

POLYMER NANOCOMPOSITES FOR HIGH VOLTAGE OUTDOOR INSULATION APPLICATIONS

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Abstract. Since last few decades, polymer based outdoor insulation materials are being increasingly used in the power industry. Polymeric insulation materials present attractive advantages such as light weight, resistance to vandalism and best performance under contaminated conditions. However, their electrical, mechanical and thermal properties could not meet the requirements of high voltage outdoor insulation applications. These properties are commonly improved by filling the base polymer with huge loadings (< 50 wt.%) of micron sized fillers. This huge filler loading makes the process ability of the polymer composite complex due to substantial rise in the viscosity of the material and outside a certain limit, the plasticity of the product also suffers. These process limitations and the recent failures in the field recommend the necessity for an alternate material with enhanced properties even at lower filler loadings. Recently nanocomposites are emerging as capable alternatives which can present the vital properties at lower filler loadings without sacrificing the plasticity in the end product as well as ease of processing. As the development of polymer nanocomposites for high voltage outdoor insulation applications is still at its immaturity, it is necessary to investigate their preparation and characterization properties desired for outdoor applications and to comprehend the various mechanisms accountable for the unique behavior of the nanocomposites. This paper presents an overview of nanocomposites as outdoor insulation at the present.

1. INTRODUCTION

Polymer nanocomposites can be described as the composites in which small quantities of nano sized fillers are homogeneously distributed in the polymers matrix by different weight percentages. The amount of nano fillers accumulated to the matrix are very diminutive (<10 wt.%). Opposite to this, the quantity of microfillers in polymer microcomposites is so high that it may reach up to 50% of the weight or higher of the total mass [1].

Tanaka et al. [1] elaborated that for better understanding of polymer nanocomposites the comparison of other two major aspects i.e., the specific surface area of the composites and filler size are important. The size of nanocomposites is in nanometer (< 100 nm), in length. The nanocomposites are

thrice smaller as compared to microcomposites. This concludes that the number density differs nine times approximately. Hence, the distance between adjacent fillers is greatly smaller in nanocomposites as compared to microcomposites. As far as specific surface area of filler is concerned it is high in the nanocomposites approximately three times larger than microcomposites. That is why nanocomposites are expected to have a great deal of interaction of polymers matrices with fillers.

As microcomposites can change different properties of composite materials (e.g., thermal and mechanical properties), on the other hand it affects the other properties negatively / adversely (e.g., electrical properties). Amazingly, the emerged polymer nanocomposites ascertain better electrical, mechanical and thermal properties [2].

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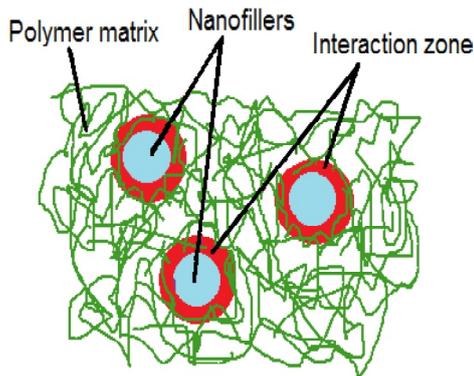


Fig. 1. Parts of polymer nanocomposites.

Another fact is that polymer nanocomposites acquire the research interest in high voltage electrical Insulation but on the other hand the chemistry and physics principles involved in the property enhancement unable to gain that much importance, hence, a lot of things remained unexplored. The research focuses on various prospective fields which can be explored. Moreover, it sums the past developments in the field of high voltage electrical technology. The chief prospects of the work are electrical discharges pertaining to surface tracking and partial discharge mechanism on polymer nanocomposites.

Generally, polymer nanocomposites consist of three main constituents, namely the polymer matrix, the nano filler and the interaction zone (the interface between the matrix and the filler), which is said to play the major role in the property enhancement of polymer nanocomposites [1,3]. A simplified diagram illustrating the constituents of polymer nanocomposites is as shown in Fig. 1. The polymer matrix can be further divided into three main categories: thermoplastics, thermosetting and elastomers. On the other hand, the nanofillers can be classified according to their dimensions: one-dimensional (or normally referred as thin platelets), two-dimensional (or normally referred as nanowires and nanotubes) and three-dimensional (or normally referred as inorganic oxides).

2. CLASSIFICATION OF POLYMERS

Numbers of materials that have high molecular weights are generally identified as polymers. Polymer may have different thermal characteristics, physical properties, chemical structure and mechanical behavior etc., depending on these properties polymers can be categorized into three major classes which are briefly narrated below.

2.2.1. Thermoplastic polymers

The behavior of this type of polymers is that on continuous exposure to thermal energy they became soft/plasticized but did not show vigilant change in their properties while considering certain precautions. Examples of these kinds of polymers are nylons, linear polyesters, Polyolefin, and polyether, PVC, sealing wax etc.

2.2.2. Thermosetting polymers

This type of polymers exhibit chemical changes by applying heating and become infusible mass. On heating the chemical reaction enables the polymers to increase their growth and cross linking of polymers chain molecules to produce giant molecule. The examples of these polymers are Phenol, resins, urea, epoxy resins, diene rubbers, etc.

2.2.3. Elastomers

Rubber has long flexible chains and weak intermolecular forces having high molecular weight polymer. Rubber has elongation at break ranging from 300-1000% and exhibits tensile strength in the range of 300-3000 psi e.g., natural and synthetic rubber.

2.3. Nanofillers

Nanofillers are normally found in the Plate-like, tube, and spherical shapes and at least one of the aforementioned dimensions is necessary to be on a nanometric scale. Nanofillers can be prepared either bottom up (oxides carbon metal and nanotubes) or by splitting large particles (nanoclay and other minerals) same like conventional filler particles. Irrespective of the fabrication procedure of nanofillers it is critical to inherit agglomeration of the nanoparticles and marvelous adhesion to the matrix. Nanosize particles can be coated or surface treated. Silanes and polyalcohol are examples of polar agents while stearic acid and fatty acids are examples of non polar acids which are coating agents for inorganic particles [4].

2.3.1. Layered silicates (LS)

Layered silicate/clay minerals belong to the class of silicate minerals, phyllosilicates. These comprise of synthetic and natural clays such as bentonite, mica, fluorohectorite, laponite, magadiite, and many more. LS belong to the 2-D nanofillers type and most widely used in various fields. LS structure can be illustrated as 2-D layer of two fused silicate tetrahe-

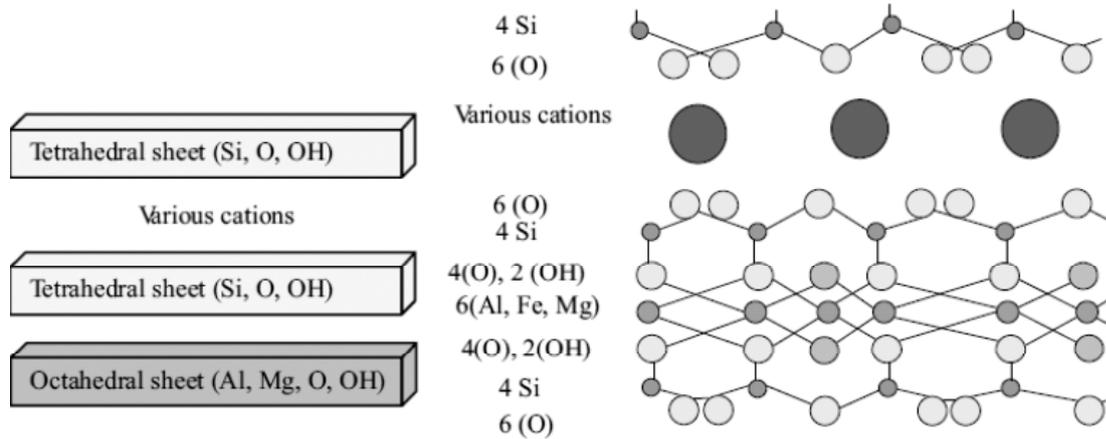
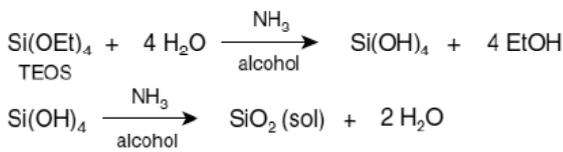
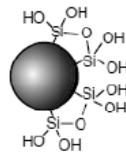


Fig. 2. Layered silicate structure.

(a) Surface unmodified silica particle

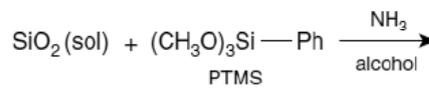


H₂O : NH₃ : TEOS : C₂H₅OH (molar ration)
11.4 : 4.0 : 1.0 : 78 (24 hr)

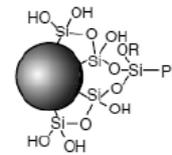


Polar surface

(b) Surface modified silica particle



H₂O : NH₃ : TEOS : C₂H₅OH : PTMS (molar ration)
11.4 : 4.0 : 1.0 : 78 : 0.11 (0.22) (24 hr)



Less polar surface

Fig. 3. Synthesis of nano-silica: (a) unmodified and (b) modified silica particle.

dral sheet with an edge shared octahedral sheet of metal atoms, like Mg or Al. Hoffmann et al. [5] proposed the model crystal structure of LS.

The sheet shape nanofillers is ~1 nm thick and their length is 100s to 1000s nanometers that is why they acquire high aspect ratio. Hence it is adequate and ideal to improve the polymer / silicate nanocomposites properties like barrier properties, stiffness and strength without changing any processing technique see Fig. 2.

2.3.2. Spherical particles

The sol-gel process is used to attain the spherical nanofillers. The spherical nanofillers can be distinguished as these nanofillers have three dimensions in the nanometer regime [6]. Organic/inorganic hybrid material can be produced by condensation reaction between the metal alkoxides and prepolymers, which results in the form of chemical bond of polymer and inorganic filler by using the sol-gel processes. This procedure proves the incorporation of filler particles in polymers through the

sol-gel process Z that avoids the aggregation of filler see Fig. 3. Silica, TiO₂, ZnO, CaSO₄, CaCO₃, ZnFe₂O₄ etc., are the old spherical amorphous nanofillers.

2.4. The interaction zones

The interaction zones take part a primary role in multi-component materials, where a meticulous understanding of their role may add to major progress, especially in nanotechnology [7]. The incorporation of inorganic nanofillers in a polymer composite improves the dielectric properties. The enhanced properties of nanocomposites are owing to the performance of the interaction zones [8]. The main features of the interaction zone are as below: (i) The mobility, owing to physicochemical bonds formation on the common surface (ii) To enhance influence of the local conductivity creation of a double layer at the interface.

As a result of above two phenomenon interfacial region gains significant boost [9].

Mobility, type and degree of change of crystallinity can be achieved by the addition of nanoparticles in the base polymer. The homogeneously distributed spherical nanofillers in a polymer, the interparticle distance between two nanoparticles is computed by Eq. (1), [10]:

$$l = r \left[\left(\frac{4\pi}{3v} \right)^{1/3} - 2 \right], \quad (1)$$

where r represents the radius of the nanofillers and v represents its volume. [11]. The space among the nanoparticles after their homogeneous distribution in the polymer matrix follow a Poisson distribution. The probability (P) of overlapping between interaction zones is given by Eq. (2):

$$P = 1 - \exp\left(-\frac{2t}{l}\right), \quad (2)$$

where t is the thickness of interaction zone. The nanoparticles surface area per unit volume of the nanocomposite is represented by Eq. (3), [12]:

$$S = \frac{3v}{r}. \quad (3)$$

The nanoparticles possess a greater surface region and because of this the interaction zones in a nanocomposite are much larger than in a polymer containing microparticles.

2.5. Modeling of interaction zones

When particles of nanometric size are introduced in a polymer matrix, an interfacial region is produced around each particle. The interfacial regions interact and contribute highly in the enhanced dielectric properties that the polymer nanocomposites express. Hence, it is very important to explore the features of the interfacial regions in great detail. The models are developed to investigate the chemical, physical structure of the interfaces and electrical properties. The enhanced properties of polymer nanocomposites are there and significant amount of technical literature is available but the cause of these properties has not been elucidated so far.

2.5.1. Lewis model

Lewis focused on the nanometric thickness by observing the interface's areas changed electrochemical and electromechanical performance [13]. By mixing the nanoparticles in an insulating material generates interfaces of nanometric dimensions, the

phenomenon gets great importance with the decrease in nanoparticles size. Lewis observed that by altering the internal charge activity a Stern layer and a diffuse Gouy–Chapman layer are produced around each nanoparticles [14,15]. The overlap of diffuse double layer will be created by the increment of nanoparticles. The overlapped layers provide a conducting path. Hence due to the internal conductivity the bulk charge accumulation is reduced and the dielectric breakdown strength of the nanocomposite is enhanced [9].

2.5.2. Tsagaropoulos model

Tsagaropoulos pointed out the glass transition behavior in various polymer/silica nanocomposites. According to his model, each nanoparticle is surrounded by two layers one is tightly bound layer and other is loosely bound layer (layer of restricted mobility). The loosely bound polymer demonstrates its own glass transition; on the other hand tightly bound layer does not participate in the glass transition. Experiments on polymer/silica nanocomposites proved that they exhibit two glass transitions, one the usual glass transition of the polymer and the other is glass transition of the loosely bound polymer. This result stems from the appearance of two $\tan\delta$ peaks [16]. At low concentrations, the inter particles distances are more vigilant and the mobility of the polymer near the tightly bound layers is not affected, Fig. 4. The gray areas to loosely bound layers, the white areas correspond to nanoparticles and black areas to tightly bound layers [16].

As a result, these regions cannot establish a second glass transition, however the first glass transition temperature of reduces. By amalgamation of more particle concentration the inter particles distances decrease whereas the loosely bond layer augment, Fig. 5. The illustration of Fig. 5 is that

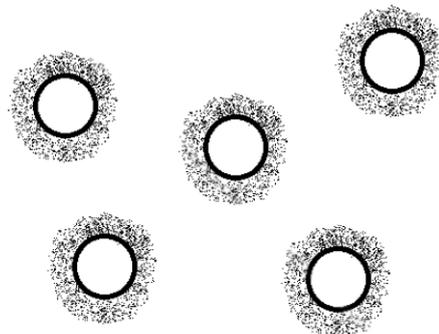


Fig. 4. Development of layers at low particles concentration.

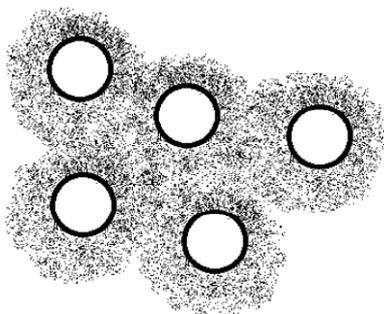


Fig. 5. Overlapping of layers at critical inter-particle distance.

gray areas show loosely bond layers, the black areas represents tightly bond layers and white areas represents nanoparticles [16].

The critical inter particles distance can be defined as the moment when the loosely bond layers start to overlap each other and display own glass transition. At this stage if we further introduce the nanoparticles amalgamation polymer regions with reduced mobility decreases, on the other hand the immobilized one increase. The gray area shows loosely bond layers, the white areas indicate nanoparticles and the black area represents tightly bond layers.

2.5.3. Tanaka's model

The Tanaka's model design refer to as multilayered model, the main objective of this model is to determine chemical and electrical of interfaces. This model is majorly used for polymer nanocomposites. This model states that as per chemical aspect by embedding of spherical inorganic nanoparticles in a polymer matrix three layers formed around it.

The initial layer is strongly bonded to polymer and nanoparticles with silane couplings, it is also called as bonded layer and it indicates a transition region. To couple inorganic nanoparticles with an organic polymer silane is normally used. With the help of monolayer two different matrices are hydrogen bonded. Outside the monolayer, the bonding holds down the mobility of polymer chain. According to multilayer model silane coupling agent is used to treat the formation of first layer surface of nanoparticle. The thickness of first layer is about 1 nm. The second layer which also called the bond layer which comprises of polymer chains tightly bonded to the first layer. The thickness of 2nd layer is between 2 nm to 9 nm. The glass transition temperature seems to be affected by the chain mobility that characterizes this region. The crystallinity is also prone interfacial interaction. A new layer of stoichiometrically cross-linked thermoset with excess

curing agent is formed around the nanoparticles when curing agents are absorbed to nanoparticles. The third layer (loose layer) is a region loosely coupled to the layer prior to it. The properties of this layer are free volume and crystallinity compared to the polymer with different chain structure and mobility. Third and second layer plays a vital role to elaborate the different properties however first layer affects indirectly [17]. The thickness is about several tens of nm.

2.6. Comparison of different models

A common assumption among all the models is that the properties of whole matrix depend upon the interfaces which are modified regions. Moreover, all models assume that every interface comprises of layers with diverse properties. The Lewis model tries to explicate the electromechanical and electrical features of interfaces, however Tsagaropoulo's model explain the material and chemical features of interfaces, i.e., physically and chemically bonding of polymer chains with nanoparticles. The multi layered model comprises of both the aforementioned models concepts so it encompass both the electrical and chemical features. Tsagaropoulos' model considers the creation of two layers around the nanoparticles. A loosely bond layer and a strongly bond layer but multicore model also illustrates the existence of third layer. The Tsagaropoulos proposed the model which concentrates on glass transition that observed in nanocomposites and is attributed to the loosely bond layer. Tanaka also agrees that the creation of layers around the nanoparticles is due to change of glass transition temperature. The multilayer model supports the lewis model regarding the electrical properties of the interfaces are concerned. Both the above models express the creation of a diffuse charge region around the nanoparticles.

There is no universal model available so far but the proposed models signify a considerable effort towards the understanding of the properties of polymer nanocomposites.

2.7. Preparation of nanocomposites

Preparation of nanocomposites can be done by various methods, either by amalgamation of the components/by in situ polymerization in the presence of a (nano) particle. If the components tolerate the blending temperature above the melting temperature of the polymer, the blending can be carried out either in a polymer melt, [18,19], or in a polymer solution, if a suitable solvent is available [20,21]. To

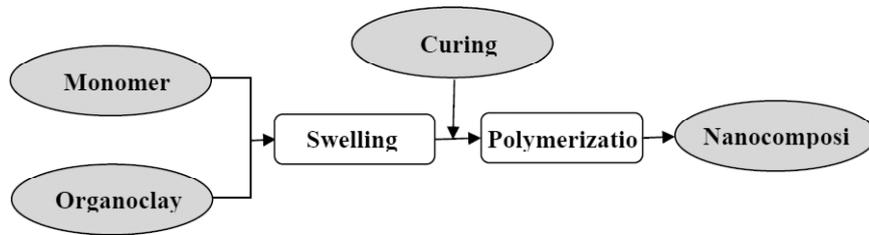


Fig. 6. In-situ polymerization.

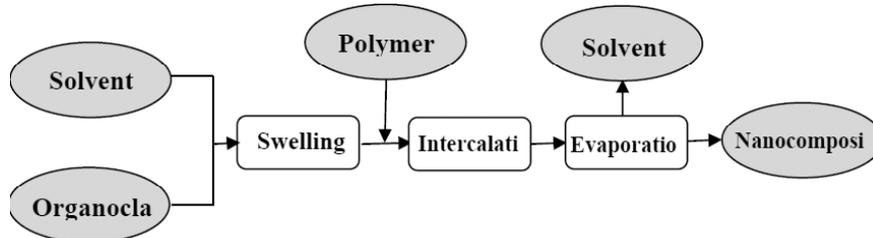


Fig. 7. Solution blending.

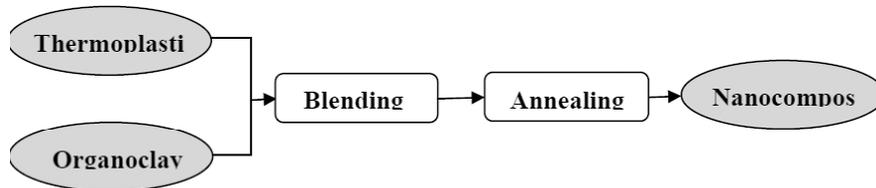


Fig. 8. Melt Intercalation.

produce a homogenous polymer nanocomposite a good compatibility between the components is crucial irrespective of the preparation method of the polymer nanocomposite [22]. In suitable external blending conditions compatibility can be enhanced like altering the temperature and the mixing intensity [23] or by chemical alteration of the filler and/or the polymer. There are different methods found in literature for preparation of nanocomposites with their inherent advantages and disadvantages.

2.7.1. In-situ polymerization method

In this method, for the creation of polymer around the intercalated layers, nanofillers are allowed to swollen within the liquid monomer solution. The polymerization can be instigated either by the incorporation of curing agent, initiator or by increasing the temperature to make it sufficiently reactive. The in-situ polymerization is shown in Fig. 6.

2.7.2. Solution blending method

This method comprises of a solvent system in this system the polymer is soluble and the nanofillers layers are swellaable. Upon mixing the polymer and nanofillers solutions, the polymer chains intercalate and displace the solvent within the interlayer of the nanofillers. The nanofillers are first swollen in a sol-

vent. When the solvent removal occurs, the intercalated structure remains, resulting in nanocomposite. Intercalation only occurs for certain polymer/solvent pairs by using this method. The drawback of this method is the use of environmentally unfriendly and economically forbidden organic solvents. The solution blending method is shown in Fig. 7.

2.7.3. Melt intercalation method

The melt intercalation technique proved to be a standard for some polymer/nanofillers nanocomposites and is also quite compatible with the industrial techniques. In this method polymer and modified nanofillers mixture are blended with shear in the molten condition. The polymer chains restate from the molten mass into the filler galleries to form either intercalated or delaminated nanocomposites. Melt intercalation method is shown in Fig. 8.

2.8. Characterization of nanocomposites

Characterization of the polymer nanocomposites is essential to examine diverse features of nanocomposite materials. Salient advantages of characterization are enlisted below:

- Features of filler dispersion inside the polymer matrix

- Consequences of filler surface alteration
- Interactions of the filler within the polymer chains
- Alteration in the process parameters on the ensuing morphology and properties.

In numerous occurrences, it is also, essential to utilize more than one characterization technique so as to precisely characterize the nanocomposite material. As these changes reflects the molecular factors of various sorts, many example found [24-27] in which electromagnetic spectrometry the standard techniques of (Raman, UV-Vis & Infra-red techniques) have been utilize to study the local interactions that occur in these regions.

Light scattering is an inexpensive way of analyzing the structure of transparent nanoparticles-containing materials [26], through sophisticated models, which may not be reliable, are needed to extort quantitative data. Wide-angle X-ray diffraction is used extensively in the literature to characterize the inter-gallery spacing in layered silicates [27].

2.9. Processing challenges

In the literature there have been some contradictory reports in regarding the effect of nanoparticles on the dielectric properties of polymer composites. In similar systems nanoparticles have shown both increase and decrease of breakdown strength [28-30]. On other hand variations are to be predictable in different systems; the effect of processing can also be a influential factor in the final properties. For example, micron fillers typically lead to drops in the breakdown strength, and similarly sized agglomerates of nanoparticles similarly perform accordingly [30,31]. This not only complicates efforts to determine whether a particular system is practically useful, but can also bias the conclusions drawn when examining the mechanisms guide to changes in properties. Therefore, it is significant to carefully consider and control the processing conditions used when making nanocomposites. Unfortunately, these systems can present additional challenges when compared to microcomposits. This can include difficulty in controlling dispersion, high relative water content of the particles and changes in the polymer microstructure.

2.9.1. Dispersion of nanofillers

Many kinds of mixers including a high shear mixing blade have been used to disperse nanofillers in materials. Generally, these blenders do not offer good results in dispersing nano-sized particles into host materials [32]. Calcinations can be used to

activate the silica surface, and an added advantage of this process is the breakdown of the silica aggregates and pellets produced during storage [33]. The concentration of silanol (Si-OH) groups on the surface reduces monotonically with the temperature when silica is heated under vacuum. According to Zhuravlev [34], most of the adsorbed water is removed at approximately 150 °C. Furthermore, results on the surface modification of SiO₂ nanoparticles with oleic acid achieved by Zongwei et al. [35] established that nanoparticles agglomeration reduces because the nanoparticles cores are separated by the surface modification layer, and the interactions between the particles are weakened. Another nonreactive modifier recommended by Seon et al. [36] is stearic acid, that allow the filler surface to become hydrophobic and similarly reduces the interactions between silica nanoparticles so that agglomerates can be broken down more easily. According to surfactant theory [37], surface modification by physical processes / techniques can be carried out with a low molecular weight surfactant, due to secondary (van der waals, electrostatic, or hydrogen bonding) forces between the nanoparticles and the modifier.

2.9.2. Dispersion characterization techniques

The employment of quantitative techniques for characterizing the dispersion in composites shuns subjective judgment of the degree of mixing. For the statistical analysis of the microstructure, the general steps are [38,39].

- Picking a micrograph of the composite.
- Selecting an image sample size representative of the structure of the material.
- Identifying particles.
- Analyzing the images.
- Making the statistical parameters that explain the dispersion.

A comparison of the TEM imaging method and FIB/SEM imaging method is shown in Fig. 9, presenting that FIB/SEM images and TEM images offer comparable information.

Proper statistical techniques are critical in quantifying the degree of blending in the nanocomposite materials. Quadrat based techniques [40,41], nearest-neighbor distance [42,44], *k*-function and Monte Carlo methods [43] are the foremost approaches used. The Quadrat technique splits the sample into cells, counts the number of particles in each cell and reports the skewness of the particle distribution [41] as in Eq. (4).

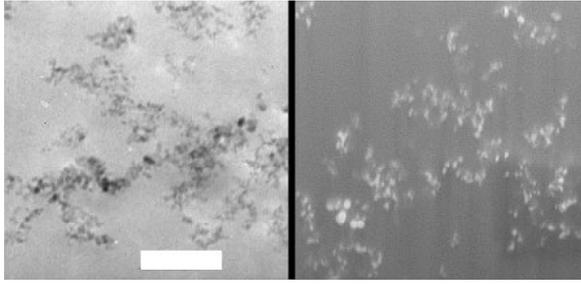


Fig. 9. TEM image (left) and SEM image (right) of 5 wt.% n-silica in polyamideimide. (Scale bar is 200 nm).

$$\frac{N}{(N-1)(N-2)} \sum_{i=1}^N \left(\frac{x_i - \bar{x}}{\sigma} \right)^3, \quad (4)$$

x_i denotes the number of particles in the i^{th} Quadrat, \bar{x} is the mean of x_i ($i=1,2,\dots,N$), and σ is the standard deviation of x_i . Skewness is the third moment of the central deviation and evaluates the asymmetry of a variable's distribution. Assuming a proper size is selected for the quadrat, the number of particles tends to be the same in each quadrat when the particles are well mixed. This will offer a skewness that is close to zero. On the contrary, aggregates will result in large number of empty or less populated quadrat. This asymmetry leads to non-zero skewness. Higher skewness offer poorer dispersion. In the nearest-neighbor distance analysis, the distance between the centers of gravity of each particle is measured. For an arbitrary particle, i , the distance between i and other particles are arranged from smallest to largest. For a sample of n particles, the k^{th} nearest neighbor distances W_k can be calculated and symbolized as [40]:

$$\{W_{ki} : i = 1, 2, \dots, n\}, \quad k = 1, 2, \dots, k. \quad (5)$$

Consider the distance W_k from a random particle to the k^{th} nearest particle. The expectation of W_k for complete spatial randomness is shown in Eq. (6).

$$E(W_k) = \frac{k(2k)!}{\{(2^k k!) \lambda^{1/2}\}}, \quad k = 1, 2, \dots, \quad (6)$$

where λ is the particle spatial density of the region to be investigated. The k^{th} nearest-neighbor distance R_k is defined as the ratio of the nearest mean distance to the expected k^{th} nearest neighbor distance under complete spatial randomness ($E(W_k)$) [40,44]. R_k is given by Eq. (7)

$$R_k = \left\{ \sum_{i=1}^n \frac{W_{ki}}{n} \right\} \left\{ (2^k k!)^2 \lambda^{1/2} \right\} / k(2k)!, \quad k = 1, 2, \dots \quad (7)$$

The first nearest neighbor distance technique utilizes only the first nearest neighbor distance. According to Eq. (7) the index for the first nearest neighbor distance is given by Eq. (8).

$$R_1 = \left\{ \sum_{i=1}^n \frac{W_{1i}}{n} \right\} 2\sqrt{\lambda}. \quad (8)$$

When interpreting the first NNI, $R_1 > 1$ indicates regularity and $R_1 < 1$ indicates clustering. The larger the departure is from the one, the more significant the regularity or clustering. Higher order NNI can give multi-scale information such as the size of the clustering size. However, it is probable to examine the pattern of the distribution by only using the first nearest neighbor distance [45,46]. Due to the simplicity of the analysis, it is utilized as the major index when the distance technique is used. In view of the fact that there is likely an interfacial volume around the nanoparticles with altered dielectric properties [47], the absolute value of the nearest neighbor distance is also imperative. When the inter particles distance becomes small enough, the majority of these interfacial volumes should overlap, leading to a shift in the response of the composite with increased loading. In the case of agglomeration, this leads to a reduction in the effective interaction volume as well as larger continuous interfacial zones. In terms of quantifying the inter particles distance, the thickness of TEM images can influence the results of the dispersion quantification, as the depth of field is typically larger than the specimen thickness [48]. In this case, two dimensional images are ideal. A comparison of simulated SEM and TEM images of different thickness are shown in Fig. 10, showing that thicker slices give a smaller obvious inter particles distance. Moreover, qualitative analysis may seem to reveal agglomerates which in fact are particles in different planes.

A qualitative comparison of composites mixed with and without this method is shown in Fig. 11.

Ultrasonic has also established usefulness in dispersing nanoparticles. Kurimoto et al. [49,50] used a novel technique which combined ultrasonic waves and centrifugal force to manufacture alumina/epoxy nanocomposites. The utilization of ultrasonic was found to be vital for good dispersion.

Likewise, Kochetov [51] combined ultrasonic processing and high shear force stirring to acquire an even spreading of the corresponding filler in the base material. The use of a dual asymmetric centrifuge has been found to be useful in dispersing nanoparticles in liquid resin systems [52]. The addition of a mixing medium is suggested in this case

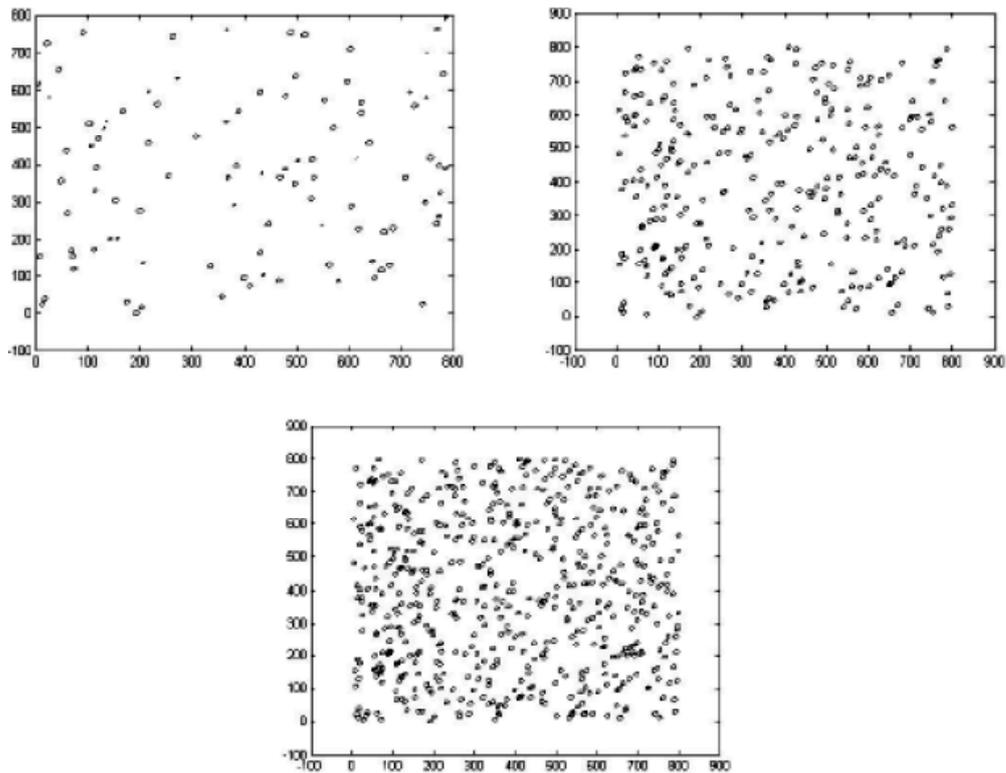


Fig. 10. Computer-generated images of a random dispersion of 5 wt.% 12 nm silica nanoparticles in XLPE. Upper left: SEM image. Upper Right: 20 nm thick TEM image. Bottom: 40 nm TEM image.

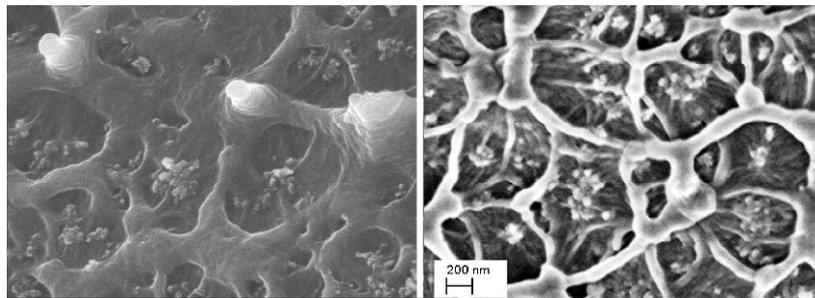


Fig. 11. SEM images of 5 wt.% silica XLPE nanocomposites (left: through pre-mixing, right: with no pre-mixing).

to facilitate break agglomerates. For example, the effect of the addition of alumina balls while mixing on the dispersion of alumina nanoparticles in a polyamide-imide system is shown in Table 1. The dispersion of the alumina nanocomposites was quantitatively studied using the nearest neighbor and quadrate techniques. At 5 wt.%, the nearest neighbor index value is closer to 1, representing enhanced particle dispersion. The skewness value also drops,

demonstrating higher particle distribution. Fig. 12 shows SEM images of these materials.

2.10. Development of nanocomposites in insulator industry

This development has been quite slow as compared to nanocomposites development in other areas. The

Table 1. Dispersion quantification of 5 and 10 wt.% alumina nanocomposites.

I.	No Alumina Balls(5%)	Alumina Balls(5%)	No Alumina Balls (10%)	Alumina Balls (10%)
Skewnes	1.74	0.71	2.0	1.73
Ist NNI	0.50	0.74	0.65	0.68

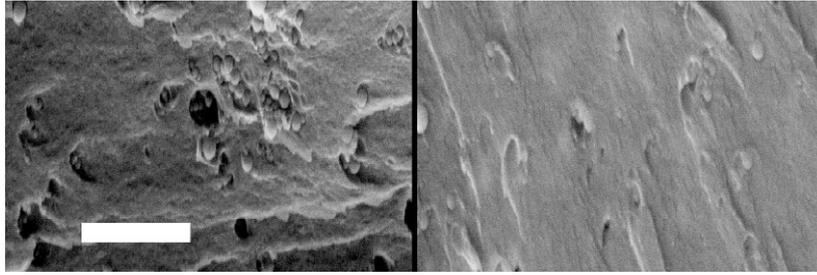


Fig. 12. SEM images of 5 wt.% alumina nanocomposites. Mixed (left: without, right: with) alumina balls. (Scale bar is 1 nm).

idea of using polymer Nanodielectric in electrical insulation was motivated by Lewis [53] in 1994 when he published a paper entitled “nanometric dielectrics”. In the paper, Lewis anticipated the property changes that would benefit electrical insulating applications due to nano-inclusion. However, the push to develop Nanodielectric was not spotlighted much at that time. It was until early 21st century that researchers began to look into it when some promising results on property changes have been successfully documented.

Due to the distinct properties of nanocomposites, researchers around the world have looked into several possibilities of nano-sized particles to be combined with base polymers. Examples of nanocomposites currently under development are polyolephins/clays nanocomposites, epoxies/inorganic oxides nanocomposites, Elastomers/carbon nanotubes nanocomposites, ethylene-vinyl copolymers/graphite nanocomposites, and polyethylene terephthalate/ceramics nanocomposites [54]. Various electrical properties of polymer nanocomposites have also been investigated for high voltage insulation application. Among them are dielectric breakdown strength, dissipation factor, permittivity space charge formation, partial discharge resistance and tracking resistance. Experimental works on these properties have shown promising results in insulation perspectives.

2.10.1. Properties of nanocomposites

The initial experimental work on polymer nanocomposites in electrical insulation perspective was credited to Henk et al. [55] and Nelson et al. [56] when they documented some potential benefits of polymer nanocomposites. In their research works, the authors highlighted the unusual properties of polymer nanocomposites, which were very different as compared the base polymer and the so called polymer microcomposits.

The dielectric breakdown strength which is found when the filler particles attain nanometric dimen-

sions is one of the most important property changes of nanocomposites. This property has in fact been widely documented in many literatures [54,57-67]. Not only this, further electrical properties, like space charge formation, dissipation factor, partial discharge, tracking resistance and permittivity were also proved to be encouraging when polymer nanocomposites were introduced.

Although there is evidence on enhanced dielectric properties of polymer nanocomposites, fundamental physics and chemistry concerning their property changes are not well understood. It is speculated that the interfacial area (interaction zone) is the main factor that contributes to the drastically enhanced insulating properties of nanocomposites [57,58,68,69]. Nelson [54] correlated the radius of particle to the surface area and proposed that when the size of the fillers is reduced, the specific surface area becomes very large. The interfacial region has high volume fraction of the high surface-to-volume ratio of the fillers between nanoparticles and the matrix [59]. As a result, the properties of the nonmaterial become altered.

For improving the dielectric strength and electrical erosion of nanocomposites the charge transport is of utmost important [70,71]. Montanari et al. [72] examined nanosilica filled polypropylene and ethylene-vinylacetate nanocomposites and observed a new relaxation process which they thought to be linked to the charge trapping at the interfaces between the nanofillers and the polymer. The magnitude of the internal charge is much less for nanocomposites and the dynamics of charge decay are much faster for nanocomposites [58]. Nelson et al. [73] showed that lower and redistributed space charge is due to the presence of homopolar charge adjacent to cathode, which is contrary to heteropolar charge near cathode for microcomposits. However, Tanaka [74] in his attempt to allocate the polarity of charge created in the composites to his proposed multi-core model, failed to draw conclusion on whether charge produced near the elec-

trodes is homo or hetero, because space charge distribution is complicated, and affected by unknown conditions. Therefore, available data is very limited and questions remain on the electrical property changes of nanocomposites.

2.10.2. Mechanical properties

To improve the mechanical performance of polymers inorganic fillers are added to the polymers [75]. To enhance the strength and toughness is the need for polymer nanocomposites [76]. The mechanical properties comprise elongation at break, tear strength, tensile modulus and hardness etc.

According to Dengke et al. [77,78] the addition of a small amount (2 - 5 percent weight) of inorganic nanofillers to polymers should be enough for mechanical steadiness and performance enhancement. Polyamide films tested by Irwin et al.[79] illustrate considerable enhancements to strength, elongation and scratch hardness. Silica nanoparticles-filled PEN composites are melt blended to enhance the mechanical properties of PEN [80].

Mechanical properties like elongation at break and tensile strength of the PA 6/tailored silica nanocomposites also illustrate a trend to enhance and then reduce with increasing silica content and have maximum values at 5 percent silica content as showed in Table 2 [81].

2.10.3. Thermal properties

The properties of materials that modify with temperature variation are known as thermal properties. Thermo-gravimetric analysis (TGA) is an instrument that is employed to monitor thermal stability by change in sample weight at elevated temperatures.

PI/SiO₂ nanocomposite demonstrates elevated thermal stability as compared to their microcomposites counterpart. The reinforcement of a silicon rubber composite with nanofillers produces

Table 2. Tensile strength with increase of percentage of fillers.

Tensile Strength,%	Nanofilles,wt.%
60	0
118	5
125	10
108	15
90	20
60	30

a superior composite with enhanced thermal properties [82]. Motori et al. [83] verified that with only 6 wt.% of nanofillers, the temperature index increases considerably as compared to the base polypropylene.

The enhanced thermal stability is credited to the action of clay layers as superior insulator and mass transport barrier to the volatile products created during decomposition as well as assisting in the formation of char after thermal decomposition [84-88]. Zhang et al. [89] reported that the heat distortion temperature and thermal decomposition were finely tuned for epoxy clay nanocomposites with 5 wt.% clay compared to pristine epoxy matrix.

Lakshmi et al. [90] compared the thermal stability of unmodified epoxy (UME) systems and clay modified epoxy (CME) systems by using different epoxy resins such as bisphenol and the triphenylphosphine unit in the HDTPP-MMT clay. A significant improvement in thermal stability has also been reported on epoxy clay nanocomposites prepared with reactive phosphorous containing organo-clay (RPC) by the evaluation of activation energy and integral procedural decomposition temperature [91].

Wang et al.[91] has reported great increase in limiting oxygen index (LOI) with the inclusion of 5 wt.% of RPC to the epoxy resin demonstrating the extraordinary improvement in flame retardancy. The char residue of clay layers will also decrease the oxygen uptake and the escape of volatile gases produced by polymer degradation [92]. Camino et al. [93] reported the mechanism of the improved fire retardancy of epoxy clay nanocomposites cured by methyl tetrahydrophthalin anhydride. An improved fire resistance was also observed in the case of epoxy carbon fiber composites with the addition of nanoclay and graphene nanosheets [94].

Gu and Liang [95] reported that thermal stability of the epoxy clay nanocomposites were influenced by the clay loading, structure and nature of the purge gas. Kaya et al. [96,97] reported that the incorporation of unmodified clay (MMT) into the epoxy resin did not affect the T_g value, while the addition of 3 wt.% of organically modified clay (OMMT) increased the T_g by about 15 °C due to the better exfoliation of clay in the epoxy matrix. Lu et al. [98] and Miyagawa et al. [99] observed an increase in T_g with the addition of clay particles to epoxy resin. Liu et al. [98] observed a decrease in T_g with increase in clay content. This was attributed to the plasticizer effect of the clay modifier.

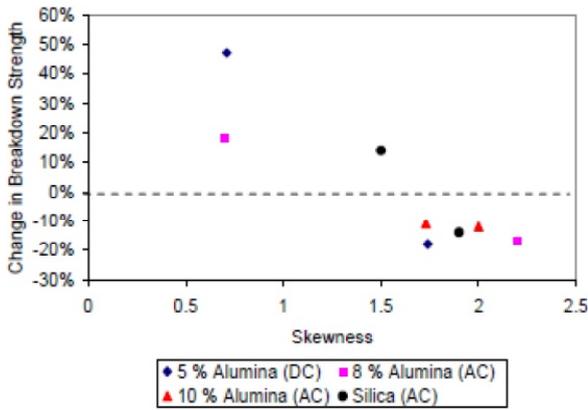


Fig. 13. Skewness and breakdown strength of alumina/PAI nanocomposites and silica/XLPE nanocomposites.

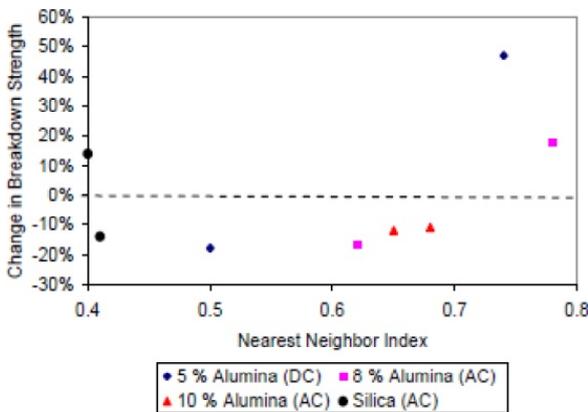


Fig. 14. Nearest neighbor index and breakdown strength of alumina/PAI nanocomposites and silica/XLPE nanocomposites.

2.10.4. Electrical properties

The electrical properties are dielectric breakdown, tracking & erosion resistance, PD resistance, space charge behavior, permittivity & dissipation factor and loss tan. The detail these properties are given in following sections.

2.10.4.1. Dielectric breakdown

The improvement in dielectric breakdown strength of nanocomposites is widely referenced in the literature [57-66]. The impact of dispersal on the dielectric properties of the nanocomposites is elaborated in Figs. 13 and 14 with a scrutiny of two diverse spread states at the equal weight in an alumina/PAI nanocomposite and a silica/XLPE nanocomposite.

The skewness and the nearest neighbor index gauge are the two diverse aspects of mixing quality and this shows that the nano silica forms fractal agglomerates. The nearest neighbor index for these particles is found to be less than one, which is prob-

ably the cause because there is no difference between the two composites. At the same time, these fractal agglomerates are well distributed and a clear trend of its influence on the breakdown strength is indicated by the skewness. In Fig. 13, a skewness of 1.5, improvement in breakdown strength was observed for both systems. In Fig. 14, with nearest neighbor index larger than 0.7, it is possible to achieve increased breakdown strength. Conversely, quantifying the degree of mixing and institute definite criteria will provide a useful reference for quality control.

Fig. 15 shows that by 7.5 wt.% for the alumina/PAI system, the breakdown strength is established to be raised. At 10 wt.%, agglomerates become widespread, and the breakdown strength drops less than that of the unfilled material.

A graph of the endurance data is depicted in Fig. 16. This data also demonstrates that when the alumina nanoparticles are inadequately mixed at 5 wt.%, the endurance life is somewhat reduced.

A fall in breakdown strength at all loadings has been found for an epoxy/ZnO nanocomposite, but the particle dispersion demonstrates agglomerates

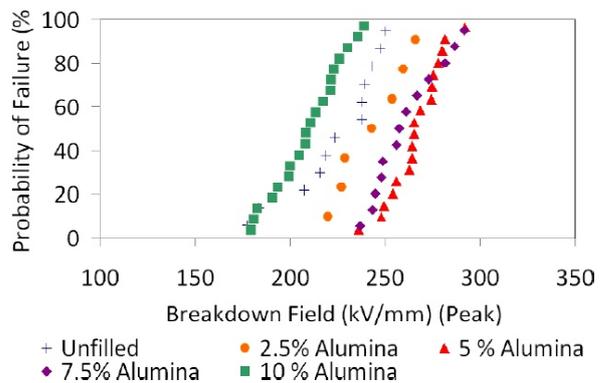


Fig. 15. Weibull plot of breakdown strength of alumina/PAI nanocomposites.

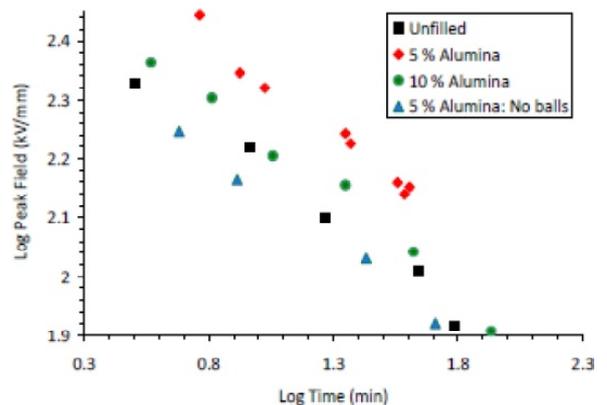


Fig. 16. AC endurance of unfilled PAI and alumina nanocomposites.

on the order of 5 nm [101]. A similar drop in breakdown strength for a ZnO/PE nanocomposite system is also seen, with no detail of particle dispersion [102]. However, other nanocomposite systems clearly show improvements in breakdown strength [103]. Where breakdown strength appears to be strongly linked to the dispersion, the effect is not as strong when dealing with corona resistance, and studies more consistently report improvements in PD resistance of nanocomposites [104].

2.10.4.2. Tracking & erosion resistance

In high voltage engineering, tracking is a process of creation of permanent conducting course across the surface of insulation due to surface erosion under voltage application. This happens to all types of polymeric insulators employed for outdoor applications. These outdoor polymeric insulators get coated with dust or moisture during service, causing the formation of conducting film on the surface. Since voltage is applied, the film will start conducting, resulting in the generation of heat, and thus causing the surface to become dry. The conducting film becomes separated due to drying, and sparks happen which damages the surface of the insulator. Since polymers are organic insulating materials, the dielectric carbonizes at the region of sparking, and the carbonized regions act as permanent conducting channels resulting in increased stress over the rest of the region. This process is cumulative, which finally resulted in the insulation failure when the carbonized track bridges the entire distance.

Over the past few decades, to increase the service life of the equipment, researchers around the world have been looking for ways to increase the tracking resistance of polymeric insulators. One of the very famous approaches is to add inorganic fillers to polymers to form the so called polymer microcomposites. For example, Piah et al. [105] studied the influence of ATH fillers on the erosion resistance and surface tracking of natural rubber and linear low density polyethylene blends. Experimental results show enhanced erosion resistance and surface tracking of the compounds. Although the use of microcomposites can achieve favorable tracking enhancement, it is said that tracking resistance of polymeric insulators should be further improved to attain greater reliability.

In 2006, tracking performance data on polymer nanocomposites was published by El-Hag et al. [106]. The authors observed the enhanced erosion resistance of nano silica filled silicone rubber as

compared to micro-filled silicone rubber. Further investigation showed that 10 wt.% of nano-filled silicone rubber gives an even better resistance for the nanocomposites. However, it is still not understandable why the increase in content up to 10 wt.% can still give favorable results in tracking resistance. This is because it is generally speculated that 5 wt.% is the optimum value to improve the properties of nanocomposites. If the content is increased further, it might cause the adverse effect to the properties.

Sarathi et al. [107], on the other hand, observed that the tracking time of aged epoxy nanocomposites is high as compared to the tracking time of pure epoxy material. The test was conducted under IEC 60587 Standards. However, it should be noted that this favorable results applies to only certain test specimens. Careful observation shows that adding nanoclay to epoxy reduces some of the specimens tracking time as compared to the pure epoxy. This is due to different ageing conditions applied to the samples. The reason behind this is unclear, and this certainly requires further experimental works.

In 2004, a study [108] was undertaken to investigate the tracking phenomena in different polymeric insulating material. It is undeniable that up to now, silicone rubber is still the best outdoor insulator. However, the study shows that high density polyethylene has good performance under alternating current (AC) test environment, and the authors recommended the addition of fillers which could further improve its tracking property. Another experimental analysis on tracking characteristics of pure high density polyethylene was conducted by Sarathi et al. [109] in 2004, and it is found that high density polyethylene would be ideal for low voltage application. It should be reinstated that the test done is based on pure polyethylene. As suggested earlier, filled polyethylene would be advantageous over unfilled polyethylene. Therefore, investigation into tracking performance of high density polyethylene nanocomposites would give an insight into the potential use of high density polyethylene nanocomposites as outdoor insulators in high voltage applications.

As mentioned earlier, partial discharge, which is a very important characteristic leading to the breakdown of high voltage insulators, happens in all kinds of polymeric insulators. There have been various experimental works on partial discharge resistance of polyethylene. However, most of the works focused on the use of low density, linear low density and cross-linked polyethylene. In addition to the insufficiency works on partial discharge previously men-

tioned, there was also very little attention drawn into partial discharge characteristics of high density polyethylene.

In 2009, the use of high density polyethylene nanocomposites in electrical insulation perspectives has just been published by Shah et al. [110]. The authors investigated various electrical properties of the nanocomposites, particularly dielectric strength, volume resistivity and surface resistivity. By increase in nano-clay content up to 5 percent in weight the dielectric strength was found to be increased considerably. Surface resistivity and volume were also found to be increased. This has yet shown the potential use of high density polyethylene nanocomposites in high voltage industries. Since the research on high density polyethylene nanocomposites is still very new, exploration into its tracking and partial discharge characteristics would certainly provide invaluable knowledge towards its electrical insulating performance as a whole.

2.10.4.3. PD resistance

Partial discharge happens in all types of polymeric insulators. It is defined as local electrical discharge which only partially bridges the insulation between conductors and that may or may not occur adjacent to a conductor. Partial discharges are in general a consequence of local electrical stress concentrations in the insulation or on the surface of the insulation.

There are mainly four types of partial discharges. They are internal discharge, surface discharges, corona and treeing. Internal discharges occurs in inclusion of low dielectric strength, usually gas filled cavities. This type of discharge is very crucial and has large impact on polymeric insulation. Meanwhile, surface discharge, occurs if there is a stress component parallel to dielectric surface. The discharges extend beyond the region where the original surface component of the electric field is high enough to cause discharges. However, this type of discharge

is less concentrated and less dangerous than internal discharge. Corona discharge, on the other hand, happens in air insulation, and is normally not dangerous. Another discharge, called treeing, is actually caused by series of internal discharge.

Since the introduction of polymer nanocomposites, there have been various experimental works conducted on partial discharge characteristics of those insulating materials. An experimental work by Kozako et al. [111] too established that only 2 wt.% of nanofillers is adequate to get better partial discharge resistance of polyamide nanocomposites.

In 2008, Tanaka et al. [112] once again highlighted that clay/epoxy nanocomposites are greater in partial discharge resistance compare to base epoxy resins. The conclusion was drawn based on the evaluation on the depth of erosion. At the same time, Maity et al. [113] researched on the surface discharge degradation of metal oxide nano-filled epoxy. It was documented that nano-alumina and nano-titania filled epoxy yielded considerably improved resistance to surface discharges. It is speculated that metal oxide particles perform as reinforcement to the bulk matrix and hence prevent erosion of the bulk matrix.

There are undeniably many experimental results published on the enhancement of partial discharge property of polymer nanocomposites. Unfortunately, most of the experimental works on partial discharge activities concentrated on surface discharges according to IEC (b) rod-plane electrodes configuration. Recall from the types of partial discharges previously defined, internal discharges are more crucial and dangerous as compared to surface discharges. Therefore, literature on internal discharges of polymer nanocomposites should have some points of discussion, since it brings larger impact on insulating materials.

Such literature on internal discharges was once published in 2001 by Henk et al. [114], who investi-

Table 3. Depth of erosion in polymer nanocomposites.

Material	Erosion Depth, μm	Remarks
Base polyamide (PA)	14	AC 6 kV, 60 Hz, 48 hrs
PA/LS Nanocomposite	2.5	IEC (b) Electrode
Base Epoxy	110	AC 4 kV, 720 Hz, 60 hrs 60 Hz
Epoxy/ LS Nanocomposite	50	equiv, Time 720 hrs Rod-gap-plane
Epoxy/ Titanate (15nm) Nanocomposite	32	Electrode
Epoxy/ Silica (40nm) Nanocomposite	27	
Epoxy/ Silica (15nm) Nanocomposite	19	

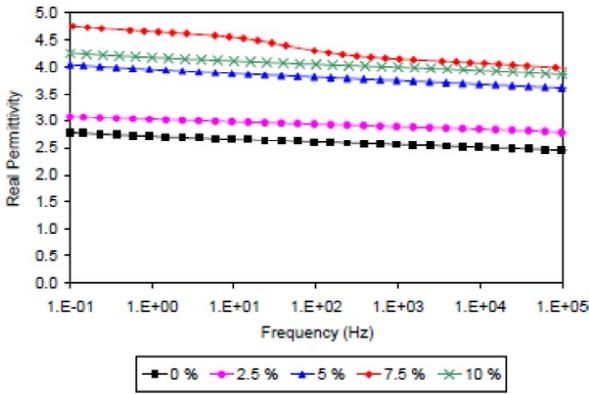


Fig. 17. Permittivity of alumina/PAI nanocomposites.

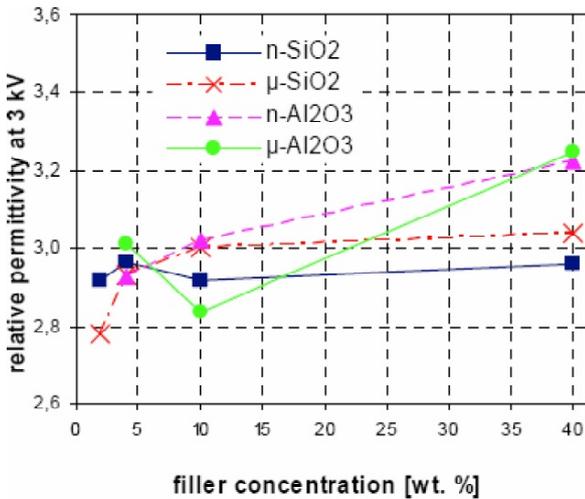


Fig. 18. Influence of filler particles on the dielectric strength of insulating materials.

gated the effect of nanoparticles amorphous silica dispersion in epoxy and polyethylene respectively. It was observed that nano-silica had strong effect of increasing partial discharge endurance of thermoset (epoxy & cross-link polyethylene). However, for thermoplastics (low density polyethylene and medium density polyethylene), no effect was observed.

Later in 2007, Lorenzo et al. [115] performed internal discharge test upon layered nanosilicates filled epoxy system. The increase of life span was established on those materials. Besides that, Weibull distributions have higher shape factor, whereby the material becomes more homogeneous (smaller content of weaker points, generally consisting of macro voids). Erosion depth in polymer nanocomposites caused by partial discharges is shown in Table 3.

Available results on internal discharges tests for polymer nanocomposites are very limited that there can hardly be any other literatures found. Whether polymer nanocomposites can really enhance the internal discharge characteristics of polymer

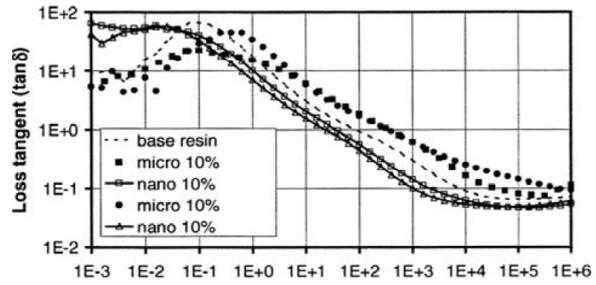


Fig. 19. Loss tangent of unfilled, micro and nano epoxy.

nanocomposites, much remains to be explored. Therefore, more available data on internal discharges of polymer nanocomposites have to be collected to further confirm the results thus far obtained.

2.10.4.4. Space charge behavior

Epoxy nanocomposites have another striking effect of nano-filler addition to polymers i.e., space charge reduction [116-118]. This is also reported that charge transport is of paramount important in enhancing the dielectric strength and electrical erosion of nanocomposites [119,120].

2.10.4.5. Permittivity & dissipation factor

According to the literature review reports, the real permittivity of the nanocomposite can drop well above or below that anticipated from volumetric mixing rules. Alumina/polyimide nanocomposites demonstrated increases in permittivity while a TiO_2 / epoxy system demonstrated the opposite effect [121]. In the PAI-alumina system illustrated in Fig. 17, the permittivity is found to increase above that expected due to mixing rules.

On filling the polymers with inorganic fillers of micrometer sizes the permittivity usually increases., The permittivity inclined to decrease with nanofillers, as found in [122,123] which is contrary. On introduction of polymer nanocomposites the dissipation factor is also originated to be encouraging [124]. The graph of relative permittivity versus filler concentration is depicted in Fig. 18.

2.10.4.6. Loss $\tan \delta$

Especially under low frequency and high temperature conditions a reduction in $\tan \delta$ is also found for epoxy-nanocomposite [125]. The graph of loss tangent of unfilled and 10% micro- and nano-filled epoxy at 293K vs. frequency is shown in Fig. 19.

3. CONCLUSION

- Surface functionalization of nanofillers aids in dispersion of nanofillers in polymer matrix. The analysis of functionalized nanofillers would help in investigation of the influence of interfacial characteristics on composites properties.
- Computation of uniform dispersion is not easy task so the methods to ascertain the degree of dispersion needs to be further investigated. SEM imaging is used to determine the dispersion of fillers qualitatively thus computational algorithms should be employed to quantify the degree of dispersion more precisely.
- Electrical performance testing such as AC dielectric breakdown and DC dielectric breakdown should be carried out as a function of environmental factors such as moisture and temperature to simulate the in service conditions.
- As 5000 hrs Multistress aging produced no considerable impact on the composites, thus it is suggested that more aging of these nano and hybrid composites should be carried out to investigate their useful life.
- The field evaluation of composites, in the form of actual insulators in the severe field environments is also necessary to fully demonstrate the advantages of these new nano and hybrid composites.
- Finally, there is a need to manufacture these nano and hybrid composites on industrial scale.

4. REFERENCES

- [1] T. Tanaka, G. C. Montanari and R. Mülhaupt // *IEEE Transactions on Dielectrics and Electrical Insulation* **11** (2004) 763.
- [2] Y. Cao, P. C. Irwin and K. Younsi // *IEEE Transactions on Dielectrics and Electrical Insulation* **11** (2004) 797.
- [3] C.D. Green and A. S. Vaughan // *IEEE Electrical Insulation Magazine* **24** (2008) 6.
- [4] N. Fuse, M. Kozako, T. Tanaka and Y. Ohki, In; *IEEE Conference on Electrical Insulation and Dielectric Phenomena* (CEIDP, IEEE, 2005), p. 148.
- [5] U. Hoffmann, K. Endell and D. Wilm // *Zeitschrift für Kristallografie Mineral Petrografie Abteilung A* **86** (1933) 340.
- [6] J. E. Mark // *Polym Eng Sci*, **36** (1996) 2905, doi: 10.1002/pen.10692.
- [7] Béla Pukánszky // *European Polymer Journal* **41** (2005) 645.
- [8] L. S. Schadler, L. C. Brinson and W. G. Sawyer // *JOM* **59** (2007) 53.
- [9] M. Roy, R. K. MacCrone, L. S. Schadler, C. W. Reed, R. Keefe and W. Zenger // *IEEE Trans. Dielectr. Electr. Insul.* **12** (2005) 629.
- [10] J. I. Hong // *Appl. Phys. Lett.* **82** (2003) 1956.
- [11] J. C. Fothergill, In: *Proc. Int. Conf. Solid Dielectrics* (UK, 2007), p. 1.
- [12] J. K. Nelson and Y. Hu, In; *Proc. Int. Conf. Solid Dielectrics ICSD'07* (UK, July 2004), p. 832.
- [13] T. J. Lewis // *IEEE International Conference on. Vol. 2.* (IEEE, 2004), p. 497.
- [14] T. J. Lewis, In: *Proc. Int. Conf. Solid Dielectrics* (2004), p. 792. .
- [15] T. J. Lewis // *IEEE Transactions* **11** (2004) 739.
- [16] George Tsagaropoulos and Adi Eisenberg // *Macromolecules* **28** (1995) 6067.
- [17] T. Tanaka, N. Fuse and Y. Ohki // *IEEE Trans. Dielectr. Electr. Insul.* **12** (2005) 669.
- [18] J.-Z. Liang // *Polym. Int.* **51** (2002) 1473.
- [19] M.-T. Ton-That, E. Perrin-Sarazin, K.C. Cole, M.N. Bureau and J. Denault // *Polym. Eng. Sci.* **44** (2004) 1212.
- [20] B. Pourabas and V. Raeesi // *Polymer* **46** (2005) 5533.
- [21] J.-M. Yeh, S.-J. Liou, M.-C. Lai, Y.-W. Chang, C.-Y. Huang, C.-P. Chen, J.-H. Jaw, T.-Y. Tsai and Y.-H. Yu // *J. Appl Polym. Sci.* **94** (2004) 1936.
- [22] U.W. Gedde, *Polymer Physics* (Chapman Hall, London, 1995).
- [23] R.B. Seymour and C.E. Carraher, *Structure-Property Relationships in Polymers* (Plenum Press, New York, 1984).
- [24] A. W. Musumeci, and J-W. Liu // *Polymer* **48** (2007) 1667.
- [25] M. Casciola and M. Pica // *Macromol. Symp.* **230** (2005) 95.
- [26] S. S. Kumar, J. Mathiyarasu and K. L. Phani // *Langmuir* **23** (2007) 3401.
- [27] M. Hernandez, J. Duchet and H. Sautereau // *Polymer* **48** (2007) 4075.
- [28] R.C. Smith, M. Landry, J.K Nelson and L.S. Schadler // *IEEE Trans. Dielect. Electr. Insul.* **15** (2008) 187.
- [29] T. Imai, T. Ozaki, T. Shimizu, S. Kuge, M. Kozako and T. Tanaka // *IEEJ Trans. Fundamental and Materials* **126** (2006) 84.
- [30] S. Singha and M. J. Thomas // *IEEE Trans. Dielectr. Electr. Insul.* **15** (2008) 12.
- [31] M. Roy, R. K. MacCrone and L. S. Schadler // *J. Mater. Sci.* **42** (2007) 3789.
- [32] Santanu Singha and M. Joy Thomas // *IEEE Conference on.* (IEEE, 2006), p. 557.

- [33] W. W. Kubiak // *Electroanalysis* **17** (2002) 1169.
- [34] L. T. Zhuravlev // *Colloids and Surfaces A: Physico Chem. Eng. Aspects* **173** (2000) 1.
- [35] Li Zongwei // *Applied Surface Science* **211** (2003) 315.
- [36] S. H. Ahn and S. G. Lee // *J. Appl. Polymer Sci.* **94** (2004) 812.
- [37] M. J. Rosen, *Surfactants and Interfacial Phenomena*, 3rd Ed. (Wiley- Interscience, 2004).
- [38] J.-L. Chermant and M. Coster, *Encyclopedia of Materials: Science and Technology* (2001).
- [39] J.K. Nelson, R. Smith and L. Hui, *EPR Report #1013790* (2007).
- [40] N. A. C. Cressie, *Statistics for Spatial Data, Revised Edition* (John Wiley, 1991). .
- [41] D. Kim, C. M. F. Barry and J. Mead // *Microsc. Res. Techniq.* **70** (2007) 539.
- [42] J. Leggoe // *Scripta Materialia* **53** (2005) 1263.
- [43] D. L. Burris, G. R. Bourne and W. G. Sawyer / *Macromolecular Materials and Engineering* **292** (2007) 387.
- [44] L. Hui, X.Wang, J.K.Nelson and L.S.Schadler, In: *IEEE Conf. Electr. Insul. Dielectr. Phenomena* (IEEE, 2008), p. 317.
- [45] L.W. Jeremy // *Scripta Materialia* **53** (2005) 1263.
- [46] A. Tewari and A.M. Gokhale // *Materials Characterization* **40** (1998) 119.
- [47] J. I. Hong and R. W. Siegel // *Appl. Phys. Lett.* **82** (2003) 1956.
- [48] L. C. Sawyer, *Polymer Microscopy*, 3rd ed.(Springer, 2008).
- [49] M. Kurimoto, K. Kato, M. Hanai, Y. Hoshina and M. Takei // *IEEE Trans. Dielectr. Electr. Insul.* **17** (2010) 1268.
- [50] M. Kurimoto, K. Kato, M. Hanai, Y. Hoshina, M. Takei and H. Okubo, In: *IEEE Conf. Electr. Insul. Dielectr. Phenomena* (IEEE, 2008), p. 706.
- [51] R. Kochetov, U. Lafont, P. H. F. Morshuis and J. J. Smit, In: *IEEE Conf. Electr. Insul. Dielectr. Phenomena* (IEEE, 2009), p. 658.
- [52] J.K. Nelson and Y. Hu, In: *International Conference on Properties and applications of Dielectric Materials* (2006),p. 150.
- [53] T.J. Lewis // *IEEE Transactions on Dielectrics and Electrical Insulation* **1** (1994) 812.
- [54] J.K. Nelson, In: *Electrical Insulation Conference and Electrical Manufacturing Expo* (Nashville, 2007), p. 229.
- [55] P.O. Henk, T. W. Kortsens and T. Kvarts // *High Performance Polymers* **11** (1999) 281 .
- [56] J.K. Nelson and J. C. Fothergill // *Nanotechnology* **15** (2004) 586.
- [57] M. Roy, J. K. Nelson, R. K. MacCrone, L. S. Schadler, C. W. Reed, R. Keefe and W. Zenger // *IEEE Transactions on Dielectrics and Electrical Insulation* **12** (2005) 629.
- [58] J.C. Fothergill, In: *IEEE International Conference on Solid Dielectrics* (Winchester, 2007), p. 1.
- [59] C.D. Green, A. S. Vaughan, G. R. Mitchell and T. Liu // *IEEE Transactions on Dielectrics and Electrical Insulation* **15** (2008) 134.
- [60] J.K. Nelson, In: *Conference Record of the IEEE International Symposium on Electrical Insulation* (Toronto, 2006), p. 452.
- [61] Gao Junguo, Ji Quanquan, Liu Jiayin, Zhang Mingyan and Zhang Xiaohong, In: *International Symposium on Electrical Insulating Materials* (Mie, 2008), p. 597.
- [62] G.C. Montanari, D. Fabiani, F. Palmieri, D. Kaempfer, R. Thomann and Mulhaupt // *IEEE Transactions on Dielectrics and Electrical Insulation* **11** (2004) 754.
- [63] Y. Murata, Y. Murakami, M. Nemoto, Y. Sekiguchi, Y. Inoue, M. Kanaoka, N. Hozumi and M. Nagao, In; *Annual Report Conference on Electrical Insulation and Dielectric Phenomena* (Nashville, 2005), p. 158.
- [64] S.S. Bamji, M. Abou-Dakka, A. T. Bulinski, L. Utracki and K. Cole, In: *Annual Report Conference on Electrical Insulation and Dielectric Phenomena* (Nashville, 2005), p. 166.
- [65] M. Roy, J. K. Nelson, L. S. Schadler, L. S. Zou and J. C. Fothergill, In: *Annual Report Conference on Electrical Insulation and Dielectric Phenomena* (Nashville, 2005), p. 183.
- [66] F. Guastavino, A. Dardano, A. Ratto, E. Torello, P. Tiemblo, M. Hoyos and J. M. Gomez-Elvira, In: *Annual Report Conference on Electrical Insulation and Dielectric Phenomena* (Nashville, 2005), p. 175.
- [67] T. Tanaka, In: *Annual Report Conference on Electrical Insulation and Dielectric Phenomena* (Nashville, 2005), p. 713.
- [68] T. Tanaka, M. Kozako, N. Fuseand Y. Ohki // *IEEE Transactions on Dielectrics and Electrical Insulation* **12** (2005) 669.

- [69] T.J. Lewis, In: *IEEE International Conference on Solid Dielectrics* (Toulouse, 2004) 792.
- [70] M. Roy, J. K. Nelson, R. K. MacCrone and L. S. Schadler // *Journal of Materials Science A* **42** (11) 3789.
- [71] R.C. Smith, C. Liang, M. Landry, J. K. Nelson and L. S. Schadler // *IEEE Transactions on Dielectrics and Electrical Insulation* **15** (2008) 187.
- [72] G.C. Montanari, F. Palmieri, L. Testa, A. Motori, A. Sacconi and F. Patuelli // *IEEE Transactions on Fundamentals and Materials* **126** (2006) 1090.
- [73] J.K. Nelson and Y. Hu, In: *8th International Conference on Properties and Applications of Dielectric Materials* (Bali, 2006), p. 150.
- [74] T. Tanaka // *IEEE Transactions on Dielectrics and Electrical Insulation* **12** (2005) 914.
- [75] L.S. Schadler, *Nanocomposite Science and Technology, Chapter 2* (Wiley, 2003).
- [76] Ralf Lach, Lada A. Gyurova and Wolfgang Grellmann // *Polymer testing* **26** (2007) 51.
- [77] C. Dengke, L. Lei and Y. J. Hui, In: *International Conference on Solid Dielectrics* (Toulouse, France, 2004), p. 800.
- [78] A. H. El-Hag, S. H. Jayaram and E. A. Cherney // *IEEE Transactions on Dielectrics and Electrical Insulation* **13** (2006) 122.
- [79] P. C. Irwin, A. Bansal and L. S. Schadle, In: *IEEE Conference on Electrical Insulation and Dielectric Phenomena* (IEEE, 2003), p. 120.
- [80] S.H.A. Kim and S. H. Hirai // *Polymer* **44** (2003) 5625.
- [81] F.O. Yang and Z.Z. Yu // *Appl. Polym. Sci.* **69** (1998) 355.
- [82] Isaias Ramirez and Edward A. Cherney // *Nanocomposites* **1** (2009) 1.
- [83] L. H. Meyer and E. A. Cherney // *IEEE Transactions on Dielectrics and Electrical Insulation* **11** (2004) 620.
- [84] Suprakas Sinha Ray and Mosto Bousmina // *Progress in materials science* **50** (2005) 962.
- [85] Ole Becker, George P. Simon and Karel Dusek, *Inorganic Polymeric Nanocomposites and Membranes* (Springer Berlin Heidelberg, 2005).
- [86] Jin Zhu // *Chemistry of Materials* **13** (2001) 4649.
- [87] LS Mc Neill, *Comprehensive polymer science* (PUBLISHED, 1989).
- [88] Giovanni Camino // *Fire and materials Fire and materials* **24** (2000) 85.
- [89] K. Zhang, F. Wang, G. Wang and Z. Li // *Appl. Polym. Sci.* **91** (2004) 2649.
- [90] N.B. Lakshmi and B.S.R. Redd // *Polymer degradation and stability* **93** (2008) 201.
- [91] Hossein Afsharian-Moghaddam and Vahid Haddadi-Asl // *Iranian Polymer Journal* **22** (2013) 757.
- [92] J. Brandt // *Arthritis Rheum* **54** (2006) 2665.
- [93] T. G. Camino, A. Frache, C. Manferti and G. Costa // *Polym* **90** (2005) 354.
- [94] Y.M. Avila, M.G.R. Carvalho and E.C. Dias // *J. Compos* **41** (2010) 41.
- [95] Qiuqin You // *Journal of Applied Polymer Science* **131** (2014) 22.
- [96] T.M. Kaya and S. Okur // *J Appl Polym* **109** (2008) 834.
- [97] Cafer Polat, Adem Dervisoglu, Hakan Guven, Ekrem Kaya, Zafer Malazgirt, Murat Danaci and Kayhan Ozkan // *The American journal of emergency medicine* **21** (2003) 208.
- [98] Hongbin Lu // *Macromolecular rapid communications* **26** (2005) 1445.
- [99] R.M. Miyagawa and L.T. Drzal // *Journal of Polymer Science Part B: Polymer Physics* **42** (2004) 4384.
- [100] C. Calebrese, L.S. Schadler and D. Schweickart, In: *IEEE 10th Int'l. Conf. Solid Dielectrics* (IEEE, 2010), p. 1.
- [101] S. Singha and M. J. Thomas // *IEEE Trans. Dielectr. Electr. Insul.* **16** (2009) 531.
- [102] C. Zilg, R. Thomann, R. Muelhaupt and G. C. Montanari, In: *IEEE Conf. Electr. Insul. Dielectr. Phenomena* (IEEE, 2003), p. 546.
- [103] M. Kozako, R. Kido, Y. Ohki, M. Kohtoh, S. Okabe and T. Tanaka, In: *IEEE Int'l. Sympos. Electr. Insulating Materials* (IEEE, 2005), p. 231.
- [104] R. K. MacCrone, R. C. Smith and L. S. Schadle // *IEEE Trans. Dielectr. Electr. Insul.* **15** (2008) 197.
- [105] M.A.M. Piah, A. Darus and A. Hassan // *Journal of Industrial Technology* **13** (2004) 27.
- [106] A.H. El-Hag, L. C. Simon, S. H. Jayaram and E. A. Cherney // *IEEE Transactions on Dielectrics and Electrical Insulation* **13** (2006) 122.
- [107] R. Sarathi, R. K. Sahu and P. Rajeshkumar // *Materials Science and Engineering A* (2007) 445.
- [108] V. Rajini, K. Kanchana, V. Gowrishree and K. Udayakumar, In: *International Conference on Power System Technology* (Singapore, 2004), vol. 2, p. 1513.

- [109] R. Sarathi, S. Chandrasekar, V. Sabari Giri, C. Venkateshaiah and R. Velmurugan // *Bulletin of Materials Science* **27** (2004) 251.
- [110] K.S. Shah, R. C. Jain, V. Shrinet, A.K. Singh and D. P. Bharambe // *IEEE Transactions on Dielectrics and Electrical Insulation* **16** (2009) 853.
- [111] M. Kozako, N. Fuse, Y. Ohki, T. Okamoto and T. Tanaka // *IEEE Transactions on Dielectrics and Electrical Insulation* **11** (2004) 833.
- [112] T. Tanaka, Y. Ohki, M. Ochi, M. Harad and T. Imai // *IEEE Transactions on Dielectrics and Electrical Insulation* **15** (2008) 81.
- [113] P. Maity, S. Basu, V. Parameswaran and N. Gupta // *IEEE Transactions on Dielectrics and Electrical Insulation* **15** (2008) 52.
- [114] P.O. Henk, T. W. Kortsen, T. Kvarst and A. Saeidi, In: *Nordic Insulating Symposium* (Stockholm, 2001), p. 1.
- [115] M. Di Lorenzo Del Casale, R. Schifani, L. Testa, G. C. Montanari, A. Motori, F. Patuelli, F. Guastavino and F. Deorsola, In: *IEEE International Conference on Solid Dielectrics* (Winchester, 2007), p. 34.
- [116] J.K. Nelson, L.A. Dissado and W. Peasgood, In: *Annual Report CEIDP* (IEEE, 2002), p. 295. .
- [117] J. K. Nelson and Y. Hu // *Annu. Rept. IEEE-CEIDP* **8-2** (2003) 719.
- [118] J. K. Nelson and Y. Hu // *Proc. IEEE-ICSD* **7** (2004) 832.
- [119] Y. Cao and P. C. Irwi // *Annu. Rept. IEEE-CEIDP* **2B-13** (2003) 116.
- [120] Y. Cao, P.C. Irwi // *EEE Trans. Dielectr. Electr. Insul.* **11** (2004) 797.
- [121] S. Raetzke and J. Kindersberger // *IEEE Transactions on Dielectrics and Electrical Insulation* **17** (2010) 607.
- [122] T. Imai, H. Hirai, S. Kojima and T. Shimizu, In: *Conf. Rec. IEEE ISEI* (IEEE, 2002), p. 37.
- [123] J. K. Nelson, R. K. MacCrone and C. W. Reed // *Annu. Rept. IEEE-CEIDP* **4-2** (2004) 314.
- [124] J.K. Nelson, In: *Electrical Insulation Conference and Electrical Manufacturing Expo* (Nashville, 2007), p. 229
- [125] J. C. Fothergill // *Annu. Rept. IEEE-CEIDP* **5A.17** (2004) 406.