12 Cross-linked Polyethylene Nanocomposites for Dielectric Applications

Abstract: Recent research for cable insulating material has shown that nano-size filler added to cross-linked polyethylene (XLPE) is electrically and physically stable. In this chapter we have tried to explore and document the role of nanoparticles in electrical breakdown characteristics. The major role of interface, different candidate mechanisms and the change in polymer morphology in the presence of nanoparticles and its synergistic effect in amplifying the dielectric breakdown strength are discussed in detail. The evidence gathered in this chapter suggests that the role of the nanoparticles is not one dimensional. The factors affecting the dielectric characteristics in polymer nanocomposites are the sum of interface, nanoparticles as scattering centres, nanoparticles as charge trapping centres and nanoparticles as defect reducing fillers.

12.1 Introduction

Nanodielectrics of polymer nanocomposites have received considerable attention due to their potential benefits as dielectrics, especially significant improvement in dielectric strength. The term “nanometric dielectrics” or simply “nanodielectrics” was introduced in 1994 when Lewis anticipated the potential property changes that would benefit electrical insulation due to nano-sized inclusion (Cao, 2004). Polymer dielectric films show very high dielectric strength (>300 kV/mm), lower dielectric loss (<0.01), and adequate mechanical flexibility (Smith, 2008). Cross-linked polyethylene (XLPE) has become the globally preferred insulation for power cables, both for distribution and transmission system applications (Jose, 2014). This insulation system provides cost efficiency in operation and procurement, as well as lower environmental and maintenance requirements when compared to older impregnated paper systems.

Electrical breakdown occurs when the applied voltage can no longer be maintained across the material in a stable fashion without excessive flow of current and physical disruption. Dielectric breakdown is categorized into (i) Intrinsic breakdown defined by the characteristics of the material itself in pure and defect free form under test conditions which produce breakdown at the highest possible voltage, never achieved experimentally, (ii) Thermal breakdown occurs when the rate of heating exceeds

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the rate of cooling by thermal transfer and thermal runaway occurs under voltage stress, (iii) Discharge-induced breakdown occurs when electrical discharges occur on the surface or in voids of electrical insulation. Ionization causes slow degradation. Corona, or partial discharge, is characterized by small, local electrical discharges and (iv) Treeing-electrical results from partial discharge. (Verweij, 1996). Under the electric field stress, nano holes of about 10 nm diameter appear in the insulation without defect initially. The breaking and rearrangement of molecular bonds caused by field and mechanical stress, affects the extension of nano hole and low density areas (LDA). Then the number of nano holes develops continuously in LDA s. More LDAs appear, thermo-electrons inject and discharge produced in LDAs leading to an increase in local conductivity, these all bring the final breakdown (Li, 2010). Under a variety of field stresses, the breakdown suffered by dielectric material presents a very strong time-dependent relationship, so it can be divided into five or more kinds by breakdown speed as shown in Table 12.1 (Fothergill, 2007). The three former are known as the short term breakdown, the others are degradation.

Table 12.1. Different kinds of electrical breakdown in time scale.

<table>
<thead>
<tr>
<th>Different breakdown mechanisms</th>
<th>Electric breakdown</th>
<th>Thermal breakdown</th>
<th>Electro-mechanical breakdown</th>
<th>PD and Electrical trees</th>
<th>Water trees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short term breakdown</td>
<td>$10^9 - 10^4$ s</td>
<td>$10^7 - 10^3$ s</td>
<td>$10^6 - 10^3$ s</td>
<td>$10^2 - 10^7$ s hrs-ys</td>
<td></td>
</tr>
</tbody>
</table>

From the point of view of insulating systems with high breakdown strength by protesting the above possible breakdown mechanisms, cross-linked polyethylene nanocomposites are the best candidates. The main parameters affecting the dielectric breakdown properties of a nanocomposites can be identified as follows: (i) filler size, material and aspect ratio, (ii) surface functionalization (iii) filler grade (iv) host material (v) type of synthesis (in-situ, ex-situ, mixing process, polymerization, etc.) (Smith, 2008). These parameters are reflected in the quality of dispersion of particles within the host material. Polymer chains usually align according to intermolecular forces. The chains that bond to a particle surface are forced to align according to their neighbouring molecules. This leads to a restructuring of the host material due to the presence of the particle and its ability to interact with the host material.

Reduction in dielectric breakdown with increasing temperature is a very important concern. Materials with a high thermal conductivity rate must be chosen to address this problem. The thermal conductivity rate of inorganic oxides is quite high. For example, thermal conductivity rate of MgO is approximately 42 W/mK, which is approximately 32 times that of silica (Jeong, 2010). Also inorganic metal oxides
are reported to show excellent characteristics for the suppression of free and space charge when used as filler in high voltage DC cable insulation materials (Ortiz, 2010). Most widely used insulation polymer at high breakdown voltage applications is XLPE and the fillers incorporated to this dielectric system to improve breakdown strength are inorganic oxides like $\text{SiO}_2$, $\text{TiO}_2$, $\text{Al}_2\text{O}_3$, $\text{ZnO}$, $\text{MgO}$ and inorganic silicates (Nelson, 2006; Jose, 2013). These hybrid organic/inorganic nanocomposites have proved their potential to have dielectric benefit in newly emerging materials and in advancement of existing dielectric materials.

A better understanding of the issues and fundamental mechanisms in nanodielectric engineering will lead to the successful development and implementation of high performance nanodielectrics for high breakdown strength materials. In this chapter, the major role of interface between polymer and filler, different candidate mechanisms giving an improvement in breakdown characteristics and the change in polymer morphology in the presence of nanoparticles and its synergistic effect in amplifying the dielectric breakdown strength are discussed in detail.

### 12.2 Candidate mechanisms leading to enhanced breakdown characteristics

The mystery behind the improvement in dielectric strength in polymer nanocomposites is not yet revealed. There are various factors and mechanisms which may be responsible for the increased dielectric strength. Basically, nanoparticles can be seen to act as barriers to the flow of electric current which restricts the breakdown mechanisms and thus higher voltage is needed to initiate the charge carrier multiplication (Takala, 2008). Due to the massive interfacial volume fraction, the overall density and depth of trap sites in the material volume may be increased which limits the mobility and energy of free charge carriers. Generally, the reduced space charge also increases the breakdown strength, as the adverse distortion of the applied field due to the local fields is reduced. On the other hand, if free charge carriers are trapped in trap sites near the electrodes forming homo charge, the field near the electrodes is mitigated which increases the voltage required for charge injection from the electrodes especially under DC voltages (Fabiani, 2009). Due to the aforementioned mechanisms, nanocomposites have also been found to be more resistant against treeing and partial discharge (Desai, 2005). The improvements in nanocomposite breakdown strength has been attributed to (1) change in space charge distribution, (2) effective interface, (3) the presence of nanoparticles as scattering centres and trapping sites for mobile charges, (4) change in polymer morphology (Frechette, 2001; Danikas, 2009). The change in polymer morphology can be further explained by the role of crystalline structures, cross-linked matrix, the mobility of polymer chains and interface in the presence of nanoparticles. The change in dielectric characteristics of polymer
Cross-linked polyethylene nanocomposites with inorganic oxide nanoparticle fillers exhibit enhanced electrical breakdown strength compared to their unfilled or micron filled counterparts (Lewis, 1994). Different mechanisms were introduced to explain the key role of nanoparticles in nanodielectrics. But the breakdown mechanism (BD) is still less clear. Models on BD of nanodielectrics chiefly consists of three, (1) coulomb block effect (CBE) (Xu, 2007), this model states that nanoparticles scatter uniformly in polymer as a coulomb island, which can raise the electric strength of the material. (2) the space charge model (Li, 2007), homo polar/hetero polar charges are accumulated to reduce/increase the electric field at the electrodes. (3) the multi core model, this model suggests that electrons lose the energy they gain from the applied voltage, because they are scattered or attracted by the coulombic force when electrons move inside the Debye shielding length. The CBE model seems more suitable for nano metal particle-polymer matrix nanocomposites. The multi-core model is better to apply in nano oxide-polymer matrix composite and it is more popular than the space charge model. It is commonly thought that in both the CBE model and the multi core model, the carrier mobility is restrained effectively by nano particle doping.

### 12.3 Experimental evidences

Smith et al. introduced a mechanism leading to improved dielectric strength in polymer nano composites [Smith, 2008]. 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 a homocharge buildup at the electrodes, which increases the voltage required for further charge injection due to blocking by the homocharge. Breakdown strength for unfilled and nanoparticle-filled resins are shown in Table 12.2.

**Table 12.2:** Breakdown strength for unfilled and nanoparticle-filled composites.

<table>
<thead>
<tr>
<th>Material</th>
<th>Dc Characteristic Breakdown Strength @ 25 °C in kV/mm</th>
<th>Ac (60Hz) Characteristic Breakdown Strength @ 25 °C in kV/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled XPLE</td>
<td>184</td>
<td>178</td>
</tr>
<tr>
<td>12.5 wt % 6 µm micro silica filled XPLE</td>
<td>162</td>
<td>139</td>
</tr>
<tr>
<td>12.5 wt % untreated 12 nm nanosilica filled XLPE</td>
<td>191</td>
<td>186</td>
</tr>
<tr>
<td>12.5 wt % vinyl silane treated 12 nm nanosilica filled XLPE</td>
<td>239</td>
<td>193</td>
</tr>
</tbody>
</table>
According to Roy et al., the improvements in nanocomposites’ electrical behaviour have been attributed to (i) the change in the space charge distribution, (ii) the reduction in internal field caused by a decrease in particle size and (iii) changes in polymer morphology (Roy, 2007). It was found that the reduction in the charge carrier mobility in nanocomposites, increase in trap depth and change in the defect size may be key to explain the improvement in properties. The characteristic breakdown voltage of different XLPE nanocomposites is shown in Table 12.3. At a high temperature region, the breakdown voltage is decreased and this can be correlated to the increased polymer chain mobility at high temperature.

Table 12.3: Characteristic breakdown voltage (kV/mm) of XLPE and several nanocomposites at a range of temperatures (Weibull shape parameter in parenthesis)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°C</td>
</tr>
<tr>
<td>XLPE +untreated nanosilica</td>
<td>269(2.49)</td>
</tr>
<tr>
<td>XLPE+AEAPS treated nanosilica</td>
<td>314(2.07)</td>
</tr>
<tr>
<td>XLPE +HMDS treated nanosilica</td>
<td>400(1.69)</td>
</tr>
<tr>
<td>XLPE +TES treated nanosilica</td>
<td>336(1.69)</td>
</tr>
<tr>
<td></td>
<td>446(1.73)</td>
</tr>
</tbody>
</table>

To investigate the nature of the charge trapping mechanism of nanocomposites, the depth of the trapping sites was evaluated using the initial rise method (Maeta, 1980). It is shown in Table 12.4. The trap depth was determined from the slope of the Arrhenius plot. However the trap depths for the second peak of AEAPS and HMDS nanocomposites is significantly higher than the other composites, which was ascribed to the formation of novel trap sites due to the polar nature of the surface modifier groups.

Table 12.4: Trap depths in all composites calculated using initial rise method from the TSC spectra

<table>
<thead>
<tr>
<th>Samples</th>
<th>Trap depth (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C5 peak</td>
</tr>
<tr>
<td>Untreated nanocomposites</td>
<td>0.37 ±0.1</td>
</tr>
<tr>
<td>Microcomposite</td>
<td>0.35 ± 0.1</td>
</tr>
<tr>
<td>Vinyl silane treated nanocomposites</td>
<td>0.41 ± 0.1</td>
</tr>
<tr>
<td>Amino silane treated nanocomposites</td>
<td>2.4 ± 0.1</td>
</tr>
<tr>
<td>HMDS treated nanocomposites</td>
<td>2.0 ± 0.1</td>
</tr>
</tbody>
</table>

The mobility of the charge carriers may be estimated using the method documented by Malec et al. [29]. \( \mu = 0.786 \frac{d^2}{t_p} V \). Where \( \mu \) is the mobility of the charge carriers, \( d \) is the sample thickness, \( t_p \) is the time at which absorption current is at its maximum (peak),
and V is the applied voltage. Carrier mobility as a function of time for XLPE and all its composites is shown in Figure 12.1. The mobility of the charge carriers also decreased with particle loading suggesting that nanoparticles scatter the carriers, reducing their mobility. The nanoparticle may alter the crystalline morphology providing another mechanism for scattering. This will be discussed in detail in another section, effect of polymer morphology on dielectric strength.

![Figure 12.1: Carrier mobility as a function of time for XLPE and all its composites](image)

Tan et al. have investigated the nanofiller considerations on dielectric breakdown strength [Tan, 2007]. The effect of fillers on composite breakdown is compared in Figure 12.2, where particles are of 20-100 nm in diameter. It is not surprising that semiconductive and partially oxidised aluminium fillers lead to lower breakdown strength. However, for the insulative fillers with breakdown strength of greater than 200kV/mm, the composite breakdown strength does not show much difference. It appears to slightly increase and saturate in the range of 500-600 kV/mm for all insulating particles. It is interesting to see that ceramic particles of higher breakdown strength do not impart the composites more endurance to a high electrical field.
**Figure 12.2**: The breakdown strength (BDS) of PEI composites increases with increasing BDS of 5 wt% various particles (Tan *et al.* 2007)

While considering the different mechanisms in nanodielectrics, the three dominant features are [11]:
(a) The magnitude of the internal charge is much less for nanocomposites
(b) The dynamics of charge decay are much faster for nanocomposites
(c) There is often a very different distribution of charge (and therefore of internal field) with nanocomposites

### 12.4 It’s all interfaces

Interfaces play a critical role in all multi-component materials, where a thorough understanding of it may put a light on the enhanced dielectric breakdown performance of polymer nanocomposites (Pitsa, 2011; Aulagner, 1995). The improved breakdown strength is directly related to the interfacial interaction zone which surrounds the nanoparticles. The characteristics of the interfacial interaction zone are the following (Pkanazky, 2005).

1. The mobility, which depends on the physico-chemical bonds created on the common surface
2. The formation of a double layer at the interface, which may affect the local conductivity
Tan et al. studied the correlation between the interface and dielectric breakdown characteristics [Tan, 2007]. When particles are smaller than 10 nm, the interfacial fraction becomes dominant, which might result in interesting physical phenomena. Figure 12.3 depicts the increasing role of particle interface with decreasing the particle sizes. With a 5 vol % particle added in a polymer, 10 nm particles will result in 40 vol % interfaces. The 5 nm particles result in 95 vol % interface of the composites. When the fillers are spheroid, more complicated filler – matrix interaction and physical properties are to be expected. According to Zou et al. polymer – particle interface are likely to extend over several atomic diameters – perhaps around 1 nm and this interaction zone would be expected to have a significant effect. For a 10 % v/v nanocomposite, with a 10 nm particle, a 1nm thick interaction zone occupies approximately 7 % of the volume, where as a 5 nm zone would occupy about 70 % of the volume. Anisotropic fillers with high aspect ratios can self assemble into superstructures, even at low concentrations (Nelson, 2002).

![Figure 12.3: The particle size dependence of the particle interfacial contribution at various loading concentrations (Tan et al. 2008).](image)

Conventional fillers tend to reduce the breakdown strength, however there are indications that well dispersed nanofillers with appropriately functionalized surface can increase the breakdown strength. Table 12.3 shows the results on cross-linked polyethylene with a variety of such fillers. The TES treated nanosilica formulation has a breakdown strength at 25 ° C of 446 kV/mm compared with 269 kV/mm for unfilled XLPE. Vaughan (Vaughan, 2006) has shown similar effects with nanoclay fillers in
PE, they have also demonstrated the effect of particle dispersion on the breakdown strength.

Figure 12.4 shows schematic representation of reactions taking place between silica and the silane (Huang, 2010).

Through the surface modification, the interface between the filler and polymer is improved and this affects positively not only the nanoparticle dispersion, but also the stability and specific surface area, resulting in enhanced electrical strength. Surface modifications of TiO$_2$ nanoparticles, with the use of polar silane coupling agents, induces enhancement in the dielectric breakdown strength. The polar groups at the interface may play the role of charge scattering centres or trap centres (Ma, 2005). Improved breakdown strength is reported for barium titanate/epoxy samples with treated nanoparticles compared to pure epoxy samples or samples with untreated nanoparticles (Siddabattuni, 2011). The improved breakdown strength is associated with the reduced Maxwell-Wagner polarization that causes the surface modification. Also covalent bonding between the nanoparticles and the polymer matrix, seems to increase the interfacial polymer density and minimize the defects (such as microvoids) in the interface, resulting in improved breakdown strength (Smith, 2008; Jose, 2014). In thermoplastics the interfacial polymer can exhibit changes in crystallinity, mobility, chain conformation, molecular weight, chain entanglement density and charge distribution (Schadler, 2007). In cross linked matrices there is an additional complication of changes in cross-link density due to small molecule migration either to or from the interface (Atkinson, 1996). It is qualitatively understood that, an attractive interface will decrease the mobility of the polymer chains and a repulsive
interface will increase the mobility (Ellison, 2003). This change in mobility of the polymer chains in the interfacial region can be estimated by the glass transition temperature, using either DSC or DMA (Takada, 2008).

A recent review of the chemistry and physics of the interface of nanodielectrics made using either spherical inorganic nanoparticles or intercalated and exfoliated layered inorganic natural and synthetic clays and micas, by Reed (Reed, 2010), highlights the progress in understanding the role of the interface, but also cites many instances of apparent contradictory results by different investigators, in properties where the measurements are typically repeatable, unlike electrical breakdown.

Alcoutlabi and McKenna (Mckenna, 2005) performed a topical review of theoretical and experimental publications on the effect of nanoparticles on melting point and glass transition temperature. They presented dynamic, thermodynamic, and pseudothermodynamic measurements reported for Tg in confined geometries for both small molecules in nanopores and for ultrathin films. They found that Tg increases, decreases, remains unchanged, or even disappears, depending on details of the experimental conditions or molecular simulation. For the same material, depending on experimental conditions, different values of Tg had been observed; it was also noted that the vast majority of the experiments had been carried out carefully and the results were reproducible. The authors conclude that existing theories of Tg are unable to explain the range of behaviours on the nanometric size scale.

On the other hand, Bendler and colleagues (Bendler, 2009) have a more positive view, and present a quantitative analysis that shows that most if not all, experimental results on the nanoconfinement of the glass transition temperature can be explained by a defect diffusion model. Their model incorporates defect-defect interaction enthalpy, defect concentrations, defect lattice geometry correlation length, and percolation fraction, to determine Tg and provides a quantitative relationship between the percolation fraction of rigid to mobile regions and Tg.

### 12.5 Theoretical models

The interfaces are consisting of layers with different electrical and chemical structures compared to the polymer. Different models were introduced to explain the electrical structure of the interface like Lewis’ model (Lewis, 2007), Tsagaropoulous model (Tsagaropoulous, 1995) and Tanaka’s model [54]. According to Tanaka’s model, when a spherical inorganic nanoparticle is embedded in a polymeric matrix, three layers are formed around it. The multi core model is presented in Figure 12.5. The bonded layer (first layer) is a transition region, which is tightly bonded to both nanoparticle and polymer by silane couplings. This bonding hinders the polymer chain mobility outside the monolayer. The thickness of the first layer is around 1 nm. The bound layer (second layer) consists of polymer chains strongly bonded to the first layer. The thickness of this layer is between 2 nm and 9 nm. Chain mobility that characterizes
this region seems to affect the glass transition temperature and crystallinity. The loose layer (third layer) is a region loosely coupled to the second layer. It has different chain structure, mobility, free volume and crystallinity compared to the polymer. Its thickness is about several tens of nm. Tanaka tried to interpret the partial discharge (PD) mechanism in polymer nanocomposites according to the multi core model. The PD degradation initiates from the third layer (amorphous region), which is the most susceptible to PDs than the other two. As soon as the PDs erode the third layer, they reach the second layer (spherulitic region) which is more resistant to PDs, PD activity continues between the second layer and the polymer matrix. The PD activity proceeds to more weak regions such as polymer regions or third layer of an adjacent nanoparticle. As a result, a zigzag path is formed around the nanoparticles due to PD activity. In this way, the enhanced PD resistance that polymer nanocomposites exhibit is achieved.

Figure 12.5: Interfaces formed around a nanoparticle embedded in a polymer matrix according to the multicore model
Due to the complexity of the composite microstructures, computational methods are usually required for study of the realistic multi component microstructures (Tanaka, 2005). Boundary integral technique (Tuncer, 2005) and finite element method (Azimi, 1994; Ang, 2003) are the commonly used computational methods, which numerically solve for interface charge density distribution and spatial potential distribution, respectively, in composites. To avoid the complication associated with them, the phase field method has recently been employed to perform computational studies of composite materials (Zhang, 2007). It calculates heterogeneous distribution of polarization, charge density, local electric field, and effective dielectric permittivity of the composites, where interphase boundary conditions are automatically satisfied without explicitly tracking interfaces. Figure 12.6 shows dipolar ordering model for nanofilled polymer composites.

![Dipolar ordering model for nanofilled polymer composites](image)

A representative figure of nanofiller-polymer interaction is shown in Fig. 12.7. It is suggested that polymer-nanoparticle interactions lead to the formation of two nanolayers around the nanoparticle. The first nanolayer closest to the nanoparticle surface is assumed to be tightly bound to the surface resulting in the polymer chains there to be highly immobile. Then there is a formation of a second polymer nanolayer with a thickness slightly more than that of the first layer and this layer contains polymer chains which are loosely bound. It seems that this loosely bound polymer in the extended layer causes a reduction in the nanocomposite glass transition temperatures at low nano-filler concentrations.
12.6 Effect of polymer morphology on dielectric breakdown characteristics

The polymer morphology has an important role in dielectric characteristics. The crystalline structure, size and shape of crystals, cross linked structure, mobility of polymer chains etc. have direct influence on dielectric breakdown strength values. While considering the crystalline morphology, size and number of crystals directly related to the breakdown process (Hoyos, 2008). In addition, the number of connecting chains between the crystals will be less in large spherulites compared to the small uniform crystals. The peculiar structure of the interface, the amorphous fraction of the polymer, which remains entrapped between boundaries, on cooling is populated by voids caused by volume contraction [Singha, 2008]. According to Hosier et al. the semicrystalline morphology drives the electrical breakdown in PE and the space filling array of lamellae results in highest electrical strength (Hosier, 2000). The enhancement in electrical breakdown can be correlated to the number and size of spherulites and the lamellar structure. The addition of additives that behave as nucleants leads to the formation of spherulites because of extensive nucleation. Also the perfectioning of the crystalline structure improves the electrical breakdown, as lamellae thicken as a consequence of adequate annealing.

The reactive grain boundaries that dominate a nonmaterial including a nanodielectric would be expected to lead to pronounced heterogeneity of the material with the following consequences (as dielectric materials): (i) high frequency dispersion, (ii) high leakage currents, (iii) high dielectric loss, (iv) accelerated ageing, (v) tendency to adsorb impurities and their precipitation at the reactive sites (Penrose, 1994). Notwithstanding these limitations, a great deal of work is being carried out in formulating composite insulating materials of commercial interest in which particles of nanodielectrics are embedded within a commonly used dielectric
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material such as polyethylene. The group of L. S. Schadler and RPI in the USA has found that such a procedure yields insulating materials having improved breakdown strength, both at room temperature and elevated temperatures (Lewis, 2005). To understand the conceptual foundations of such an improvement, it is important to observe first that the percentage of embedded nanoparticles must be quite low. This is because of low nanoparticle percolation threshold (Danikas, 2009) particularly for the commonly used particles. If the nanoparticle content increases beyond the percolation threshold, the nanoparticle tends to lose its beneficial effects. This arises because the nanoparticles act as a sort of hindrance to the propagation of electron avalanches found during dielectric breakdown, below the percolation threshold limit and this hindrance tends to be short circuited above the threshold limit. That the nanoparticles in polymer matrix behave as barriers for electron propagation can be looked at from different conceptual angles as follows:

(i) Nanoparticles, because of their extended surface area change the very nature of the polymer, alter the depth and density of trap sites in the language of solid state physics, thus reducing charge carrier mobility and energy.

(ii) The structure between the polymer and the nanoparticle is the key to the trapping mechanism, this is where the change layer (double layer) develops and nanoparticles present an elongated scattering path to the charge carriers.

(iii) Since area of the interfaces between the nanoparticles and the polymer is very large, the whole polymer matrix may be essentially treated as the interfacial region. The outcome is a set of strengthened nanometric double layer interfaces (Ildstad, 2001).

Goshowaki et al. have studied the influence of crystallinity on electrical conduction in LDPE and XLPE (Goshowaki, 2007). The degree of crystallinity of XLPE is less than that of LDPE i.e. the crystalline region of LDPE is decreased by cross linking. The experiments confirmed that the leakage current flowing in XLPE is greater than that in LDPE. This phenomenon suggests that charged particles move more easily in XLPE, in which a greater non crystalline region exists, as compared with LDPE. Figure 12.8 shows TSC spectra for XLPE, microcomposites, untreated and treated nanocomposites. Both the microcomposite and the untreated nanocomposites show a peak at ~54 °C. For the base polymer, a peak appears in a similar temperature region and is referred to as the C4 peak (Roy, 2007), which originates from the amorphous–crystalline interface of the polymer. However, at higher temperatures, the TSC spectra for the microcomposite and untreated nanocomposite are different. The smaller peak at 78 °C for the untreated nanocomposite is overshadowed by a rapid increase in current in the microcomposite. This increase in current is attributed to Maxwell–Wagner interfacial polarization and this peak is identified as the q-peak. Charges trapped at the interface of microparticles are responsible for such peaks (Ma, 2004). Figure 12.8 also depicts the TSC spectra for the surface treated nanocomposites. The TES nanocomposite which shows a peak at similar temperature to the C4-peak
shown by the untreated nanocomposites, but shifted upward ~5 °C. The shift in the peak is attributed to the higher viscosity of TES nanocomposites compared to the base polymer and the untreated nanocomposites (not shown here). The height of the peak for the TES nanocomposites is roughly similar to that of the untreated nanocomposite. The AEAPS and HMDS treated composites show similar behavior to the untreated nanocomposite at low temperatures, but the C4 peak is shifted slightly to lower temperatures (51 °C for the AEAPS nanocomposites and 47 °C for the HMDS nanocomposite). At higher temperatures, however, they both show a clear peak at 91 °C, much different from the microcomposite peak and the other nanocomposites. These may originate from the charge carriers trapped by the polar surface groups. Such groups will create surface states with deep trap sites.

![Thermally stimulated Current spectra for silica-filled composites](image)

Figure 12.8: Thermally stimulated Current spectra for silica-filled composites

According to Pitsa et al. by adding nanoparticles in a base polymer, the aforementioned mobility, type and degree of crystallinity change occurs (Pitsa, 2011). Experimental results have shown that polyimide nanocomposites present higher crystallinity than pure polyamide (Fuse, 2004). Increase in crystallinity has also been reported for silica/ XLPE nanocomposites, where the higher crystallinity was attributed to the vinyl silane treated silica nanoparticles. These results are directly correlated to the polymer chain mobility and thus breakdown strength. It is reported that as silica nanoparticle concentration exceeds 10 wt. %, the polymer mobility is severely restricted and immobilized above 20 wt % particle concentration.

Wang et al. investigated the breakdown strength of the silane grafted XLPE samples before and after immersion in distilled water (30°C) for 30 days, were reported
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It should be noted that the dielectric breakdown behaviour of the silane grafted XLPE before hydration is quite similar to its dependence of gel content on VTMS (Vinyl trimethyl silane) concentration and strongly supports the aforementioned considerations.

![Figure 12.9: Characteristic dielectric strength for silane grafted XLPE samples](image)

**12.7 Conclusions**

The researchers have tried to reveal the important factors at play in the enhancement of dielectric strength in polymer nanodielectrics. The evidence gathered in this review suggest that the role of the nanoparticles is not one dimensional. The factors affecting the breakdown characteristics in polymer nanocomposites are the sum of interface, nanoparticles as scattering centres, nanoparticles as charge trapping centres, nanoparticles as defect reducing fillers etc. The most likely mechanism that could be used to explain the increase in breakdown strength in the nanocomposites is the scattering created by both particle/polymer interfaces and possibly disrupted crystalline structures. A more attractive interface between nanofiller and polymer can contribute more towards property enhancement. The mechanism leading to the subtle differences in breakdown strength due to surface treatment of the nanofillers is either due to the defect reduction via chemical linkage between particle and polymer or, due to the introduction of deep trap sites in the polymer due to surface modifier groups. It is clear that continued developments in chemistry and materials sciences are critical to electrical insulation research in the field of nanodielectrics.
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