

Polypropylene nanocomposite for power equipment: a review

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Abstract: Polypropylene (PP), with high breakdown strength, low dissipation and good processability, is one of the most widely used dielectric material for power equipment, especially in power capacitors and power cables. The improvement of PP-based dielectric material can benefit the properties enhancement of power capacitors and cables, and thus to meet with the rapid development of the power system. Nanocomposite provided a promising orientation to reach the target and recent research approaches of PP nanocomposite for power equipment were reviewed in this paper. In this paper, we linked the nanofillers to the improved properties of PP nanocomposite, and categorised the research works into nanoclay/PP composites, metal oxide/PP nanocomposite, conductive particles/PP nanocomposite, and PP core-shell nanocomposites chronologically, corresponding to the enhanced thermal and mechanical property, breakdown strength property and energy storage property, respectively. Based on the achieved approaches, prospective for future research was proposed, providing a worth-considering direction for the future work.

1 Introduction

It is commonly agreed that development of nanocomposite greatly diversifies the application of dielectric, for fillers in nanoscale can effectively improve the performance including thermal, mechanical and electrical properties compared with conventional dielectric material [1–4]. As early as in 1988, a US patent has already issued, showing enhanced corona-resistance of epoxy resin with the addition of organoaluminate or organosilicate as insulation material [5]. Afterwards, Lewis introduced a landmark theoretical work in 1994, which is now generally quoted as the beginning of the nanodielectrics initiative [6]. Then, possibilities of nanodielectrics development were highlighted by Nelson *et al.* in 2002 [7], their experimental data interested the attention worldwide and officially announced the advent of nanodielectrics. For dielectric material, nanocomposite is commonly defined as the conventional polymer/nanofiller system, where nanofillers homogeneously disperse in organic polymer matrix, leading to improvement of material properties [8, 9]. With continuous development of nanocomposite, plenty of achievements of nanocomposite for power equipment have been gained, particularly; XLPE/MgO nanocomposite submarine cable has been fabricated in Japan [10]. Thus, nanocomposite is considered to be the most promising orientation to corporately enhance different properties of dielectrics [11–14].

Additionally, developments of nanocomposite for the application of power equipment have been achieved these years, such as epoxy nanocomposite for electric motors, polyethylene (PE) for the power cable, and PP for power capacitors, etc. [15–17]. For epoxy resin, Imai *et al.* [18] prepared epoxy/modified layered silicate, which exhibited enhanced thermal, mechanical, insulating and dielectric properties compared with pure epoxy resin, Li *et al.* [19] found that a slight filler of Al₂O₃ in epoxy resin can promote electrical strength than pure epoxy resin. In addition, it was found that even conduction nanofiller can also improve breakdown strength, Wang *et al.* [20] presented that epoxy/nanosilver nanocomposite showed an increase at a slight filler loading. Also, for low density PE (LDPE), it was found that appropriate Al₂O₃ filler loading in LDPE can traumatically improve the permittivity and breakdown properties [21], and MgO nanofiller in LDPE can effectively increase volume resistivity and

promote breakdown strength [22]. For PP, Cao *et al.* [23] prepared PP/MgO nanocomposite, the DC breakdown strength of which increased apparently with 1 wt% nano-MgO loaded, and Takala *et al.* [24] found that PP/silica nanocomposite with 5 wt% filler content has better DC and AC breakdown strength compared with neat PP.

Specialised for PP, with considerable high breakdown strength and relatively low dielectric losses [25, 26], has manifested itself as the dominant dielectric materials for power capacitors. Meanwhile, PP has drawn more and more attention to the application of power cable and cable accessories since it is easy-processing and more environmentally friendly than XLPE [27, 28]. As the rapid development of power system, power equipment is required to exhibit enhanced properties. For instance, higher permittivity of PP film should be gained to satisfy the promotion of energy density of power capacitors, and for cables applications, the mechanical property and better stability to operation stresses of PP are urgencies to be settled.

Thus, it can be concluded that high permittivity, required for high energy storage, and superior electrical strength, required for operating stability, are two key factors that need to be reinforced when applying for real occasions [29, 30]. As introduced previously, PP is the good matrix with excellent properties regarding two aspects. However, PP nanocomposites can further improve the properties of PP to some extent, thus it draws broad attention. To achieve this goal, extensive research works have been carried out by introducing nanofillers such as nanoclay, metal oxide, high *k* material nanoparticles and so on. Good experimental results including permittivity, dielectric loss, space charge, conductivity, breakdown, electrical tree, corona resistance, etc. were obtained [12, 31–33], and such improved properties are considered to result from an extensive interphase between the polymer matrix and nanofillers. As a result, several models have been raised to physically illustrate the effect of interphase.

Double-layer structure model, proposed by Lewis [34, 35], pointed that each atom and molecule in the interfacial area can be interacting with its surroundings by a combination of both short and long range forces, however, this model did not provide a description regarding physical processes at the interfacial area.

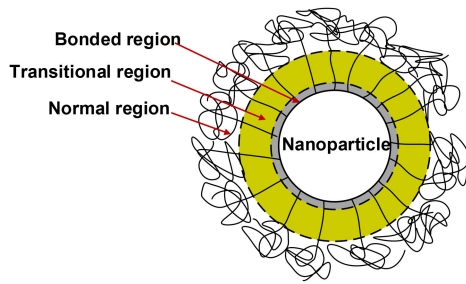


Fig. 1 Multi-region structure model of polymer nanocomposite dielectrics [31]

Then, the multi-core model was a rather complex and flexible theoretical construct, proposed by Tanaka *et al.* [12, 33], he pointed that spherical nanoparticles of several tens of nm diameter are homogeneously dispersed in a distance similar to the diameter, this model presented that nanoparticle sphere consists of a bonded layer, bound layer and a loose layer, where an electric double layer overlapping the former three layers was also considered. Interactions of the aspherical inorganic particle with the surroundings, Li *et al.* [19, 31, 36] concluded the relations between short-time breakdown properties (electrical breakdown and flashover) as well as long-time degradation properties and nanofiller type, particle content, cohesive energy in the polymer matrix. Based on the conclusion, they proposed a multi-region model, which consisted of bonded, normal and transition regions, as shown in Fig. 1. Abundant unsaturated bonds, hydrogen and organic groups exist on the surface of particles so that particles can interact with molecular chains of the polymer matrix by covalent, ionic and hydrogen bonds. The tight junction area, extending about 1 nm outside the surface of the nanoparticle, was bonded region. In this region, interaction strength between nanofillers and polymer molecular chain was determined by particle surface state, polarization and matrix initial property together. Namely, interaction strength in bonded region will be weak if without being treated by coupling reagent, particle surface lacks hydrophilic organic groups. On the contrary, interaction strength will be strong correspondingly if the particle surface is treated with proper coupling reagent.

Compared with the model raised by Tanaka, the most visible different feature is on clarification on alternation effect of shallow and deep traps. By combining with the model mentioned, deep traps and shallow traps can be figured out, where different kinds of traps showed dominate effect at various nanofiller content, lots of phenomena thus can be explained from the microscopic perspective. Trap distribution and effect is regarded as a main factor of charge transport property, which may bring contributions to macroscopic electrical behaviour. It was obvious that this model provided a new perspective to investigate mechanism of performance improvement with a deep insight.

Different kinds of nanofillers, with different dielectric constant, conductivity, morphology etc. were employed in the PP polymer and consequently introduce different interfaces with varies trap characteristics. So how to link the kinds of nanofillers to the expected properties is the key issue for the study of PP nanocomposites. In this review, we focused on nanoclay, metal oxide and high k material (such as carbon nanotube (CNT), graphene and metal), correspond to promotion on thermal and mechanical properties, breakdown strength property and energy storage property respectively.

For thermal and mechanical properties, intensive researches were conducted on PP-nanoclay [37]. The mechanical properties of PP-based nanocomposites containing 1, 3, 5 and 7 wt% nanoclay have been studied by Liu and Wu [38]. The tensile strength and tensile modulus were enhanced with increasing nanofiller content from 1 to 5 wt%, and the trend was weakened when the content is beyond 5 wt%.

However, as mentioned above, researchers gradually realized that promotion of thermal and mechanical properties cannot meet up with the demand of power capacitors, thus dielectric properties including permittivity and breakdown field are required to be

enhanced. Then oxide gradually came into the sight. Li *et al.* [31] summarized the dielectric breakdown characteristics with different filler content, type and size, and interface region model is proposed to interpret the dielectric breakdown mechanism. Zha *et al.* [39] found that the nanocomposites with 0.5 phr surface-treated MgO effectively suppressed the space charge accumulation compared to PP/SEBS blends and improved its breakdown strength. It was also found that the charge transport and space charge suppression in the PP nanocomposites were closely related to the different structure of ZnO [40].

In addition, with the advent of new material, more options regarding filler election were considered. Yu *et al.* [41] showed that the incorporation of multi-walled nanotube (MWNT) greatly increased the dielectric permittivity of PP/BT (barium titanate) nanocomposites, through the surface medication of MWNT, the percolation threshold was reduced to 2–3 wt%, ϵ_r was greatly enhanced from 5 to 15 at 10^2 Hz with 2 wt% m-MWNT. Polshnikov *et al.* [42] showed that the dielectric constant of PP/graphene nanocomposites was greater than 30 throughout the measured frequency range with 2.9 vol% GNP. However, the high permittivity of conductive nanocomposite was usually accompanied with the large dielectric loss, because of the high leakage current which arises from direct contacts between conducting fillers in composites near the percolation threshold. A challenge in achieving high permittivity while retaining low loss was to prevent contact between conductive fillers in the polymer matrix by confining fillers within individual interface layers and improved the dispersion of conductive fillers in the polymer.

Furthermore, it was noticed that, apart from the component of nanocomposite, the structure also brought contributions to the performance of PP nanocomposite, for an appropriate gradient of permittivity and a mean dispersion especial attract researchers' attention. Lanagan and co-authors, Marks *et al.* have done an array of researches on dielectric properties and energy storage of PP nanocomposites with core-shell nanostructures [43–46]. A high dielectric constant was obtained and relatively high energy storage density of PP/BT@Al₂O₃ nanocomposites is estimated as high as 9.4 J/cm³ [43]. Furthermore, the same core materials with Al₂O₃ shell of different thickness introduced into PP were studied. The dielectric losses were dramatically suppressed with the increase of the shell thickness while the dielectric constant kept at the same level.

The objective of this paper is to give an overview of the researches carried out over the past years that have contributed to the development of nanocomposite for power equipment in a broad sense. With the consideration of linking the nanofiller to the enhanced properties of PP nanocomposite, we summarized the different phases of nanocomposite development, which can be categorized into four parts, namely nanoclay/PP composites, metal oxide/PP nanocomposite, conductive particles/PP nanodielectric materials, and PP core-shell nanocomposites. Based on the past investigation work and current research status, we also proposed some perspectives for future research, providing worth-considering directions for the future work.

2 Development and application of PP nanocomposite

2.1 Nanoclay/PP composites

Nanoclay have been most widely investigated in polymer-based nanocomposites because the clay materials could be easily obtained and surface modification was also easier than other particles. The inorganic exchange cations in the galleries of native clay silicate structure by surfactants could improve the compatibility of nonorganic silicate and a hydrophobic polymer. The electrical, thermal, or mechanical properties of the polymer could be improved by nanoclay filled.

Nanoclay was a kind of phyllosilicates, also called layered silicates. A silicate consisted of Si and O (base formula SiO₄), formed a tetrahedral structure. Since each tetrahedral had an excess of negative net electrical charge, the silicate had some metal cations to achieve electrical neutrality. These metals, such as Fe,

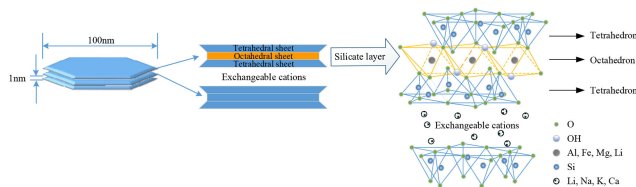


Fig. 2 Structure of 2:1 layered silicate

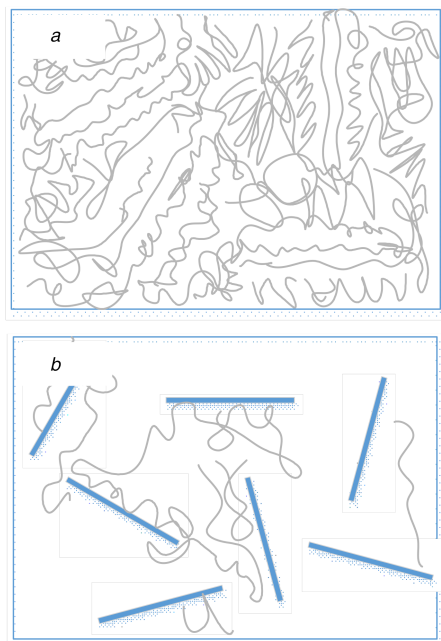


Fig. 3 Schematic illustration of (a) Intercalated nanocomposites, (b) Exfoliated nanocomposites

Mg, K, Na and Ca had the fundamental purpose to bind together the different silicate tetrahedral structures [47]. The typical structure of phyllosilicates was two-dimensional layers where two external tips of silica tetrahedrons were fused by a central octahedral sheet of alumina, as shown in Fig. 2 [48].

The layered structure of montmorillonite (MMT) was the most common layered silicates used in nanocomposites dielectric. The compound of MMT was a centre sheet of Al–O octahedral and two Si–O tetrahedrons. The ions of Na⁺, K⁺, or Ca⁺ were existing in the layers to balance the excess negative charge. As the layers were kept together by relatively weak forces, polar molecules could penetrate in the interlayer gap and swell the interlayer distance [49, 50]. The originally layered silicates were hydrophilic and could be dispersed only in hydrophilic polymers. A modification could transform nanoclay to hydrophobicity, thus miscible with more polymers [51–54]. The intercalated and exfoliated nanocomposites were the two different types of polymer/layered nanocomposites, see Fig. 3 [55]. In the exfoliated nanocomposites, individual clay lamellae were completely separated in a continuous polymer matrix. The average distance of lamellae depended on the clay loading, and usually content of clay was low (<3 wt%) in exfoliated nanocomposites. Intercalated composites were characterised by the polymer chains inserting into the interlayer. A distance of interlayer silicate increased and the piled structure was maintained in the clay. Alternative polymeric and inorganic layers were well-ordered in the multilayer structure. Nanocomposites consisted of non-polar polymer (e.g. PE, PP) and clay often had the intercalated structure.

The intercalated nanocomposite of PP/clay was firstly successfully prepared by Usuki *et al.* [56] and then nanoclay became an important filler to improve PP properties. Four common techniques have been employed to prepare the polymer nanocomposites, including the in-situ polymerisation, the solvent approach, the sol–gel method and the melt blending. In the preparation of PP/clay nanocomposites, the melt blending, i.e. melt interaction was an attractive method, especially in a commercial

generation. In the melt interaction method, the polymer was first melted at high temperature (i.e. higher than the melting temperature of PP) and the filler was then blended with the polymer melt under shear. This technique had an advantage that no solvent was required for the nanocomposite synthesis. The polymer could intercalate between the interlayers if the silicate surface was modified in some way. What's more, high temperature (>200°C) could improve homogeneous mixing, but it was inevitable to lead to the ageing process of surface modifier and polymer chains, hence temperature determination also needed to be paid attention [57]. As this method was environmentally friendly and did not require the usage of large amounts of solvents, and also owing to its simplicity and economic viability, the melt intercalation method had been widely used for the synthesis of polymer nanocomposites with a large number of polymer materials [58].

In early research of PP/clay nanocomposites, thermal and mechanical properties were concerned. Those properties of the nanocomposites were better than pure polymer. Improvements of nanocomposites, with a higher modulus, were more stable under the action of heat and strength. The mechanical properties of PP-based nanocomposites containing 1, 3, 5 and 7 wt% nanoclay were studied by Liu and Wu. The tensile strength and tensile modulus were enhanced with increasing nanofiller content from 1 to 5 wt%, and the trend was weakened when the content beyond 5 wt% [38]. In the test of dynamic mechanical analysis (DMA), nanocomposites with different nanoclay contents showed enhancement of the moduli over the investigated temperature range, which indicated the plastic and elastic responses of PP towards deformation were influenced by nanoclay [59]. The thermal properties of PP-based nanocomposites included heat distortion temperature (HDT) and thermal stability. HDT was the retention of a polymeric material in applied heat and load. Most of the studies reported the nanoclay in the PP matrix promoted a higher HDT [60]. The improvement of HDT originated from the mechanical stability since the melting temperature of nanocomposites did not show the obvious increasing trend. Volatile products caused weight loss at high temperature. The inorganic clay acted as a superior insulator and mass transport barrier, which improved the thermal stability of nanocomposites and mainly assisted in the formation after thermal decomposition. The incorporation of clay into the nanocomposites was the significant reason for thermal stability flammability [61].

To improve the dielectric properties, nanoclay was also introduced into the PP matrix. The AC breakdown strength and resistance to partial discharges were significantly improved with 1, 2, 4, 8 wt% contents of synthetic and natural nanoclay. The addition of nanoscale synthetic nanoclay to PP resulted in a moderate, up to ~12% increase in ac breakdown strength. At the partial discharge voltage of 9.7 kV, the mean times of breakdown of composites with 2 wt% nanoclay were about 16 h, while it was only 0.032 h for PP. The DC conductivity of nanocomposites was higher than unfilled PP. Dielectric losses were increased by nanoclay filled over a broad frequency and temperature ranges, and the composite with natural clay showed higher losses than the one containing synthetic clay at higher frequencies and temperatures [62, 63]. After 10 kV/mm DC electrical field applied for 75 min, more positive heterocharge layer remained in vicinity of the cathode in composites than PP. The increase of space charge accumulation might result from the filler dispersion process [64].

Propagating of electrical treeing was an important parameter to evaluate the insulation life of a polymer. PP was a typical kind of semi-crystalline polymer, and the growth of electrical treeing was determined by the complex non-uniform state of aggregation structure. A greater thermodynamic driving force for electrical treeing grown along the interface of crystalline and amorphous, due to the free energy of interface. The new branches of electrical treeing were initiated at the interface, then developed along the amorphous and occupied it eventually, as shown in Fig. 4 [65–67].

The distribution of interface and amorphous had an important role in the development of electrical treeing. The nanoclay doped in the composites had two main effects on preventing electrical treeing, one was heterogeneous nucleation effecting on the crystallisation, and the other was acted as a barrier of inorganic

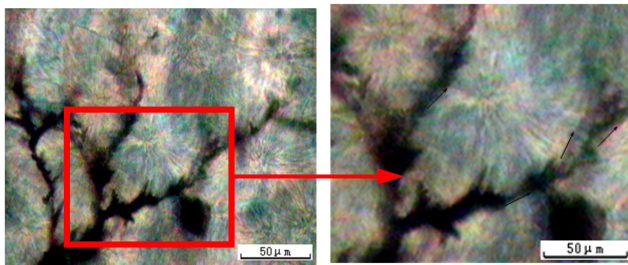


Fig. 4 Electrical treeing developed along the interface of crystalline and amorphous in PP

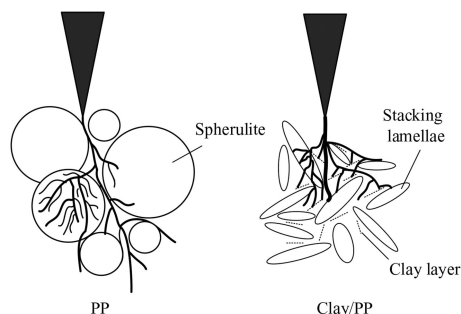


Fig. 5 Effect of heterogeneous nucleation and barrier for electrical treeing growth [68]

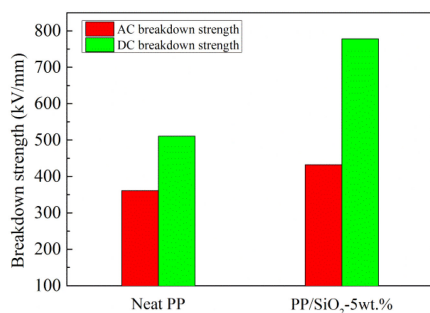


Fig. 6 AC and DC breakdown strength results of neat PP and PP silica nanocomposite

layers, as shown in the schematic diagram in Fig. 5 [67]. The effect of heterogeneous nucleation characterised by the crystallinity degree of improving and the crystalline size reducing, and these increased the interface of crystal and then increased the branching probability of electrical treeing. The inorganic layered structure of nanoclay presented a barrier for electrical tree development. The tree branch exhibited difficulty in penetrating the layer, and only developed along the surface layer instead of penetrating the layer when tree branches grew in nanoclay layers. This occurrence was an obstacle for electrical treeing growth [68].

2.2 Metal oxide/PP nanocomposite

Since the PP dielectric is mostly used as the solid insulating material for high voltage power capacitors and power cables [69, 70], the dielectric breakdown problem is the most important property for the application. Due to its irreversible nature of solid dielectrics, dielectric breakdown is a major cause of catastrophic failure of insulation in the electrical equipment. The development of nanotechnology has provided new ideas and solutions for the development of dielectric insulating materials suitable for higher voltage level. Polymeric dielectrics doped with appropriate metal oxide nanoparticles can obviously improve the dielectric and electrical insulation properties [23, 71–83]. DuPont has developed a nano-doped polyimide film (100CR) with excellent electrical performance and it has been serving in wind generator and aerospace applications. In-depth study of the mechanism of the introduction of metal oxide nanoparticles on dielectric breakdown can provide experimental guidance and theoretical support for the

development of nanocomposite dielectrics with higher breakdown strength.

In general, the breakdown performance of nanocomposite dielectrics is affected by many factors such as the surface state, particle size, content, type and dispersion of the particles. Inappropriate choice of fillers even induces the decreased breakdown strength [84]. However, most reports evinced that nano-doping is beneficial for the dielectric breakdown performance of PP matrix. The dispersion of nanoparticles is the key factor that affects the breakdown of the composite [71]. It is shown that polymer nanocomposites prepared by in-situ and ex-situ exhibit different breakdown characteristics. In-situ polymerised samples showed excellent breakdown performance with significantly higher breakdown field strength than ex-situ polymerised samples. Rytoluoto *et al.* [81] found that the optimum silica filler content was at the low fill fraction level (~ 1.0 wt%), where it was more probable to achieve a good-quality dispersion of nanosilica. It is considered that the increased DC breakdown strength may be attributed to the deep traps at the interfaces between nanoparticles and polymer matrix that reduce the charge carrier mobility and the scattering effects of the nanoparticles [73]. Jiang and co-authors found that AC breakdown strength increases with the concentration of MgO nanofillers. The increase of AC breakdown strength may be due to the presence of nanofillers, which can render the breakdown paths more difficult to form [23]. Zha *et al.* [83] found that the PP/SEBS/MgO nanocomposites filled with 0.5 phr MgO presented excellent space charge suppression due to a certain amount of deep traps induced by 0.5 phr MgO which can directly capture the space charge and suppress the accumulation of space charges. Nevertheless, it is worth noting that inorganic nanoparticles, e.g. magnesia, silica, alumina or titania, are typically doped into polymers. The regularity of nanodoping on dielectric breakdown is much different [23, 73, 78, 80–83]. Regarding the effect of the different nanoparticle content and type of breakdown characteristics, we give some experimental results. Takala *et al.* found that the PP silica composite with 5 wt% silica filler gave higher AC and DC breakdown strengths than the neat PP, as shown in Fig. 6 [72] and the increment of DC breakdown strength was higher than AC breakdown strength.

DC breakdown strength of PP nanocomposites with different nano-doping contents is shown in Fig. 7 [23]. DC breakdown strength increases apparently with the loading of nano-MgO, but when the nanoconcentration reaches higher than 1 wt%, the breakdown strength has a slight decline compared with 1 wt%. It is clarified that space charge and electric field distortion are well restricted with the addition of nano-MgO, while this effect is not obvious with the nanoconcentration reaches 6 wt%. Low nanofiller concentration in MgO/PP shows better electrical insulation properties compared with pristine PP and high nanofiller concentration composites.

DC breakdown strength of PP nanocomposites with different nanoparticles at different nano-doping contents [73] is shown in Fig. 8. Considering the electrical properties investigated, the optimal content for MgO, TiO₂, ZnO and Al₂O₃ nanoparticles is about 3, 1, 1 and 1 phr, respectively. Among these four kinds of nanoparticles, MgO and TiO₂ nanoparticles are more capable than ZnO and Al₂O₃ nanoparticles to modify the electrical properties of PP.

In general, nano-doping imparts significant effects on the dielectric breakdown for the PP matrix. It is widely accepted that the changed dielectric performance of nanocomposites come from the interface regions between the nanoparticles and polymer matrix [11–15]. The interface region is the bridge to connect the nanoparticles and the polymer matrix. As with the interface region, Tanaka *et al.* [33] proposed the multi-cores model of the interface region and considered that electrons decelerated by trapping and scattering effect were the major reason to improve dielectric breakdown strength. It is believed that the change in trap characteristics of the composite due to the interface region is an important reason for the change in dielectric properties [68–70], consequently, affecting the space charge transport, conductance and electrical performances. Li *et al.* [19, 31] proposed the potential barrier model of the multi-region structure and considered that the

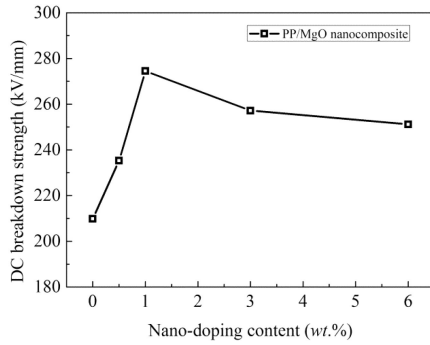


Fig. 7 DC breakdown strength of PP nanocomposites with different nano-doping contents

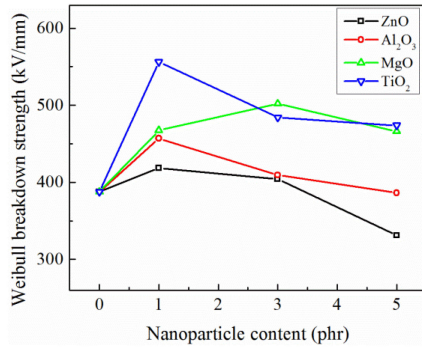


Fig. 8 DC breakdown of PP nanocomposites with different nanoparticles at different nanodoping contents

changed trap distribution which determines the dielectric breakdown performance. And it is likely that the deep traps can be formed in the multi-core model for nanocomposites by a small amount of nanofillers (~1 wt%), which enhanced the trapping effect and thus reducing the carrier mobility and energy, finally induced the improved breakdown strength.

It is reported in literature that the properties of the nanocomposites depend on the properties of the nanoparticles (e.g. shape, size, type and content) and the interaction between the nanoparticles and polymer matrix. Also, the coupling agent would significantly influence the properties of the nanocomposites. Therefore, it is difficult to establish a filler selection rule to guide the design of polymer nanocomposites with desired properties [85]. The dispersion of nanoparticles is a challenge that nanocomposite is hard to be applied on a large scale which remains to be solved. In short, the excellent performance of nanocomposite dielectrics makes it have a wide range of applications in the future.

The enhancement of breakdown strength has always been a heated topic and will last in the future for a long-time. The different working conditions of power equipment decide the different requirements of PP-based dielectric material. For power cables and filter capacitors, the dielectric material should be working under the electric field for at least thousands of hours or even several decades, so a good performance of long-term breakdown is necessary. For impulse capacitor, which is charged with DC voltage source and generate impulse voltage/current by the rapid output of power, short-term breakdown properties are more important. However, most of the current researches only focused on the short-term breakdown strength. According to Li's model [31] as mentioned in Section 1, there was a conflict between short-term and long-term breakdown properties depending on the different nanofillers loading. As a result, the research on the breakdown properties should aim at the requirement of power equipment, whether it's the short-term or the long-term.

2.3 Conductive particles/PP nanocomposite

In order to improve the dielectric permittivity (ϵ_r) of polymer, one approach was to disperse high- ϵ_r ceramic powders into the polymer to prepare 0–3 type composites [71, 85–87]. To achieve a high

permittivity, very high filler loading was necessary in general, usually over 50 vol%. Such high loading of ceramic powders significantly deteriorated the mechanical performance of composites and increased the dielectric loss. An alternative strategy is to develop high- ϵ_r percolative composites filled with conductive fillers, such as metal particles, CNTs and graphite nanoplates. As described by the power law, the ϵ_r of PP composites could be dramatically increased by the introduction of conductive fillers (several tens times higher than the polymer matrix) near the percolation threshold f_c according to the formula [88]

$$\epsilon_r = \epsilon_{pp}(f_c - f)^{-s}, \quad \text{for } f < f_c$$

where the ϵ_r is the dielectric constant of PP, f_c is the percolation threshold and s is the critical exponent. The percolation threshold of different systems will fluctuate by one order of magnitude with respect to the theoretical value, 0.16. Specifically, for most spherical conductive fillers, the experimental percolation threshold values were distributed in a broad range, from 0.013 to 0.17 [89–95], most of which were far lower than the theoretical value of 0.16. Monte Carlo simulations demonstrated the influence of the aspect ratio of ellipsoidal fillers on percolation threshold as

$$f_c \propto \frac{1}{p}$$

where p is the ratio of the length of the long axis to the short axis. For instance, nanocomposites filled with $p \approx 12$ carbon fibre [96], $p \approx 200$ exfoliated graphite nanoplates [97], and $p \approx 1000$ graphene sheets [98], presented rapidly decreasing f_c values of 0.074, 0.010 and 0.001, respectively, as a result of the increase in the aspect ratio.

If they also have the high dielectric breakdown strength and low loss dissipation factor. Such percolative systems will offer a potential alternative to conductive filler/polymer nanocomposites as a nanodielectric material for high- U_c capacitors because of their extremely high dielectric permittivity as well as very low filler loading required.

There are two main types of nanotubes available at present. Single walled nanotubes (SWNT) [99, 100] consisted of a single sheet of graphene rolled seamlessly to form a cylinder with a diameter of the order of 1 nm and length of up to centimetres. MWNTs consisted of an array of such cylinders formed concentrically and separated by 0.35 nm, similar to the basal plane separation in graphite [101]. MWNTs can have diameters from 2 to 100 nm and lengths of tens of microns. However, effective utilisation of CNT is hindered by the complexity of their dispersion in a polymer matrix and high cost. One of the alternatives is graphene, the material, which has become one of the hottest topics in physics and materials science.

Graphene, a true two-dimensional material with many unique properties, has aroused tremendous scientific and industrial interests since it was found by Geim's group in 2004 (Fig. 9a). The properties, including high Young's modulus (~1 TPa) and fracture strength (~130 GPa), high thermal conductivity (~5000 W/(m K)), high electrical conductivity (~6000 S/cm), and high surface area (~2600 m²/g), make it very attractive for various applications. Graphene oxide (GO) was an oxidised graphene derivative (Fig. 9b), which could be widely used as an alternative or precursor for graphene materials due to its high dispersibility and processability in an aqueous environment [102–105]. It is produced from mineral graphite flakes by thermal oxidation method invented by Hummers and modified by successors. By incorporating within a polymer matrix, these atomically thin carbon nanosheets can significantly improve the physical properties and the dielectric constant of the host polymer at very low filler loading. Therefore, numerous reports have focused on the preparation and structure property investigation of graphene/polymer and CNTs composites in the past few years.

Since the discovery of CNTs, their superior electrical, thermal and mechanical properties made them very attractive for incorporation in polymer materials for a range of applications

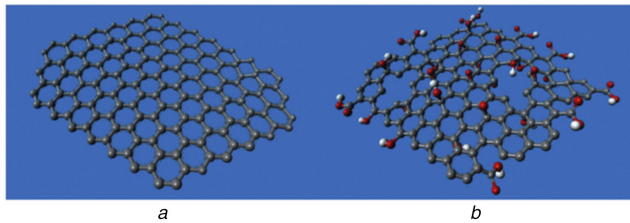


Fig. 9 Atomistic structures of individual sheets of basic graphene [105]
(a) GO, (b) Atoms are colour-coded: grey – carbon, red – oxygen, and white – hydrogen

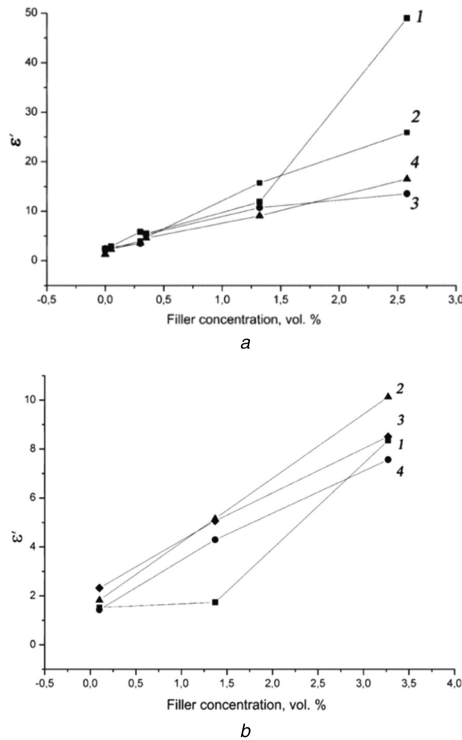


Fig. 10 Concentration dependence of dielectric permittivity at different frequencies (1–3.2 GHz, 2–4.8 GHz, 3–6.6 GHz, 4–11 GHz) [42]
(a) Composites with pristine GNP, (b) Composites with sonicated GNP

including electrostatic dissipation, electro-magnetic interference shielding, electro-thermal nanoprobes, dielectric materials with high dielectric permittivity and conductive adhesives [52, 106–108]. Yu *et al.* [41] showed that the incorporation of MWNT greatly increases the dielectric permittivity of PP/BT nanocomposites. After the surface modification of MWNT, the percolation threshold was reduced from 3–5 to 2–3 wt%. For the binary nanocomposite with 2 wt% m-MWNT, ϵ_r was greatly enhanced from 5 to 15 at 10^2 Hz. At a given frequency, the addition of MWNT improved the dielectric permittivity of the PP/BT nanocomposites, which was related to the formation of nanocapacitors between MWNT and PP/BT. As long as the loading of MWNT was insufficient to form a conductive network, they were isolated and covered by the insulating PP matrix, hence forming a large number of nanocapacitors in which the insulating PP/BT components could be considered as the dielectric layers with higher ϵ while the conducting MWNTs acted as the electrodes. Tjong *et al.* [109] showed that PP/MWNT nanocomposites prepared with a Haake mixer under a higher shear rate exhibited a very low percolation threshold of 0.22 vol%. Prashantha *et al.* [110] showed that PP/MWNT nanocomposites exhibited a percolation threshold of 2 wt%. For the nanocomposite with 2 wt% MWNT, ϵ_r was greatly enhanced from 2.1 to 11.5 at 10^2 Hz. For the PP matrix and PP containing 1 wt% MWNTs, the loss factors of the samples exhibited an initial increase at lower frequency followed by a decrease above 10^2 Hz. However, for the PP nanocomposites containing 3 and 5 wt% MWNTs, a peak of

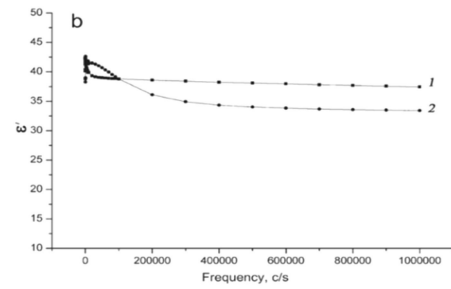


Fig. 11 Dependence of permittivity on frequency, the concentration of GNP in composite: 1–2.9 vol%, 2–5.6 vol % [42]

loss factor was observed at 40 Hz. No peaks were observed for composites bearing 2 and 4 wt% nanotubes. The first increase in loss factor at low frequency could be attributed to dipole polarisation. As the frequency increased further, the dipole polarisation effects reduced, and the value of the loss factor declined accordingly. For the nanocomposites containing >1 wt% of MWNTs, the decrease of loss factor is no longer observed leading to higher values of dielectric loss compared to PP. In case of nanocomposites with 3 and 5 wt% MWNTs peak was observed at 10^4 and 10^5 Hz, respectively. These results indicated the presence of dielectric relaxation characteristics.

Polschikov *et al.* [42] showed that nanocomposites of PP and graphene nanoplatelets were synthesised by in situ polymerisation in liquid monomer in the presence of highly effective isospecific homogeneous metallocene catalyst. Composites isotactic PP/GNP showed high dielectric permittivity (Figs. 10 and 11). Dielectric permittivity (ϵ') increases sharply with increasing filler content, which apparently was caused by high interface surface in composites.

Sonication of GNP powder was found to essentially affect dielectric permittivity and its dependence on the concentration of GNP dielectric permittivity of composites with sonicated GNP is much lower than composites with pristine GNP. This may be due to the different aspect ratio, found for sonicated particles seem to be the primary factor. Sonication was found to decrease the aspect ratio of these aggregates in the composite to 31 from X-ray phase analysis data.

Wang *et al.* [111] showed that reduced GO/PP (rGO/PP) composites with an ultra-low percolation threshold as low as 0.033 vol% and the appearance of the PP latex efficiently prevented the aggregation of rGO nanosheets. When the rGO content approached about 0.03 vol%, which was accompanied by a dramatically increased dielectric permittivity (the dielectric permittivity is 160 and 40 at 10^2 and 10^3 Hz) (Fig. 12). For composites incorporated with conductive fillers, the dielectric loss is mainly caused by the leakage current in the composites. Higher content of conductive fillers could construct more conductive pathways and thus resulted in more significant leakage current and dielectric loss.

In a percolative system, conducting particles are isolated by thin dielectric polymer layers to form a heterogeneous system, which could readily serve as a dielectric with excellent characteristics for energy storage. The high permittivity of this type of nanocomposite is, however, offset by the large dielectric loss, because of the high leakage current which arises from direct contacts between conducting fillers in composites near the percolation threshold. A challenge in achieving high permittivity while retaining low loss is to prevent contact between conductive fillers in the polymer matrix by confining fillers within individual interface layers and improve the dispersion of conductive fillers in the polymer.

Xu *et al.* [112] showed that nanocomposites prepared from PP and surface-functionalised with ionic liquids (MIL), the percolation threshold of MWCNTs/PP ($f_{c-MWCNTs}$) nanocomposites is 3.2 vol% and the percolation threshold of MIL/PP was 9.7 vol%, the dielectric permittivity of the MIL/PP composite at 10^2 Hz was ~ 354 and the dielectric loss tangent was ~ 0.8 when f_{c-MIL} was 11.1 vol%. The dielectric loss tangent of MWCNTs/PP nanocomposites was 3.8 when $f_{c-MWCNTs}$ was 3.3 vol%. The non-conducting shell around MWCNTs should prevent direct contact of

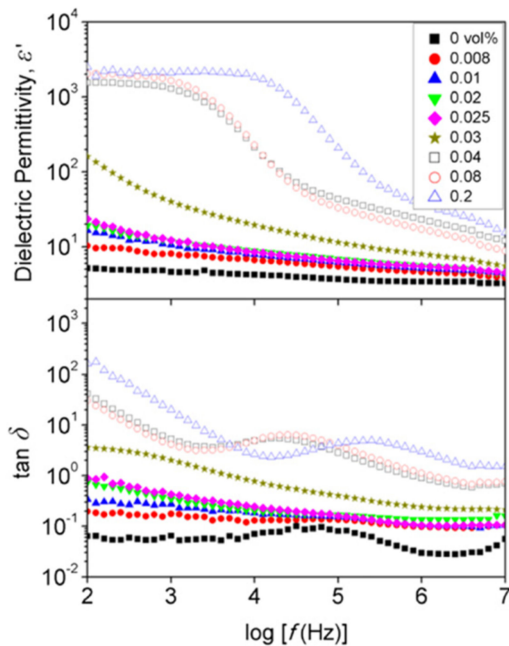


Fig. 12 Dielectric permittivity (ϵ') and loss factor ($\tan \delta$) of the rGO/PP composites with the different volume fraction of rGO as a function of frequency at room temperature [111]

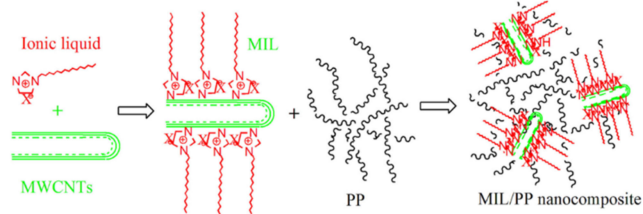


Fig. 13 Schematic diagram of preparation of the MIL/PP nanocomposite [112]

MWCNTs with each other when blended with PP, as shown in Fig. 13. Thus, it could be inferred that formation of a layer of non-conducting ionic liquid on the surface of the MWCNTs will change the dielectric properties of the composite material to make f_c for the MIL/PP nanocomposites was much higher than that for the MWCNTs/PP nanocomposites.

Despite the enhanced dielectric constant achieved by nanoparticles doping, the dielectric loss still needs attention, since, for power capacitor application, the requirement of high energy storage density is always accompanied with the guarantee of low losses. Besides, to adjust the lab-level measurement electric field to the practical working condition of power equipment is necessary, especially for the PP nanocomposite of extremely high permittivity as much more complicated relaxation polarisation shall be introduced.

2.4 PP core-shell nanocomposites

Core-shell nanostructures are the composite nanoparticles consisting of at least two different ingredients, one at the centre forms the core and the surrounding layer acts as the shell. The nanomaterials have attracted a great deal of attention because of their combined superior properties that cannot be possessed by their corresponding single components [113]. Compared to single nanoparticles introduced in a polymer matrix, polymer/core-shell nanocomposites show an excellent dispersion and an appealing dielectric property [114, 115].

Core-shell nanostructures, according to their diverse structures, can be categorised into three parts including core-shell nanoparticles (CSNs), hollow CSNs (HCSNs) and yolk-shell nanoparticles (YSNs), as shown in Fig. 14. Thereinto, CSNs whose shells are appressed to the cores are much more common than the

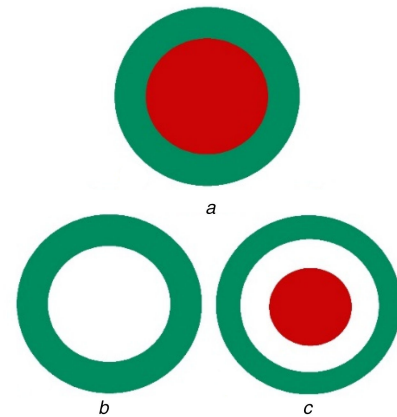


Fig. 14 CSNs
(a) Core-shell, (b) HCSNs, (c) YSNs

other two particles, as shown in Fig. 14a. An extra shell can endow the core with new properties and enlarge its applications.

However, CSNs have limited storage capacity, and then another core-shell nanostructure has been invented, which is called hollow core-shell nanoparticles, as shown in Fig. 14b. Kim *et al.* [116] prepared hollow Pd nanoparticles by removing the silica core through a solvent (HF) and the particles showed excellent catalytic activities in Suzuki cross-coupling reactions. Hollow Pd nanoparticles can maintain their high catalytic activity after used repeatedly. The high surface area of Pd spheres resulting from the hollow structure can account for the high catalytic activity.

Despite the outstanding properties provided by HCSNs, one of their main defects that cannot be neglected is the lack of the inside core [117]. Thus, to combine the merits possessed by both core-shell and hollow core-shell nanostructures in one structure, YSNs (also known as rattle core-shell) were proposed, as shown in Fig. 14c. YSNs could be described as special HCSNs which have been injected a mobilisable core. Due to the exciting structures and the combined properties, YSNs have attracted intensive research attention and show promising for wide applications, such as catalysis, drug delivery, biosensors, etc [118, 119].

The initiation of CSNs for energy storage properties improvement was first adopted in poly(vinylidene fluoride) (PVDF). Yao *et al.* [120] synthesised core-shell structured $\text{BaTiO}_3@ \text{Al}_2\text{O}_3$ (BT@ Al_2O_3) nanoparticles as the filler and PVDF as the polymer matrix. They found that the BT@ Al_2O_3 /PVDF nanocomposites had larger dielectric constant and lower dielectric loss compared to BT/PVDF nanocomposites at the same volume fraction (such as 2.5 vol% fillers). Later, researchers started to investigate the application of PP/core-shell nanocomposites due to its higher breakdown strength and lower dielectric loss than PVDF.

Guo *et al.* [43] synthesised a series of PP/core-shell nanocomposites via in situ olefin polymerisation as shown in Fig. 15. In the progress, the methylaluminoxane (MAO) coated on the surface of the cores could form a thin Al_2O_3 coating by its ambient exposure and the Al_2O_3 coating acted as a dielectric buffer layer between high-permittivity fillers and low-permittivity PP matrix. When the cores were BaTiO_3 , rod-shaped TiO_2 and ZrO_2 , respectively, the relative permittivity of could be up to 6.1, 4.9 and 6.9, much higher than pure PP ($\epsilon_r \sim 2.2$). The paper also predicted that the PP nanocomposites with BaTiO_3 cores could reach a high energy density of 9.4 J/cm^3 . The good dielectric performances resulted from Al_2O_3 layer moderating the incompatibilities between fillers and matrix which lead to nanoparticle deagglomeration.

Furthermore, the same research group [44] studied the dielectric properties of PP/core-shell nanocomposites with variable shell thickness. Al_2O_3 shell with different thickness was achieved by controlling the number of MAO coating cycles. The results showed that the dielectric loss and leakage current were obviously suppressed with the increase in the thickness of the Al_2O_3 shell, as shown in Fig. 16. Leakage current and dielectric loss not only lead

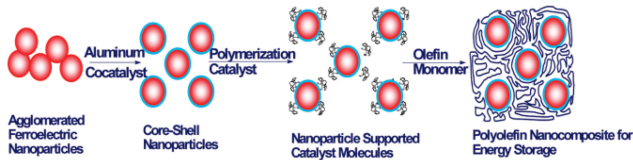


Fig. 15 Synthesis of PP/CSNs nanocomposites [43]

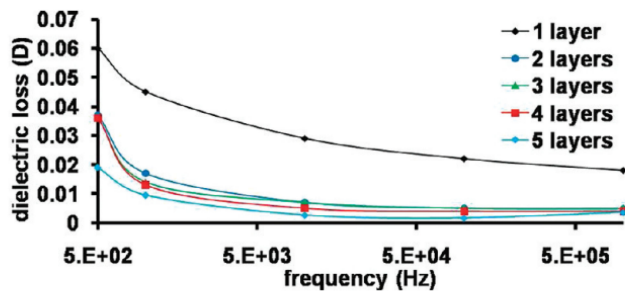


Fig. 16 Dielectric loss of PP/BaTiO₃@Al₂O₃ nanocomposites as a function of the number of shell layers [44]

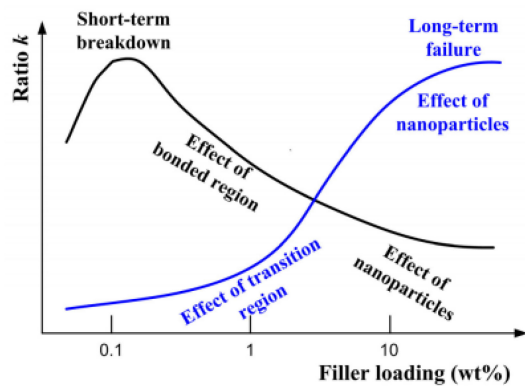


Fig. 17 Schematic diagram of the short-term breakdown and the long-term failure [31]

to the dissipation of energy but also produce undesired thermal effects in the film. Suppressed leakage current and dielectric loss show a promising application in small capacitors with large energy storage density. In the meantime, Fredin *et al.* [45] studied the relationship between dielectric loss and nanoparticle surface area in the PP/core-shell nanocomposites. Results showed that the loss at 100 MV/m scales was nearly linearly with the total internal surface area, regardless of the core materials. The results indicated that the optimum nanocomposite loss characteristics could be obtained by incorporating high permittivity particles with dimensions sufficiently large (i.e. >100 nm) to suppress excessive loss.

As for inorganic/inorganic core-shell nanocomposites applied in PP nanocomposites, the shells have a lower dielectric constant than the inside cores but higher than the matrix. Thus, the shells with moderate permittivity act as an effective buffer layer between high-permittivity nanoparticles and low-permittivity PP matrix. The shells can reduce the disparity in the electric fields within the constituent phases, minimise discontinuities in the local electric fields at the interfaces, and thus enhance the dielectric properties [45]. As a result, the shells can lead to good dispersion of the nanofillers due to the beneficial effect of grading the large permittivity contrast between the nanoparticles and the polymer matrix.

As a result, the CSNs with conductive core (Al@Al₂O₃) was studied that the permittivity as high as 15.4 was achieved [46], which solved the problem mentioned in Section 2.3 that conductive nanofillers introduced into polymer could highly raise the permittivity of the matrix by the percolation theory, but the addition of conductive fillers can lead to a high dielectric loss, a high leakage current and low breakdown strength simultaneously. As for PP/core-shell nanocomposites with conductive fillers as the core and insulating materials as the shell, the insulating shell can

effectively suppress leakage current by preventing the cores from forming the conductive percolation network for the composites, leading to a very low dielectric loss. In fact, the insulating shells often have lower surface energy compared to the conductive cores, resulting in a good dispersion of the fillers, which can also make great contributions to higher dielectric performances.

Basically, most of the PP core-shell nanocomposites are designed for the energy storage application in a capacitor. All the PP films in capacitor should be biaxially oriented, which is called BOPP. The orientation process shall cause the change of crystalline properties comparing with the cast or pressed PP film, and consequently, the electrical properties shall be influenced at the same time. So the research of BOPP nanocomposite films is necessary and of great value for the industrial development of PP nanocomposite in the future.

3 Prospective

3.1 Short term versus long term

In most research works, the method to evaluate the modified nanocomposite PP ramp up DC voltage breakdown test. However, only a few equipment working conditions such as impulse capacitor is short-term, a large number of PP dielectric material working conditions are more closely relating to long-term performance. Though the aging is an old topic for traditional polymer dielectric materials, for nanocomposite PP, papers about aging and degradation can be rarely seen. Besides, the published works proved that degradation of nanocomposite PP is faster than the neat one [72, 121], so more works need to be carried out to evaluate the electrical properties of modified nanocomposite PP.

In Li's work [31], short-term breakdown and long-term breakdown of the nanocomposite were systemically studied, and a nanofiller model that consisted of the bond region, transition region and the normal region was introduced. It was presumed that the long-term properties have a significant improvement with increasing filler content. The short-term breakdown strength is reduced due to the volume of bonded region increasing. Thus, the mechanism of the short-term breakdown and the long-term failure may be schematically represented in Fig. 17.

From aging to the degradation, to the evolution of breakdown process, the aging process occurs on the nanolevel, while the degradation occurs from the nanometre to the micronlevel [31]. The research on the breakdown of nanodielectrics should not be limited to the short-term, but to be extended to the long-term, and to reveal the insulation failure mechanism from nanometres to microns and then to mm. Therefore, it is necessary to investigate the mechanism of aging and degradation of nanodielectric materials and improve the operating reliability of nanodielectric materials in a variety of working conditions.

3.2 Necessity of lower losses

When it comes to breakdown strength or dielectric constant, dielectric loss is often neglected, since losses do not contribute to the electrical performance directly, i.e. cannot bring any contributions to electrical properties. However, dielectric losses raise much attention in the industrial application of dielectrics. For the application of capacitor, the loss is a kind of active power that can influence the efficiency of reactive power compensation, which is one of the main functions of power capacitor. For the use of cable, high losses could bring about the temperature rise and accelerate the thermal aging process. Therefore, losses do not contribute to the energy storage density or breakdown strength but affect the dielectric performance for the practical application.

Generally, the loss is considered to be originated from two aspects, namely conduction and relaxation polarisation. Both to lower down the charge carrier density and carrier mobility can suppress conductivity, but it becomes more complex for relaxation polarisation. Polarisation can be divided into two categories, displacement polarisation and relaxation polarisation. Displacement polarisation will not cause dielectric losses but the contribution from it to dielectric constant is very limited. As a result, the only way to enhance dielectric constant is to encourage

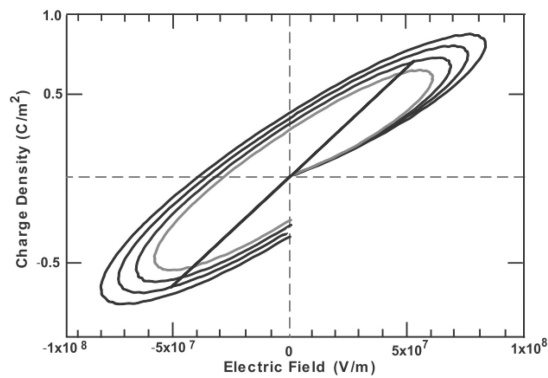


Fig. 18 Energy storage properties of nanocomposite PP under different electric field [74]

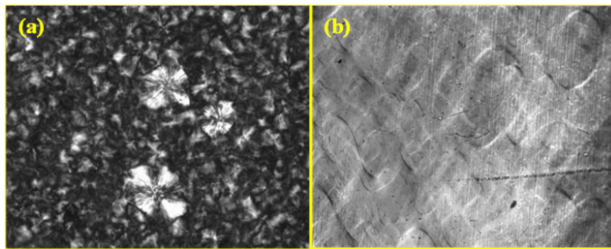


Fig. 19 Polarised light microscope image of PP film
(a) Hot-pressed PP film, (b) BOPP

relaxation polarisation and consequently, the dielectric loss is raised.

For neat PP, electron displacement polarisation holds the dominant position, and the ionic polarisation caused by impurities inevitably is the major part of relaxation polarisation. For nanocomposite PP, the dielectric loss mechanism is rarely discussed. In Zhang *et al.*'s work [122], nano-BaTiO₃ doped PP was prepared and the effect of space charge induced interfacial polarisation on dielectric losses was investigated. It was concluded that the interfacial polarisation between nanofillers and matrix played an important role in the failure and dielectric losses due to the large permittivity and conductivity contrast. In Zhu's work [73], the orientation, ionic and interfacial polarisations were discussed, and dipolar polarisation is found to be the most promising mechanism for high dielectric constant and low loss polymer dielectrics among a number of approaches, if the dipolar relaxation peak can be pushed to above the gigahertz range.

In this regard, how to achieve high energy density while keeping low losses is somewhat difficult to answer and a question thus can be raised for scholars to conduct further researches.

3.3 Measurement under high field

Generally, most dielectric responses are measured under low electric field (1–3 V), but the operation condition of PP, no matter for cable or capacitor application, is much higher than the measurement field. For instance, the field for cable application is around 20 kV/mm, and the working field of shunt capacitor for reactive power compensation is even higher than 50 kV/mm, while this value comes to be >100 kV/mm for HVDC filter capacitors, and the field of impulse capacitors could reach >300 kV/mm. Thus, to measure and evaluate the nanocomposite PP film under the high field, which is comparable to working condition, is extremely necessary.

On the one hand, the mechanism of dielectric response varies in the different applied field. Firstly, the dominant charge carriers could turn from ions to electrons when the electric field increases, and according to the Schottky and Pool–Frenkel effect, the number of free electrons will increase since the decreased barriers can benefit the electrons hopping process. Secondly, the barrier for ions hopping will also decrease and lead to the enhanced ionic polarisation. As for nanocomposite PP, the new energy level of traps shall be introduced by doped fillers, so the dielectric response

may be more active and different from traditional PP especially under the high field. In Fredin *et al.*'s research [74], the stored energy could not be released thoroughly when the applied field was higher than 50 kV/mm in Al@Al₂O₃/PP nanocomposite as shown in Fig. 18, and this was never observed in neat PP before.

On the other hand, the high field could link the polarisation and conduction. Polarisation process and conduction process compose the dielectric response. Under low electric field, these two processes are independent, while under the high field, there will be an interaction between them in some way. In general, the distance between positive and negative charge centres when polarised at the low field is about nanometre scale, while the transportation distance of charge carriers could be millimetre scale, to move through the dielectric material and form conduction. When the applied field goes up, the distance between positive and negative charge centres shall increase, and this distance can even increase to micrometre scale if the field is high enough. This value is comparable to the millimetre scaled transportation distance of charge carriers, so both the polarisation and conduction processes are promoted.

3.4 From normal PP to BOPP

It is commonly agreed that the dielectric films in the capacitor are BOPP film, which has totally different crystallisation properties and much higher electric properties than normal cast or hot-pressed PP film. The orientation could bring about a new deformation mechanism based on rotation and splitting of the woven structure, with the *c*-axis parallel to the stretching direction, and the *b*-axis perpendicular to the surface of the film [69, 123]. After orientation, the microstructure turns from spherulite to crater-like and rough surface can be formed in consequence as shown in Fig. 19, which makes it possible to use BOPP film to replace capacitor cellulose paper since the rough surface can largely benefit the impregnation of capacitor oil. At the same time, both crystallinity and density increase by orientation, and therefore, the breakdown strength can be improved a lot that reaches >600 kV/mm (DC), and together with the enhancement of mechanical properties that enables the feasibility of PP films wound into capacitor units.

However, most of the current researches on PP nanodielectrics are based on cast film or hot-pressed film. Though many good results have been achieved, the feasibility of these modification methods is still uncertain to some extents. As a result, to develop the research work of PP nanodielectrics from normal PP to BOPP is necessary and key problems faced are the manufacturing challenge and mechanism study.

Manufacturing challenge. Different from most of other insulation materials, the thickness of commercial BOPP film for capacitor application is usually <20 μm, sometimes even several micrometres only, so to ensure good dispersion of nanoparticles in such thin films is very difficult for practical manufacturing, since the size of a small nanofiller agglomerate can be easily more than several hundred nanometres, which may act as a weak point in BOPP films. Rytoluoto *et al.* tried the nano-SiO₂ and nano-CaCO₃ filled BOPP films with different mixing methods [123, 124]. Results showed that in general, the distribution of nanofillers was acceptable, but large cluster with the diameter about 1 μm was still inevitable. As shown in Fig. 20, the breakdown strength was improved with relatively low filler content, while the error bar increased obviously with the rising of filler content, which was the consequence of poor filler dispersion with higher loadings.

Mechanism of nanocomposite PP after orientation. The orientation could bring about the recrystallisation process to form a crater-like crystalline [69, 123], so the mechanism of nanocomposite BOPP should vary from nanocomposite PP. However, at present only a few of researchers performed dielectric research on the nanocomposite BOPP film, and mainly focused on the results presentation. For the mechanism of nanocomposite BOPP, such as the behaviour of nanofillers during the orientation process, the evolution of the interphase region brought by orientation, and even the systematically study of the electrical properties before and after orientation are still absent. Only to make clear of the mechanism of nanocomposite BOPP, the current

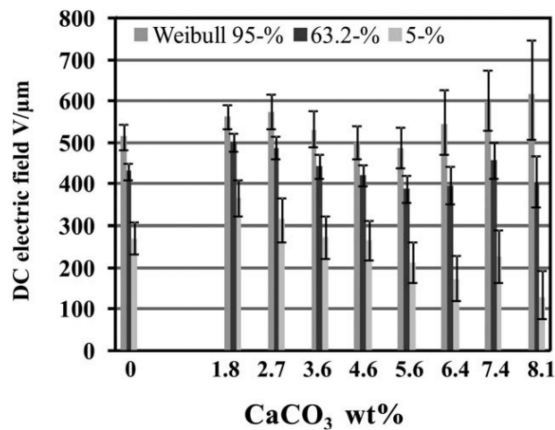


Fig. 20 DC breakdown strength of nano- CaCO_3 doped BOPP film presented by Weibull distribution [123]

research on cast or hot-pressed nanocomposite PP film can be more directive to the practical industry application.

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