INFLUENCE OF FILLER CONTENT ON TRAPS AND CONDUCTIVITY OF EPOXY RESIN NANOCOMPOSITES

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Abstract: Epoxy resin nanocomposites have high resistivity and high breakdown voltage and perform excellent in suppressing space charge accumulation, which is important for the development of DC power equipment. However, how nanofiller content impacts on the resistivity of nanocomposite still remains to be unclear. Therefore, a method, based on the structure model of interaction zones, is proposed to investigate densities of deep and shallow traps of nanocomposite. Then trap densities as a function of nanofiller content is obtained. With an increase in nanofiller content, shallow trap density gradually rises up, while deep trap density shows an increase firstly and then a decrease due to the overlapping of interaction zones. Additionally, at higher nanofiller content, it is found that shallow trap density goes up quantitatively and mean-distance between shallow traps decreases rapidly, thus carriers are easier to hop and migrate in shallow traps and mobilities of carriers controlled by shallow traps increase correspondingly. Then, a charge transport model is introduced to investigate charge distribution, electric field distribution and conductivity property of epoxy/TiO_2 nanocomposites. It turns out that, with an increase in nanofiller content, space charge accumulation near cathode/dielectric surface goes up firstly and is followed by a decrease, correspondingly electric field distortion in cathode/dielectric field gets strengthened firstly and weakened afterwards, and the same tendency takes places in conductivity. Actually, in bulk composites, conductivity is dominated by deep traps at lower nanofiller content, while shallow traps will gradually come to domination with increasing nanofiller content. In conclusion, experimental results are in good agreement with theoretical deduction, and method and model proposed in this paper may be applied to other occasions.

Keywords: Epoxy resin nanocomposite, interaction zone, trap, conductivity

1 INTRODUCTION

Due to excellent performance of confronting short-time breakdown and long-time degradation, nanocomposites are widely used in many fields such as ultra-high voltage power equipment, high energy storage devices and equipment, aerospace and aviation, which is also a main development focus of electrical insulation material [1-5]. Previous studies manifest that nanofillers can increase conductivity of nanocomposites, breakdown electric field, energy storage density as well as flashover voltage, and decrease space charge accumulation [1, 2, 5-9]. It is generally believed that interaction zone between nanofillers and polymer matrix is the key factor for nanocomposite properties, therefore it is significant to investigate the properties of traps in interaction zones of nanocomposites as well as its influence on conductivity.

Previous studies have proved that conductivity of nanocomposites is closely relating to the nanofiller content, namely, conductivity shows a decrease firstly and then goes up with an increase in nanofiller content [10-12]. Li et al [10] investigated complex conductivity properties of epoxy/TiO_2 nano–comoposite dielectric with Broadband dielectric spectrum, finding that dielectric losses at low frequencies are caused by DC conductivity, and DC conductivity appears an increase firstly and then decreases with increasing TiO_2 nanofiller content. Murakami [1] tested volume resistivity of low-density polyethylene at various MgO nanofiller content under electric field of 40 and 80 kV/mm respectively, it was indicated that volume resistivity also shows an increase firstly and is followed by a decrease with an increase in nanofiller content. Moreover, Cao [12] investigated the volume conductivity of polyimide TiO_2 nanocomposite material as a function of nanofiller content at temperatures of 100 ^oC and 150^oC, and it is concluded that conductivity reaches the minimum value with 2wt% nanofillers.

In recent few decades, many models are developed to explain nanocomposite properties including permittivity, dielectric loss, space charge, conductivity, breakdown, electrical tree, corona resistance, etc [1-5]. Some typical models are single-layer structure model, proposed by Lewis [13, 14]; multi-core model, introduced by Tanaka [3, 4]; multi-region model, raised by Li et al [2, 10, 15]. All these models provide theory preparation for further research on nanocomposites.

Based on nanocomposite interaction zone structure model, a method that can be applied for calculating deep and shallow trap density in interaction zones is proposed in this paper. With this calculation method, both shallow and deep trap density change as a function of nanofiller content can be obtained. Then, charge transport model is introduced for investigating how conductivity of nanocomposite changes at various nanofiller content, which turns out that density variation in shallow and deep traps determines the distribution of space charge and electric field in bulk of dielectric, as well as conductivity property of nanocomposites. All these work provide theoretical evidences for understanding nanocomposite properties comprehensively.

2 STRUCTURE AND TRAP PROPERTIES OF NANOCOMPOSITE

2.1 Structure model of nanocomposite

Li et al [2] concluded relations between short-time breakdown properties (electrical breakdown and flashover) as well as long-time degradation properties and nanofiller type, particle content, cohesive energy in polymer matrix. Based on the conclusion, they proposed a multi-region structure model of polymer nanocomposite dielectrics, which is composed of bonded, normal, and transition regions, as shown in Figure 1. Abundant unsaturated bonds, hydrogen and organic groups exist on the surface of particles, so that particles can interact with molecular chains of the polymer matrix by covalent, ionic, and hydrogen bonds. The tight junction area, extending about 1nm outside the surface of the nanoparticle, is bonded region. In this region, interaction strength between nanofillers and polymer molecular chain is impacted by particle surface state, polarization and matrix initial property together. Namely, interaction strength in bonded region will be weak if without being treated by coupling reagent, particle surface lacks hydrophilic organic groups. On the contrary, interaction strength will be strong correspondingly if particle surface is treated with proper coupling reagent.

The region outward extending about 10nm from the surface is transitional region, mainly composed of molecular chains of polymer matrix. In the transitional region, distribution and regulation of molecular chains are influenced by interaction strength and properties in bonded region. For nanofillers not treated by proper coupling reagent, transitional region is thin due to weak interaction strength in bonded region. While for those experiencing proper treatment, transitional region is thick with higher volume fraction due to strong interaction strength in bonded region, which can change crystalline structure dramatically and probably enhances degree of crystallinity. Additionally, nanofiller doping will lead in vast defects such as impurity and nano-hole, resulting in more appearances of traps. All these traps can capture injected charges, change distribution of space charges and electric field, and impact conductivity, breakdown and flashover properties of dielectric materials. Normal region lies in the region outward extending more than 10nm from the surface, where molecular chains surrounds the nanofillers randomly. Normal region has similar properties with polymer matrix [2].

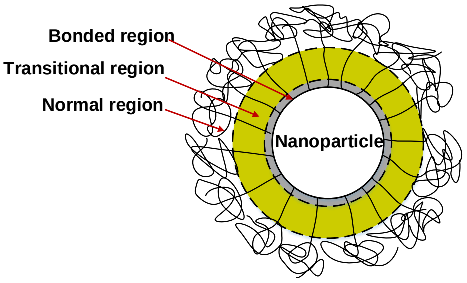

Figure 1: Multi-region structure model of polymer nanocomposite dielectrics.

2.2 Trap properties of nanocomposite

Mean-distance between nanofillers is in a close relation to its type and content. Under ideal conditions, nanofillers uniformly distribute in the polymer matrix without conglomeration. In this section, mean-distance between particles as a function of nanofiller content will be induced and analysed.[4, 16] Here supposing diameter of particle as d, distance between surface of one particle to another is d_{ss}, f_V denotes the half volume fraction of the nanofillers in the composite, then d_{ss} can be expressed as

$$d_{ss} = \left[\left(\pi / 6 f_V \right)^{\frac{1}{3}} - 1 \right] d \tag{1}$$

Assuming nanofiller density is ρ_n, polymer matrix density is ρ_m, the mass percent of the nanofiller in the composite dielectric is f_m, parameters including f_m, ρ_n, ρ_m as a function of d_{ss} can be obtained through equation (1) together with mass percent and volume fraction.

$$d_{ss} = \left[\left(\frac{\pi}{6} \frac{\rho_n}{\rho_m} \frac{1}{f_m} \left(1 - f_m \left(1 - \frac{\rho_m}{\rho_n} \right) \right) \right)^{\frac{1}{3}} - 1 \right] d \tag{2}$$

Equation (2) implies that, with increase of nanofiller content, mean-distance between particles tend to decrease remarkably and nanofillers in per unit volume will rapidly increase. Since each nanoparticle will form an interaction zone with the polymer matrix, thus more interaction zones will be formed promptly with higher nanofiller content. In addition, in accordance with structure model of nanocomposite, with increasing surface distance of nanofillers, molecular chains in interaction zones will get more disordered and energy level of traps will decline correspondingly. To simplify the process mentioned, it is considered that deep traps play an essential role in the bonded region and transitional region, while normal regions are dominated by shallow traps. For overlapping of interaction zones brings so tiny contribution to shallow trap, it is reasonable to neglect impact brought by shallow traps. Under this simplification, shallow trap density in interaction zone can be denoted as:

$$N_{ST(n)} = \xi \big/ (d_{ss}+d)^3 \qquad (3)$$

where ξ is a constant, denoting the trap amount leaded into nanocomposite by one interaction zone, which may relate to polymer matrix, nanofiller type, nanofiller surface treatment, polarization difference of polymer matrix and nanofiller, etc.

It is noticed that deep trap couples in bonded and transitional region are impacted by overlapping of interaction areas, so percolation effect needs to be considered when calculating parameters of deep traps brought by interaction zones in nanocomposites.

$$N_{DT(n)} = \frac{\xi}{(d_{ss}+d)^3}\exp\left(-\frac{f_w}{f_{w0}}\right) \qquad (4)$$

where f_{wo} denotes a constant that describes degree of nanofiller overlapping in polymeric nanocomposites.

Supposing the thickness of interaction zone is d_{iz}, then the percent by volume of the area not occupied by the nanofillers and the interaction zone is represented as:

$$f_{no} = 1-\tfrac{4}{3}\pi(d/2+d_{iz})^3 \big/ (d_{ss}+d)^3 \qquad (5)$$

It is further supposed that densities of shallow and deep traps in neat polymer matrix are $N_{ST}(m)$ and $N_{DT}(m)$ respectively, which turn to be $N_{ST(m)}f_{no}$ and $N_{DT(m)}f_{no}$ respectively when nanofillers leaded in. With combination of equation (3) and equation (4), it can be concluded that densities of shallow traps and deep traps in polymetric nanocomposites can be expressed as $N_{ST}=N_{ST}(m)f_{n0}+N_{ST}(n)$ and $N_{DT}=N_{DT}(m)f_{n0}+ N_{DT}(n)$.

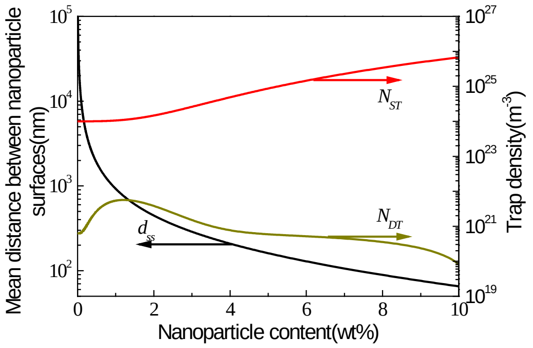

Figure 2: Interparticle distance from surface to surface, shallow trap density, deep trap density as a function of filler content in epoxy resin based titanium oxide nanocomposites.

Figure 2 gives out the dependent relations between the nanofiller content and the mean-distance of nanofiller surfaces, as well as shallow traps densities. As mentioned above, nanofiller in this paper refers to TiO_2 with 25nm in diameter, ratio of the nanofiller density to the epoxy matrix is 2.19, constant ξ and f_{w0} are 5×10^4, 0.4wt% respectively. Figure 2 indicates that, with increase of filler content, mean-distance between nanofiller surfaces drops rapidly, while shallow trap density rises up. When filler content keeps in a low status, deep trap density goes up with the increase of nanofiller content, since overlap of interaction zones haven't appeared. However, at higher nanofiller content, overlapping appears and leads to percolation effect, making the deep shallow trap density fall down with rise of filler content.

3 CHARGE TRANSPORT MODEL FOR NANOCOMPOSITE

3.1 The shallow traps of the nanocomposite control the carrier mobility

Figure 3 demonstrates the carrier mobility controlled by shallow traps as a function of nanofiller content. During the model solution, energy level of shallow traps and temperature are set as 0.5eV and 100K respectively. In this way, when α is a constant, carrier mobility controlled by shallow traps goes up gradually with increase in ξ, since increase of ξ indicates that more shallow traps are brought into dielectric, mean-distance between shallow traps decreases, enabling carriers get easier to hop among traps, thus carrier mobility goes up in this way. When ξ is larger than 2×10^4 and more nanofillers are brought into polymer matrix (5wt% for example), increase of shallow traps density has a slight impact on carrier mobility, and tunnel effect cannot be neglected in this occasion. When ξ is a constant, carrier mobility goes down remarkably with increase in α, which indicates that impact of mean-distance of traps on carrier mobility becomes more and more evident.

3.2 Charge transport model

Under the effect of applied electric field, cathode injects electrons to bulk dielectric, and injection of electron is relating to barrier height at electrode, dielectric surface, electric field intensity and temperature, etc. In accordance with Schottky thermal emission [17-20],

$$j_{in}(t) = AT^2\exp\left(-\frac{E_{in}}{k_BT}\right)\exp\left(\frac{\sqrt{eF(0,t)/4\pi\varepsilon_0\varepsilon_r}}{k_BT}\right) \qquad (6)$$

where j_{in} denotes current density injected by electrode, A represents Richardson constant, E_{in} denotes barrier at cathode and dielectric surface, $F(0,t)$ denotes field intensity at cathode and dielectric surface, ε_0 represents vacuum permittivity, ε_r denotes relative permittivity of nanocomposite

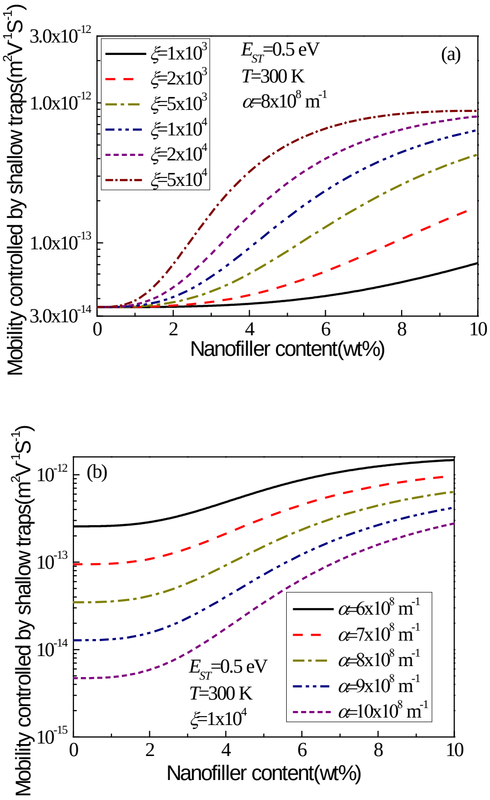

Figure 3: Shallow trap controlled carrier mobility as a function of nanofiller content, (a) at various, (b) at various α.

under high frequency, t is duration that applied voltage keeps.

In the bulk dielectric, injected electrons will migrate to anode by thermally assisted hopping in shallow traps, current density $j_c(x,t)$ caused by electron migration in shallow traps are closely relating to electron density $q_{ST}(x,t)$ in shallow traps, mobility μ_S and electrons field $F(x,t)$ [17-20].

$$j_c\left(x,t\right)=q_{ST}\left(x,t\right)\mu_S F\left(x,t\right) \tag{7}$$

where x denotes variable position in bulk dielectric.

It needs to be clarified that electron migrating in shallow traps can also be captured by deep traps and further become deep trap charges. Similar with shallow traps, thermal assisted hopping may take place in deep traps and charges then continue migrating to anode. Charge density change in shallow and deep traps at any positions as a function of time is equal to difference of flow-in current density and flow-out current density. Namely, the process mentioned above satisfies charge continuity equation [17-20].

$$\frac{\partial q_{ST}\left(x,t\right)}{\partial t}+\frac{\partial q_{DT}\left(x,t\right)}{\partial t}+\frac{\partial j_c\left(x,t\right)}{\partial x}=0 \tag{8}$$

While charges in bulk dielectrics obeys Poisson's equation:

$$\frac{\partial^2\phi\left(x,t\right)}{\partial x^2}=-\frac{q_{ST}\left(x,t\right)+q_{DT}\left(x,t\right)}{\varepsilon_0\varepsilon_r} \tag{9}$$

Then finite element method is applied to solve charge injection, charge conductivity, charge continuity equation, Poisson's equation and charge capture-detrapping dynamic equation. In this way, properties of charge density distribution, field distribution, and conductivity when applied voltage keeps can be obtained [17, 18].

4 SIMULATION RESULTS AND ANALYSIS

In accordance with experimental results, relative permittivity has been set as 3.5, charge injection barrier at anode-dielectric surface is 1.15eV, energy of shallow and deep traps are 0.5eV and 0.9eV respectively, coefficient ξ and α are 1×10^4 and $8\times10^8\text{m}^{-1}$ respectively, densities of shallow and deep traps can be obtained by interaction zone trap model. Additionally, carrier mobility controlled by shallow traps can be obtained by charge hopping model. Here, temperature of epoxy/TiO_2 composite dielectric sample is set as 300K and thickness is 0.5mm. Then properties of space charge distribution, field distribution and conductivity of bulk epoxy nanocomposites can be obtained by charge transport model.

Cathode injects electrons to bulk dielectric under the effect of applied voltage, electrons in shallow traps migrate to anode by thermally assisted hopping. During this period, some carriers are captured by deep traps and space charges gradually accumulate in bulk dielectric. With electrons' being captured continuously, charges reduce gradually in shallow traps, while charges in shallow and deep traps decline dramatically with increase of distance from cathode. What's more, accumulation of space charges around cathode will lead to weakening of electric field near cathode, which will further result in that electron injection from cathode to bulk dielectric falls down with extension of time that applied voltage keeps. When it comes to conductivity, dual effect of space charge accumulation and field distortion make charge injection as well as transport gradually become steady and finally come to a dynamic equilibrium. Thus, a steady distribution of space charges and electric field are formed, and steady conductivity come into being in external circuit.

Considering many interaction zones are formed in polymer due to nanofiller, many independent interaction zones are established at low nanofiller content. Deep trap in interaction zones is a main factor for charge transport in nanocomposites. When deep trap density in interaction zones increases, more injected charges will be captured and more space charges will gather around the cathode/dielectric surface, shown as Figure 4(a). Furthermore, Figure 4(b) manifests that more space

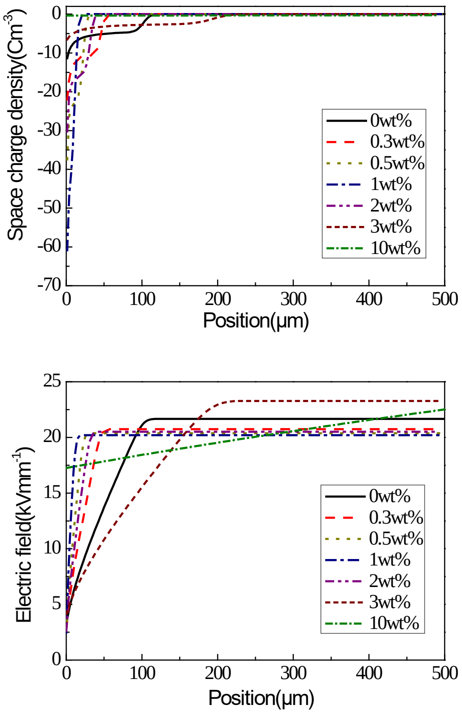

Figure 4: Distributions in polymer nano-composites after applying voltage for 1×10^{4}s. a) Space charge, b) Electric field.

charge accumulation will weaken electron field at cathode/dielectric surface severely, reduce electron injection from cathode and lead to decline of conductivity. At higher nanofiller content, overlapping of interaction zones will appear gradually and result in weakening of deep traps or decrease of trap density. On the other hand, increasing shallow traps in interaction zones will further lead to larger mobility. Overall, conductivity will increase dramatically under dual effect of deep traps decrease and shallow traps increase in interaction zones.

Figure 5 manifests epoxy/TiO$_2$ nanocomposite conductivity as a function of nanofiller content as a solution of charge transport model, which turns out to be similar to experimental results. Furthermore, tiny graph in Figure 5 illustrates epoxy/TiO$_2$ nanocomposite conductivity at various nanofiller content [10]. Finally, both calculation and experimental results imply that nanocomposite conductivity increases firstly and then decreases with more nanofiller involved. It is noticeable that, when nanofiller content is less than about 1wt%, conductivity is greatly dominated by deep traps in interaction zones; while nanofiller content further increases, impact brought by overlapping of interaction zones appears obvious and impact of deep traps gradually become inconspicuous, and impact of shallow traps strengthened, conductivity will gradually be dominated by shallow traps.

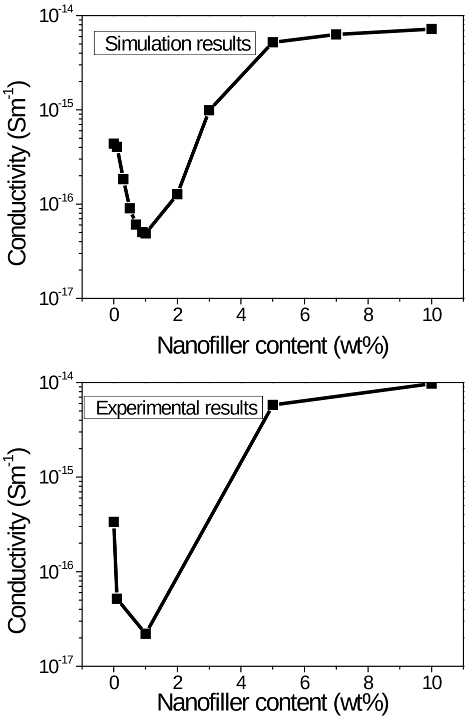

Figure 5: Conductivity of epoxy/TiO$_2$ nano-composites calculated by charge transport model as a function of filler content. Inset: Experimental results of Conductivity of epoxy/TiO$_2$ nanocomposites as a function of filler content. a) Simulation results, b) Experimental results.

5 CONCLUSION

Above all, properties of traps in interaction zones as well as its impact mechanism on space charge distribution and epoxy nanocomposite conductivity have been investigated. Main results can be concluded as follows:

1) Based on a multi-region structure model, a method of calculating densities of shallow and deep traps in interaction zones has been proposed, by which densities of both shallow and deep traps as a function of nanofiller content was deduced. It manifests that when nanofiller content goes up, density of shallow traps also increases gradually while the density of deep traps increases firstly and falls down afterwards due to impact of interaction zones overlapping.

2) Mobility of carriers (controlled by shallow traps) as a function of nanofiller content has been given. It can be concluded that, with an increase in nanofiller content, more shallow traps in bulk dielectric emerge and mean-distances of shallow traps are shortened, leading to carriers' becoming easier to hop in shallow traps. In this way, mobility of carriers controlled by shallow traps rises up with increase of nanofiller content.

3) Charge transport model is introduced to investigate the space charge distribution, electric field distribution and conductivity properties. It indicates that, with increase of nanofiller content, space charge accumulation around the cathode/dielectric surface goes up firstly and then declines, thus distortion at cathode/dielectric surface gets strengthened firstly and weakened afterwards, conductivity turns on an initial increase and is followed by a decrease.

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