Effect of different surface treatment agents on the physical chemistry and electrical properties of polyethylene nano-alumina nanocomposites

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Abstract: Generally, the electrical properties of nanocomposite are affected by the type, size, filling concentration and surface treatment process of the nanoparticle. In this study, nanocomposites of polyethylene (PE) with varying filling contents of nano-alumina particles were prepared by the melting blending method and three different kinds of coupling agents were applied for surface modification properties of the nanoparticles. Two of them were silane based and the other was titanate based. The effect of different coupling agents on the dielectric properties was studied. Fourier-transform infrared spectroscopy and thermo-gravimetric analysis were used to verify their compositions. Scanning electron microscope and polarised optical microscopy were used for morphology study. Dielectric permittivity, direct current (DC) volume resistivity and DC breakdown strength characterised their improved insulation performance with nano-alumina as filler. Thermal stimulated current results revealed that adding nano-alumina particles into low-density PE could provide more deep traps and increase DC resistivity.

1 Introduction

Nanodielectric has been given special attention in the cable insulation field in the last two decades due to its low dielectric loss, high breakdown strength and enhanced thermal conductivity compared with traditional composite materials [1]. The concept of nanocomposite was first introduced by Lewis [2] in 1994. A multiple layered model was subsequently proposed by Tanaka *et al.* [3] in 2005 in order to explain the possible mechanism of how nanoparticles interact with the base material. Recent researches published by Zhou *et al.* [4] also show that the introduction of different nanoparticles could significantly improve the electrical properties of polymer cable insulation materials. Currently, more researchers focus on optimising the size and filling the content of nanofillers [4–7].

Polyethylene (PE) is one of the most popular matrix materials for extruded high-voltage (HV) cable insulation due to its excellent insulating characteristic. Cross-linked PE (XLPE) cables have been widely used in HV alternative current and HV direct current (HVDC) power network which could operate under 90°C because of its structure. However, the degassing process and by-products of crosslinking bring the adverse effect on dielectric performance in the long-term operation. Besides, its crosslinked structure makes it hard to recycle. Recently, PE incorporating different nanoparticles has shown comparable electrical strength to XLPE cables, which makes it possible to be used as HVDC cable insulation.

It is well-known that the interface between the base polymer and nanofillers can play a dominating role in determining both the physical chemistry and dielectric properties [3, 8–12]. The interface region is usually modified by applying additives known as coupling agents before the nanoparticles are mixed with the base polymer material. These coupling agents are compatible with the interface between the nanoparticle and the polymer matrix by modifying the surface chemistry of the nanoparticle. A wide range of coupling agents is available for most common filler–polymer combinations [13–15]. Furthermore, coupling agents on surface-treated nanoparticles may affect charge transportation within the nanocomposite. The relationship between charge movement and electrical strength was studied in [13, 16–18]. Enhanced

breakdown strength has been achieved through different surface treatments for silica/XLPE in [19]. The charge distribution and trap level were also analysed through thermally stimulated current (TSC) measurements and peaks associated with traps appeared after surface modification of the filler. The results suggested that more deep traps have been introduced after adding the surfaced-treated fillers. Deep traps could lead to the increase of breakdown strength as they reduce the charge mobility and the mean-free path of electron acceleration through capturing the charge carriers [20, 21]. Moreover, the trap density and shallow traps also have an effect on breakdown strength but the relationship between these parameters is not fully clear yet [6, 7, 22–24].

Another problem for polymer insulation is the charge injection by Schottky injection or tunnelling from the electrode–dielectric interface when a voltage is applied [25, 26]. Under high electric fields, charges may accumulate within the bulk of the polymer. When the total amount of charge is large, it will result in the distortion of the local electric field, which can lead to insulation degradation [21, 27]. Therefore, how to supress charge injection into polymer insulation is another important issue to address. When the surface-modified nanoparticles are introduced, the charge injection barrier is increased. In addition, the charge would be injected into deep traps and this will decrease the apparent charge mobility. Zhou *et al.* [28] proved that adding inorganic nano-MgO into polypropylene could efficiently introduce more deep traps.

In this paper, attempts have been made to study the effect of surface modification of nanoparticle on physical chemistry as well as the dielectric properties of the nanocomposites by using three different coupling agents. It also explores the possible mechanism of how nanoparticles enhance the dielectric properties. The melt-blending method was adapted to make low-density PE (LDPE)/ nano-alumina composite film samples to study its feasibility as a high-performance recyclable HVDC cable insulation. In comparison to the dielectric properties of virgin LDPE samples, LDPE nanocomposite samples showed some interesting dielectric performance.
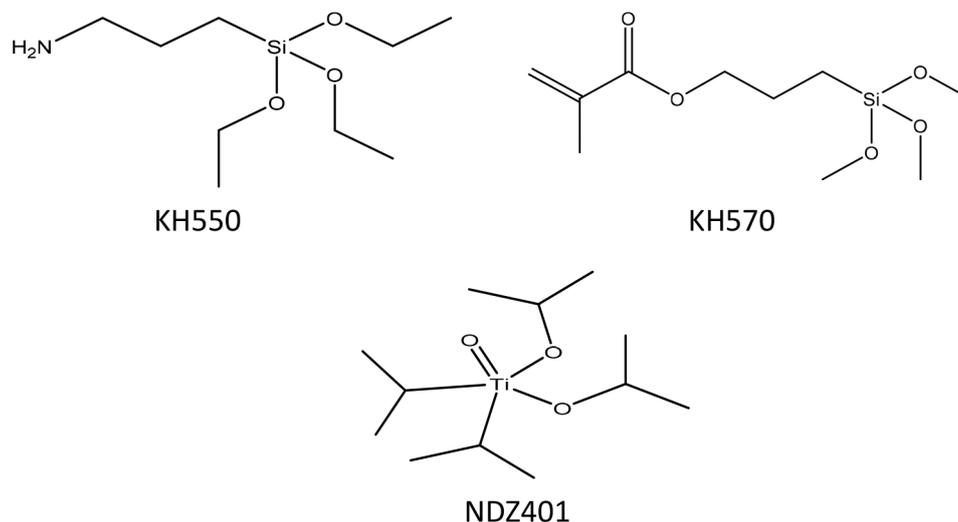
Fig. 1 *Molecular structures of the coupling agents used in this study*

2 Experiments

2.1 Materials

Linear LDPE was purchased from ExxonMobil and had a melt flow index of 3.5 g per 10 min, a density of 0.924 g/cm^3 and a melting point of 124°C. Alumina nanoparticles with an average diameter of 30 nm were obtained from Aladdin Industrial Inc., China. The silane coupling agents, used for modifying the surface of nanoparticles: 3-aminopropyltriethoxysilane (KH550) and γ-methacryloxypropyltrimethoxysilane (KH570), were bought from Sinopharm Chemical Reagent Co. Ltd, China. The titanate coupling agent, tetraisopropyl di(dioctylphosphate) titanate (NDZ401), was obtained from Nanjing Shuguang Chemical Group Co. Ltd, China. The molecular structures of these three coupling agents are as shown in Fig. 1. KH550 and KH570 are both silane-based inorganic molecules but with an amino group and oxy group, respectively, thus giving compatibility with different polymer bases. As for NDZ401, it is a typical titanate coupling agent containing isopropyloxy and three long organic chains which makes it widely used for surface treatment. The hydroxide groups on the surface of nanoparticles can easily react with the isopropyloxy on the coupling agent to form a chemical bond by forming isopropyl alcohol. For most of the coupling agents, a monomolecular film will be formed to cover the surface of particles which modifies the surface properties.

2.2 Surface modification of nanoparticles

The nano-alumina particles were firstly dried in a vacuum oven at 100°C for 24 h. Then the nanoparticles were dispersed in xylene solution followed by ultrasonic mixing for 60 min to achieve homogeneous dispersion in the solution. The mixture was transferred into a three-neck flask, connected with a condenser and a mechanical stirrer, and the coupling agents were added. The mass of the coupling agent was around 1 wt% of nanoparticle. The mixture was refluxed in an oil bath at 80°C for 12 h before undergoing centrifugation with pure xylene for three times. Lastly, the surface-modified nanoparticles were placed in the vacuum oven at 60°C until dried. This process was used for the surface treatment using KH550, KH570 and NDZ401.

2.3 Nanocomposite sample

Prior to the melt blending, all polymer pellets and both surface-modified and untreated nano-alumina particles were dried in a vacuum oven at 100°C for 6 h. The rotation speed of the internal mixer was set at 60 rpm. The temperature setting for PE and was 170°C. The filling contents of the nanocomposite were listed in Table 1. 1 phr means 1 g nanoparticle was added to 100 g base polymer and the labelled names would be referred in other sections

Table 1 Sample name and description

Name	LDPE, g,)	Nnao-Al$_2$O$_3$, g	Silane coupling agent
LDPE	50	0	none
LDPE/Al$_2$O$_3$–Pure@0.5 phr	50	0.25	none
LDPE/ Al$_2$O$_3$-Pure@2 phr	50	1	none
LDPE/ Al$_2$O$_3$-Pure@5 phr	50	2.5	none
LDPE/Al$_2$O$_3$-KH550@0.5 phr	50	0.25	KH550
LDPE/Al$_2$O$_3$-KH550@2 phr	50	1	KH550
LDPE/Al$_2$O$_3$-KH550@5 phr	50	2.5	KH550
LDPE/Al$_2$O$_3$-KH570@0.5 phr	50	0.25	KH570
LDPE/Al$_2$O$_3$-KH570@2 phr	50	1	KH570
LDPE/Al$_2$O$_3$-KH570@5 phr	50	2.5	KH570
LDPE/Al$_2$O$_3$-NDZ401@0.5 phr	50	0.25	NDZ401
LDPE/Al$_2$O$_3$-NDZ401@2 phr	50	1	NDZ401
LDPE/Al$_2$O$_3$-NDZ401@5 phr	50	2.5	NDZ401

in this paper. Pure LDPE granules were processed in the same condition without any additive as reference batch.

The next step was to press the composite granules into thin film samples with a thickness of 100 and 200 μm by compression moulding under 15 MPa at 200°C. The films were then annealed to room temperature by circulating water while the compression mould was still maintained at a pressure of 15 MPa. Finally, all the samples were labelled and stored in a dry and clean place. Before each test, the film samples were put in a vacuum oven at 100°C for 12 h to remove the moisture from the sample surface. All different kinds of samples were listed in Table 1.

2.4 Characterisation

In order to study the effect of surface treatment on nanoparticles, the chemical structure of modified and unmodified nano-alumina particles was checked using thermo-gravimetric analysis (TGA) and Fourier-transform infrared (FTIR) spectroscopy. TA Q500 instrument from TA Instrument, US was employed to conduct TGA for pure nano-Al$_2$O$_3$, KH550-treated nano-Al$_2$O$_3$, KH570-treated nano-Al$_2$O$_3$ and NDZ401-treated nano-Al$_2$O$_3$, with a heating rate of 10°C/min until 800°C. Moreover, FTIR spectra of them were acquired between 400 and 4000 cm^{-1} by using the Thermo Fisher Nicolet iS10 spectrometer, USA.

The distribution of nanoparticles within the base material was characterised by field emission scanning electron microscope (FE-SEM), Hitachi 8010, Japan. The nanocomposite samples were immersed in liquid nitrogen and then snapped into two halves. The
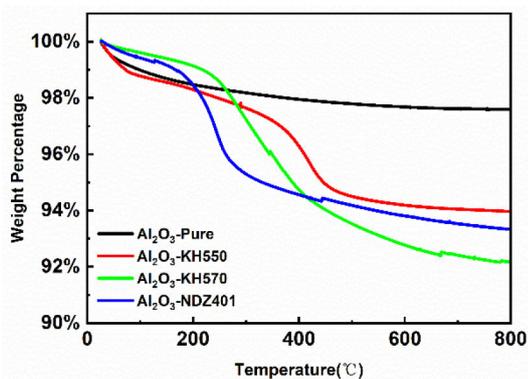
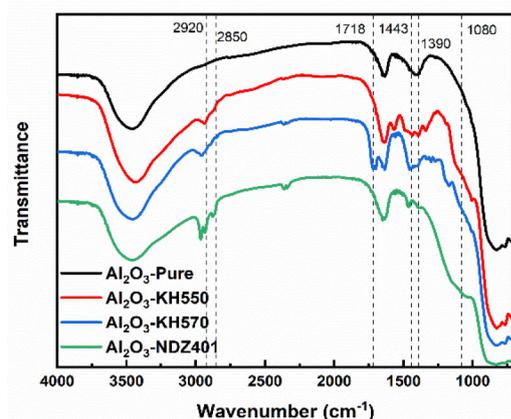**Fig. 2** *TGA curves of nano-alumina powders*

Fig. 3 *FTIR spectrum of different nano-alumina samples*

cross-section at the broken edge was then sputtered with gold to avoid charge accumulation when observed under the SEM.

The spherulite size of the LDPE nanocomposites was observed through polarised optical microscopy (POM) and it was conducted by employing a Nikon Eclipse microscope (LV1100NPOL) with a polariser. The pieces of film samples were placed between microscope glasses and then were put on a hot stage (LTS420, Linkam). The sample was firstly heated at 200°C and maintained for 20 min. The sample was then quickly cooled to its crystallisation temperature (135°C for LDPE composites) and kept at this temperature for 15 min to allow for isothermal crystallisation before observation.

Dielectric permittivity and loss tangent of PE and PE composite film samples with a thickness of 100 μm were sputtered with gold electrode before testing using an Alpha-A high-performance frequency analyser (Novolcontrol GmbH Concept 40, Germany) over the frequency range of 10^{-1}–10^6 Hz at 30°C.

DC breakdown strength of nanocomposites was measured by a dielectric strength tester (Z-VI, Suzhou Industrial Park HaiWo Technology Co., LTD, China) with a pair of 20 mm-diameter ball electrodes at room temperature. The negative DC voltage applied was increased continuously at a uniform rate until breakdown occurs (according to IEC 60243). We have chosen a rate of ~1 kV/s and the thickness of film samples was 100 μm. The applied voltage was recorded by the tester when the breakdown happened. For each category of film sample, 25 test results were repeated. Later, according to IEEE Standard 930–2004, all the valid data were analysed by using a two-parameter Weibull statistical distribution model.

DC volume resistivity was determined using a standard three-electrode system equipped with a digital Keithley 2635B electrometer, which has a minimum display resolution of 0.1 fA. Samples, coated with gold as conductive areas, with about 100 μm thickness were measured under 40 kV/mm at 30°C. The leakage direct current values were directly logged at intervals of 600 s. For each kind of nanocomposites, measurements on three film

specimens were performed to calculate an average DC volume resistivity.

TSC was conducted by a broadband dielectric spectrometer (Novocontrol GmbH Concept 40, Germany). The 100 μm thickness samples were sputtered with gold electrodes before the test. The sample was firstly polarised at 50°C under 6 kV/mm for 30 min and then cooled down to −80°C by liquid nitrogen with a cooling rate of 10°C/min. The depolarisation current was recorded along with the changing temperature from −80 to 100°C with a heating rate of 3°C/min.

3 Results and discussion

3.1 TGA and FTIR results

Fig. 2 shows the TGA results of nano-alumina particles with and without surface modification. The weight loss of nanoparticles <200°C is mainly due to the water desorption. The weight loss between 150 and 600°C is mainly caused by the loss of organic groups grafted the nanoparticles surface. Different peaks mean three different coupling agents have different thermal decomposition characteristics. There is limited influence on the application of nanocomposite material for cable insulation as the operation temperature is <200°C. For pure Al_2O_3 powder, the total loss is around 2% and this is due to the loss of absorbed moisture. However, the weight loss is up to 7% for KH570-modified Al_2O_3 powder and about 6% for the other kinds of samples. Except for the similar loss of pure Al_2O_3 particles, the rest of the weight is ascribed to the total mass of organic silane coupling agent. The titanite coupling agents usually decompose above 230°C and this is observed from the TGA results. It reveals that KH550, KH570 and NDZ401 were successfully grafted on the surface of nano-Al_2O_3 particles from the test results.

The FTIR results also demonstrate the success of surface treatment for nano-Al_2O_3 particles as displayed in Fig. 3. After modification, some characteristic peaks for KH570 are found on the spectrum of KH570-Al_2O_3 powder. The new absorption peaks at 2920 and 2850 cm^{-1} are characteristic stretching and bending bonds of –CH_2– bond. The distinctive C=O stretching peak of KH570 at 1718 cm^{-1} is also evident in the spectrum of the Al_2O_3-KH570 particles. In addition, compared with unmodified nano-Al_2O_3, peaks at 1443, 1390 and 1080 cm^{-1} suggest the Si–O–CH_2CH_3 bond exists after surface modification. The same peaks of –CH_2– bond and Si–O–CH_2CH_3 bond were also found on the spectrum of KH550-Al_2O_3 powder which means it was also successfully grafted onto nano-alumina particles. As for NDZ401-Al_2O_3 powders, except the peak of –CH_2– bond, new peaks were found at 1063 and 1232 cm^{-1} which are the characteristic peaks of O–P bond and O–Ti–P bond, respectively. Together with the TGA results, nano-alumina particles and all coupling agents were strongly chemical bonded.

3.2 SEM images

The distribution of nanoparticles within the base polymer was studied by SEM and is shown in Fig. 4. The dispersion of particles plays an important role in determining the electrical properties of nanocomposites. Without surface treatment, as shown in Fig. 4a, nanoparticles are agglomerated and the diameter of nanoclusters is up to 2.5 μm. On the contrary, the average dimension of surface-treated nanoparticles, shown in Figs. 4b, c and d, is <250 nm with limited aggregation. Combining the TGA and FTIR results, it is concluded that surface treatment of nanoparticles by all three coupling agents can effectively change the surface of the particles and help with the homogeneous distribution within the polymer.

3.3 Crystalline morphology

In order to find the possible relationship between changing morphology and changes of electrical performance, polarised optical images of LDPE and LDPE composites were obtained, as shown in Fig. 5. As the size of PE spherulites is too small to
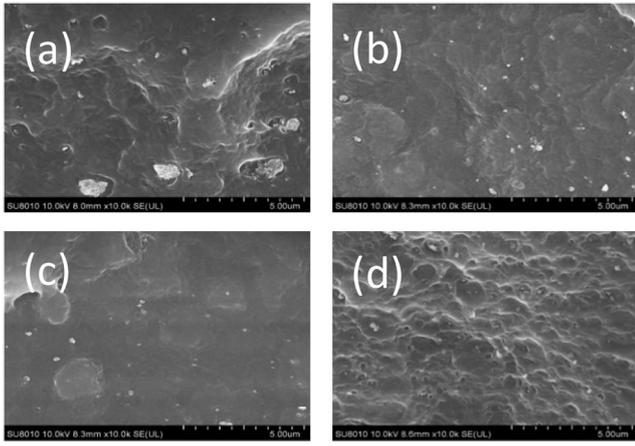
Fig. 4 *SEM images of both modified and unmodified LDPE composites with 5 phr content*
(a) LDPE/Al$_2$O$_3$-Pure@5 phr, *(b)* LDPE/Al$_2$O$_3$-KH550@5 phr, *(c)* LDPE/Al$_2$O$_3$-KH570@5 phr, *(d)* LDPE/Al$_2$O$_3$-NDZ401@5 phr
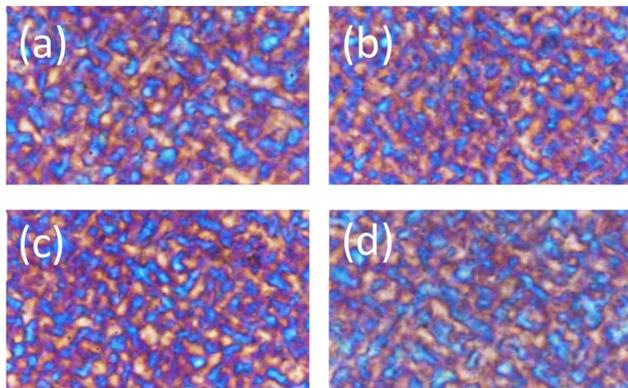
Fig. 5 *POM images of LDPE and LDPE composites with 0.5 phr content*
(a) LDPE/Al$_2$O$_3$-Pure, *(b)* LDPE/Al$_2$O$_3$-KH550, *(c)* LDPE/Al$_2$O$_3$-KH570, *(d)* LDPE/Al$_2$O$_3$-NDZ401

measure, all the results were assured by qualitative observation which was the light colour region (yellow spots). Compared with pure LDPE, a nucleation effect was observed after doping with nano-alumina particles resulting in an increased total number of spherulites and a reduced spherulite size as determined from the POM images. No major difference in the behaviour of the crystallinity was observed between the different coupling agents.

3.4 Dielectric permittivity and loss tangent

Fig. 6 describes the frequency-dependent dielectric permittivity and loss tangent of LDPE and LDPE/nano-alumina composites with different surface modifications. From Fig. 6*a*, adding nano-alumina particles has limited the influence on the dielectric constant, which suggests that both PE and its composites could be used in a wide frequency range. As for the loss tangent, all the values are in the order of 10^{-3} and stay stable with changing frequency and content. The reason for the strong relaxation peak at 1 kHz might be some agglomeration or impurities in this kind of the test sample, which results in the strong interfacial polarisation compared with other samples. It could be concluded that low filling content of nano-alumina particles into LDPE would not affect the permittivity of composites over a wide range of frequencies. In a word, PE and its composites have suitable dielectric properties between 0.1 and 10^6 Hz.

3.5 DC breakdown strength

DC breakdown strength was characterised by a two-parameter cumulative Weibull distribution function, which is a widely used
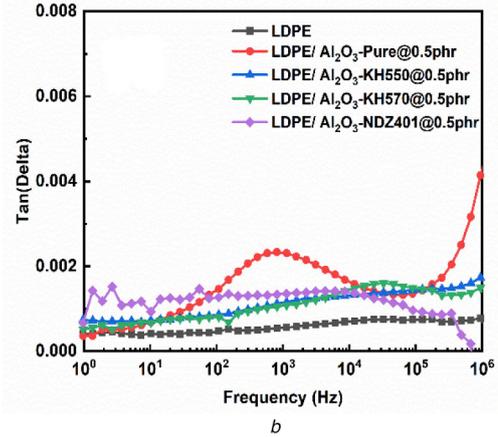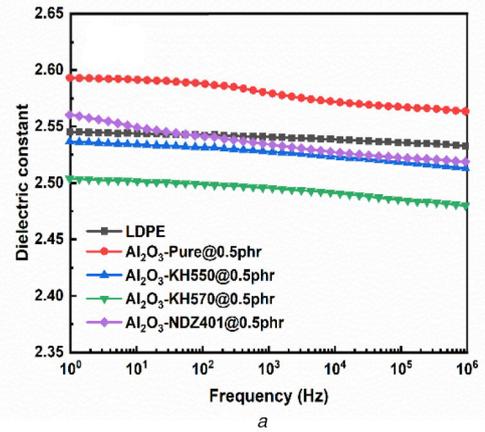

Fig. 6 *Dielectric spectra of PE and PE composites*
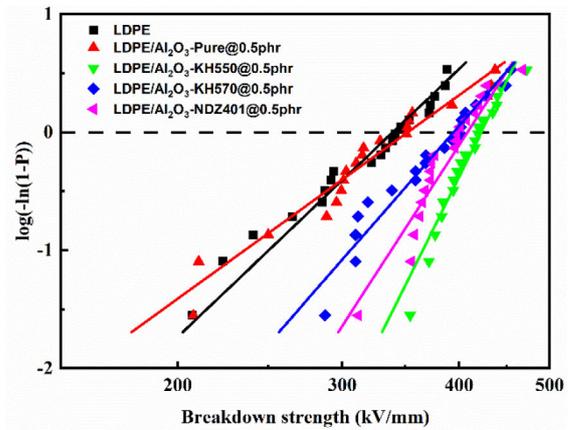*(a)* Permittivity of LDPE/ nano-Al$_2$O$_3$, *(b)* Tan (delta) of LDPE/ nano-Al$_2$O$_3$

Fig. 7 *Weibull distribution plots of the DC breakdown strength of PE composites*

method to analyse the breakdown voltage data of solid insulating materials (1):

$$P = 1 - \exp\left[-\left(\frac{E}{E_0}\right)^{\beta}\right] \quad (1)$$

where E is the experimental electric breakdown field, E_0 is the characteristic breakdown strength and represents the breakdown strength at 63.2% cumulative breakdown probability, and β is a shape parameter of Weibull distribution which describes the dispersion of the experimental results [29]. The Weibull plots of DC breakdown strength of pure PE and their composites with and without surface treatment are presented in Fig. 7. The characteristic breakdown strength of the LDPE sample is 339.7 kV/mm. Adding the pure nano-alumina particles does not seem to have any significant effect on the breakdown behaviour of the polymer.
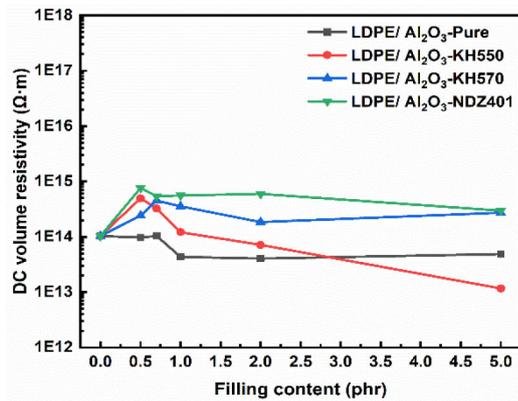
Fig. 8 *DC volume resistivity of LDPE composites with different content*

Fig. 9 *Trap level distribution in LDPE and its composite at 2 phr filling content*

However, the addition of surface-treated nanoparticles has a significant effect on the breakdown behaviour increasing the characteristic breakdown strength. The LDPE/KH550-Al$_2$O$_3$ showed the highest characteristic breakdown strength among composite samples and it reached 422.4 kV/mm, 24.3% improved compared with the LDPE sample. The results showed all types of coupling agents that have enhanced the DC breakdown strength.

Generally, the introduction of nanoparticles creates interface areas between nanoparticles and base material. The interface might influence the trap level and distribution within the composite, which improves the electrical breakdown strength according to [8, 30]. In addition, the total length of the channel the breakdown must form is one of the determining factors influencing the DC breakdown strength. The conducting channel for breakdown follows the interface between rather than through the nanoparticles. When nanoparticles are well treated and the filling content is appropriate, the agglomeration is limited and the particles are well distributed within the polymer. Before the intrinsic breakdown happens, local breakdown exists between each individual particle and base polymer. However, due to the limited size of nanoparticles and reduced spherulite size, the total length of the breakdown path increases, which enhances the breakdown strength of the composite system [7, 24, 31, 32]. When the loading content is 0.5 phr, all the surfaced modified samples exhibit higher DC breakdown strength compared with the virgin LDPE sample. This shows all three kinds of chosen coupling agents have been proved to be effective options to modify the surface of the nanoparticle, which increases both the density and energy of deep traps. The changes of deep traps increase the DC breakdown strength [24]. In conclusion, the composite samples using surface-treated nanoparticles exhibit higher breakdown strength than the base polymer, which means adding nano-alumina into PE has a positive impact on insulation performance.

3.6 DC volume resistivity

Another important parameter is DC volume resistivity, which defines the dielectric loss under DC electrical field. The resistivity values were calculated by the recorded current at 600 s after the voltage was applied. The nanoparticles act as a nucleating agent within the nanocomposite system. When a small number of nanoparticles is added, the total number of spherulites increases thus increase the amorphous–crystalline interaction area. This results in the introduction of new deep traps. In addition, the structure becomes more uniform which reduces the electron mean-free path. Hence, the volume resistivity is improved [7, 33]. As can be seen in Fig. 8, most of the nanocomposites have shown enhanced DC volume resistivity compared to the base polymer. The LDPE/Al$_2$O$_3$-NDZ401 with 0.5 phr has maximum resistivity among LDPE composites and it is about one order higher than that of pure LDPE. With the same filling content, the DC volume resistivity of surface-treated nano-alumina LDPE composite samples at filler contents lower than 2 phr is always higher than those for nanocomposites without surface treatment. The LDPE-
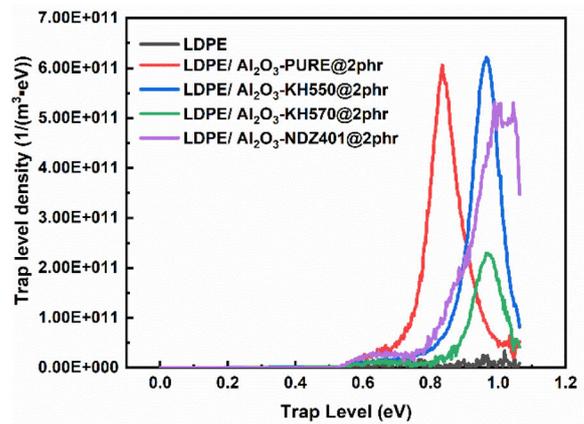
based surface-treated nanocomposites with <2 phr filling concentration therefore shows advantages in the DC dielectric loss.

3.7 TSC and trap distribution

The TSC spectrum of LDPE and its nanocomposites was firstly obtained. According to the modified TSDC theory (which allows the trap distribution to be calculated based on the TSC) [23], the trap level distribution then was calculated and presented in Fig. 9. The shallow peak of all five samples was at 0.65 eV and it was stimulated by the glass transition of LDPE. The peak of deep trap for virgin LDPE was located at 1 eV with a trap density of 2.0×10^{10} m^{-3}/ eV and the peak of deep trap for LDPE/Al$_2$O$_3$-pure with 2 phr was located at 0.8 eV with a trap density of 6.0×10^{11} m^{-3}/eV. From the result, the peak of deep trap shifted towards 1.1 eV with different coupling agents. The LDPE/titanate-coated alumina had the widest trap level range and the peak was about 1.05 eV. The trap distribution is tightly linked with the electrical performance of nanocomposites. The deep trap is believed to have the ability to capture more charge carriers and therefore reduce the carrier charge mobility [22–34]. This can also be verified by the enhanced DC resistivity of LDPE/nano-alumina with surface modification. For the nano-alumina particles with 2 phr filling content, the sample with NDZ401 has the largest number of deep traps so that its DC resistivity is highest.

4 Summary and conclusion

In this paper, the effect of different coupling agents on different DC dielectric properties has been explored. The process of surface modification by three kinds of coupling agents for nanoparticles and their blending with polymer samples have been described. To characterise new nanocomposite material, chemical, morphological and electrical study was conducted. The TGA and FTIR results have proven the success of surface modification by KH570 for nanoparticles. The SEM images showed a better distribution of nanoparticles within base material and improved the non-agglomeration of nanoparticles. The effect of nanoparticles on altering DC breakdown strength and DC volume resistivity of LDPE nanocomposites has been demonstrated and possible explanations for the changes observed have been discussed. Specifically, both KH550 and NDZ401 have better compatibility for the LDPE composite system compared with KH570. Sample of LDPE/KH550-Al$_2$O$_3$ with 0.5 phr shows the highest DC breakdown strength and increased by 24% compared with virgin LDPE sample. The presence of deep traps in the interfacial region decreases the charge carrier mobility and improves the DC resistivity at several times the number of magnitudes. On all accounts, the results on the DC electrical properties of nano-Al$_2$O$_3$/ LDPE composite reveal that surface modification is a necessary process for nanocomposite material and it can significantly affect their electrical properties as future recyclable HVDC cable insulation.

5 Acknowledgments

6 References

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