides the defect reduction via chemical linkage between nanoparticles and polymer or the introduction of deep trap sites in the polymer due to the surface modifier groups [32].

From all the above reports it is clear that there are many factors that influence the breakdown strength of nanocomposites, but the involved dominant breakdown mechanism is partly dependent on the temperature conditions, as for example a temperature increase will reduce the polymer mechanical strength. Regarding water tree retardation in nanocomposites, the addition of MgO nanoparticles in LDPE and XLPE in different concentrations managed to improve the nanocomposite strength in water tree growth as well as to observe the temperature effect on its development [33]. In [34, 35] the influence of the interface mechanical strength in barium titanate-polyvinylidene fluoride nanocomposite breakdown strength was investigated. In the interface area the titinate-covered barium nanoparticles were cross linked to the polyvinylidene fluoride matrix forming an organically integrated body, which posed a potential barrier which prevented charge carriers to cross through the interface area. The charge carriers are confined in the polymer area only, which promotes energy storage, while, with the tetrafluoroaphalic acid nanoparticle treatment, a passivation layer around the interfacial area is formed, thus reducing the generation of charge carriers which may results in ionic or dc conduction and the decrease of the breakdown strength. Yet in other publications, it was proved that nanoparticle treatment which resulted in covalently-bonded interface polymer-particle nanocomposites exhibit improved breakdown strength [36, 37]. It is quite clear from the above
that interfaces and their treatment are dominant factors in defining the breakdown strength of polymer nanocomposites.

Interface models were proposed in the past that tried – at least partially – to interpret the behavior of polymer nanocomposites. This subject was already partly treated [38, 39] and it will be treated in more detail separately in a future publication, consequently interface models only briefly will be mentioned here. Interface models are extremely useful for better understanding the interfacial properties of nanocomposites and they basically treat the areas around the nanoparticles, offering thus interpretations as to why polymer nanocomposites have improved electrical behavior compared to their conventional counterparts. Main interface models – referring to nanocomposites – are the Lewis model, the Wilkes model, the Tanaka multi-core model, Tsagaropoulos’ model, the potential barrier model, the interphase model, the polymer chain alignment model, the water shell model, the dual layer model, the physical model for the explanation of surface degradation mechanism, the physical model for tree growth, Chen’s model and the percolation model. All the above mentioned models – as said to be discussed in a future paper – represent a significant effort towards the understanding of the properties that emerge in polymer nanocomposites. There is not, however, a universal model so far, that will cover all the experimental facets that are simulated by all these models.

IV. BREAKDOWN AND RELATED MECHANISMS

Various models have been proposed for the breakdown of polymers. Partial discharges (PD) is a major source of electrical degradation and occur in voids, de-laminations and other defects in an insulation system. PD may cause electrical treeing. Electrical treeing is the main indication of aging and ultimately leads to insulation breakdown and eventual failure of the electrical equipment. Various models have been proposed for the breakdown of polymers. Niemeyer, Pietronero and Wiesmann (NPW) [40, 41] introduced a stochastic model in which the evolution of the tree-like patterns are explicitly depend on local electric field strength and a factor which modulates the randomization of the process. The fractal dimensions of the experimentally obtained tree-like patterns, are in general, in accordance with the patterns obtained from the breakdown simulations, which advocates in favor of the fractal characteristic of the electrical trees. An improved model was proposed in [42], where there was a generalization by introducing a breakdown criterion for tree formation, so that the branches could only be added if the local field at a branch tip exceeded a critical threshold field for growth, and by introducing an internal field within the tree channels that would add to the electrode potential at the tip of the tree, implying thus that the tree channel could not be considered without resistance. More recently, Dodd [43] presented his deterministic model which successfully in simulating electric trees in dielectric without the need of a random variable, a requirement of previous stochastic models. Instability in the spatial development of partial discharges within the tree structure takes the role of the stochastic element as used in previous models to produce branched tree structures. In yet another model, electric treeing is simulated with the use of von Neumann Cellular Automata (CA) theory. More specifically, it is presumed that electric charges in the electrode tip create electric field that surpasses the dielectric strength of the polymer insulator and a gradual tree-like channel formation is spread in it. On every step the local potential on every point is being recalculated, due to local dielectric permittivity fluctuations caused by the tree channel propagations [44, 45]. Dissado and Sweeney [46] proposed a deterministic quantitative physical model for the breakdown of solids by discharges originating from voids or channel tips. It is found that fractal tree-like structures are formed only when the local electric fields at the tree tips are allowed to fluctuate about their Laplace values. By considering the local-field enhancement factor as a white noise, which is produced by the breakdown mechanism itself, it is shown that the amount of branching depends only on the range of fluctuations allowed.

Noskov’s model took into account PD erosion or the real distribution of the electric field due to space charges, and also that the electric trees had to emanate always from matrix defects. The model could estimate electrical tree propagation and PD activity within growing tree channels. The local electric field and the damage accumulation in the dielectric material were constituent into the tree growth, while the increase of the damage was proportional to the PD energy release in the channels. The electric field distribution was determined by the charge deposition within the tree structure and the electrode geometry, while charge distribution changes within the channels during PD. PD starts when the electric field along the channels exceeds a threshold inception value and stops when the field falls below the threshold quenching value [47]. Although the above mentioned publications refer mainly to conventional polymers, their ideas could also apply to nanocomposites. The CA model, for example, was applied to simulate electrical treeing in nanocomposites [48]. However, a drawback of the CA model is that it does not consider in detail the interface region around the nanoparticles. On the other hand, this is understandable since there is no generally accepted model for the interfaces as yet. Generally speaking, in the various models, in order an electrical tree simulation to take place in nanocomposites, local fluctuations are used, fluctuations of factors that simultaneously comprise variables of functions that determine the conditional representation of the discrete cells of the polymer matrix and of the nanoparticles of the nanocomposite. Factors that can be used as variables, are the electric field or the released energy due to PD activity, with the first to be greatly preferred because it can be easily calculated. The CA model considers as decisive factor the local change – even slightly – of the dielectric constant that in turn affects the local electric field [48].

V. TREEING SIMULATIONS

Treeing simulations in nanocomposites were based on the model developed in [48]. As nanocomposites consist of different materials, it is only logical to try to develop the simulations on previous treeing models of conventional polymers [44, 45]. More specifically, the initial CA model for nanodielectrics, had analysis 5000x5000 cells, a point-plane electrode arrangement and every nanoparticle was presented in just one cell. Generally the design concepts of a previous model [44, 45] are applied to nanocomposite treeing simulation.
the electric field vector and radius.

For electric tree propagation an algorithm is executed first to the cells at the electrode tip and when the electric field exceeds the nanocomposite breakdown strength, the cells are converted to tree cells and this procedure is repeated to all cells until the tree propagation stops. The cell potential is calculated solving Laplace or Poisson equations as well as the boundary conditions determined as described in [44, 45]. The potential distribution is also affected by interactions between the nanoparticles due to their proximity. Cox in his work [49] in a model with two spheres calculated accurately enough sphere potentials $\Phi_a$, $\Phi_b$, with $E$ the external electric field, $d$ the distance between sphere centers, $a$ sphere radius, $k$ the sphere permittivity ratio to that of the polymer, $\lambda=\cos\theta$, $A=\cos\Theta$ and $P_n$ a Legendre n grade polynom. When in the nanocomposite there is a defect or microparticle the potential is $\Phi=-(3/(\varepsilon_2/\varepsilon_1)+2)E r \cos\theta$, where $\varepsilon_1$ the polymer permittivity and $\varepsilon_2$ that of the microparticle while $r$ is it’s radius and $\theta$ the angle between the electric field vector and radius.

$$\Phi_a = \frac{E_a}{2} \sum_{n=1}^{\infty} a_n [\left(\frac{a}{d}\right)^{n+1} + \frac{2n+1}{n(k-1)} (1)^n P_n(\lambda)]$$

$$\Phi_b = \frac{E_b}{2} \sum_{n=1}^{\infty} a_n [\left(\frac{a}{d}\right)^{n+1} + \frac{2n+1}{n(k-1)} (-1)^n P_n(A)]$$

Simulations regarding the influence of space charges on the development of electrical treeing with the model described briefly above as well as in [48] gave results qualitatively not different from those reported in [50, 51]. Specifically, it was shown that space homocharges around the high voltage tip electrode, hinder further charge diffusion from the electrode into the matrix, as well as electric tree growth and breakdown of the nanodielectric. It was shown also that electrical tree deployment through the nanocomposite, was taking place only through the polymer matrix deviating from the nanoparticles, which increased significantly the lengths of electrical tree paths to the opposite electrode, resulting in increased breakdown strength and delayed breakdown. Furthermore, the effect of the size of nanoparticles included in a nanocomposite was simulated (Figures 1 and 2). It is evident that smaller size nanoparticles (which means more nanoparticles per volume) have a beneficial effect on hindering electrical treeing, in accordance with experimental results published in [52]. In other words, an increase in wt% nanoparticle content, offers a longer treeing path and thus a higher breakdown strength. It must, however, kept in mind that not only the size of nanoparticles in important but also, among other factors, the coupling agents. Coupling agents in nanocomposites are more effective in small sizes of nanoparticles and increase tree breakdown time [52]. An interesting parameter which was investigated was the presence of air voids in a nanocomposite (Figures 3 and 4).
Simulations with the model described above [48], indicated that voids cause –as in conventional polymers– problems. As shown in Figures 3 and 4, in the presence of an air void, electrical treeing is encouraged despite the existing nanoparticles. With two air-filled voids, treeing propagation becomes even worse. The outcome of all the above simulations and cited technical literature converge to a general conclusion, that the increase of the nanoparticle content -up to a certain percentage– may impede electric tree propagation and PD activity and erosion in nanocomposites. However, even nanocomposites must avoid defects, such as air-filled voids, that are detrimental to all kinds of insulation systems.

VI. CONCLUSIONS

In this paper, a background as to the some aspects of polymer nanocomposites was given. Some advantages of these materials as well as some of their problem areas were commented upon. Simulations of electrical tree propagation, based on a CA model, were presented. It was shown that the size of the nanoparticles plays a crucial role in determining the treeing path and propagation. It was also pointed out that conventional polymers as well as polymer nanocomposites “suffer” both from defects, such as air-filled voids. Experimental results seem to justify some of the simulations shown here.

REFERENCES


[38] M. G. Danikas, R. Sarathi, “Interfaces in high voltage engineering: A most important question for conventional solid insulating materials as well as for nanocomposite polymers”, Funktechnikplus#journal, Vol. 1, No. 4, pp. 7-31, 2014


