Understanding insulation failure of nanodielectrics: tailoring carrier energy

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Abstract: Owing to the formation of interface and new feature of which, the properties of nanodielectrics can be improved. ‘Hard/soft interface’ and its trap distribution can be tailored by functionalised groups. Molecular simulation results show that the interaction energy and electrostatic potential are larger for the soft interface, which indicates the greater bonding strength with the polymer matrix and electrostatic force on charge carriers. Charge transport simulation indicates that the accumulation of homocharges would form a reverse electric field and distort electric field distribution. The injection depth would be restricted at the vicinity of sample/electrodes due to the greater trapping effect of deep traps, thus weakening the distortion in the sample bulk, thereby decreasing carrier energy and delaying the formation of impact ionisation. Based on the accumulation of carrier energy, 2, the idea of suppressing electron free path and carrier energy to enhance the insulation breakdown is confirmed. The classified effects of nanofillers during dc breakdown and corona-resistant are further understood from carrier energy. The introduced interfacial trap is effective in trapping carriers due to the low carrier energy under dc voltage, while ineffective in blocking the energetic charges during corona-discharge, but nanoparticles exert blocking and scattering effect against the energetic charges.

1 Introduction

Engineering dielectrics have important applications in power equipment and electronic devices [1]. The study of the relationship between microscopic theories, mesoscopic phenomenon, and macroscopic property (3M) is of great significance for the improvement of engineering dielectrics [2]. The polymers have polymer chemical (first-level) structure, polymer chain (second-level) structure, aggregate structure (third-level), and texture (high-level) as listed in Table 1. The polymer has complex structures, which is affected by chain conformation and arrangement, molecular weight, and crystalline, amorphous etc. whilst a tiny difference in polymeric structure would lead to a big difference in electrical properties [4]. Understanding the relationship between molecular structure and electrical performance is important but complex and difficult.

The greatest truths are the simplest. Reductionism is a theory that restores complexity to simplicity and then reconstructs complexity from the simplicity [1]. A. Einstein once summed it up briefly: the supreme trial for physicists is to reach those basic laws that are universal, and then deduce the universe from the laws. Is this universal? We have encountered some difficulties in polymer researches. Reductionism seems to be difficult to understand the relationship between polymer structure and its performance at each hierarchy. The Nobel Prize winner P. W. Anderson questioned the reductionism and proposed the emergent phenomenon. It was considered that the behaviour of complex aggregates of a large number of elementary particles cannot be understood by a simple extrapolation based on the nature of a few particles, and instead by a new feature presented in each level [1]. For example, for carbon atoms, presenting in different hierarchy or atomic arrangement, demonstrate as much different properties, such as graphite, fullerene, diamond, and carbon nanotubes, as shown in Fig. 1. Science is constantly improving, and the methods and theories of scientific research are stepping forward. Based on dialectical philosophy, substances and theories cannot be absolute and should be viewed dialectically. In the face of reductionism and emergent theory, they should be complementary to each other in scientific research [5].

Not only the complex structure of the polymer matrix, but also interface region (interaction region) is formed between the polymer matrix and the nanoparticle due to the large specific surface area of nanoparticle for nanocomposites [6, 7], as shown in Fig. 2. In addition, the interface region has different physical and chemical properties compared to polymer matrix and nanoparticles [8–11]. The properties of nanocomposites are difficult to be understood because of its structural complexity and the irregularly distributed nanoparticles. Hence, the interaction between the polymer and the nanoparticle becomes more complicated. Since the improved electrical performance of nanocomposites, which indicates 1 + 1 does not necessarily equal 2 in the field of nanocomposites. Comprehensively, the formation of interface region is a new

Table 1 Polymeric structural hierarchy and its properties [3]

| Polymer structures | Properties |
|--------------------|------------|
| chain structure    | first level | constitution, tacticity, branching, crosslinking. | stability, intermolecular interaction, chain flexibility, dielectric constant. |
| second level       | molecular weight and distribution, size and shape. | mechanical strength, thermal property, flexibility, processability. |
| aggregate structure| third level | crystalline, amorphous, liquid crystal states. | physical and mechanical properties, optical property, breakdown strength. |
| high level structure| fourth level | texture structure | mechanical and dielectric properties. |
A flexible molecule is 'soft interface' [1]. Hence, the flexibility and characteristics can be significantly affected, thus affecting the performance for nanodielectrics. However, interface region is still a key factor [12, 18]. The basic facts are that the molecular chains have pure polymers originates from the interface regions [13]. Based on the proposed interface model [8–10], the charge transport characteristics can be significantly affected, thus affecting the conductivity and electric field distribution, finally demonstrated as the changed breakdown performance. In addition to being the scattering center for charge carriers [14], the introduced interfacial deep traps are considered to be effective in restricting carrier energy [10, 15–17]. Around with interface region, two interfacial models of nanodielectric composites are commonly adopted. The Lewis interface is an electric double layer formed by the spontaneous transfer of charges caused by band structure difference [6]. The other is the multi-core model proposed by Tanaka et al. [10]. For Tanaka interface, in which charge density decays in exponentially with distance according to the Born approximation [10]. The two models are helpful to understand the improved performance for nanodielectrics. However, interface region is still occupied by molecular chains, while Lewis and Tanaka model only considered the distribution of charge and potential distribution on particle surface. The basic facts are that the molecular chains have a classification of rigidity and flexibility discriminated by the rotational energy barrier. The higher rotational energy barrier is, more difficult for molecule to rotate, the worse the flexibility. Besides, the flexibility and interaction energy between grafted molecules on particles and matrix molecules would affect the molecule arrangement in the interface region. The interface formed by rigid molecule is ‘hard interface’, and the interface formed by flexible molecule is ‘soft interface’ [1]. Hence, the flexibility and interaction between surface-functionalised groups and polymer matrix is a key factor [12, 18].

The interfacial structure between the inorganic particles and polymer is affected by the type of nanoparticles [19], particle surface treatment [20], particle surface functionalised groups [12], and the polarity and flexibility of the polymers [21] etc. The molecules in the interface region were occupied by the nanoparticles surface grafted molecules and the matrix molecules. The cohesive energy density reflects the flexibility and interaction between molecules [11]. The interaction energy obtained by molecular simulation would affect the bonding strength between molecules [12], which further affect the interfacial structure and potential barrier distribution, finally affecting the charge transport process. The nature of the hard/soft interface is greatly affected by the interaction between molecules. Since the different molecular chains would affect the bonding strength, it is considered that the surface-functionalised groups on nanoparticles would affect the interaction between the nanofiller and polymer matrix. Knowing about this is helpful to understand the property of hard/soft interface and the composite performance.

Can we modulate hard/soft interface property through surface functionalisation of nanoparticles, and thus affecting the nanocomposite property? Yes, a more fundamental and refined understanding of the interfacial effect on electrical properties indicated that the hard/soft interface is closely related to breakdown performance [12]. Two functionalised POSS (Tri Silanol Isobutyl POSS 1450 and Tri Silanol Phenyl POSS 1458) were blended with polypropylene (PP). DC breakdown showed that the breakdown strength of PP/POSS 1450 composite increased by 18.2% (from 237.5 to 280.8 kV mm$^{-1}$) compared to pure PP, while that of PP/POSS 1458 decreased by 17%. The improved breakdown strength corresponds with the composite possessing better intermolecular compatibility and deeper traps. The molecular simulation further reveals that hard/soft interface and trap energy are affected by interaction energy and electrostatic potential (ESP) [12], as shown in Fig. 3. Different functionalised groups lead to different interaction energy interacted with PP molecules, which results in different interfacial compatibility. For flexible isobutyl group, the interaction energy interacted with PP molecules is 50.21 kJ/mol, which is much bigger than that of rigid phenyl group with 32.15 kJ/mol. Larger interaction energy enhances the bonding strength and reduces interfacial defects. Larger ESP has greater electrostatic force on charge carriers in the interface, demonstrating as the enhanced potential barrier (trapping effect) [8]. The PP/POSS 1450 composite with larger intermolecular interaction energy and ESP distribution would be more effective in restricting the charge carriers’ migration and its energy, and finally resulting in different interfacial compatibility and deeper traps.
Comprehensively, the structure of hard/soft interface was proposed to interpret the improved breakdown performance [8, 11, 12], as shown in Fig. 5.

3 Analysis of trap modulated carrier energy and electrical breakdown

For the study of traps information, methods of TSDC [22] and surface potential decay [23] can be adopted. Also, the variation of trap characteristics can be intuitively demonstrated by different \( j-V \) characteristics [24]. Generally, electronic conductivity dominates at the high electric field and low temperature, in which the electrons mainly originate from the electrode injection. In the ohmic region, \( j = nE \), and \( n = 1 \). For the Child law, scale index \( n = 2 \). For Mott law with traps, obeying the scaling law, \( j \sim V^n \). On account of the complex energy band structure (energy spectra, including physical shallow traps, chemical deep traps etc.) of polymers, thus resulting in the deviate from the square law of \( n \), as shown in Fig. 6. By measuring the \( j-V \) characteristics, it is possible to reflect the trend of changes in trap energy and density. The change in the energy band structure (trap distribution) of the material (induced by filler doping, ageing etc.) leads to changes in conductivity characteristics. For Dupont® pure polyimide 100HN and its composite 100CR [25], the TSDC results showed that the trap centre of 100CR moved to shallower trap energy, which was consistent with the increased conductivity, as shown in Fig. 7. For the \( j-V \) curves of 100HN and 100CR, the changes of \( j-V \) originate from the changes in trap characteristics of the polymer.

The most studied is the change of trap characteristics modulated by nanofillers. Results of TSDC showed that the trap energy for small amount and large amount of nanofillers would change greatly [22, 26]. The correlation between traps and breakdown strength was analysed [12, 26–28]. Deep traps energy is positively related to the dc breakdown strength, as shown in Fig. 8. Specifically, incorporating with a small amount of nanofillers is contributed for deeper traps, whilst the decreased trap energy was found by incorporating with a large amount of nanofillers. Based on the proposed interfacial models, it was considered that a vast distortion of potential occurs in bonded region and deep traps are introduced [8]. Outwards from the surface of nanoparticles, the overlapped interface regions gradually take a dominant role [8, 29]. For composites with large amount of nanofillers, the shorter distance between the nanoparticles causes the overlapped interface regions.

In addition, the density of shallow traps gradually increases, thereby forming the percolation conductance path [30]. The deep trap energy increases, resulting in a decrease in carrier mobility and the suppression of carrier energy [17]. Consequently, the breakdown strength increases as an increase of deep trap energy due to the effective suppression of carrier energy and its multiplication process [31, 32].

4 Understanding insulation breakdown from carrier energy tailored by electric field distortion and electron free path

Space charge transport is closely related to electric breakdown. Pulsed electro-acoustic results showed that the injected charges amount increases with time, and the electric field distortion becomes more severe until breakdown occurs [33]. Bipolar charge transport model, including charge injection, migration, trapping, de-trapping, and recombination process [32]. Charge transport and accumulation had been confirmed to be of great influence on electric breakdown according to simulation of space charge modulated electrical breakdown model [32, 34, 35]. Besides, the enhanced trapping effect of deep traps would affect charge transport process. According to the equation of carrier energy accumulation, \( \Phi = E\lambda \), which is affected by electric field strength and electron free path [17, 36], as shown in Fig. 9. If the electric field and the free volume are large enough, the carrier energy will increase rapidly in a short time, so that it can overcome the potential barrier and continue to migrate, and its energy will be accumulated from the electric field until the impact ionisation process is triggered.
According to the Positron Annihilation Lifetime Spectra (PALS) theory, the long-lived component ortho-positronium (o-Ps) would preferentially localise in the free volumes, and the annihilation of which make it a microprobe of free volume [37]. The radius of the free volume cavity \( R \) (in nm scale) can be obtained by the Tao–Eldrup equation. The PALS spectra of pure PP and PP/Al\(_2\)O\(_3\) nanocomposites were shown in Fig. 10, and the free volume cavity \( R \) was in the illustration. It showed that the radius of free volume in the composite is still nearly the same as that for pure PP even at high nanofiller content (15 wt%). It indicated that the free path of carriers has not changed, whereas the trap energy changed much along with the nanofiller contents. Hence, the trap energy should dominate in the process of affecting charge transport and electric field distribution.

Based on the equations of bipolar charge transport, the charge injection and electric field distribution varied with time under a constant voltage (20 kV) were simulated, as shown in Fig. 11. For 150 μm pure PP with trap energy of 1.17 eV, the simulated results indicated that the charge amount was 0 at the initial time \( t = 0 \) s, and the electric field was uniformly distributed in the sample, i.e. a straight line. With time going on, the charges were continuously injected into PP material, and the distortion of electric field occurred. After the charges injection into the material, they are quickly trapped to form a homo-charges distribution [17, 34]. Deeper traps inhibit the migration of charges into the inner depth, thus inducing the accumulation of homo-charges at the vicinity of electrode/sample, and forming a reverse electric field, thereby...
weakening the electric field here. As a result, the electric field at the vicinity gradually decreased, whilst the electric field inner the material gradually increased. The carrier energy in the sample bulk was larger than that at the vicinity due to the uneven electric field distribution according to the energy accumulation of $Ee\lambda$.

The simulated results for composites with different trap energy were shown in Fig. 12. The results indicated that the charge amount and injection depth were increased as the trap energy decreased. Deeper traps inhibit the migration of charges into the inner depth of the sample, thus leading to the larger charge accumulation and the reverse electric field at the electrode/sample vicinity. And the weakened electric field at the vicinity suppressed subsequent charges injection. Due to the larger electric field in the sample bulk and larger distortion of electric field for sample with smaller trap energy, thus leading to the decreased breakdown strength since the breakdown strength is determined by the intrinsic breakdown strength, i.e. the electric field for sample with shallower traps would priority reach the threshold value (intrinsic breakdown strength), as shown in Fig. 13. Besides, the more increased (distorted) electric field in the sample bulk with shallower traps leads to the larger carrier energy according to $\Phi = Ee\lambda$, thus easier triggering impact ionisation and charge multiplication. Hence, the breakdown strength of which possessed shallower traps decreased.

Carrier energy is a key parameter affecting the insulation breakdown property. Based on the idea, a new super-insulator prototype of 1D gas-solid Al$_2$O$_3$ NPT (nanopore template) was constructed and a novel thought for constructing nanostructured dielectrics by restricting the charge multiplication and its energy was proposed [38]. The results showed that the breakdown strength Al$_2$O$_3$ nanocell was much higher than air, and of which increased with the nano-pore size decreasing, as shown in Fig. 14.

5 Classified effects of nanofillers on dc breakdown and corona-resistance

For DC breakdown, the carrier energy is small due to the small free path and low mobility in the sample bulk, generally with few eV [31]. Hence, for DC breakdown, the interfacial trapping effect is effective to trap charges due to the small carrier energy. However, for the corona-resistance, owing to the extremely uneven electric field and discharge, surface degradation is caused by the energetic charged ions that directly collide with the polymer molecules [39].
To distinguish the effects of nanoparticles in the breakdown and corona-resistance process, a comparison of dc breakdown and ac corona-resistance experiments were carried out. The corona-resistance of nanocomposites with higher filler content exhibits longer failure time compared with the most improved dc breakdown strength at low filler contents [28]. Furthermore, for nanocomposites with high filler contents, the eroded area appears more spreading on the sample surface. Several distinguishable eroded layers surrounding the hole can be observed [25, 28].

According to the fluid models of gas discharges, the electron energy distribution function (EEDF) was obtained by Boltzmann equation solver BOLSIG + [40]. For the needle electrode with 7 kV AC voltage and 1 mm gap distance, the simulated result of EEDF was shown in Fig. 15a. It indicated that the charges energy is distributed in several tens eV, which is much larger than the interfacial trap (usually with few eV). Hence, the potential barrier in the interface is weak when suffering the energetic charges, whilst the ‘hard’ nanoparticles itself would play a role in energy dissipation by nanoparticle scattering effect. Inspired by the eroded layers on the sample surface, a corona-resistance model for nanocomposites was proposed on the basis of synergistic effects of energy dissipation by scattering effect of nanoparticles [25, 28], as shown in Fig. 15b. Scattering effect of nanoparticle arises from the ‘hard’ collision against energetic charges. The area below the needle tip, which suffers the most erosion is therefore protected. The scattering effect against energetic charges plays an important role in energy dissipation.

For the scattering effect of nanoparticles act during the corona-resistance, compared with the trapping effect for improving dc breakdown, the nanoparticles act on the two processes are much different. For dc breakdown, the interfacial trapping effect is effective due to the small carrier energy induced by the small free path and low mobility in the sample bulk, especially when electric field is not high, while for corona-resistance, the interfacial trapping effect is ineffective due to big carrier energy induced by the large free path in the air ionisation process. Comprehensively, the classified effects of nanofillers on dc breakdown and corona-resistance can be better understood from the perspective of carrier energy.

6 Conclusion

Hard/soft interface is affected by the interaction between matrix molecule and surface-functionalised molecule. Intermolecular interaction energy between grafted groups and polymer molecule, and ESP would affect interfacial traps distribution. Larger interaction energy increases bonding strength. Larger ESP has a greater electrostatic force on charge carriers, demonstrating as the enhanced potential barrier (trapping effect). The breakdown strength increases as an increase of deep trap energy due to the effective suppression of carrier energy and its multiplication process. Different trap characteristics result in different space charge accumulation and electric field distortion. The bipolar charge transport simulation shows that the electric field for sample with shallower traps would priority reach the threshold value (intrinsic breakdown strength), and the more increased (distorted) electric field in the sample bulk leads to the larger carrier energy, thus easier triggering impact ionisation and charge multiplication. Weakening the carrier energy by increased trap energy and the inhibiting the electron free path would improve the insulation breakdown performance. Classified effects of nanoparticles on dc breakdown and corona-resistance can be further understood from the perspective of carrier energy.

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Fig. 14 Process of electron moving in gas
(a) In macro-gap without transverse confinement, (b) In nanocell with transverse confinement, (c) Improved breakdown characteristics of different voltage forms of Al2O3 NPT vary with nanocell size compared with normalised nano-air-column [38]

Fig. 15 Corona-resistance model
(a) Calculated EEDF for needle-plate electrodes by BOLSIG +, (b) Interfacial weak resistance and scattering effect of the nanoparticles for long-term corona-resistance
