Review of interface tailoring techniques and applications to improve insulation performance

Mingxiao Zhu\(^1\) | Jianyi Xue\(^2\) | Yanhui Wei\(^3\) | Guochang Li\(^3\) | Guanjun Zhang\(^2\)

\(^{1}\)College of New Energy, China University of Petroleum (East China), Qingdao, China
\(^{2}\)State Key Laboratory of Electrical Insulation and Power Equipment, School of Electrical Engineering, Xian Jiaotong University, Xian, China
\(^{3}\)Institute of Advanced Electrical Materials, Qingdao University of Science and Technology, Qingdao, China

Correspondence
Guanjun Zhang, College of New Energy, China University of Petroleum (East China), 28 Xianning West Road, Xi'an, Shaanxi 710049, P R. China. Email: gjzhang@xjtu.edu.cn

Associate Editor: Shahab Farokhi

Funding Information
National Natural Science Foundation of China, Grant/Award Numbers: 52007198, 11175175, 51827809; Natural Science Foundation of Shandong Province, Grant/Award Number: ZR2019QFE014; Fundamental Research Funds for the Central Universities, Grant/Award Number: 19 CX02015 A

Abstract
Interfaces between different materials, for instance, electrode–dielectrics and vacuum/air/SF\(_6\)-insulators and oilpaper, are universal in high-voltage insulation systems. Targeted tailoring of the interfacial properties, e.g., chemical structures, micro-/nanoscale morphology, the charge injection barrier, trap states, and surface conductivity, is thought to be an effective approach to improve insulation properties such as breakdown and flashover strength, corona/tracking resistance, and wettability. In this article, the authors review recent progress in interface tailoring methods and their application to improve various insulation properties. The potential application scenarios of interface tailoring in different facilities are first summarised, and the desired insulation properties of various applications are highlighted. Interface tailoring methods are classified as physical/chemical surface modification and surface coating (inorganic, organic and composite), and the features of different techniques are described in detail. The structure–property relationships between interfacial states and various microscopic parameters such as charge injection barrier, trap distribution and surface conductivity are discussed together with the tailoring mechanisms for different insulation properties. Finally, the future development prospects of interface tailoring methods and their applications, e.g., multifunctional coating and stimuli–response smart coating, are presented.

1 | INTRODUCTION

Interfaces between different materials, for instance, electrode–dielectrics and vacuum/air/SF\(_6\)-insulators and oilpaper, are universal in high-voltage insulation systems such as pulsed-power equipment [1, 2], outdoor insulators [3, 4], gas-insulated switchgear (GIS) [5, 6] and power transformers [7, 8]. The different dielectric parameters on both sides of the interface give rise to multiple effects, e.g., the rearrangement of electric field distribution, accumulation of space charge on the interface and changes in the discharge inception and propagation processes [9, 10]. For these reasons, interfacial properties have a significant influence on insulation performance. For example, the charge injection barrier and trap energy at the electrode–dielectrics interface strongly affect the breakdown strength of bulk materials [11, 12]; the surface flashover voltage at vacuum/air/SF\(_6\)-insulator interfaces is dominated by several interfacial properties such as surface conductivity and trap distribution [13–15]; the corona/tracking resistance of insulators is closely related to that of the surface layer because it acts as the spearhead against discharge bombarding; and surface free energy and micro-/nanoscale morphology determine the hydrophobicity and anti-icing properties of insulators [16–18].

Targeted tailoring of interfacial properties, e.g., chemical structures, micro-/nanoscale morphology, charge injection barrier, trap distribution, surface conductivity and permittivity of the surface layer, is thought to be an effective approach to improve insulation properties such as breakdown and flashover strengths, corona/tracking resistance and wettability. For example, wide-bandgap inorganic and organic films such as boron nitride [11, 19], silicon dioxide [20] and polytetrafluoroethylene (PTFE) [8] were deposited on the surface of
polymer dielectrics to elevate the charge injection barrier at the electrode–dielectric interface and consequently give rise to increased breakdown strength. Surface modification techniques including fluorination [14, 15], plasma treatment [21–24] and surface coating [25, 26] were employed to regulate surface conductivity and trap distributions, thereby suppressing surface charge accumulation and improving flashover performance. Surface functionally graded materials (SFGMs) with spatially graded distributions of permittivity/conductivity at the gas–space interface were fabricated by dip coating [27], magnetron sputtering [28, 29] and gradient fluorination [30] methods and showed promising application in suppressing electric field distortions and elevating flashover voltages. Apart from improving electrical properties, numerous techniques such as lithography, etching, templating, chemical vapour deposition (CVD) and surface coating methods have been presented to build superhydrophobic surfaces by altering surface micro-scale/nanoscale structures or surface free energy and have a range of applications in waterproofing, self-cleaning, anti-icing and anticorrosion [16–18]. As indicated, numerous studies have been conducted to improve various levels of insulation performance by tailoring the interfacial properties, but most works have merely taken advantage of the single tailoring effect of interface modification. In fact, interface tailoring techniques in various applications, including fabrication methods, structure–property relationships, characterisations and underlying mechanisms, can be investigated in a unified manner.

Here, the fabrication methods, structure–property relationships and modification mechanisms of interface tailoring techniques, and their applications in improving insulation properties, are reviewed. Section 2 summarises the potential application scenarios of interface tailoring. In Section 3, interface tailoring methods including physical/chemical modification and surface coatings (inorganic, organic and composite coatings) are illustrated. In Section 4, the applications of interface tailoring in improving various microscope interfacial parameters and corresponding insulation properties are demonstrated, and the structure–property relationships between interfacial states and performance are discussed. Section 5 summarises applications of interface tailoring in improving insulation-related performance such as corona/tracking resistance and wettability. Finally, the conclusions and future perspectives are summarised in Section 5.

2 | POTENTIAL APPLICATION SCENARIOS OF INTERFACE TAILORING

Several potential application scenarios of interface tailoring are shown in Figure 1. The charge injection barrier and trap depth at electrode–dielectric interfaces have a significant effect on breakdown strength, electrical conduction loss and the space charge and charge–discharge efficiency of dielectrics, which can be modified by depositing a wide-bandgap surface layer. For example, hexagonal boron nitride (h-BN) and SiO2 layers were deposited on the surface of polymer films by CVD and plasma-enhanced CVD (PECVD) methods to block the charge injection and consequently reduce electrical conduction and improve charge–discharge efficiency at elevated temperatures [11, 20]. In a similar application, nanostructured PTFE and Al2O3 films were fabricated on cellulose insulation pressboard with a magnetron sputtering technique and could act as a functional barrier layer to suppress charge accumulation and elevate breakdown strength [8, 31].

In composite insulation systems, the mismatch of dielectric parameters at vacuum/air/compressed gas–solid interfaces causes electric field concentration and surface charge accumulation that can lead to partial discharges and even flashovers over spacers. For instance, surface flashover and charge–discharge are serious problems faced in vacuum–solid insulation and has gained wide attention in many fields such as spacecraft, pulsed-power devices and vacuum circuit breakers [1, 2]. As another example, the spacers in gas-insulated transmission lines and substations (GIL/GIS) suffer from the problem of surface charge accumulation under DC stress that distorts the local electric field and may initiate flashover at the compressed gas–solid interface [5, 6, 32]. It is widely accepted that the dynamic processes of surface charge accumulation and dissipation are dependent on surface trap states and electrical conductivity that can be modulated by many interface tailoring techniques. Using interface tailoring methods such as fluorination [14, 15], plasma treatment [21–24] and non-linear surface coating [33–35], shallow traps can be introduced on the spacer to effectively accelerate charge dissipation and improve flashover strength. From another perspective, deep traps can be formed by elaborate regulation of the types and concentrations of nanofillers in the surface coating to capture injected charges and lead to homo-charge accumulation, thus reducing the electric field in the vicinity of electrodes [36, 37]. Therefore, charge injection from electrodes is inhibited, which leads to suppressed accumulation of surface charges and elevated flashover strength.

In addition to surface flashover at the air–solid interface, outdoor insulators suffer from problems such as deposition of water film, pollution, ice, snow or their mixtures that may lead to electrical and mechanical failures [3, 4]. Advanced coatings have been developed as an effective interface tailoring method to improve the performance of outdoor insulators in harsh environments. For example, superhydrophobic coatings with a water contact angle higher than 150° and sliding angle lower than 10° have been fabricated by many methods such as templating, etching and spray coating and offer the advantages of water repellence, self-cleaning ability, low ice-adhesion strength and delayed freezing time [4, 17, 18]. In contrast to superhydrophobic coatings that passively reduce ice accumulation, semiconducting silicone coatings with electrothermal effects [38] and sunlight-responsive coatings with photothermal effects [39, 40] have been developed for active de-icing. Moreover, superhydrophobic–electrothermal synergistic anti-icing coatings have also been used [41].

For inverter-fed rotating machines and outdoor insulators, corona discharge and dry-band arcing at the air–solid interface can cause serious surface damage or tracking leading to partial or complete loss of insulation [42, 43]. Higher inorganic filler content is usually incorporated into polymers to significantly
enhance the partial discharge (PD) or arcing resistance, which may result in the aggregation of fillers and consequently a reduction in breakdown strength. As alternative approaches, interface tailoring methods such as electron beam irradiation [44], fluorination [45, 46] and surface coating can enhance resistance to corona and arcing discharges with little effect on breakdown strength.

3 | INTERFACE TAILORING METHODS

The general routes for tailoring interfacial properties can be classified as surface modification and surface coating. For the first approach, surface microscopic morphology can be physically changed by etching and templating methods, whereas the chemical composition on the surface can be modified by several methods such as electron beam irradiation, ozone treatment, fluorination and plasma modification. In the surface-coating approach, a new layer of coating film, which can be inorganic, organic or composite, is deposited onto the dielectrics by various methods such as magnetron sputtering, CVD, PECVD, electrodeposition, brushing, spraying and dip coating. A brief description of some important techniques is provided in the subsections that follow.

3.1 | Physical modification methods—etching and templating

For insulators with an inherently smooth surface, roughening the surface can increase the vacuum flashover voltage significantly for μs pulse, 50 Hz, and DC voltages [1]. This is possible because rougher surfaces are less sensitive to the impacts of electrons at shallow angles and thus suppress the secondary electron emission avalanche process [47]. For instance, Yamamoto et al. [48] and Naruse et al. [49] investigated the influence of surface roughness on flashover voltage for different materials such as Al₂O₃, SiO₂ and PTFE, indicating that rougher surfaces present higher flashover voltages. A CO₂ laser generator was adopted to create scratched lines on the
surface of alumina ceramics in [50], and it was found that a much higher flashover field strength was gained with a larger scratching density. Chang et al. theoretically and experimentally confirmed that a periodically grooved surface could effectively suppress multipactor development and increase the transmitted power of high-power microwave [51].

In addition, surface roughness is a key factor contributing to the formation of superhydrophobic surfaces [16–18]. Surface roughening methods by simple etching or templating can be used to fabricate superhydrophobic surfaces for various materials. Etching can be classified as dry etching and wet chemical etching. Plasma and reactive ion etching are typical dry etching methods, in which the reactive atoms and ions in a gas discharge creating anisotropic etching of the surface [52, 53]. In wet chemical etching, acid or base solutions are used to etch dislocations or impurities on materials. Chemical etching is a relatively simple approach that can be easily scaled-up, while the etching process may be hazardous and not environmentally friendly [54, 55]. Templating, another common method to construct micro- and nanoscale roughing morphology, uses an intermediate surface as the master template [56]. The master template with desired specifications can be replicated on material surfaces with a moulding process. For example, Liang et al. fabricated a superhydrophobic silicone rubber using a templating method in which laser beam–processed H13 mould steel was used as the master template [57].

### 3.2 Chemical modification methods

Electron beam irradiation has been employed to improve the surface flashover voltage and PD resistance of polymers by chemical modification. The samples are usually irradiated by an electron gun in a vacuum chamber, as shown in Figure 2a. Gao et al. stated that electron beam irradiation induced cross-linking reactions within the samples, and the improved cross-linking structure gave rise to enhanced PD resistance [44]. The influence of electron beam irradiation on the surface flashover of an epoxy resin/Al2O3 composite was investigated by Li et al., and they found that deep trap density and energy levels increase with the electron beam energy [58–60]. As a result, the introduced deep traps enhanced the ability to capture primary emitted electrons, thus suppressing the secondary electron emission process. In addition, the trapped charge carriers can cause homo-charge accumulation near the electrodes, reducing the electric field around the triple junction points, thereby improving surface flashover strength.

Fluorination and ozone treatments are frequently employed to improve flashover performance using highly reactive F2 or O3 to chemically modify the surface molecular structures. Four steps—desiccation, vacuuming, fluorination and exhaust—are involved in the direct fluorination of the samples, which is usually conducted in a stainless reaction vessel, as shown in Figure 2b. In the fluorination process, C–F, C–F2, and C–F3 groups are generated by disrupting C–H bonds and grafting F atoms, due to the higher bond energy of the C–F bond compared with the C–H bond [14, 15, 61]. It has been reported that the thickness of the fluorinated layer on the epoxy resin (EP) is submicrometer, and SEM images showed that fluorination also increases surface roughness [14, 15, 61, 62]. In ozone treatment, O3 reacts with hydroxyl and forms carbonyl in molecular chains [63]. Numerous studies have indicated that fluorination and ozone treatment can reduce the energy levels of surface traps and elevate surface conductivity to accelerate charge dissipation speed and suppress charge accumulation. The suppressed charge accumulation causes little distortion of the surface electric field and reduces the occurrence probability of initial effective electrons. As a result, DC flashover voltage can be improved by fluorination and ozone treatment [14, 15, 61]. For example, An et al. found that the DC flashover voltage of truncated cone EP samples in 0.1 MPa SF6 increased from 85.27 to 97.06 kV (by 13.8%) after the EP sample was fluorinated for 30 min, as shown in Figure 3 [14].

Although fluorination and ozone treatment can improve flashover voltage, a sealed reaction vessel or complex experimental equipment is required, which restricts their industrial application. As an alternative approach, non-thermal plasma with an F-containing (e.g. CF4) or O-containing (e.g. open air) working gas can be used to treat material surfaces in a manner similar to that of direct fluorination and ozone treatment. In material modifications, atmospheric pressure non-thermal plasma is usually generated by dielectric barrier discharge (DBD) [21, 23], radiofrequency plasma generator [64] and plasma jet (APPJ) [22, 65], as shown in Figure 4a,b. Lopez-Garcia et al. [64] and Zhang et al. [65] used CF4 as a
working gas in plasma modification to treat the material surface and found that the C–H bond is substituted by the C–F bond on the treated surface. In studies by Shao et al. [23] and Chen et al. [21], the plasma treatment was conducted in open air, and it was found that the plasma introduces an O element into the polymer surface, and the chemical reactions produce carbonyl groups. It was found that the plasma treatment method with CF₄ and air as the working gas chemically modified the material surfaces in a manner similar to fluorination and ozonation; thereby, flashover strength can also be effectively improved.

3.3 | Inorganic surface coating

The dielectric parameters of inorganic materials have a wide range of values. For example, relative permittivity ranges from 4 of BN to 1000 of BaTiO₃ or even higher, and the bandgap ranges from 3 eV of BaTiO₃ to 9.5 eV of Al₂O₃. As a result, many electrical properties such as electric field distribution, charge injection barrier and trap distribution can be purposefully tailored by introducing specific inorganic materials on the surface of insulators, thereby improving various dielectric properties such as breakdown voltage and flashover strength.

Physical vapour deposition (PVD) and CVD are the most used methods to build an inorganic layer on the dielectric surface. Among different PVD methods, magnetron sputtering has been used for many applications in both inorganic and organic surface coating due to its broad applicability to various target materials. For example, Hao et al. fabricated an Al₂O₃ film on cellulose insulation pressboard with a magnetron sputtering technique that increased the charge injection barrier and elevated breakdown strength [31]. A coating layer of BN was deposited on both sides of polyimide film using magnetron sputtering in [19], and the BN layer effectively suppressed the charge injection by increasing the barrier height, consequently improving breakdown strength and discharging energy density. In [36], a Cr₂O₃ coating was deposited on an EP surface with a magnetron sputtering machine, which introduced a large number of deep traps with high energy levels. The charge injection process is inhibited by the reversed electric field formed by the high-density trapped charges in the Cr₂O₃ coatings. To homogenise the electric field distribution in GIL, a concept using SFGM was proposed by Du and Li et al. [28, 29]. Using the magnetron sputtering method, continuously graded permittivity and conductivity layers were fabricated by depositing BaTiO₃ and ZnO films with gradient thickness on the insulator surface to regulate the electric field distribution under AC and DC applied voltages, respectively.

CVD is a reproducible and scalable method for the synthesis of several materials that can be used to build an inorganic coating on the dielectric surface. In [11], b-BN films were prepared from CVD and readily transferred onto polyetherimide (PEI) films, resulting in greatly improved discharged energy density and charge–discharge efficiency at elevated temperatures. Due to the mild reaction conditions, PECVD is more frequently employed in surface deposition to improve various properties such as flashover strength, breakdown voltage and hydrophobicity. Abbasi-Firouzjah et al., Shao et al. and Xie et al. used tetraethoxysilane as the precursor in plasma treatment to build SiO₂ thin films on the substrate, which increased the surface conductivity and flashover voltage [24, 66, 67]. Due to the broad bandgap of SiO₂, a similar method was adopted by Li et al. to raise the injection barrier at the electrode–dielectric interface, which consequently improved breakdown strength and energy density [20].

3.4 | Organic surface coating

Organic polymers with specific properties can be coated on dielectric surfaces to improve various types of performance, e.g. room temperature vulcanised silicone rubber is widely used to improve the hydrophobicity of outdoor insulators. Other polymers containing hydrophobic groups such as polydimethylsiloxane (CH₃) and PTFE (CF₃) can be used for the same purpose. PTFE functional film was sputter coated on cellulose insulation by Hao et al., and they found that breakdown strength and hydrophobicity was improved [8]. In addition,
organic coatings can be fabricated by many scalable methods such as brushing, dipping, spraying and lamination, and external stimuli such as heat treatment and UV radiation are usually needed to trigger the solidification process. For example, heat treatment is required for thermosets such as EP and PEI), whereas UV radiation is needed for UV-curable resins [69, 70].

3.5 Composite surface coating

A composite coating composed of polymer and fillers is thought to be a flexible and scalable technique for interface tailoring in which the polymer mainly acts as the adhesive and binding components, and various properties can be flexibly controlled by changing the doping scheme of the fillers. Various insulation properties such as flashover voltage, breakdown strength, PD resistance and superhydrophobicity can be effectively improved by elaborately designed composite coating. Composite coating can be readily fabricated by spraying, brushing or electrospinning well-blended suspensions of polymer precursors, nanofillers and approximate solvents or dipping the substrate into as-prepared solution, which are easier to implement than most other methods such as plasma treatment, fluorination, PVD and CVD [4, 16]. As an example, 6-BN layers were transferred on both sides of polycarbonate films via electrospinning technology, and it was found that composite film has high breakdown strength, low leakage current density and excellent high-temperature energy density [71].

Composite coatings with different fillers have been brushed on insulators to tailor surface properties such as electrical conductivity and trap distribution, thereby improving charge accumulation behaviour and flashover strength. For example, Tu and Qi et al. investigated the effects of SiO$_2$/epoxy and TiO$_2$/epoxy coatings on the dynamic behaviour of surface charge and found that the coating film can effectively restrain charge accumulation [25, 26]. Non-linear conductive fillers such as micron-scale SiC and ZnO were also used in the composite coating to increase surface conductivity and thus accelerate charge dissipation [13, 33–35, 72, 73]. Moreover, SiC/epoxy coatings can reduce the maximum electric field and homogenise surface electric field distribution, which further
increases flashover voltage. In [74], a nano-laminar coating with aligned montmorillonite (MMT) sheets in polyvinyl alcohol (PVA) polymer was fabricated to improve flashover strength.

Artificial superhydrophobic surfaces present broad applications in outdoor insulators because of their multiple functions such as waterproofing, anti-icing and self-cleaning [16]. Constructing microscale and nanoscale hierarchical structures and lowering surface free energy are the main routes to create a superhydrophobic surface. Among the different methods, surface coating is a convenient and facile approach to produce a superhydrophobic surface. For instance, Lu et al. and Cao et al. developed a ‘paint + spray adhesive’ strategy to fabricate superhydrophobic coatings applicable to various polymers and microscale/nanoscale fillers [17, 18]. For instance, superhydrophobic coatings using binding polymers such as epoxy [75, 76], thermoplastic elastomer [77, 78], PDMS [79] and supramolecular silicone polymer [80], and fillers such as TiO$_2$ [79, 81], silica [75, 76] and carbon nanotubes [77] have been reported.

High inorganic filler content is usually introduced into polymers to improve corona/tracking resistance, which may severely reduce breakdown strength [44]. The corona/tracking resistance of insulators is closely related to that of the surface layer because it acts as the spearhead against discharge bombardment. As a result, corona/tracking resistance can be improved using a thin layer of coating with a high concentration of inorganic fillers, which has little effect on bulk breakdown strength. Furthermore, both corona/tracking resistance and breakdown strength can be effectively improved by separately tailoring the nanofillers in the bulk material and surface coating.

Composite coating is a flexible method for interface tailoring in which the type of binding polymers, physical parameters (permittivity, conductivity, bandgap), shape, size, volume fraction, distribution of fillers and thickness of coating film can be readily controlled to achieve different properties. For instance, the permittivity and conductivity of coatings can be regulated by changing the type, shape and volume fraction of fillers as well as the thickness of the coating film to homogenise the electric field distribution or accelerate charge dissipation. The trap energy level may be controlled by choosing polymers and fillers with desired bandgaps, e.g., deep traps with energy levels higher than 1 eV can be introduced by introducing narrow-bandgap fillers into wide-bandgap polymers [37, 82, 83]. In addition, by reasonably choosing polymers and fillers, ‘stimuli–response’ coatings can be fabricated. For example, photothermal fillers such as carbon nanotube (CNT) and polydopamine (PDA) particles can be used with photoradiation to actively remove ice adhering to insulators [39, 40].

4 | APPLICATIONS IN TAILORING INTERFACE PROPERTIES AND CORRESPONDING INSULATION PERFORMANCE

Many dielectric properties in insulation systems such as breakdown strength, space charge, flashover voltage, high-field conduction and energy density are determined by the carrier injection process at the electrode–dielectric interface as well as carrier transfer characteristics [8, 11, 19, 20]. As a result, various insulation properties can be improved by regulating microscopic interfacial parameters such as the charge injection barrier, trap distribution, surface conductivity, permittivity of the surface layer and surface morphology via interface tailoring. For this reason, analysing the relationships between interfacial physical/chemical structures and microscopic parameters is critical for understanding the modification mechanism and rational design of the interface tailoring method, which will be discussed in detail in this section.

4.1 | Charge injection barrier

The charge injection process depends on various factors, the most important of which are the energy barriers from the electrode Fermi level to the polymer conduction and valence bands [12]. For this reason, several insulation problems faced with typical power equipment such as capacitors and cables can be addressed by increasing the injection barrier. For instance, the space charge density in polymers can be reduced by increasing the injection barrier, which lowers the distortion of electric field distribution in the power cable and thereby increases breakdown strength and reduces the possibility of electrical ageing–induced insulation failure [84]. In addition, electrical conduction loss in the energy-storage dielectric can be effectively reduced, which improves energy density and charge–discharge efficiency, especially under elevated temperature.

The schematics of the energy diagram of an electrode–polymer interface are depicted in Figure 5. Before contact, the isolated polymer and metal electrode share the same vacuum level. When the two materials are contacted, the unaligned Fermi levels of the metal and organic materials create a dipole layer, resulting in a shift of the vacuum level at the interface ($\Delta \phi$) [12, 85], as shown in Figure 5. The injection barriers for electron $\phi_e$ and hole $\phi_h$ can be expressed as...
$\phi_e = \psi_m - VEA + \Delta \varphi$

$\phi_h = -\psi_m + VIP - \Delta \varphi$  \hspace{1cm} (1)

where $VEA$ and $VIP$ are the electron affinity and ionisation energy of the polymer, respectively, and $\psi_m$ is the metal work function. Moreover, $\phi_e$ and $\phi_h$ follow the following equation:

$\phi_e + \phi_h = E_g$  \hspace{1cm} (2)

where $E_g$ is the bandgap of the polymer. As can be seen from Equation (2), wide-bandgap materials such as PTFE, polyethylene (PE), BN, SiO$_2$ and Al$_2$O$_3$ are easier to use for forming high-injection barriers. For materials with a similar bandgap, such as PTFE and PE, the values of $\phi_e$ and $\phi_h$ depend on $VEA$, $VIP$ and $\Delta \varphi$, which can be precisely calculated from Equation (1) using first-principle simulations [12, 85].

The $b$-BN film was transferred onto PEI to improve the charge–discharge efficiency and energy density [11]. The potential barrier at the electrode–dielectric interface changes due to differences in the bandgap and electron affinity of PEI and $b$-BN. The $b$-BN has a wider bandgap of 5.97 eV compared with that of PEI at 3.16 eV. As a result, an electron barrier greater than 5.1 eV is established at the $b$-BN/Au interface, which is significantly more than the barrier height at biaxially oriented polypropylene/Au of 3.2 eV and PEI/Au of 2.93 eV [11]. With the same purpose, Li et al. coated a SiO$_2$ layer on various polymers using the PECVD method [20]. The established energy diagram at the electrode–dielectric interface is shown in Figure 6a,b. Due to the higher LUMO (i.e. the lowest unoccupied molecular orbital) level and lower HOMO (i.e. the highest occupied molecular orbital) level of SiO$_2$, the injection barrier at the electrode–dielectric interface for electrons and holes are raised from 3.9 and 1.3 eV to 4.3 and 4.7 eV, respectively. As a result, the space charge density is much reduced at both room temperature and elevated temperature, and breakdown strength and electrical resistivity are significantly improved, as shown in Figure 6c,d. In [31], an Al$_2$O$_3$ layer with bandgap of 9.5 eV was deposited on cellulose paper to improve insulation performance in transformer oil.

Fluorination and PTFE film were also employed to improve insulation properties by raising the injection barrier. For example, a nanostructured PTFE layer was formed onto cellulose paper using magnetron sputtering, and thereby,
various properties of oilpaper insulation were improved [8]. In another study, CF₄ DBD was used as a surface modification method to improve the dielectric properties of cross-linked polyethylene film, and breakdown strength and dielectric loss were improved [84]. To clarify the underlying mechanisms, the charge injection characteristics of PE and PTFE oligomers were investigated using first-principle calculations, and the results indicated that the charge injection barrier is higher at the metal/PTFE interface in the case of chemisorption [85].

It is worth noting that the practical injection barrier at the electrode–polymer interface is much lower than the theoretical values, e.g. the experimentally observed injection barrier at the metal/PE interface is about 1 eV, while the theoretical value is around 4 eV [86]. Several researchers have hypothesised that the injection barrier values are probably reduced by various imperfections such as impurity states or physical deformation created at the interface [87–89]. For example, El-Shahat et al. found that the presence of common chemical impurities such as carbonyl, vinyl and conjugated double bond impurities creates impurity states in the bandgap of PE and lowers the injection barrier [90]. However, the presence of chemical impurities is not sufficient to explain the significantly reduced charge injection barriers. More work is still needed to understand the underlying mechanism that could guide interface tailoring methods for raising the injection barrier.

4.2 Interfacial charge trap distribution

It is widely accepted that the dynamic processes of carrier transportation at the vacuum/gas/oil–solid interface (or the surface layer) and in bulk insulation are dependent on trap states, which have a tremendous influence on surface flashover and bulk breakdown strength, as shown in Figure 7a,b. Isothermal surface potential decay [91] and thermally stimulated depolarisation current [92] methods are generally used to extract trap parameters and describe the relationship between trap parameters and insulation performance.

Numerous studies have investigated the influence of trap energy on flashover voltage, with various surface tailoring methods adopted to regulate surface trap states [13, 21, 74]. By summarising the experimental results in [23, 33, 35, 63, 74, 93], the relationship between flashover voltage at the gas–solid interface and trap energy are portrayed in Figure 7c, in which both flashover voltage and trap energy are normalised to those of pristine polymers. Charge carriers captured by deep traps cause homo-charge accumulation near the electrodes, reducing the electric field around the triple junction points and suppressing the secondary electron emission process, thereby improving surface flashover strength, as depicted in zone III in Figure 7c. In zone II, shallow traps are beneficial to charge dissipation, thereby suppressing surface charge accumulation.
and increasing the surface flashover voltage [92]. However, the excessively large surface conductivity in zone I increases the leakage current along the spacer surface, which deteriorates surface insulation strength.

For bulk breakdown, Smith et al. and Li et al. concluded that the increased deep trap energy of bulk materials can enhance DC electrical breakdown strength because of the reversed electric field caused by homo-charges and restricted injection depth in the vicinity of the sample–electrode interface [93–95], as shown in Figure 7bd. That is, the dielectric strength of polyethylene can be significantly improved by adding clay nanoparticles [96]. As shown, breakdown strength is closely related to the trap states in the vicinity of the sample–electrode interface but less dependent on traps in the bulk regions far from the electrodes. As a result, interface tailoring techniques such as grafting polar groups by chemical modification or intercalation of polymer or composite layers have been employed to introduce deep traps at the electrode–dielectric interface to inhibit charge injection and improve bulk insulation properties [97–101]. Using these approaches, both flashover voltage and breakdown strength can be effectively improved by interface tailoring techniques.

Chemical modification is thought to be an effective method to tailor trap states in polymers. It is widely accepted that fluorination, ozone treatment and CF₄/air plasma can reduce surface trap depth to accelerate charge dissipation along the material surface to improve flashover voltage [14, 15, 21–24, 30, 61, 63]. An et al. declared that the introduction of fluorine atoms inevitably leads to a significant structural change or disorder that introduces physical defects with shallower traps in the surface layer [14]. Electron beam irradiation, the other chemical modification method, can generate free radicals and terminal groups on the EP to convert shallow traps into deep traps and elevate flashover performance [63].

Li et al. found that high mobility of charge carriers [82] and increasing the surface flashover voltage [92]. However, the excessively large surface conductivity in zone I increases the leakage current along the spacer surface, which deteriorates surface insulation strength.

For bulk breakdown, Smith et al. and Li et al. concluded that the increased deep trap energy of bulk materials can enhance DC electrical breakdown strength because of the reversed electric field caused by homo-charges and restricted injection depth in the vicinity of the sample–electrode interface [93–95], as shown in Figure 7bd. That is, the dielectric strength of polyethylene can be significantly improved by adding clay nanoparticles [96]. As shown, breakdown strength is closely related to the trap states in the vicinity of the sample–electrode interface but less dependent on traps in the bulk regions far from the electrodes. As a result, interface tailoring techniques such as grafting polar groups by chemical modification or intercalation of polymer or composite layers have been employed to introduce deep traps at the electrode–dielectric interface to inhibit charge injection and improve bulk insulation properties [97–101]. Using these approaches, both flashover voltage and breakdown strength can be effectively improved by interface tailoring techniques.

Chemical modification is thought to be an effective method to tailor trap states in polymers. It is widely accepted that fluorination, ozone treatment and CF₄/air plasma can reduce surface trap depth to accelerate charge dissipation along the material surface to improve flashover voltage [14, 15, 21–24, 30, 61, 63]. An et al. declared that the introduction of fluorine atoms inevitably leads to a significant structural change or disorder that introduces physical defects with shallower traps in the surface layer [14]. Electron beam irradiation, another chemical modification method, can generate free radicals and terminal groups on the EP to convert shallow traps into deep traps and elevate flashover performance [63].

To reduce space charge accumulation in bulk materials and enhance breakdown strength, several interface tailoring methods such as grafting of polar groups by (oxy)-fluorination [97, 98] and intercalation of polymer layers (e.g. low-density polyethylene modified with carbonyl groups [99], fluorinated ethylene propylene copolymer [100] and polyvinyl fluoride [101]) were employed to build blocking layers at the electrode–dielectric interface. Deep traps are thought to be formed in blocking layers that could effectively capture homo-charges and create a reversed electric field. However, it is confusing that some chemical modification methods such as fluorination play opposite roles in surface flashover and charge injection at the electrode–dielectric interface—specifically, charge transport in surface flashover and charge injection processes are promoted and restricted, respectively [14, 97, 98]. For this reason, although some modification methods have been proposed, more theoretical works such as first-principle simulations are needed to understand the underlying mechanism and guide the trap regulation.

Incorporation of inorganic or organic fillers into polymers is another extensively used method to tailor trap distribution in bulk insulation. Composite surface coating is thought to be a flexible method to tailor the interfacial trap states between vacuum/gas/oil–solid and electrode–dielectrics to improve flashover and breakdown strength, respectively. The trap states in composites or coatings depend on several factors such as bandgap, interfacial structure and volume fractions of fillers, as described in Figure 8. A multiregion model is usually used to describe the interfacial region between the polymer matrix and fillers and can be divided into bonded, transient and normal regions [102–104]. A stern layer or interface shell is thought to exist in the bonded region and to form a high-energy barrier for charge injecting the fillers, as shown in Figure 8c–h [103, 104]. Moreover, deep charge traps can be introduced in filler cores or transient regions. Li et al. stated two probable reasons for carriers becoming trapped in the transition region, e.g. reduction of carrier mobility due to collision with defects and local traps capturing charge carriers [104].

Two representative types of traps were introduced based on combinations of nanofillers and polymers: type I such as a PE (10 eV)/MgO (7.8 eV), and type II such as an epoxy (4 eV)/SiO₂ (9 eV) [105]. Figure 8g shows the interface energy diagram of type I. Electrons transport in the conduction band of the polymer in a trap-controlled conduction mode to reach the interfacial region, which can be readily trapped in the transient region. The electrons cannot hop the barrier ΔF₂ at a low electric field but could be injected through the interface shell into the filler core via field emission at high field and then deeply trapped in the conduction band of the fillers, as shown in Figure 8g. For type II, since the bandgap of nanofillers is wider than that of polymers, deep traps cannot be formed in the fillers and thus only exist in the transient region, as depicted in Figure 8e. By comparing Figure 8e,g, we find that much deeper traps can be formed by type I combinations of polymer and fillers, and the trap energy level can be further deepened using narrow-bandgap fillers such as conductive or semi-conductive materials. For instance, a deep trap with an energy level higher than 1.5 eV can be introduced by employing semi-conductive all-organic fillers or graphene [83].

In addition, from the above analysis, surface modification of nanofillers with narrow-bandgap or conductive polymers is a promising method to deepen trap energy for type II fillers [106, 107].

As nanofiller concentration increases, overlapped transient zones are formed by local agglomeration of fillers [103], as shown in Figure 8b. In this circumstance, carriers gain enough energy in the transient region to hop the barrier ΔF₂, which is beneficial for transporting charges and leads to deterioration in insulation performance. This situation is more serious in the type I combination of polymer and fillers because the carriers can readily transfer in the narrow-bandgap fillers after hopping the barrier ΔF₁ in the bonded region, which can be observed in Figure 8b. For this reason, the optimal volume fraction of conductive or semi-conductive fillers is usually much lower than that of wide-bandgap fillers [37, 82]. For type I fillers, Du et al. found that a proper content of nanographene (GR) raises the trap energy and density of EP/GR composite coating, which increases flashover voltage [37]. Zhang et al. introduced fullerene C₆₀ into EP to increase trap density and restrict the mobility of charge carriers [82]. Li et al. found that high-
electron-affinity molecular semiconductors give rise to a large trap energy level of about 1.5 eV, thereby providing high energy density and discharge efficiency of up to 200°C [83]. Many researchers have filled type II fillers such as SiO₂, BN nanosheet and Al₂O₃ into bulk materials to improve the insulation properties of various polymers. It has been found that insulation performance such as breakdown strength and energy density also depend on the local electric field distribution and scattering effects of nanofillers related to various properties of nanofillers, e.g. bandgap, permittivity, shapes (particle, nanowire, nanosheet), volume fraction and distribution (for instance, random, horizontally aligned and vertically aligned) [108–111] that will not be discussed here.

Most existing research has tried to control the internal space charge and improve breakdown strength by filling the entire bulk material with nanofillers [94, 112], as shown in

**FIGURE 8**  Energy diagram at the polymer-nanofillers interface. (a) Schematic of multiregion model. (c) Schematic of the charge distribution around an isolated filler. Energy diagram at the polymer-nanofillers interface for isolated type I (g) and type II (e) fillers. (b) Schematic of overlapped fillers. (d) Schematic of the charge distribution around overlapped fillers. Energy diagram at the polymer-nanofillers interface for overlapped type I (h) and type II (f) fillers. E/C, E/V, and E₀ are the bottom edge of conduction band, the top edge of valence band, and the band gap, respectively.

Figure 9a; uniformly doping fillers while avoiding agglomeration is difficult work. As an alternative approach, deep trap composite coatings can be inserted between the dielectric and electrodes to act as the blocking layer for charge injection due to the reversed electric field generated by trapped charges (see

**FIGURE 9**  Schematic of improving bulk properties by filling nanofillers. (a) Filling nanofillers in the entire bulk material. (b) Depositing a composite blocking layer on the dielectric surface.
Figure 9b). For instance, Teyssedre et al. used an Ag/ SiO, C,H composite layer to control the charge injection of low-density polyethylene [113]. As described above, the type, interfacial structure and volume fraction of fillers can be controlled to optimise the inhibiting effect.

Until now, most works have been concerned with the trap states of composites filled with one kind of filler. In the case of hybrid fillers or hierarchically structured nanofillers, traps may be formed at the interfaces between different fillers. As a result, the trap distribution can also be regulated by tailoring the interface properties between different kinds of fillers, e.g. simultaneously filling wide-bandgap inorganic fillers such as Al2O3 and a conductive filler such as graphene and designing hierarchical structures such as core–satellite and embedded structures, as shown in Figure 10.

4.3 Surface conductivity and permittivity of surface layer

The surface conductivity and permittivity of surface layers have a strong influence on insulation performance by affecting the charge transportation process and electric field distribution, which can be tailored by many methods, e.g. controlling the fluorination time, regulating the materials and thickness of the inorganic coating, and manipulating the type, shape, loading and distribution of nanofillers in the composite coating. These methods have been applied to accelerate the charge dissipation process on spacer surfaces and homogenise the electric field distribution in GIS/GIL.

As described above, chemical modification methods such as fluorination and plasma treatment can increase surface conductivity and promote charge dissipation, thereby increasing flashover voltage [14, 15, 21–24]. Another effective method is depositing non-linear composite coating filled with a high concentration of semi-conductive fillers such as SiC or ZnO [33–35]. Du et al. and Zhang et al. investigated the effects of non-linear coating on surface charge behaviour and flashover voltage [33–35]. They found that the non-linear coating increases the charge carrier mobility, which suppresses charge accumulation and decreases the possibility of occurrence of effective electrons, as shown in Figure 11a. Moreover, the electric field-dependent non-linear conductivity properties of the non-linear coating can homogenise the surface electric field, thus hindering the propagation of surface streamer and contributing to improvement in the flashover voltage [35], as shown in Figure 11. The physical properties and geometric distribution of fillers have a substantial effect on surface conductivity and flashover voltage, so they should be carefully selected when designing the composite coatings. Zhang et al. fabricated a nano-laminar coating with aligned deployment of MMT nanoclay sheets in PVA polymer to increase surface conductivity, thereby improving flashover voltage [74]. This work provides new insight into improving surface conductivity by controlling the orientation and distribution of nanofillers.

Du and Li et al. proposed the concept of SFGMs to build spatially graded distributions of permittivity/conductivity on the insulator surface layer [9, 29, 30]. Without changing the bulk properties, it is feasible to suppress the electric field distortions on the insulator surface and to consequently elevate flashover voltages. Magnetron sputtering and gradient fluorination methods have been used to fabricate the ε-SFGM and σ-SFGM insulators. To maximise the electric field homogenisation effect of the ε-SFGM insulator, the spatially dependent thickness of the BaTiO3 sputtering layer was optimised by an iterative method. During the sputtering process, the sputtering time and layer thickness distributions, namely the permittivity
of the BaTiO$_3$ layer, were controlled by a rotating mask with a designed gap above the insulator [9, 29, 30], as shown in Figure 12. The maximum electric field of the optimal $\varepsilon$-SFGM insulator was reduced by $\sim$70%, and the AC flashover voltage was improved by $\sim$20% in air. With similar procedures, they also fabricated a $\sigma$-SFGM insulator by sputtering ZnO on the insulator [29]. It should be noted that both magnetron sputtering and gradient fluorination methods require complex experimental facilities that restrict their use to industrial insulator applications. As an alternative approach, spray coating is probably more suitable for the industrial fabrication of SFGMs in which the permittivity/conductivity of the surface layer can be tailored by controlling the flow rate, gas pressure and moving speed of the spray gun.

5 | APPLICATIONS OF INTERFACE TAILORING IN IMPROVING INSULATION-RELATED PERFORMANCE

Interface tailoring methods can also be employed to improve other insulation-related properties such as corona/tracking resistance, wettability, adhesiveness of coating layer and ‘stimuli–response’ properties, all of which are discussed in this section.

5.1 | Corona/tracking resistance

It is recognized that the carrier energy in the breakdown process of polymers is relatively small due to the limited free path and low mobility in the bulk, generally with few eV [103]. As a result, the trap is effective in trapping carriers under DC voltage. However, the charged energy in corona/tracking processes calculated by the Boltzmann equation solver BOLSIG+ can reach tens to hundreds eV, which is much higher than that of the traps (usually with few eV) [103]. Under this circumstance, a more compact molecular structure, e.g. a higher degree of cross-linking, crystal structure, and introduction of inorganic fillers, is needed to resist the bombardment of high-energy carriers.

Several methods such as electron beam irradiation, fluorination and incorporation of inorganic fillers have proved effective in improving corona resistance. Gao et al. used a 7.5 MeV electron beam to improve the corona resistance of EP/Al$_2$O$_3$ nanocomposites and found that electron beam irradiation promoted cross-linking reactions in the samples, and therefore, the improved cross-linking structure gives rise to enhanced PD resistance [44]. Li et al. and An et al. found that fluorination treatment could improve corona ageing and tracking properties [45, 46, 114]. A much narrower and thinner
tracking path is formed on the fluorinated samples than on the virgin sample after surface flashover, as shown in Figure 13a. Filling inorganic fillers is another effective method to improve corona resistance, wherein the ‘hard’ fillers play a role in energy dissipation by scattering effect [103], as depicted in Figure 13b. For this reason, the nanocomposites with higher filler content usually exhibit longer failure time, whereas breakdown strength is usually reduced at a high concentration of fillers. To resolve this problem, a thin composite coating film with a high content of inorganic fillers can be used to improve corona/-tracking resistance with potentially little effect on breakdown strength.

### 5.2 Wettability

In a humid and polluted environment, the wettability of insulators has a tremendous influence on flashover voltage due to the adherence of water droplets or contaminants. As a result, hydrophobic surfaces are preferred in these cases, especially for outdoor applications. Young’s, Wenzel’s, and Cassie–Baxter equations have been proposed to explain surface wettability on different surfaces, as shown in Figure 14. It is well recognised that lower surface tension and higher solid materials roughness lead to an increase in the contact angle. It is known that alkyl and fluorine chemical groups such as CH$_2$, CH$_3$, CF$_2$, CH$_2$F and CF$_3$ possess low surface energy, and consequently, polymers containing these groups such as organosilicon and PTFE are generally used as hydrophobic materials [76, 79]. Surface roughness is the second critical factor for improving hydrophobicity. Thabet et al. found that surface roughness, hydrophilic site arrangement and dipole/dipole interactions can be changed by filling different types and concentrations of nanoparticles into polymers to further modify the wettability of nanocomposites [115, 116]. Following these rules, superhydrophobic coatings with water contact angles higher than 150° and sliding angles lower than 10° have

---

**Figure 13** (a) Surfaces of virgin and surface fluorinated samples after flashover test. Reproduced with permission [114]. (b) The scattering effect of nanoparticles on corona ageing [103].

**Figure 14** A liquid droplet on different surfaces: (a) Young’s model; (b) Wenzel’s model; (c) Cassie–Baxter model.
been fabricated by tailoring the chemical composition and creating hierarchical roughness on the surface, thus offering the advantages of water repellance, self-cleaning ability, low ice adhesion strength and delayed freezing time.

Physical modification methods including etching and templating have been used to create hierarchical microscale/nanoscale morphology to fabricate the superhydrophobic surface [57]. A composite coating prepared by spraying, dipping and brushing methods is another flexible way to achieve superhydrophilicity, in which fillers form the hierarchical roughness, and polymers act as binding media [17, 18]. For instance, Lu et al. and Cao et al. developed a universal ‘paint + spray adhesive’ strategy to fabricate superhydrophobic coatings that is applicable to various polymers and microscale/nanoscale fillers [17, 18]. Superhydrophobic coatings using binding polymers such as epoxy [75, 76], thermoplastic elastomer [77, 78], PDMS [79] and supramolecular silicone polymer [80] as well as fillers such as TiO$_2$ [79, 81], silica [75, 76] and carbon nanotubes [77] have been reported. We have fabricated a multifunctional coating by spraying ZnO particles and CNTs dispersed in a PDMS matrix that endowed various dielectric materials with the multifunctionality of high DC flashover strength, a superhydrophobic surface, and self-cleaning capability [117].

Although various methods have been adopted to create the superhydrophobic surface, superhydrophobicity is easily lost under the effects of external stresses such as mechanical force, water immersion and ultraviolet radiation. As a result, developing a superhydrophobic surface with high mechanical robustness or self-healing properties is urgently desired. Deng et al. fabricated a robust superhydrophobic surface by structuring surfaces at two different length scales with a nanostructure design to provide water repellence and a microstructure design to provide mechanical durability [118].

5.3 | Adhesiveness and mechanical durability

The adhesiveness and mechanical durability of coating layers are crucial for the long-term operation of surface tailored insulators. There are two pathways to enhance the adhesiveness between the coating layer and bulk materials, i.e. chemical anchoring and physical attachment [119]. Physical attachment strategies, e.g. supramolecular interaction and metal coordination interaction, involve easy implantation but often suffer from weak and unstable adhesion of coating films. Inspired by natural marine mussels, polydopamine has been used extensively as a universal adhesive group to coat PDA-based polymers onto both organic and inorganic surfaces through both covalent and non-covalent interactions [120, 121]. Various interactions such as hydrogen bonding, coordination, π–π stacking and cation–π interaction can be formed by the catechol groups and benzene rings of PDA [80]. For instance, PDA was introduced into supramolecular silicone polymers to achieve high binding strength on various substrates, as shown in Figure 15a–c [80]. Silanization of hydroxy-rich materials is thought to be an effective approach...
to covalently anchor polymer-based coatings onto diverse solid surfaces, including glass, silicon and ceramics [122]. In this method, different types of functional silanes can be used to modify the surface of these substrates by hydrolysis reaction with the hydroxy group, and then long-chain polymers can be covalently cross-linked with the terminal functional groups in silanes such as amino and epoxy groups. Yang et al. developed a universal coating strategy that attached various epoxy-modified functional polymers onto diverse aminated surfaces via a ‘one-step’ ring-opening reaction [119] in which the reaction between epoxy and amino groups form a covalent interaction, as shown in Figure 15d. Establishing a covalent interaction between the coating layer and substrate is an effective route to enhance the adhesiveness and mechanical durability of coated samples.

Although interface tailoring methods have been extensively applied to improve various insulation properties, adhesiveness and mechanical performance tests of the coating film have not attracted sufficient attention. The adhesiveness and mechanical durability of coating layers can be examined by several methods including sandpaper abrasion tests, the Taber Rotary Abraser test (ASTM D4060), sand dropping test, pencil hardness tester and crosscut standard test (ASTM-D3359-17) [4, 75, 76]. Moreover, the chemical stability of coating films can be tested by UV radiation, immersing the samples in acidic or alkaline solutions and long-term thermal ageing experiments.

5.4 | ‘Stimuli–response’ properties

Many polymers and inorganic materials present stimuli-responsive properties; for instance, the photothermal effect of CNT and PDA particles, the fluorescence luminescence of various materials under UV radiation and the electroluminescent characteristics of ZnS phosphors [123]. The stimulus-response characteristic is essentially an energy-transfer phenomenon. Composite coatings formed by these materials endow the resultant insulators with smart functions that can reversibly respond to external stimuli. These smart coatings present a broad range of potential applications in active anti-icing, power equipment condition monitoring, self-healing coatings and other related areas and have not yet received enough attention. For example, Jiang et al. and Yang et al. prepared sunlight-responsive and robust anti-icing/de-icing coatings by incorporating photothermal SiC/CNTs and nanocarbon fibres, respectively [39, 40]. As can be seen from Figure 16, the maximum surface temperature of prepared coatings rose to about 120°C in tens of seconds, and the spherical ice was melted by the continuous irradiation [39].

5.5 | Summary of applications of interface tailoring to improve insulation performance

In much high electric field equipment, the states of interfaces between different materials, for instance, electrode–dielectrics, vacuum/air/SF6-insulators, and oilpaper (film), have a great influence on most insulation properties. For this reason, interface tailoring methods have been applied to improve various insulation properties such as flashover voltage, breakdown strength, corona/arcing resistance, charge–discharge efficiency and superhydrophobicity. The applications of interface tailoring methods in improving insulation performance are comprehensively summarised in Table 1.
| Microscopic parameters and insulation-related properties | Tailoring methods | Application |
|----------------------------------------------------------|------------------|-------------|
| Charge injection barrier                                 | Depositing wide-bandgap layer: | • Inhibiting space charge accumulation |
|                                                          | • Raising breakdown strength | |
|                                                          | • Inorganic layer h-BN, SiO$_2$, Al$_2$O$_3$: CVD, PECVD, magnetron sputtering | • Reducing the electrical conduction loss |
|                                                          | • Organic layer: magnetron sputtering, fluorination, CF$_4$ dielectric barrier discharge | • Improving the energy density and charge–discharge efficiency |
| Charge trap distribution                                  | Chemical modification: | • Increasing flashover strength at vacuum/gas/oil–solid interfaces (surface trap distribution) |
|                                                          | • Fluorination, ozone treatment and CF$_4$/air plasma to lower surface trap depth | • Improving breakdown strength (trap states at the electrode–dielectric interface) |
|                                                          | • Electron beam irradiation to deepen surface trap depth | • Inhibiting space charge accumulation (trap states at the electrode–dielectric interface) |
|                                                          | • Grafting of polar groups and intercalation of polymer layers to introduce deep traps at electrode–dielectric interface | |
| Inorganic coating:                                       | • Magnetron sputtering: Cr$_2$O$_3$ etc. | • Improving the energy density and charge–discharge efficiency (trap states at the electrode–dielectric interface) |
| Composite coating:                                       | • Incorporating narrow-bandgap nanofillers (conductive or semi-conductive) to form deep traps in the core fillers | |
|                                                          | • Incorporating wide-bandgap nanofillers to introduce deep traps at the nanofiller-matrix interfaces | |
|                                                          | • Adopting hybrid fillers or hierarchically structured nanofillers | |
| Surface conductivity and permittivity of surface layer   | Chemical modification: | • Increasing flashover strength at vacuum/gas/oil–solid interfaces |
|                                                          | • Fluorination, ozone treatment and plasma treatment to increase surface conductivity | |
| Inorganic coating:                                       | • Magnetron sputtering of BaTiO$_3$ and ZnO to regulate the permittivity and conductivity, respectively | • Fabricating SFGMs to homogenise electric field distribution |
| Composite coating:                                       | • Manipulating the type, shape, loading and distribution of fillers in the composite coating, e.g. EP/SiC coating | • Suppressing surface charge accumulation |
| Corona/tracking resistance                               | • Chemical modification: fluorination, electron beam irradiation | • Breaking the trade-off between corona/tracking resistance and breakdown strength |
| Wettability                                               | Composite coating | • Fabricating superhydrophobic surfaces with the advantages of water repellance, self-cleaning ability, low ice adhesion strength and delayed freezing time |
| Mechanical durability and adhesiveness                    | • Physical modification: etching, templating | • Strengthen the mechanical durability and adhesiveness of coating film |
|                                                          | • Chemical modification: plasma treatment | |
|                                                          | • Composite coating: spraying, dipping, brushing | |
| Stimuli–response properties                               | • Incorporating PDA in coating film | • Active anti-icing, power equipment condition monitoring, self-healing coatings, and other related areas |
|                                                          | • Establishing a covalent interaction between coating layer and substrate | |
|                                                          | • Composite coating composed of polymers and inorganic fillers with stimuli-responsive properties. | |

Abbreviations: CVD, chemical vapour deposition; PDA, polydopamine; PECVD, plasma-enhanced chemical vapour deposition; SFGM, Surface functionally graded materials.
CONCLUSIONS AND FUTURE PERSPECTIVES

Various interface tailoring methods such as physical and chemical surface modifications and inorganic, organic and composite coatings have been applied to improve various insulation properties. Insulators modified with interface tailoring methods have been shown to possess great improvements in flashover voltage, breakdown strength, corona/arcing resistance, charge–discharge efficiency and superhydrophobicity in comparison with pristine samples. Microscopic parameters such as charge injection barrier, surface trap distribution, surface conductivity, permittivity and surface morphology can be flexibly tailored by several methods, e.g. controlling fluorination time, regulating the materials and thickness of the inorganic coating, and changing the type, shape, loading and distribution of nanofillers in the composite coating. Although some methods such as fluorination and magnetron sputtering are effective in improving interfacial properties, a scaled reaction vessel or complex experimental equipment is required, which restricts their use to industrial applications. As a result, alternative methods such as spray coating can be attempted with similar applications such as the fabrication of SFGM.

By reasonably designing the preparation scheme, interface tailoring techniques can be extended to more applications, including areas such as the following. (1) By independently tailoring the interfacial and bulk states, it is possible to simultaneously improve multiple properties such as corona resistance and breakdown strength, which is difficult to achieve by the single modification method. (2) Multifunctional coating can be achieved by reasonably choosing the type and volume fraction of fillers in the composite coating, and multiple microparameters such as roughness, surface conductivity and PD resistance can be simultaneously regulated to improve multiple insulation performance. (3) Rational design of interfacial states, by which molecular simulations such as quantum chemical computation can be used to understand the underlying mechanism and structure–property relationship of interface tailoring techniques, and high-throughput computation is probably an efficient approach for rationally designing interfacial states. (4) Stimuli–response smart coatings with different functions can be fabricated using polymers and fillers with stimuli–response properties that present broad prospects for potential applications in active anti-icing, power equipment condition monitoring, self-healing coatings and related areas.

ACKNOWLEDGEMENTS

This work is supported by the National Natural Science Foundation of China (52007198, 51827809, 11775175), the Natural Science Foundation of Shandong Province of China (ZR2019QEE014) and the Fundamental Research Funds for the Central Universities (19 CX02015 A).

ORCID

Mingxiao Zhu https://orcid.org/0000-0001-6154-7147
Guochang Li https://orcid.org/0000-0002-8268-0729

REFERENCES

1. Miller, H.C.: Flashover of insulators in vacuum: the last twenty years. IEEE Trans. Dielect. Insul. 22, 3641–3657 (2015)
2. Zhang, G.-J., et al.: Pulsed flashover across a solid dielectric in vacuum. IEEE Trans. Dielect. Insul. 25(6), 2321–2339 (2018)
3. Gubanski, S.M.: Modern outdoor insulation - concerns and challenges. IEEE Electr. Insul. Mag. 21, 5–11 (2005)
4. Arshad, et al.: Properties and applications of superhydrophobic coatings in high voltage outdoor insulation: a review. IEEE Trans. Dielectr. Electr. Insul. 24, 3630–3646 (2017)
5. Li, C., et al.: Understanding surface charge accumulation and surface flashover on spacers in compressed gas insulation. IEEE Trans. Dielectr. Electr. Insul. 25, 1151–1166 (2018)
6. Amer, M., et al.: New experimental study on the DC flashover voltage of polymer insulators: combined effect of surface charges and air humidity. High. Volt. 4(4), 316–323 (2019)
7. Qu, G., et al.: Substantial improvement of the dielectric strength of cellulose-liquid composites: effects of traps at the nanoscale interface, J. Phys. Chem. Lett. 11, 1881–1889 (2020)
8. Hao, J., et al.: Preparation nano-structure polytetrafluoroethylene (PTFE) functional film on the cellulose insulation polymer and its effect on the breakdown voltage and hydrophobicity properties. Mater. 11, 851 (2018)
9. Li, J., et al.: Promising functional graded materials for compact gaseous insulated switchgears/pipelines. High. Volt. 5(3), 231–240 (2020)
10. Kumara, S., et al.: DC flashover characteristics of a polymeric insulator in presence of surface charges. IEEE Trans. Dielectr. Electr. Insul. 19(3), 1084–1090 (2012)
11. Azizi, A., et al.: High-performance polymers sandwiched with chemical vapour deposited hexagonal boron nitrides as scalable high-temperature dielectric materials. Adv. Mater. 29, 1701864 (2017)
12. Sato, M., Kamada, A., Hidaka, K.: First-principles studies of carrier injection in polyethylene (PE) and ethylene-vinyl acetate copolymer (EVA) oligomers. IEEE Trans. Dielectr. Electr. Insul. 24(1), 574–582 (2017)
13. Xue, J.-Y., et al.: The regulation mechanism of SiC/epoxy coatings on surface charge behaviour and flashover performance of epoxy/alumina spacers. J. Phys. D. Appl. Phys. 52, 405502 (2019)
14. Que, L., et al.: Improved DC flashover performance of epoxy insulators in SF6 gas by direct fluorination. IEEE Trans. Dielectr. Electr. Insul. 24, 1153–1161 (2017)
15. Li, C., He, J., Hu, J.: Surface morphology and electrical characteristics of direct fluorinated epoxy-resin/alumina composite. IEEE Trans. Dielectr. Insul. 23, 3071–3077 (2016)
16. Nguyen-Tri, P., et al.: Recent progress in the preparation, properties and applications of superhydrophobic nano-based coatings and surfaces: a review. Prog. Org. Coating. 132, 235–256 (2019)
17. Lu, Y., et al.: Robust self-cleaning surfaces that function when exposed to either air or oil. Sci. 347, 1132–1135 (2015)
18. Li, Z., et al.: Surface-embedding of functional micro-/nanoparticles for achieving versatile superhydrophobic interfaces. Matter. 1, 661–673 (2020)
19. Cheng, S., et al.: Polymide films coated by magnetron sputtered boron nitride for high-temperature capacitor dielectrics. IEEE Trans. Dielectr. Electr. Insul. 27(2), 498–503 (2020)
20. Zhou, Y., et al.: A scalable, high-throughput, and environmentally benign approach to polymer dielectrics exhibiting significantly improved capacitive performance at high temperatures. Adv. Mater. 30, 1805672 (2018)
21. Guan, H., et al.: Mechanisms of surface charge dissipation of silicone rubber enhanced by dielectric barrier discharge plasma treatments. J. Appl. Phys. 126, 093301 (2019)
22. Fang, Z., et al.: Hydrophobic surface modification of epoxy resin using an atmospheric pressure plasma jet array. IEEE Trans. Dielectr. Electr. Insul. 23, 2288–2293 (2016)
23. Shao, T., et al.: Surface modification of epoxy using an atmospheric pressure dielectric barrier discharge to accelerate surface charge dissipation. IEEE Trans. Dielectr. Electr. Insul. 24, 1557–1565 (2017)
70. Wang, C., et al.: UV-cured nanocomposite coating for surface charging mitigation and breakdown strength enhancement: exploring the combination of surface topographical structure and permittivity. RSC Adv. 10, 16422–16430 (2020)
71. Liu, G., et al.: Sandwich-structured polymers with electrosprun boron nitrides layers as high-temperature energy storage dielectrics. Chem. Eng. J. 389(1), 124443 (2020)
72. Donzel, L., Greuter, F., Christen, T.: Nonlinear resistive electric field grading Part 2: materials and applications. IEEE Electr. Insul. Mag. 27(2), 18–29 (2011)
73. Volpov, E.: Dielectric strength coordination and generalized spacer design rules for HVAC/DC SF/sub 6/gas insulated systems. IEEE Trans. Dielect. Electr. Insul. 11(6), 949–963 (2004)
74. Zhang, B., et al.: A self-assembled, nacre-nimic, nano-laminar structure as a superior charge dissipation coating on insulators for HVDC gas-insulated systems. Nanoscale. 11, 18046 (2019)
75. Elzaabalawy, A., Meguid, S.A.: Development of novel superhydrophobic coatings using siloxane-modified epoxy nanocomposites. Chem. Eng. J. 398, 125403 (2020)
76. Zhang, X., et al.: Robust superhydrophobic epoxy composite coating prepared by dual interfacial enhancement. Chem. Eng. J. 371, 276–285 (2019)
77. Li, L., et al.: A superhydrophobic smart coating for wearable sensing electronics. Adv. Mater. 29, 1702517 (2017)
78. Wang, F., et al.: A superhydrophobic coating to create multi-functional materials with mechanical/chemical/physical robustness. Chem. Eng. J. 381, 122539 (2020)
79. Liu, J., et al.: Elastic superhydrophobic and photocatalytic active films used as blood repellent dressing. Adv. Mater. 32, 1900008 (2020)
80. Cao, C., et al.: Sprayable superhydrophobic coating with high processability and rapid damage-healing nature. Chem. Eng. J. 392, 124834 (2020)
81. Liu, M., et al.: Inorganic adhesives for robust superwetting surfaces. ACS Nano. 11, 1113–1119 (2017)
82. Zhang, B., et al.: Surface charge accumulation and suppression on fullerene-filled epoxy-resin insulator under DC voltage. IEEE Trans. Dielectr. Electr. Insul. 25, 2011–2019 (2018)
83. Yuan, C., et al.: Polymer/molecular semiconductor all-organic composites for high-temperature dielectric energy storage. Nat. Commun. 11, 3919 (2020)
84. Zhao, A.X., et al.: Surface modification of XLPE films by CF4 DBD for dielectric properties. AIP Adv. 9, 015102 (2019)
85. Chen, X., et al.: First-principle investigation of the charge injection barriers of polyethylene and polytetrafluoroethylene oligomers. J. Appl. Phys. 126, 035101 (2019)
86. Teyssedre, G., Laurent, C.: Charge transport modelling in insulating polymers: from molecular to macroscopic scale. IEEE Trans. Dielectr. Electr. Insul. 12(5), 857–875 (2005)
87. Huzayyin, A., Boggs, S., Ramprasad, R.: Quantum mechanical study of charge injection at the interface of polyethylene and platinum. In: Annual Report Conference on Electrical Insulation and Dielectric Phenomena. 800–803 (2011)
88. Unge, M., Christier, T., Christen, T.: Space charges and deep traps in polyethylene—Ab initio simulations of chemical impurities and defects. In: IEEE International Conference on Solid Dielectrics, 935–939 (2013)
89. El-shahat, M., Huzayyin, A., Anis, H.: Effect of morphological deformation on barriers to charge injection at the interface of copper and polyethylene. IEEE Trans. Dielectr. Electr. Insul. 25(6), 2178–2182 (2018)
90. El-Shahat, M., Huzayyin, A., Anis, H.: Effect of chemical impurities on charge injection barriers at the interface of Copper and polyethylene. IEEE Trans. Dielectr. Electr. Insul. 26(2), 642–647 (2019)
91. Simmons, J.G., Tan, M.C.: Theory of isothermal currents and the direct determination of trap parameters in semiconductor devices and insulators containing arbitrary trap distributions. Phys. Rev. B. 7(8), 3706–3715 (1973)
92. Li, S.: Improvement of surface flashover in vacuum. High Volt. 5(2), 122–133 (2020)
93. Du, B., et al.: Carrier mobility and trap distribution dependent flashover characteristics of epoxy resin. IET Gener. Transm. Dis. 12(2), 366–471 (2018)
94. Li, S., et al.: Linking traps to dielectric breakdown through charge dynamics for polymer nanocomposites. IEEE Trans. Dielectr. Electr. Insul. 23, 2777–2785 (2016)
95. Smith, R., et al.: The mechanisms leading to the useful electrical properties of polymer nanodielectrics. IEEE Trans. Dielectr. Electr. Insul. 15(1), 187–196 (2008)
96. Thabet, A.: Experimental enhancement for dielectric strength of polyethylene insulation materials using cost-feWER nanoparticles. Int. J. Elec. Power. 64, 469–475 (2015)
97. An, Z., et al.: Correlation between space charge accumulation in polyethylene and its fluorinated surface layer characteristics. J. Phys. D. Appl. Phys. 45, 035302 (2012)
98. Teyssedre, G., et al.: Interface tailoring for charge injection control in polyethylene. IEEE Trans. Dielectr. Electr. Insul. 24, 1319–1330 (2017)
99. Tanaka, Y., et al.: Space charge distribution in low-density polyethylene with charge-injection suppression layers. J. Phys. D. Appl. Phys. 28, 1232–1238 (1995)
100. Hori, T., et al.: Space charge distribution in low-density polyethylene with blocking layer. In: IEEE Conference on Electrical Insulation and Dielectric Phenomena. 197–200 (2003)
101. Xia, J., et al.: Blocking effect of PVF on space charge injection into low density polyethylene. In: Proceedings of International Conference on Solid Dielectrics, Potsdam 379–382 (2010)
102. Tanaka, T., et al.: Proposal of a multi-core model for polymer nanocomposite dielectrics. IEEE Trans. Dielectr. Electr. Insul. 12(4), 669–681 (2005)
103. Li, S., Xie, D., Lei, Q.: Understanding insulation failure of nanodielectrics: tailoring carrier energy. High, Volt. 5(6), 643–649 (2020)
104. Min, D., et al.: The coupling effect of interfacial traps and molecular motion on the electrical breakdown in polyethylene nanocomposites. Compos. Sci. Technol. 184(10), 107873 (2020)
105. Tanaka, T.: A quantum dot model for nanoparticles in polymer nanocomposites. IEEE Trans. Dielectr. Electr. Insul. 26(1), 276–283 (2019)
106. Zhou, Y., et al.: Interface-modulated nanocomposites based on polypropylene for high-temperature energy storage. Energy Stor. Mat. 28, 255–263 (2020)
107. Li, S., et al.: Tailoring interfacial compatibility and electrical breakdown properties in polypropylene based composites by surface functionalised POSS. Appl. Surf. Sci. 471(1), 451–458 (2019)
108. Ai, D., et al.: Tuning nanofillers in situ prepared polimide nanocomposites for high-temperature capacitive energy storage. Adv. Energy Mater. 10, 1903881 (2020)
109. Li, H., et al.: Enabling high-energy-density high-efficiency ferroelectric polymer nanocomposites with rationally designed nanofillers. Adv. Funct. Mater. 31, 2006739 (2020)
110. Huang, X., et al.: High-k polymer nanocomposites with 1D filler for dielectric and energy storage applications. Prog. Mater. Sci. 100, 187–225 (2019)
111. Shen, Z.H., et al.: Phase-field modelling and machine learning of electric-thermal-mechanical breakdown of polymer-based dielectrics. Nat. Commun. 10, 1843 (2019)
112. Diaham, S.: Modulation of the dielectric breakdown strength in polyimide nanocomposites by deep traps tailoring in interphase regions. IEEE Trans. Dielectr. Electr. Insul. 26(1), 247–252 (2019)
113. Milliere, L., et al.: Silver nanoparticles as a key feature of a plasma polymer composite layer in mitigation of charge injection into polyethylene under DC stress. J. Phys. D. Appl. Phys. 49, 015304 (2015)
114. An, Z., et al.: Improved flashover performance and tracking resistance of silicone rubber by direct fluorination. J. Appl. Polym. Sci. 137(15), 48556 (2020)
115. Thabet, A., Elshahed, A.A.: Controlling on attraction forces of water droplets on surfaces of polypropylene nanocomposites coatings. Trans. Electr. Electron. Mat. J. 19(5), 387–395 (2018)
116. Thabet, A., Elnahwaleed, A.A.: Improvement of surface energy properties of PVC nanocomposites for enhancing electrical applications. Measurement. 110, 78–83 (2017)
117. Zhu, M-X., et al.: Superhydrophobic and high-flashover-strength coating for HVDC insulating system. Chem. Eng. J. 404, 126476 (2021)
118. Wang, D., et al.: Design of robust superhydrophobic surfaces. Nature. 582, 55–59 (2020)
119. Mao, S., et al.: A universal coating strategy for controllable functionalised polymer surfaces. Adv. Funct. Mater. 30, 2004633 (2020)
120. Xie, C., et al.: Mussel-inspired hydrogels for self-adhesive bioelectronics. Adv. Funct. Mater. 30, 1909954 (2020)
121. Kang, S.M., et al.: One-step multipurpose surface functionalisation by adhesive catecholamine. Adv. Funct. Mater. 22, 2949–2955 (2012)
122. Yuk, H., et al.: Tough bonding of hydrogels to diverse non-porous surfaces. Nat. Mater. 15, 190–196 (2016)
123. Hu, L., et al.: Harnessing the power of stimuli-responsive polymers for actuation. Adv. Funct. Mater. 30, 1903471 (2020)

How to cite this article: Zhu, M., Xue, J., Wei, Y., Li, G., Zhang, G. Review of interface tailoring techniques and applications to improve insulation performance. High Voltage. 2021;1–21. https://doi.org/10.1049/hve2.12094