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Research Article

Development of Innovative Functional Electrical Insulating Composites

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Abstract

Recently, a strong demand arises for improving functionality such as electrical insulation, thermal and mechanical properties of insulating polymer composites by filling a small amount of inorganic fillers instead of conventionally adding large amount of fillers up to 50 to 80 vol%. Functionally graded materials (FGM) also provide a special functionality such as electric field grading and adding a non-linearity in the electrical conduction. This review paper presents fundamentals and application of innovative functional electrical insulating composites and their characterizations, which are mainly performed jointly with Professor Tanaka under his guidance. The article begins with recent research trend of development of the functional electrical insulating composites, and then presents nano-alumina coating technique for electrical insulation, filler orientation technique by electric fields for attaining high thermal conductivity, nanocomposite technique for improvement of electrical Insulation, and application to voltage limiting devices as well.

Keywords: functional insulating composites, filler orientation, high thermal conductivity, nano micro composites

1.Introduction

Masayuki Hikita (MH) first met Professor Toshikatsu Tanaka when he was a researcher at the Central Research Institute of Electric Power Industry in 1980's. At that time, he had introduced a mini-computer, which is now called IoT, to research in the field of electrical insulation by applying it to partial discharge (PD) measurement for the first time. MH was also strongly impressed by Prof. Tanaka's theoretical consideration in the complex mechanisms of water and electrical tree generation and growth in polyethylene cable solid insulating materials.

Later, as Professor Tanaka was working on laser induced lightning as a Visiting Professor at Kyushu University, MH often met him at meetings in the field of dielectric and insulation technology in the same Kyushu area as MH, who was also stimulated by his active research activities with heated discussions.

At that time, Prof. Tanaka was advocating the importance of developing polymeric nanocomposite (NC) materials for aiming all-solid-state substations in the future. In 2002, he was appointed as a professor to start Graduate School of Information, Production and Systems (IPS) of Waseda University in Kitakyushu district, and then Masahiro Kozako (MK) joined Prof. Tanaka's laboratory as an assistant professor. Prof. Tanaka and MK started their NC research from literally "zero" in 2002 at the newly established IPS. It took about two years to set up a research facility that could develop practical NC materials such as epoxy resin and silicone rubber, starting from the evaluation of available samples.

In the beginning of the research, they started with the discovery of the development of PD resistance by NC technology, and then studied the development of NCs for insulating substrates and silicone rubber NCs for polymer insulators.

After MK left Waseda University in 2005 and joined Kyushu Institute of Technology (Kyutech) in 2008 where MK has collaborated with MH, while MH and MK continued joint research with Prof. Tanaka and received a lot of useful advice to pursue the research on development of new functional insulating materials used for electric power apparatus and power electronics equipment.

In the next chapter, we will introduce some of the results of these studies collaborated with Prof. Tanaka and those under his guidance and advice.

2. Development and characterization of functional composite insulating materials

2.1 Development of polymer nanocomposite insulating materials

Polymer nanocomposites (polymer NCs) are composite materials in which fine particles (nanofillers) with a size of 100 nm or less are uniformly dispersed in a polymer matrix. Wide unit surface area of NCs enables to exhibit new functions. Polymer NCs has been attracting worldwide

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attention in the field of dielectric and insulating materials since around 2000. Polymer NCs are expected to contribute to high integration, compactness, high functionality, and high efficiency of devices in the electric power and electronics fields.

Tab. 1 and Tab. 2 summarize results of research on polymer NCs at Kyushu Institute of Technology, and the material control technologies used so far and evaluations, respectively. We are developing polymer NCs insulating materials for power equipment, cables, outdoor insulation, power modules, new functional materials by controlling filler electric field orientation, and evaluating electrical insulation properties of new fillers and new base polymers. Based on these results, we aim to achieve high thermal conductivity, high heat resistance, weather resistance, long life, and good electrical insulation, as well as practical application.

Table 1. Research topics and outcomes on polymer nanocomposites in Kyushu Institute of Technology

Target	Purpose	Polymer	Filler
1) Outdoor Polymer Insulator	Improvement of Resistance to Erosion	Silicone rubber	Nano-SiO_2, Nano-AlO(OH)
2) Substrate for Power Module	Both Increasing Withstand Volt. & Th. Conductivity	Epoxy resin	Micro-filler + Nano-SiO_2, Nano-Al_2O_3
3) Coating for Insulators	Antistatic by Controllable Resistivity	Epoxy resin	CNT
4) Enamel Wires	Improvement of Resistance to Inverter Surge	PEI, PI	Several Nano
5) GIS Spacer	Improvement of FOV, Downsizing	Epoxy resin	Nano-Micro

Table 2. Technology used for development of functional insulating materials in Kyushu Institute of Technology

Technology or Material	Characteristics	Possible Application
6) Dilectro-phoresis	Filler Alignment to Extract Filler Feature	various
7) Electrophoresis	Filler Density Distribution Control	Electric Field Relaxation
8) Nano-Alumina Coating	Modification to Insulation	various
9) C60, Fullerene	Improvement of Insulation	various
10) Hydrocarbon Thermosetting Resin	Low Viscosity, Improvement of Insulation	Molding for HV/HT Devices
11) Microporous Polymer	Low Permittivity, Increment of PDIV	Enamel Wires

Nanosilica-filled silicone rubber nanocomposites were developed and evaluated for their tracking and erosion resistance, arc resistance, flame retardance, mechanical properties, and electrical properties. It was found that the addition of a small amount of nanosilica improved the tracking and erosion resistance, arcing resistance, flame retardance, and other properties. [1, 2] Fig. 1 shows the average values of erosion depth after the inclined plate test for each sample. As shown in the Fig. 1, the erosion resistance, including the tracking resistance, is dramatically improved by the addition of 0.5 wt% nano-beamite alumina AlOOH. Note that even the specimen with 0.5 wt% boehmite (AlOOH) nanofillers exhibits sufficiently improved resistance to surface tracking, while 3 wt% is needed for silica nanofiller. This superior AlOOH addition effect is caused by the presence of the hydroxyl group or crystal water which reacts as flame retardant.

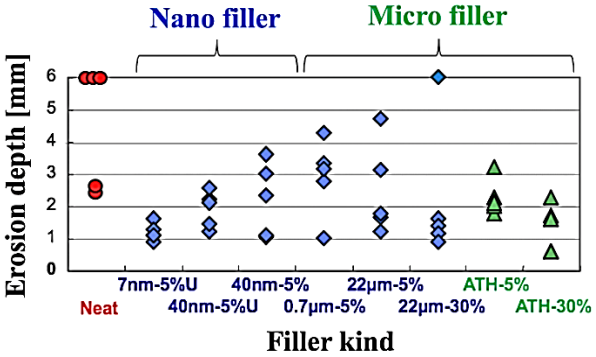

Fig. 1. Average erosion depth for each specimen after the inclined plane test. U and ATH stand for nanocomposites prepared using a ultrasonic homogenizer and composites mixed with micro-sized acid tri-hydride filler.

2.2 Development of olefin-based thermosetting resin insulating materials

Poly-dicyclopentadiene (P-DCP), a hydrogen-based thermosetting resin, and its high heat-resistant type, poly-tricyclopentadiene (P-TCP), were mainly tested to investigate their applicability to electrical insulating materials. Evaluation was made on the viscosity of the main agent, glass transition temperature, flexural strength, flexural modulus, linear expansion coefficient, water absorption coefficient, dielectric properties, volume resistivity and dielectric breakdown strength of the neat resins [3]. Fig. 2 shows the molecular structural formulae of P-DCP and T-DCP. Tab. 3 lists various properties of P-DCP and T-DCP in comparison with epoxy resin. Fig. 3 shows the temperature dependence of DC conductivity of P-DCP and T-DCP. It can be seen in the Fig. 3 that the olefinic thermosets present lower conductivity than epoxy resins up to the high temperature range of 250 to 300 ºC. These results show that hydrocarbon thermosets are promising as electrical insulating materials.

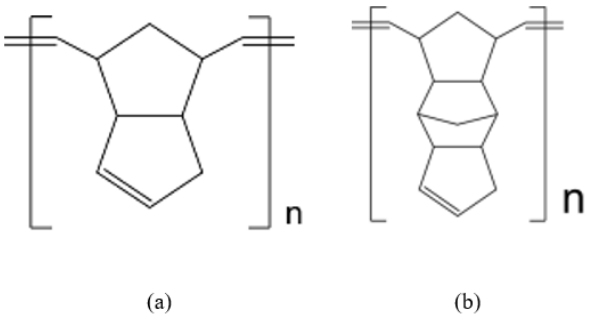

Fig. 2. Molecular structure of (a) P-DCP and (b) T-DCP.

In order to investigate the above dielectric and conductive properties, an attempt was made to estimate the permittivity of DCP and TCP with the basic unit of monomer structure and the degree of polymerization n=1 to 5 from the polarization rate calculation by quantum chemical calculation using density functional theory (DFT) [4].Calculation was also made to estimate the energy gap φ_g defined by a difference in the energy level between HOMO (highest occupied molecular orbital) and LUMO (lowest

unoccupied molecular orbital).

Table 3. Properties of P-DCP and T-DCP as compared with epoxy resin [3].

		P-DCP		P-TCP		Epoxy
Main resin		PENTAM 8000MS (RIMTEC)		(RIMTEC) PENTAM		jER828 (Mitsubishi Chemical)
Hardener		PENTAM 8000CS (RIMTEC)		8000CS (RIMTEC)		jER113 (Mitsubishi Chemical)
Viscosity of main resin in liquid form	(mPa·s)	3		9		12,000
Specific gravity	(g/cm^3)	1.04		1.09		1.13
T_g (DMA)	(°C)	156		278		161
Flexural strength	(MPa)	81		95		113
Flexural modulus	(GPa)	2.0		3.1		2.7
Coefficient of linear expansion	(ppm/K)	83.3		60.6		65.5
Moisture absorption A (at 130 °C, 85% RH, 4 days)	(%)	0.05		–		1.71
Relative permittivity ε, (at 63.1 Hz, 20 °C)	(−)	2.82		2.81		4.20
tanδ (at 63.1 Hz, 20 °C)	(−)	0.0058		0.0052		0.0093
Volume resistivity ρ, (at 23 °C)	(Ω·cm)	4.2×10^{18}		7.9×10^{18}		2.8×10^{18}
Breakdown strength (at 23 °C)	(kV$_{rms}$/mm)	110.8		106.1		92.2

The quantum chemical calculations allow us to calculate a microscopic physical quantity, i.e. the polarization coefficient. Assuming that the Lorentzian internal electric field can be applied, the relative permittivity ε_r, which is a macroscopic physical quantity, is calculated. ε_r of DCP and TCP was calculated to be 2.62 to 2.68 in the range of polymerization degree n=5. The calculated ε_r were found to be in good agreement with measured values of 2.86 and 2.81 for DCP and TCP, respectively[4].

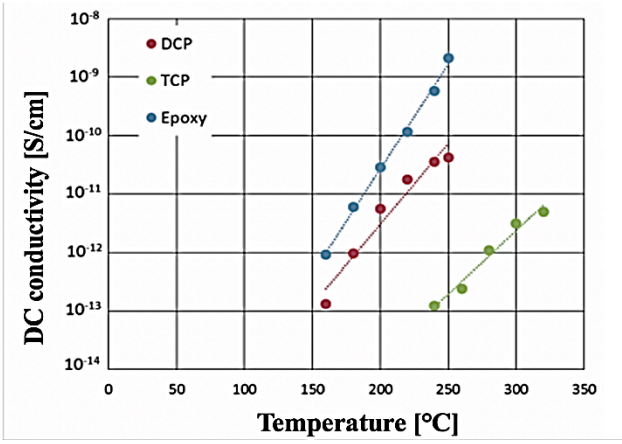

Fig. 3. Temperature dependence of DC conductivity of P-DCP and P-TCP as compared with that of epoxy resin.

On the other hand, the energy gaps φ_g of DCP and TCP were evaluated to be 6.55 to 6.86 eV and 6.60 to 6.88 eV, respectively[4]. These values are larger than φ_g of 4.76 to 5.61 eV in epoxy. This difference in φ_g can explain the difference in σ_{dc} for each sample shown in Fig. 3, if it is assumed that DC conductivity is dominated by electronic carriers.

2.3 Development of Functional Insulating Materials by Electric Field Alignment

As a method to realize the functionality of composites with a small filler lodging, we develop epoxy composites with fillers by electric field orientation as shown in Fig. 4. The concept of filler orientation includes polarization charge, interparticle interaction, and chain structure, and it is possible to derive particle properties even at low content. Alumina, boron nitride, barium titanate, zinc oxide (micro varistors), and nano alumina coated conductive particles were used as fillers. The bridge condition of the prototype filler oriented composite was confirmed using scanning electron microscope (SEM) and transmission electron microscope (TEM) images. Measurements were also made on thermal conductivity, permittivity, resistivity, and withstand voltage in the filler oriented composites.

2.3.1 Development and Evaluation of Insulating Materials with High Thermal Conductivity

Fig. 5(a) to (c) show SEM images of the fractured surface of the field-aligned samples for uniform dispersion of plate-like alumina filler in shape, AC voltage application and DC voltage application, respectively. The thermal conductivityκ of the samples (a) to (c) in Fig.5 were evaluated to be 0.34, 0.73 and 9.87 W/mK, respectively. Namely, the high thermal conductivity of the composite material is achieved by controlling the filler orientation and collection.

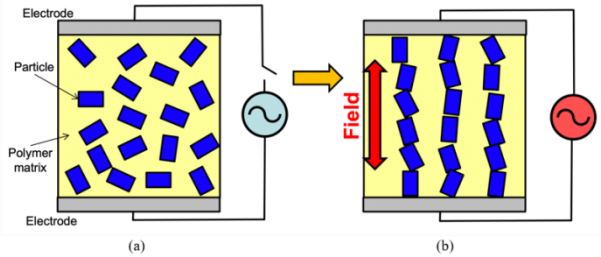

Fig. 4. Principle of electric field orientation of filler in matrix polymer. Coulomb force due to polarization charge forms filler chain structure. (a) Before electric field application and (b) Electric field application during cure process.

In addition, hybrid technology with nanocomposites to improve the insulating performance of electric field filler oriented samples has succeeded in improving the thermal conductivity by a factor of two while maintaining the

dielectric strength. Fig. 6 shows the relationship between dielectric breakdown strength (E_B) and thermal conductivity κ for samples with micro-sized spherical alumina (μS) and plate-like alumina (μP) added to epoxy resin, samples with nano-sized alumina added to P (n+μPS), and samples oriented in an electric field of 2 kV/mm (-E). As shown in the Fig. 6, the electric field alignment effect provides two times higher κ, and the nano-sized filler addition brings the breakdown strength by 8% increase. As a result, the hybrid effect of nanocomposite and filler orientation improve both thermal conductivity and dielectric strengths. The role of each filler is considered as follows: micro spherical filler and plate-like filler contribute to suppression of viscosity increase and increase of thermal conductivity, respectively, and nano filler provides increase of dielectric strength.

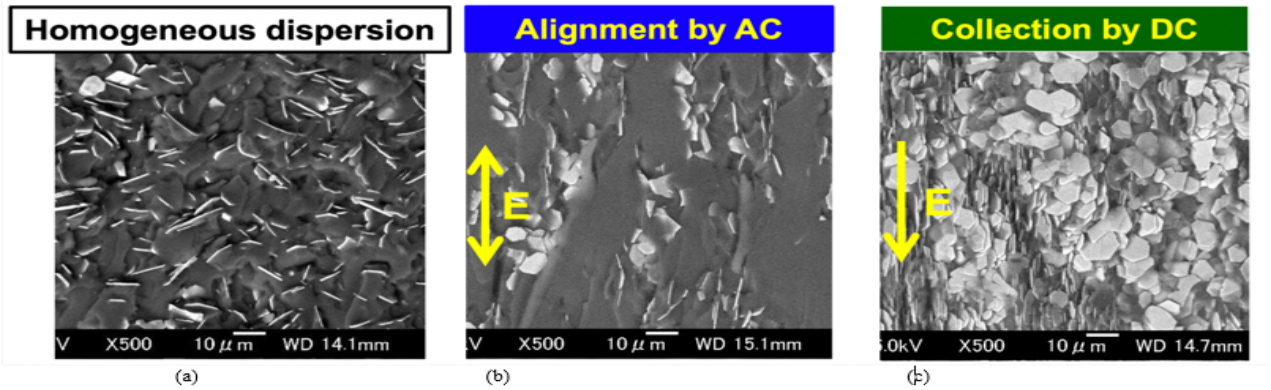

Fig.5. SEM image of plate-like alumina filler orientation by AC and DC electric field E application during curing process of epoxy resin. (a) 10 vol%, κ = 0.34 W/m K (b) 10 vol%, κ = 0.73 W/m K (c) 20 vol% (locally 40 vol%), κ = 9.87 W/m K.

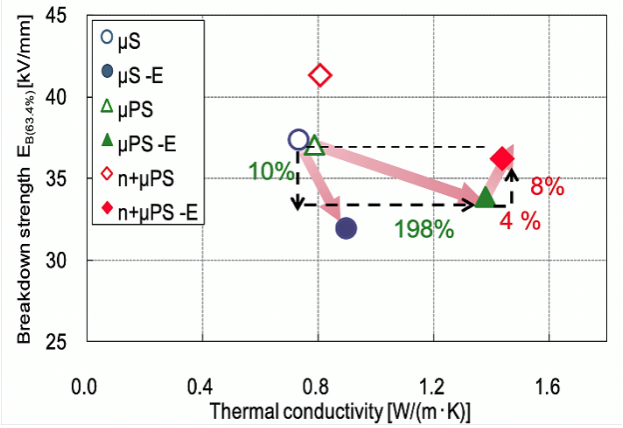

Fig.6. Relation between breakdown strength and thermal conductivity of various type alumina fillers added epoxy resin composites with and without the electric field application E of 2 kV/mm. n stands for nano-sized Al_2O_3 of 1 vol%, μS : micro-sized spherical Al_2O_3 of 35 vol%, μPS : micro-sized plate-like and spherical Al_2O_3 of 7 and 28 vol%, respectively.

Fig. 7(a) to 7(b) show SEM images of n+μPS (without field; homogeneous dispersion) and n+μPS-E (with field; filler alignment) used in Fig. 6.Fig. 7(c) and (d) show magnified SEM images of the center region of SEM images shown in Fig. 7 (a) and (b).It is seen in Fig. 7(a) and 7(b) that the plate-like micro particles are uniformly dispersed in the absence of electric field, while they orient among spherical particles due to the electric field orientation. Furthermore, as can be seen in Fig. 7(c) and (d), nano alumina particles are also uniformly dispersed without electric field, while the electric field application causes nano particles to move to the gap among the plate-like micro particles. It seems that presence of the nanoparticles surrounding the microparticles results in the electric field relaxation in micrometer range.

This superior breakdown strength is caused by the presence of nanofillers (charge trap) and/or a nano-effect due to closely packed nanofillers (electric field relaxation). In summary, high thermal conductivity and high permittivity can be simultaneously demonstrated with the low filler content using the electric field induced micro-sized particle alignment. Furthermore, the breakdown strength can be improved using the nanocomposites. Combination of the above would be very attractive to enhance the thermal conductivity property as well as insulation performance in the polymer composites.

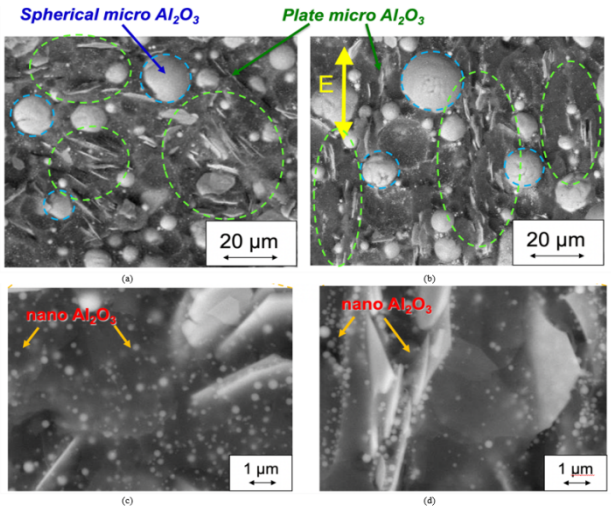

Fig.7. SEM images and enlarged ones of nano and micro Al_2O_3 fillers added epoxy resin n+μPS and n+μPS-E with and without the electric field alignment, respectively. (a) n+μPS (without field; homogeneous dispersion), (b) n+μPS-E (with field; filler alignment), (c) Enlarged SEM of center region of (a) and (d) Enlarged SEM of center region of (b).

2.3.2 Development of micro varistor epoxy composite materials

Composite material varistor consists of micro μ varistor (semiconductor particles with ZnO as main component as shown Fig. 8(a)), and epoxy resin. An electric field was applied during the curing of the resin to create composite material varistors with a thickness of 0.6 to 3.2 mm (equivalent to a varistor voltage of 180 to 960 V) using μ varistors with a single particle varistor voltage of 300 V/mm.

Fig. 8(b) shows example of chain of μ varistors formed in the epoxy. Simulation of filler behavior during the electric field orientation was also performed, and good agreement was obtained with the measured filler behavior [5]. Fig. 9 shows voltage-current (*V* - *I*) characteristics of the micro varistor epoxy composites with different sample thicknesses. As shown in the Fig. 9, excellent nonlinear resistance characteristics are successfully obtained even with low filling rate. In order to seek for the application of this composite material varistor, investigation is also made on its surge absorption capability against continuous surge and its control method [6].

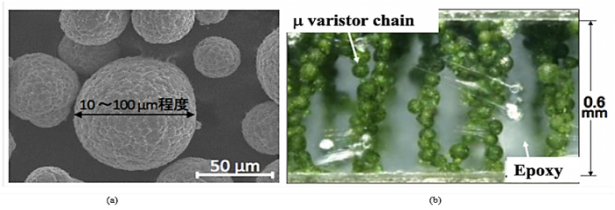

Fig.8. Microvaristor particles and epoxy composite varistor with field application. (a) Microvaristor particles and (b) Composite varistor.

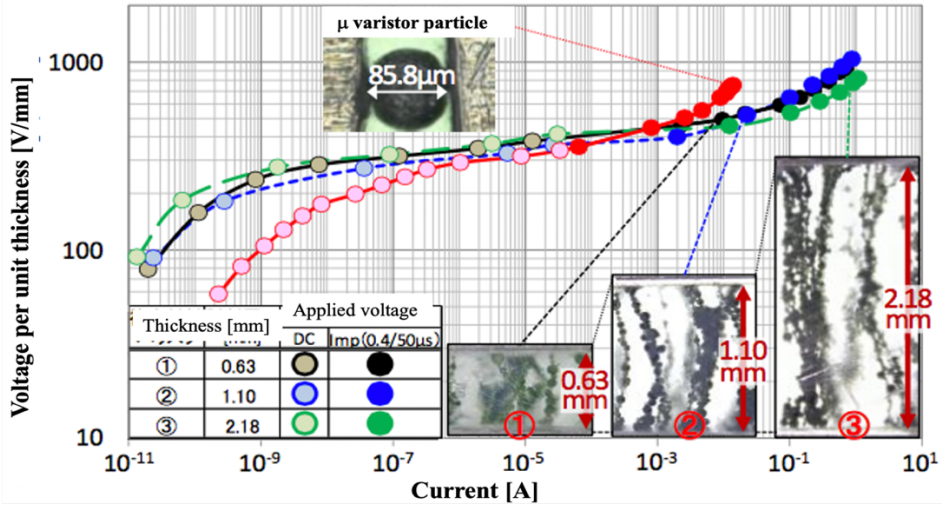

Fig. 9. Voltage-current characteristics of composite varistor with different thicknesses.

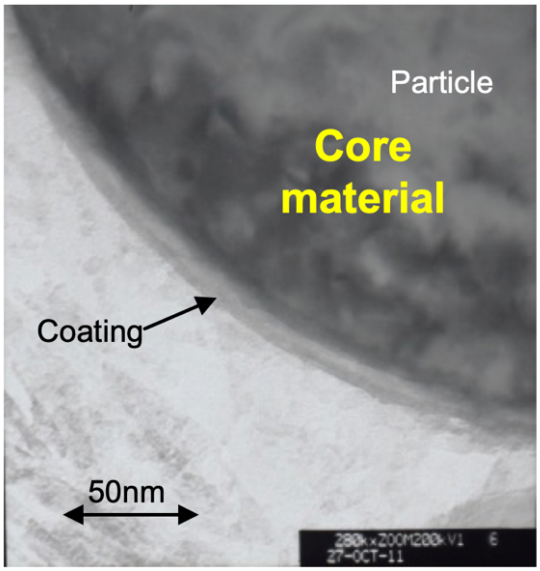

Fig. 10. TEM image of nano-alumina coated spherical aluminum.

The method of nano-alumina coating is as follows. First, hydrothermal synthesis is performed using alumina powder and acetic acid as catalyst so as to prepare dispersion of nanoboehmite. Secondly, the target particles are added to wet coat the nano-beohmite. This technique takes advantage of the property of nano-beohmite to adhere to the target and become stable. Then, they are dried and crystallized to form a thin film of 50 nm in solid content on the surface of the target.

After the coated particles were filled in epoxy resin, the volume resistivity ρ, thermal conductivity κ, permittivity ε were measured. It was found from the measurements that neat epoxy EP,EP with 24 vol% graphite of average particle size 15 μm (GP/EP) and GP/EP with nano alumina coating on the graphite (nBA coated GP/EP) exhibit κ = 0.2, 0.5 and 0.5 W/m K, respectively. Whilest EP, GP/EP and nBA coated GP/EP showed $\kappa=10^{16}$, 4.9×10^{6} and 3.2×10^{15}Ωcm, respectively.

Fig. 11(a) and (b) show schematic diagram of the mechanism of electrical and thermal conduction with and without nano alumina coating on conductive particles, respectively. Fig. 11(a) shows general micro-particles without alumina coating dispersed in the matrix. In this case, the paths of electronic and thermal conduction are directly transmitted between the particles. On the other hand, in Fig. 11(b), where alumina particles are coated, heat conduction is the same as in Fig. 11(a) because of alumina's high thermal conductivity of 30 W/m K. While the electron conduction does not occur in the entire matrix, because the path of electron conduction is blocked by the insulating alumina

2.4Development of functional insulating materials by nano-alumina coating

Thermal conductive fillers can be broadly classified into insulating and conductive ones. Alumina and aluminum nitride are commonly used in insulating systems. On the other hand, conductive fillers have high intrinsic thermal conductivity in nature, so that they can provide even higher thermal conductivity.

Boehmite alumina (BA) was coated on a core filler material at a few 10 nm by collaboration with Sato Research Co. The size and shape of the primary particles of BA can be controlled and it has good adhesive properties. This means good insulation by alumina coating, applicable to many materials; e.g. conductive material such as Al、Cu、Zn、carbon as well as semi-conductive material as SiC、ZnO etc. Fig. 10 shows TEM image of nano-alumina coated spherical aluminum.

coating.

2.5Development of Functional Insulating Materials by Adding Fullerenes

Fullerene (FL) is a general term for compounds in which carbon atoms form a spherical structure, as typified by C_{60}, which has a soccer ball-shaped molecular structure. Fullerene is likely to form aggregates so that it is difficult to disperse it well in a polymer matrix. Few reports have been made on electrical insulation properties of FL filled composite as electrical insulating material. Composite materials added with FLs of 0.1, 0.3, and 0.6 wt% were prepared in a plate shape with a thickness of 0.5 mm using two different dispersion methods, i.e. fullerene dissolved solution addition method and FL direct mixing method.

In the FL dissolved solution addition method, FL epoxy composite is prepared as follows: A FL solution dissolved in toluene with impurities removed is mixed with epoxy dissolved in toluene. Afterwards, the toluene is removed, and the mixture is cured to form a resin. It has been reported that the electrical insulating properties of FL/EP composites prepared by the FL dissolved method are greatly improved. Fig. 12 shows fullerene content dependence of ac breakdown strength E_B of FL/epoxy composite prepared by the dissolved solution method and the direct mixing method [7]. As shown in the Fig. 12, E_B increases as the filling ratio increases in both cases. It should be noted that E_B of fullerene/EP composite with the dissolved method providing good dispersion greatly increases by 30 %. The prominent increase in E_B is interpreted in terms of improved dispersion of the FLs, providing good performance as electron acceptors so as to suppress the generation of electron avalanches in the composite.

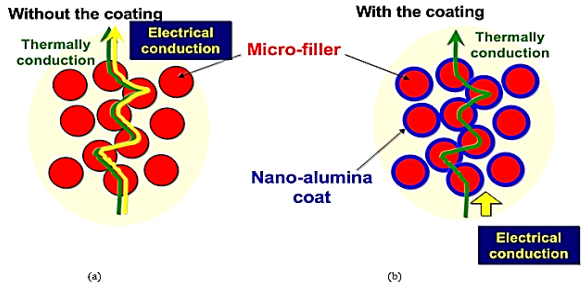

Fig.11. Thermal and electrical conduction paths in epoxy matrix containing conductive particles with and without nano-alumina coating. (a) Without nano-alumina coating and (b) with nano-alumina coating.

In addition, we investigate AC breakdown strength of EP resin mixed with different types of fullerene (higher order FLs) [8]. An attempt is also made to discuss the mechanism of the improvement effect of FL addition on E_B of the composite by evaluating the electronic state of EPs with different FL fillers and curing agent using quantum chemical calculation. As a result, it is shown that the introduction of C_{60} and C_{70} into EP considering the curing agent introduces electron traps of 0.64 and 0.72 eV in depth, respectively [8]. The introduced electron traps suppress the electron avalanche, and consequently improves the breakdown strength.

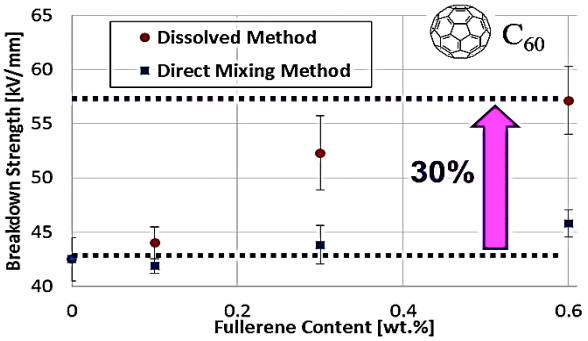

Fig.12. Fullerene content dependence on breakdown strength of epoxy composite prepared with the dissolved method and the direct mixing method.

3. Conclusions

This paper outlines the development, evaluation, and application of functional insulating materials conducted at Kyushu Institute of Technology. Our research on the development and evaluation of nanocomposite electrical insulating materials was triggered and inspired by Professor Toshikatsu Tanaka. The research originally guided by him has led to our current research on new functional insulating materials for applying to electric power equipment such as generators, switchgear, and transformers. In addition to electric power equipment insulation systems, this research has led to the development and application of functional insulating materials for power modules and power electronics equipment insulation.

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