

Polyethylene/Aluminum Nanocomposites: Improvement of Dielectric Strength by Nanoparticle Surface Modification

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ABSTRACT: The effect of the surface modification with a silane coupling agent (octyl-trimethoxysilane) of aluminum (Al) nanoparticles on the dielectric breakdown behaviors of polyethylene (PE)/Al nanocomposites was investigated in comparison of the influence of the improvement of the interfacial adhesion between Al nanoparticles and PE using a compatibilizer (maleic anhydride grafted polyethylene). It was found that when compared with the other modification approaches, the surface-treated Al nanofiller with the silane coupling agent makes it possible for the PE/Al nanocomposites to still keep the relatively higher breakdown strength even in the higher Al

loading level above 14 vol %, which can be understood in terms of the better interfacial adhesion between the surface-treated particle dispersion and the matrix. The combined effects of the Al nanoparticles on the different factors which influence the dielectric breakdown processes in polymer matrix such as microstructure, conductivity, and crystallinity of the nanocomposites were discussed in detail. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3577–3584, 2009

Key words: dielectric properties; polyethylene (PE); aluminum; nanocomposites; surface modification

INTRODUCTION

Polymer composites loaded with metallic fillers can have high dielectric constants and are highly desirable for use in various branches of application, such as electric stress control, electromagnetic shielding, and higher storage capability of the electric energy. Recently, polymer composites filled with metal nanoparticles have invoked much interest because of their low percolation threshold and high dielectric constant.^{1–3} It should be noted that, although several polymer/metal nanocomposites with very high dielectric constant have been prepared up to now, but that few paper have dealt with the systematic investigation on the dielectric strength of the nanocomposites yet.¹

The dielectric breakdown behaviors of the nanocomposites are of great importance from the viewpoint of their practical applications in the aforementioned high voltage engineering.³ Of interest is to grasp how to prepare the polymer composites not only with the expectable high dielectric constant, but also with high electrical breakdown strength. Actually, because the

metal nanoparticles generally have high specific surface and surface tension, they are favorable to self-aggregation in most polymer matrix, which has been understood as one of the main reason why the dielectric loss increases and breakdown strength decreases in the polymer/metal nanocomposites.⁴

To resolve these problems, quite necessary is that effective approaches should be introduced so as to realize the better particle dispersion in the polymer matrix⁵ and to reduce the electrical conduction between the neighboring particles as possible as could.

Recently, the authors have focused on the electrical properties of polyethylene (PE)/aluminum (Al) nanocomposites, and shown that PE/Al nanocomposite can be a promising material for stress control in the power cable terminations.^{3,6} This paper aims to discuss the effect of a silane coupling agent (octyl-trimethoxysilane) and a compatibilizer (maleic anhydride grafted polyethylene) on improvement of the interfacial adhesion between Al nanofillers and polyethylene and the increase in dielectric strength of the PE/Al composites.

EXPERIMENTAL PROCEDURE

Materials

The Al nanoparticles with an average diameter 100 nm were supplied by Hongwu Nanomaterials

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(Xuzhou, Jiangsu, China). The polyethylene used was linear low density polyethylene from ExxonMobil in Saudi Arabia. Octyl-trimethoxysilane (OTMS) from Degussa (Germany) was used as a coupling agent. A maleic anhydride grafted polyethylene (Ma-PE) donated by Shanghai SUNNY New Technology Development (CMG9904, Shanghai, China) was used as a compatibilizer. The molecular structures of OTMS and Ma-PE were shown in Scheme 1.

Sample preparation

As used in our previous research,^{3,6,7} the solution compounding method was adopted to prepare the PE/Al nanocomposites. The surface modification of the Al nanoparticles with OTMS was carried out by using the dry toluene reflux method and described in detail elsewhere.⁷ For the composites using the Ma-PE as a compatibilizer, the following equation was used to determine their compositions:

$$\text{LLDPE (vol \%)} + \text{compatibilizer (vol \%)} + \text{Al (vol \%)} = 100\% \quad (1)$$

where, compatibilizer (vol) = 15% Al (vol).

Thin films with thickness of around $250 \pm 10 \mu\text{m}$ were used for measurement. The films were obtained using compression molding at 140°C under a pressure of about 10 MPa. To avoid or minimize the influence of residual internal stresses on the experimental results, each sample was kept in a desiccator for at least 7 days before the dielectric breakdown strength were measured.

The nanocomposites were denoted using the following notation: particle pattern-coupling agent or compatibilizer-particle volume fraction, thus N-2.0, S-2.0, and L-2.0 indicate the nanocomposites with 2.0 vol % Al particles without modification, with

2.0 vol % Al nanoparticles modified with OTMS and the composites prepared with the Ma-PE as a compatibilizer, respectively.

Sample measurements

Morphologies of fractured surfaces of the PE/Al composites were characterized by scanning electron microscopy (JEM-7401F, Japan). Cylindrical samples were broken in liquid nitrogen and sputtered with thin layers of gold to avoid the accumulation of charge.

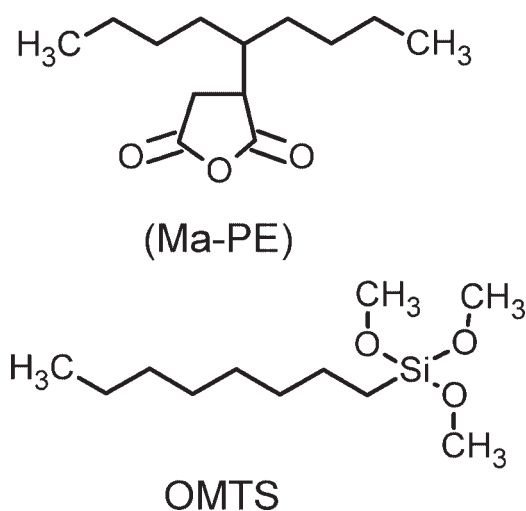
Dielectric breakdown strength was measured using an AHDZ-10/100 alternating-current dielectric strength tester (Shanghai Lanpotronics Corporation, China) according to ASTM D 149-2004. The specimens were placed between two 10-mm-diameter copper ball electrodes and the electrode system containing the measured sample was immersed in the pure silicon oil to prevent the surface flashover. The test voltage was applied across two ball-typed electrodes and was increased with a rate of 2 kV/s until the sample was punctured. Twenty breakdown tests were repeatedly performed on each specimen. To assure the accuracy of the dielectric breakdown test, the dielectric breakdown data for each sample were statistically treated using two-parameter Weibull distribution analysis.⁸ The Weibull statistical distribution in the case of step or ramp voltage test can be written as

$$P(E) = 1 - \exp\left[-\left(\frac{E}{E_0}\right)^\beta\right] \quad (2)$$

where, E is an experimental breakdown strength, P is the cumulative probability of electrical failure, β is the shape parameter which is a measure of the spread of breakdown strength, E_0 is the scale parameter that represents the breakdown strength at the cumulative failure probability of 63.2%, which is often used to compare the dielectric breakdown intensities of various samples with one another.

DC current measurements were performed by using a Keithley 6517A Electrometer/High Resistance Meter. Gold electrodes were evaporated on the front and rear surfaces of the samples (the front electrode, 2 cm in diameter, surrounded by a guard ring, and the back electrode deposited on the whole rear surface). A given voltage (1 kV/mm) was applied for 20 min, and the charging current was recorded. The dc current was measured after applying the dc voltage to the specimens for 1 min according to ASTM D257.

The crystallinity of the samples was analyzed using a Perkin-Elmer Pyris-1 DSC. All the samples were accurately weighted ($\approx 5.0 \text{ mg}$) and had the same shape and size – a circular film with the same diameter as the sample pan. The samples were heated from 20°C to 170°C at a heating rate of $10^\circ\text{C}/\text{min}$, and the



Scheme 1 The molecular structures of Ma-PE and OTMS.

endothermic curves were recorded as a function of temperature. The crystallization of degree X_c can be determined with $X_c = \Delta H_f / (\Delta H_m(1 - \phi))$, where ΔH_f is the heat of fusion determined by integrating the area under the normalized melting curves from 40°C to 130°C and ΔH_m is the enthalpy corresponding to the melting of a 100% crystalline sample and $\Delta H_m = 293 \text{ J/g}$ for PE. ϕ is the weight fraction of the particles in the composites. All of DSC measurements were performed under N_2 atmosphere. The instrument was calibrated with an Indium standard.

RESULTS AND DISCUSSION

Breakdown strength of the composites

Figure 1 displays the dependences of the characteristic breakdown strength (Weibull scale parameters) on the loading level of the Al nanoparticles for the composites Ns, Ls, and Ss. It should be noted that the significant effects of the surface modification of the nanofiller and the compatibilizer are more and more apparent as the loading level of the nanofiller increases. Of interest is that only the surface modification of the Al nanofiller with the silane coupling agent makes it possible for the PE/Al composites to still keep the relatively higher breakdown strength even in the higher Al loading level above 14 vol %.

As shown in Figure 1, three kinds of nanocomposites considered show lower values of dielectric breakdown strength when compared with the neat polymer, which can be understood in terms of the roles of the Al nanoparticles and clusters as the electrical defects. It is well known that metallic particles and clusters in the polymer matrix act as the defects which can locally amplify the electric field intensity around the interfaces between the filler particles and the polymer matrix.

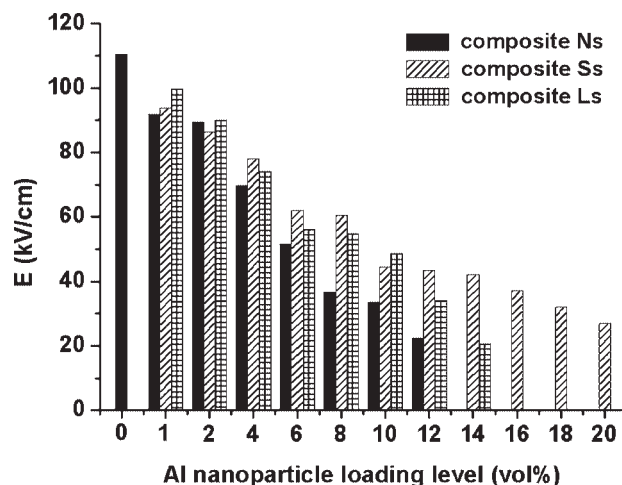


Figure 1 The breakdown strength at the cumulative failure probability of 63.2% for various nanocomposites.

Effects of dispersion of nanoparticles and interfacial adhesion on breakdown strength

Here, it is worth noting why the different kinds of composites show different dielectric breakdown behaviors in spite of the fact that the loading levels of Al nanofiller are the same with one another. Firstly, this phenomenon should be attributed to the difference of the degree of dispersion of Al nanoparticles in PE matrix. As can be seen from Figure 2, the fractured surfaces of the PE/Al composites observed in this study show the obvious differences in microstructure from one another, depending both on the surface state of the nanofiller and on whether or not the compatibilizer has been used. When compared with the samples N-12 and L-12, the morphology of the composite S-12 displays a good visual distribution: Al nanoparticles are dispersed into PE matrix without any agglomerates larger than 1 μm . However, the dispersion of the Al nanofiller without any surface modification in the sample N-12 is so poor that some larger agglomerates with arbitrary shapes can be observed in SEM photographs. Although some agglomerates of several micrometers in size can be observed in the sample L-12, it shows relatively better dispersion when compared with N-12. According to our large number of SEM observations for other samples, the compatibilizer, Ma-PE is shown to significantly improve the dispersion of the Al nanoparticles without any modification and to create the interfacial interactions between the polymer phases and the Al nanoparticles when the loading levels of the Al nanofiller are less than 14 vol %. Beyond 14 vol %, as shown in Figure 2(e), any improvement of Al nanoparticle dispersion cannot be found and the introduction of the Ma-PE results in deteriorating the dispersion of the Al nanoparticle when compared with the composite Ns. For the composites Ss, however, all the samples show the significantly improved dispersion when compared with the composites Ns (Fig. 2). These results suggest that OTMS can increase the interfacial adhesion between the Al nanoparticles and the polymer matrix whereas the Ma-PE can only improve the dispersion of Al nanoparticles of the low loading levels in PE. According to eq. (1), the fraction of Ma-PE added in the composites with low nanoparticle loadings is also small. In this case, it is considered that the Ma-PE is well dispersed in PE matrix. A primary mechanism in improving the dispersion of Al nanoparticles involving lowering the interfacial tension between the separated phases and preventing coalescence of the nanoparticles during processing. At higher nanoparticle loading levels, however, the fraction of Ma-PE is also larger according to eq. (1), in which case the composites may consist of Ma-PE-rich phase and PE matrix. On the

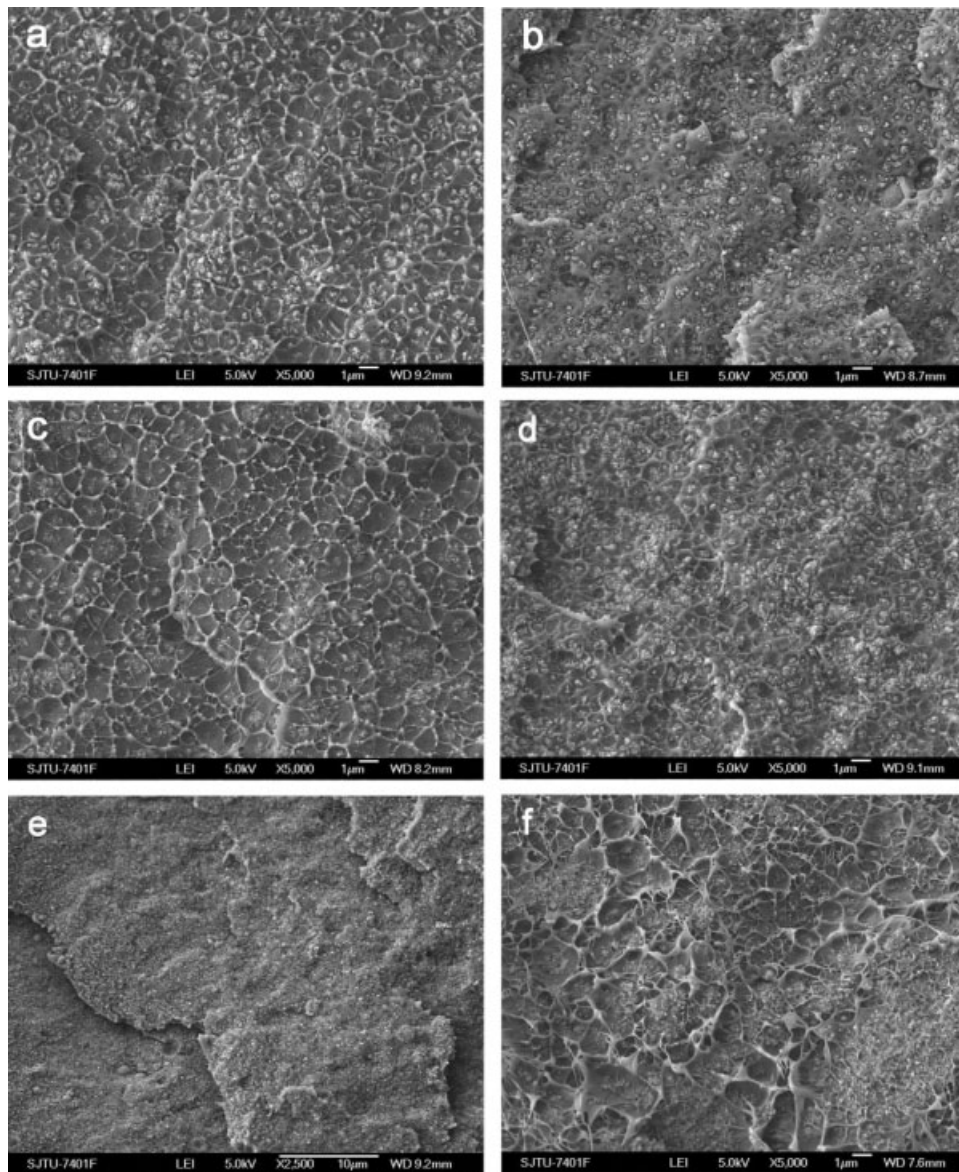


Figure 2 SEM morphologies of the fractured surfaces of composite N-12 (a), S-12 (b), L-12 (c), N-16 (d), S-16 (e), and S-16 (f).

other hand, the Al nanoparticles tend to be located in Ma-PE-rich phase because of their hydrophilic surface. Therefore, the Ma-PE can result in deteriorating the dispersion of the Al nanoparticles at high loading levels when compared with the composite Ns.

As well known, two Weibull statistical parameters, e.g., the scale (E_0) and shape (β) parameters are representative of the characteristic value and the scatter of dielectric breakdown strength, respectively⁹: the greater the scale parameter, the higher dielectric breakdown strength; the smaller the shape parameter, the severer the scatter of the measurement data for the dielectric breakdown strength. Especially in the case of polymer composites loaded with metal or non-metal particles, the scatter of the breakdown

strength data is closely related to the dispersion characteristics of the fillers in the polymer matrix.

Figure 3 presents the different behaviors of the Weibull statistical distribution for the electrical breakdown strength behaviors of the neat PE, N-8, S-8, and L-8 samples, which shows the significant effects of the silane coupling agent and compatibilizer on the interfacial interactions between the Al nanoparticles and polymer matrix.

In PE/Al composite systems considered here, the β values are found as 11.58, 11.34, 10.14, and 6.39 for the neat PE, S-8, L-8 and N-8, respectively: N-8 has the minimal β value, indicating the greater data scatter of dielectric breakdown strength resulting from the worst particle dispersion among three kinds of the composites studied, which also strongly supports

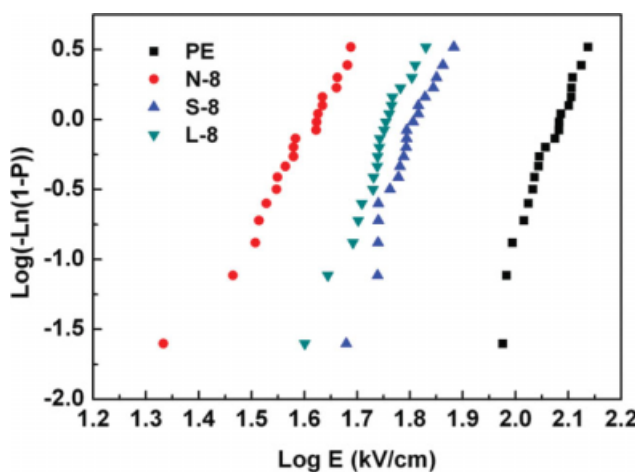


Figure 3 Weibull plots of ac dielectric breakdown strength of PE, composite N-8, S-8, and L-8. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the aforementioned microstructure investigation results.

Another factor that can affect the breakdown strength is the interfacial adhesion between the metallic particles and the matrix. Detailed chemical characterization of coated nanoparticle surfaces was described in elsewhere.^{7,10} It has been found that ~ 1 wt % of OTMS silane coupling agent covalently bonded to the Al surface and that the surfaces of the OTMS coated nanoparticles were more hydrophobic when compared with the surfaces of the as received nanoparticles because of the introduction of non-polar octyl groups on the surfaces. The schematic of surface characteristics for a silane treated Al nanoparticle is presented in Figure 4.

After the surface modification, the non-polar octyl groups on the surface of the Al nanoparticles

make the particles have better interfacial adhesion between the particles and the matrix. This compatible interface reduces the possibility of the formation of small voids and pores in the interface, which may be another reason why the values of dielectric breakdown strength are higher in the composite Ss and Ls than in the composite Ns. For the composite Ls with low Al loading level ($\leq 14\%$), the introduction of the Ma-PE is observed to improve the interface adhesion between the metallic particles and the matrix, so further increasing the breakdown strength when compared with the composite Ns. It also should be noted that the composite L-1 and L-2 have higher breakdown strength than those of composite Ss, which may be explained in terms of the charge trapping and scattering effect of polar groups in the Ma-PE. It is well known that because of their high polarity the polar groups can not only trap the movable charged particles, but also decrease the acceleration of electrons in the local discharged regions formed by the applied electric field high enough to cause the local dielectric breakdown in the relatively weak defects, e.g. voids and the other imperfections, thus decreasing the chance of their initiating a dielectric breakdown.¹¹ On the other hand, the voids probably formed during the sample preparation processes can be additively filled with the high polar Ma-PE, which can be another reason why the incorporation of the Ma-PE further increase the dielectric breakdown strength of the PE/Al composites than the surface modification of the nanofillers with the silane coupling agent when the Al loading levels are very low. As the nanoparticle loading levels further increase, however, the van der Waals forces among the particles can reach such a high level that the Ma-PE can not show a dispersion effect, this leading to the reduction of breakdown strength of the composites.

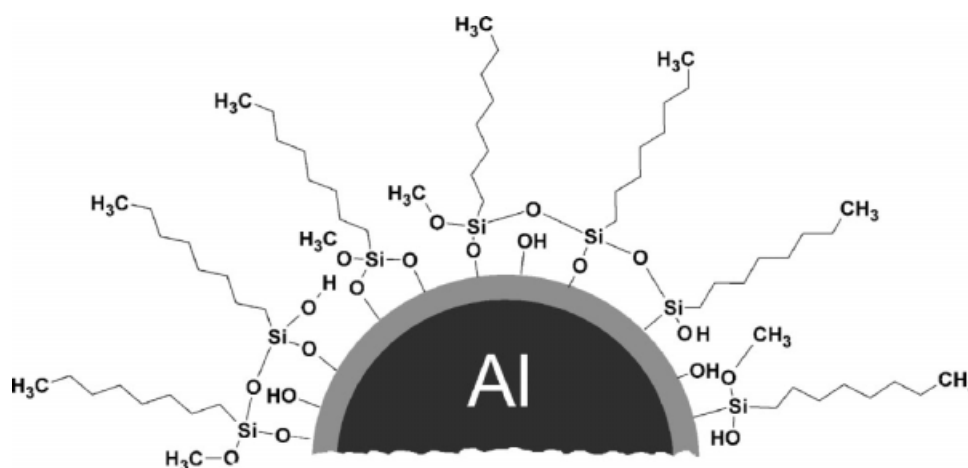


Figure 4 Schematic of surface characteristics for a silane treated Al nanoparticle.

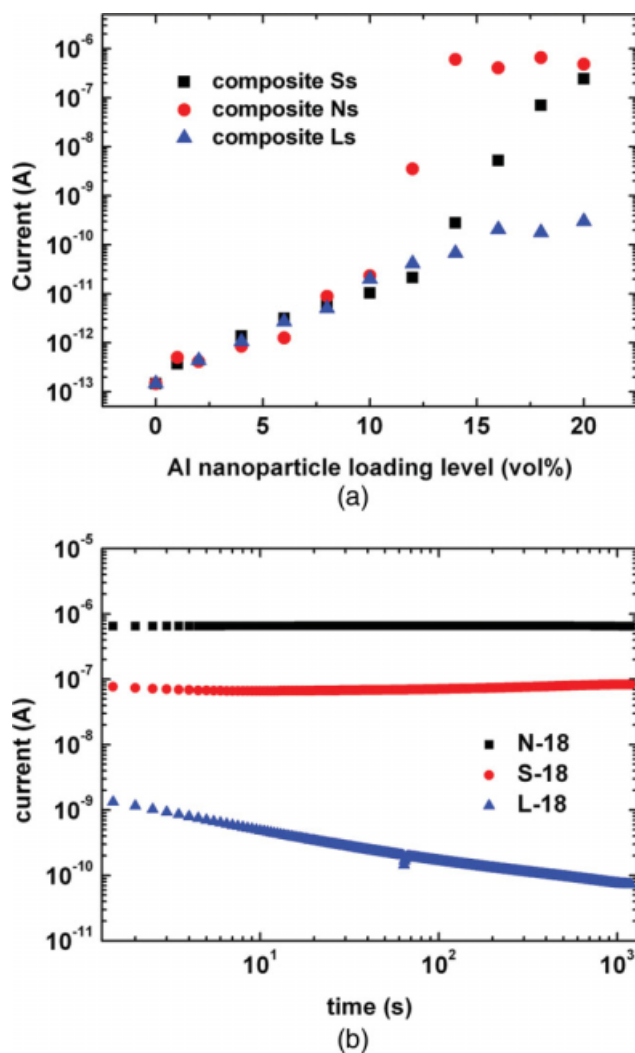


Figure 5 (a) Plots of dc charging current versus the loading level of nanofillers and (b) time dependence of dc charging current for the nanocomposites (the applied field and temperature: 1 MV/m, 303 K). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Effects of conductivity on breakdown strength

According to dc current measurement results for the three kinds of composites (Fig. 5), the incorporation of Al nanoparticles with and without the surface modification tends to increase the dc conductivity of the composites when compared with the neat PE, while the surface modification clearly decreases the dc conductivity of the composite Ss with high loading level than that of the composite Ns with the same Al loading level. It is also should be noted that the composites Ns just lose their dielectric strength when the conductivity of the composites reaches its maximum value at Al loading level of 14%. Therefore, it is expected that the loss of dielectric strength for the composites with high Al loading levels may

be partly attributed to their high electrical conductivity. However, the increase of electrical conductivity cannot be used to explain all the dielectric strength results of the three kinds of composites. As seen from Figure 5: (i) all the three kinds of composites with the loading level less than 10% have the similar conductivity; (ii) the composite Ls with Al loading level higher than 14% have a lower electrical conductivity than the composite Ss with the same Al loading levels. It is interesting to know why the composite Ls with high loading level have a lower conductivity in comparison with the composite Ns and Ss. As mentioned above, the incorporation of Ma-PE can lead to very poor dispersion of nanoparticles in the high loading levels, causing some large agglomerates of several micrometers in diameter to be seen, which makes the formation of the conducting path of nanoparticles difficult. The time dependence of the dc current for the nanocomposites, shown in Figure 5(b) strongly supports this assumption: the decreasing characteristic of the time dependence of dc current can be no longer found for N-18 and S-18, whereas the dc current of the composite L-18 is found to significantly decrease with time and the conductivity value is much less than those of N-18 and S-18. Combined with the observation results on the microstructure of the nanocomposites, the main factor to determine the dielectric strength characteristics of the PE/Al nanocomposites is considered to be the particle dispersion properties, e.g. the size, shape and spatial distribution of the particle clusters, while the externally-introduced charge carriers may only be the secondary factor in our cases.

Effects of crystallinity and crystalline morphology on breakdown strength

It has been known that the crystallinity and crystalline morphology can affect the breakdown strength of polyolefins.¹² Therefore, it is important to evaluate the influence of Al nanoparticles on the crystallinity and crystalline morphology of the PE matrix. Figure 6 presents the crystallinity changes of PE in the composite Ns and Ss with Al loading levels. It can be seen from Figure 6 that all the composite samples have the similar values of crystallinity with the neat PE, ranging from 40 to 50%. The difference between the two kinds of composites is found to be within the experimental errors and considered to be insignificant. Therefore, it can be concluded that the nanoparticles with and without surface modification do not cause any significant differences of the crystallinity of PE. Although the initial and final melting temperatures of the composite Ns and Ss are higher than those of the neat polyethylene (Fig. 7), there is no significant difference between the two kinds of

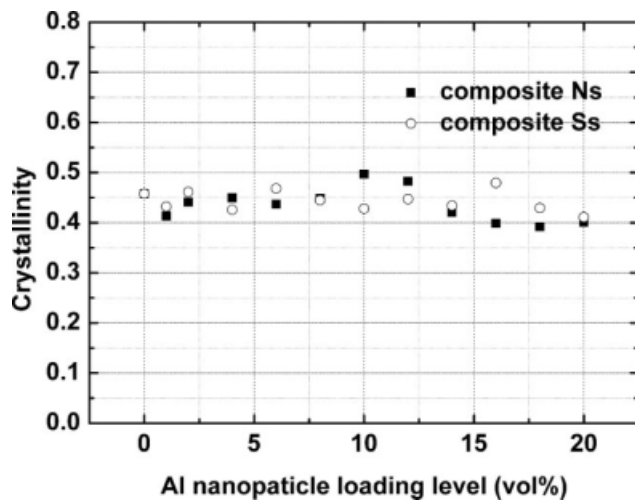


Figure 6 Changes in crystallinity of composite Ns and Ss with Al loading levels.

composites. According to Gibbs-Thomson equation,¹³ the observed values of melting temperatures of the LDPE/Al composites indicate similar size and size distribution of the LDPE crystals. These results lead to the following conclusions: (i) the decrease of the dielectric breakdown strength in the composites could not be linked to any changes of the crystallinity of the polymer matrix; (ii) the differences in breakdown strength between composite Ns and Ss could not be attributed to the changes of crystal size of PE.

Data analysis using Beale and Duxbury's model

According to Beale and Duxbury's model used to describe the dielectric breakdown characteristics of metal-loaded dielectric composites,¹⁴ the breakdown strength E_{bre} decreases logarithmically with the linear dimension L of the composites when the volume fraction of the metal p_{metal} is below the percolation threshold p_c and behaves as

$$E_{bre} = \frac{(p_c - p_{metal})^v}{\ln L} \quad (3)$$

According to eq. (3), the breakdown strength tends to zero if the metal fraction in the insulating matrix reach the percolation threshold. Detailed discussion of the percolation threshold of the composites is not an emphasis here; this was covered in another article.¹⁰ Briefly, it was found that the values of the electrical percolation threshold were 9.7% for composite Ns and 12.1% for composite Ss, respectively.

For the composite Ss, however, the breakdown strength is observed to still have relatively high values when the Al loading levels are beyond the percolation threshold, which may be mainly attributed to the existence of very thin barriers of polymeric mate-

rial between metallic clusters. After the surface modification, the Al nanoparticles with the non-polar octyl groups attached on their surfaces have good adhesion with the polymer matrix, which makes it easy for the adsorption of the polymer chains onto their surface to occur. The absorbed polymer chains can act as the dielectric barrier governing the tunneling conduction between the neighboring Al cores; on the other hand, the absorbed polymer chains make it impossible for the complete contacts to be realized between the nanoparticles. The self-passivation characteristics of Al particles may be another reason why the PE/Al composites still have relatively high breakdown strength even when the nanoparticle contents are beyond the percolation threshold.^{5,6} The passivated oxide layer around the metallic core surface can also act as the dielectric barrier governing the tunneling conduction between the neighboring Al cores.^{5,6} Combined with the experimental fact that high dielectric constant only can be realized for the composites with comparatively high nanoparticle loading levels,^{3,10} it is worth noting that the above-mentioned composites with high particle loadings still have good dielectric breakdown characteristics, this being of a great significance for practical applications.

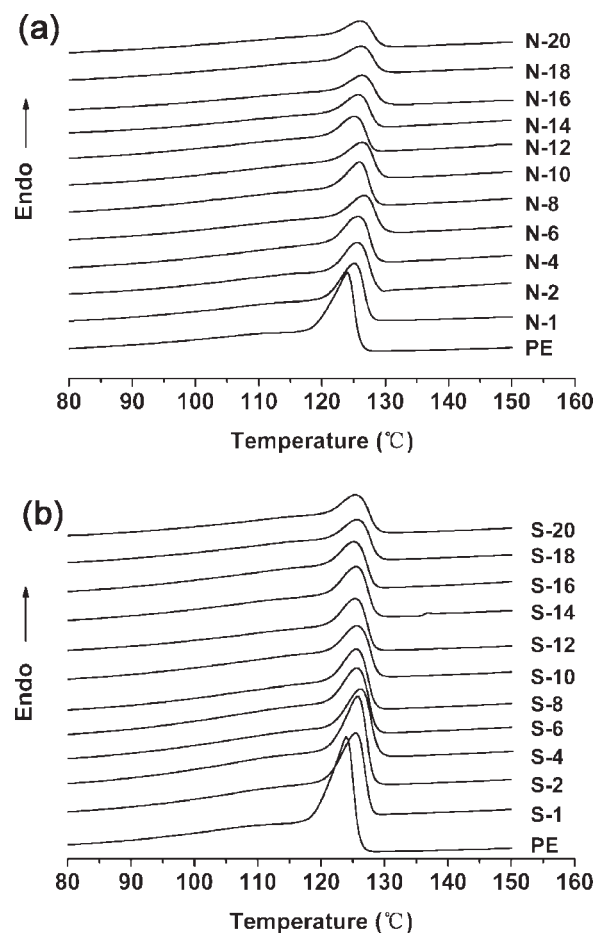


Figure 7 Melting curves of composite Ns and Ss.

CONCLUSION

We have discussed the effect of the surface modification of Al nanoparticles or the introduction of a compatibilizer on the dielectric breakdown behaviors of polyethylene/Al composites. It has been shown that Al nanoparticles play the multiple roles in the breakdown mechanisms for the polymer matrix. Dispersed Al nanoparticles or cluster not only act as the defect centers for the electric field enhancement but also increase the dc conductivity, which are the main reasons why the breakdown strength of the composites is lower than that of the neat PE. The relatively higher breakdown strength of the composites prepared with surface-treated nanoparticles in comparison with those prepared with the original nanoparticles may be attributed to the better particle dispersion combined with good interfacial adhesion between the surface-treated nanoparticles and the matrix. It is also concluded that the main factor to determine the dielectric strength of the PE/Al composites is the particle dispersion properties and the externally-introduced charge carriers may play a secondary role. The above investigation hints at that the surface modification of the metal nanoparticles is surely necessary for preparing the useful polymer/metal nanocomposites with high dielectric constant

but without any significant reduction of their dielectric breakdown strength.

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