China Corner

Research Development of Nanodielectrics in China

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1. Overall

Nanodielectrics have attracted more and more attention from universities, research institutions and companies in China due to their potential benefits as dielectrics. Since Xiangshan-science conference whose topic was the multilevel structure and macro perfor-mances of nanodielectrics was held in Beijing in 2009, some progresses have been made in nanodielectrics research field.

The homogeneous distribution of nanoparticles in polymer matrix is a problem of nanodielectrics researches. Nanoparticles are chiefly dispersed in matrix by shear force diffusion and chemical modification in the majority of experiments. The viscosity of the matrix is an important factor for shear force diffusion. Chemical modification will alter the surface states of nanoparticles to increase the electrostatic force between fillers and matrix.

As a result, the experimental results of nanodielectric properties have little comparability and poor reproducibility, owing to the different preparation processes. The interfaces around the nanoparticles are hard to describe clearly at the present stage, but important for understanding the physical and chemical properties of nanodielectrics.

2. Properties of Nanodielectrics

Nanodielectrics exhibit a series of unique outstanding properties, such as electrical, mechanical, optical and magnetical, owing to nanoparticles with a giant specific surface area, quantum size effect and the special interface between particles and polymer matrix.

The surface activity, surface energy, surface tension, and surface area of nanoparticle increase with decreasing the particle size. The surface atoms exhibit high chemical activity, and they are easy to bond with other atoms. This will lead to nanometer fillers difficult to uniformly disperse in the preparation process. On the other hand, this will result in the strong interaction between the particles and the polymer matrix to form a very complex interface structure, thus changing the electrical, thermal, mechanical and other properties of the material, which is the theoretical basis of the modified nano-doping.

It has been known that the polarity of polymeric matrix, the type and the surface states of nanoparticles have a combinative influence on the interface. The interface is widely recognized to play a key role in determining the macroscopic electrical performance, short-term breakdown, long-term aging properties. Its detailed structure and properties need to firstly be understood.

3. Research Development of Nanodielectrics in China

It is very urgent to develop new high insulation materials with higher breakdown field and superior ageing-resistant performance to meet the need in super/ultra-high voltage electrical equipment, high energy storage devices and equipment, aerospace and so on. Nanodielectrics as the third generation insulating materials with superior electromechanical performance open a new window for the industry development as well as correspond to the development strategy. Therefore, it is significant to investigate and develop nanodielectrics.

In the recent years, researchers in China have done a lot of works and have made great progress in the field of nanodielectrics. Various methods were used to prepare nanodielectrics and various polymer matrixes such as polyethylene (PE), silicone, epoxy resin (EP), polyamide (PA), polyimide (PI) doping various fillers such as alumina (Al_2O_3), titania (TiO_2), silica (SiO_2), layered silicates.

The current research is concentrated on invesitigating the properties of nanodielectrics, such as, dielectric response behaviores, breakdown properties, space charge effect, partial discharge (PD) resistance, electrical aging resistance and so on.

3.1 Dielectric Properties of Nanodielectrics

It was reported that the relative permittivity will be deviated from the original value when there are trace amount of nanoparticals in the polymer matrix.

3.1.1 Development of high permittivity nanodielectrics

Dielectric materials with a high dielectric constant are expected to be used as dielectric materials of flexible multi-layer capacitors. In general, nanopaticles, such as Al_2O_3, TiO_2, $BaTiO_3$, are used as fillers to improve the relative permittivity of polymers.

PI/nano $BaTiO_3$ composite films were prepared by direct mixing poly (amic acid) and silane coupling agent modified $BaTiO_3$ particles followed by imidization. Experimental result showed that the dielectric properties of the composites displayed good stability within a wide range of temperature and frequency. The dielectric constant of this nanocomposite increased with an increase of the volume fraction of $BaTiO_3$ particles. For example, the dielectric constant was 35 at 10 kHz when the content of $BaTiO_3$ was 50 vol%, which was 10 times of that of the pure polyimide.

Stearic acid gel method was used to prepare nanocrystalline $BaTiO_3$ composites. It was found that dielectric constant of nanocrystal was much larger than that of bulk materials. As the particle size decreased, the dielectric constant of nanocrystal initially increased and then decreased to a small value.

3.1.2 Development of low permittivity nanodielectrics

Nanometer silicon tube was added in PI to reduce the dielectric constant. When the content of nanometer silicon tube was less than 3 wt%, the complex dielectric constant decreased with increasing the content of nanometer silicon tube.

The low density polyethylene (LDPE) and EP doping with various concentration of nano Al_2O_3 and TiO_2 fillers were studied. It was found that the dielectric constant of nanocomposites show a reduction as long as the concentration of nano particles in an appropriate range. The reduction of dielectric constant is due to the increase of free volume and the restriction of dipolar around the interaction zone.

3.2 Volume Resistivity of Nanodielectrics

The PI/Al_2O_3 nanocomposite films were prepared by sol-gel process. With the volume resistivity test of polyimide/nano-alumina composite film, it was found that the volume resistivity was the highest and higher by an order of magnitude than pure polymer when the content of nano-alumina was about 10%.

LDPE and EP doping with various concentration of nano Al_2O_3 and TiO_2 fillers were investigated. It was found that the conductivity of nanocomposites showed a reduction as long as the concentration of nano particles in an appropriate range. The reduction of charge mobility is likely to be the reason for the decrease of conductivity.

The high field conductivity of LDPE with nano-SiO_2 particles was studied. It was found that the high field conductivity of LDPE was based on space charge limited current, while that in LDPE/Nano-SiO_2 was based on ion hopping conductance.

Some metal nano particles, such as Ag, Sn, also have influence on polymer volume resistivity when their contents are very low. Some researches showed that the volume resistivity could be increased by an order of magnitude when the content of nano-metal was about 0.1%. The invesitigation on the DC volume resistivity and high field conductivity of nano-Ag/EP polymer composite showed that after trace addition of Ag nanoparticles with small sizes, the composite had obviously higher volume resistivity than pure EP. The increase of resistivity was related with the size and addition of Ag particles, and characteristics of base polymer. High field conductivity tests showed that the coulomb blockade effect appeared when Ag particles of small nanosize disperse uniformly in the polymer. When the addition of Ag nanoparticles was too much or their size was too big, the composite showed space charge limited current property.

The investigation on the volume resistivity of nano-Ag/PVAc nanocomposite found that the conductivity decreased to lower than 10% of the original ones at a certain the nano-Ag addition. However, when the addition of metal nanoparticles increased, the polymer might transit to good conductor.

Carbon nanotube CNT was used to add into polymer to acquire the expected properties. The different properties were found in the multi-wall carbon nanotube (MWNT)/polymer-based composites with the MWNT before and after chemical modification. The percolation threshold was very low in the composites with one dimension MWNT compared with that of composites with conducting sphere particles in micron size. When the content of original MWNT fillers was 0.02 vol%, the conductance of the composite was highest which was 5×10^{-4} S/m, while that for TFP-MWNT composite was 10^{-2} S/m.

3.3 Electric Breakdown Performance

Breakdown strength of dielectric is an extremely important electrical parameter for dielectric material in engineering. Researchers in China have studied the electric breakdown performance of nanodielectrics, and found that the BD performance was dependent on the addition of nanoparticles.

Ag/PVA nano-polymer matrix composites have been prepared by the sol-gel method, and the electrical properties were investigated. The results showed that the composite with a proper nano-Ag addition had a high breakdown strength, which was obvious at cryogenic temperature.

The breakdown strength of nanocomposites initially increased and then decreased with nano particle addition. Under power frequency applied field (ac), breakdown field of nanocomposites reached to the maximum at nanoparticle concentration of about 1 wt%. For example, it was about 43 kV/mm for epoxy nanocomposite, which had an increase of 16% compared with pure epoxy (37 kV/mm). For LDPE nanocomposite, ac strength had a maximum value of 50 kV/mm, indicating an increase of 19% compared with pure LDPE (42 kV/mm). Under DC applied field, the maximum breakdown fields were 125 kV/mm and 400 kV/mm for epoxy nanocomposites and LDPE nanocomposites, which could be improved 13.6% and 33.3%, respectively.

Although quiet a lot of research works on nanodielectric breakdown properties under ac, dc and pulse voltage have been done so far. It is unfortunate that the results of breakdown properties of nanodielectrics have little comparability and poor reproducibility until now. This may be caused by the polymer matrix, type of nanoparticles, dispersion situation of nanoparticals, sample thickness, voltage waveform and so on.

In order to conveniently comment on the BD properties of nanocomposite, a ratio *k*, which is defined as the breakdown voltage of composite divided the breakdown voltage of polymer matrix, was introduced in 2010. And it was found that the cohesive energy density (CED) of polymer matrix strongly affects the BD properties of nanocomposites, and the breakdown performance could be improved as long as nano particle addition in an appropriate range.

3.4 Long-term Ageing

At present, the investigation on the ageing resistance of nanodielectrics in China is booming. Although the results from different researchers have little comparability, and the mechanism of ageing resistance is different, the ageing resistance of polymer will be great improved for the introduction of nanopaticles.

The nano-TiO_2 particles was introduced to the PI by using in-site dispersion polymerization. It was found that the corona-resistant lifetime of the nanodielectrics was 40 times longer than pure PI film at the electrical stress of 12 kV/mm, when the TiO_2 addition was 15%.

The aging resistance of PI with nano-SiO_2 particles was investigated. It was found that the nano-SiO_2 particles would extremely improve the aging resistance of PI. The investigation on the effect of TiO_2 on the aging resistance of nanodielectrics found that the nano-TiO_2 particles could moderate the electric field distribution, increase the heat conduction and extend the lifetime of nanodielectrics. At the same time, the nano TiO_2 precipitate formed an electron and UV shielding layer to capture the electric charge and absorb UV generated by corona.

In order to extend the lifetime of variable frequency motor, investigation on the aging resistance PI films 100CR found that this material could increase the corona inception voltage and breakdown voltage.

In order to investigate the relation between the nanoparticle content and ageing resistance, the ratio *k* was introduced and defined as electrical ageing performance of nanocomposite divided by that of matrix. It was found that adding micro and nano particles could effectively improve the ageing resistance and with the ageing time prolonging, nano-composite was superior to micro-composite.

4. Application Prospect of Nanodielectrics

Nanodielectrics have broad application prospects in electrical engineering.

Capacitor insulation: Nanodielectrics have high breakdown field strength at the same time keeping relative high dielectric constant. It will develop the performance of the storage density of capacitor, miniaturize the capacitor. The excellent anti-aging properties can ensure the stable performance of the capacitor during the work.

HVDC cable: The excellent space charge properties of nanodielectrics can moderate the internal electric field. Meanwhile, the operating voltage level and reliability of HVDC cable will increase owing to the breakdown performance and anti electrical aging properties of nanodielectrics.

Generator insulation: The application of nanodielectrics will be favor to the reduction of the size of generator, increase the reliability of generator, and reduce the cost. In addition, the lifetime of generator will been extended for the corona-resistant property of nanodielectrics.

Insulating paint: Nanodielectrics can be used as insulating paint due to the waterproof, fire resistance and flashover properties.

Insulation in extreme work environment: Nanodielectrics can be used as the insulation of spacecraft and nuclear reactor.

In addition, nanodielectrics can be used in micro electronic device, optical device, electrostriction material and sensor.

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