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Dielectric Properties of Epoxy/Clay Nanocomposites — Effects of Curing Agent and Clay Dispersion Method — (Final draft (Post-print) version)

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ABSTRACT

Effects of the differences in the curing agent and filler dispersion method on the dielectric properties were examined for epoxy/clay nanocomposites. Irrespective of the clay dispersion method, relative permittivity and electrical conductivity are higher in the samples cured with the amine. Moreover, negative heterocharge accumulates in the vicinity of the anode in the amine-cured samples, whereas positive homocharge accumulates in the acid anhydride-cured samples. From the results of UV photon absorption and PL measurement, the bandgap or the energy at which the photon absorption increases drastically is smaller in the amine-cured samples than in the acid anhydride-cured samples. Ion migration can occur easily in the amine-cured samples whose electrical conductivity and relative permittivity are higher than the acid anhydride-cured samples. The curing agent gives the strongest effect, while the existence of clay affects secondly and the filler dispersion method has the weakest effect.

Index Terms — Epoxy nanocomposite, curing agent, filler dispersion method, space charge distribution, permittivity, conductivity

1 INTRODUCTION

RECENTLY, various polymer nanocomposites (NCs) are attracting much attention as new materials with superior properties in many fields^{1 2 3 4 5 6 7 8 9 10}. The NCs

1 B. Andrew, “Nanocomposites technology takes off”, *Eur. Plast. News*, Vol. 27, No. 8, p. 31, 2000.

2 J. W. Gilman, C. L. Jackson, A. B. Morgan, R. Harris, Jr., E. Manias, E. P. Giannelis, M. Wuthenow, D. Hilton, and S. H. Phillips, “Flammability properties of polymer-layered-silicate nanocomposites. Polypropylene and polystyrene nanocomposites”, *Chem. Mater.*, Vol. 12, pp. 1866- 1873, 2000.

are mixtures of base polymer and nanosized fillers. In the electrical insulation field, NCs with polyethylene, polyamide, epoxy resin, and other polymers have been studied. In this paper, we focus on epoxy/clay NCs, in which nanosized clays are added to a base epoxy resin. Although sulfur hexafluoride (SF₆) gas has been very widely used as a superior insulating substance for high voltage power apparatus, it shows a very high greenhouse effect, about 24,000 times as high as CO₂. On this point, epoxy/clay NC is expected to take the place of SF₆ gas. Using epoxy/clay NCs for electrical insulation in power apparatus has another advantage of significant reduction in size.

In order to create a good NC dielectric material and to clarify its electrical properties, it is important to figure out the factors to determine its properties. There would be two factors in epoxy/clay NCs: curing agent and filler dispersion method. Epoxy resin is a thermosetting resin, which is formed by adding a thermal treatment to a mixture of a base resin and a curing agent. Since chemical reactions are involved in the curing process, the chemical structure of a cured epoxy resin depends on the curing agent in addition

to the base resin. Furthermore, the condition of clay dispersion should affect the dielectrics behavior of a NC. From such viewpoints, we studied the effects of curing agent and clay dispersion method on the dielectric properties of epoxy NCs.

2 SAMPLES

Table 1 shows the curing agent and clay dispersion method used for each sample, together with its reference code. The base resin, diglycidyl ether of bisphenol A, was

3 C. Chen, M. Khobaib, and D. Curliss, "Epoxy layered-silicate nanocomposites", *Prog. Org. Coatings*, Vol. 47, No. 3/4, pp. 376-383, 2003.

4 J. K. Nelson and Y. Hu, "The impact of nanocomposite formulations on electrical voltage endurance", *IEEE Intl. Conf. Solid Dielectrics*, pp. 832-835, Toulouse, France, 2004.

5 J. C. Fothergill, J. K. Nelson, and M. Fu, "Dielectric properties of epoxy nanocomposites containing TiO₂, Al₂O₃ and ZnO fillers", *IEEE Conf. Electr. Insul. Dielectr. Phenom.*, Boulder, Colorado, USA, pp. 406-409, 2004.

6 J. C. Fothergill, J. K. Nelson, and M. Fu, "Dielectric properties of epoxy nanocomposites containing TiO₂, Al₂O₃ and ZnO fillers", *IEEE Conf. Electr. Insul. Dielectr. Phenom.*, Boulder, Colorado, USA, pp. 406-409, 2004.

7 T. Tanaka, M. Kozako, N. Fuse, and Y. Ohki, "Proposal of a multi-core model for polymer nanocomposite dielectrics", *IEEE Trans. Dielectr. Electr. Insul.*, Vol. 12, No. 4, pp. 669-681, 2005.

8 T. Tanaka, "Dielectric nanocomposites with insulating properties", *IEEE Trans. Dielectr. Electr. Insul.*, Vol. 12, No. 5, pp. 914-928, 2005.

9 M. F. Frechette, C. W. Reed, and H. Sedding, "Progress, understanding and challenges in the field of nanodielectrics", *IEEEJ Trans. FM*, Vol. 126, No. 11, pp. 1031-1043, 2006.

10 T. Kikuma, N. Fuse, T. Tanaka, Y. Murata, and Y. Ohki, "Filler-content dependence of dielectric properties of low-density Polyethylene/MgO nanocomposites", *IEEEJ Trans. FM*, Vol. 126, No. 11, pp. 1072-1077, 2006.

cured either by an amine curing agent (4,4'-diaminodiphenylmethane) or by an acid anhydride curing agent (methylhexahydrophthalic anhydride). The filler added to the epoxy resin is nm-sized clay, mainly composed of montmorillonite, and its content is 5 wt%. Figure 1 shows the chemical structure of epoxy resin¹¹. For clay dispersion, an organo method and a solubilization method were adopted. In the former method, a modifier with organic chains such as ammonium ions is introduced into the clay interlayers, whereas clays organized by an organo method and swollen in a polar solvent such as dimethylacetamide are introduced in the latter method. Table 2 shows the average clay interlayer distance in each sample, measured by TEM^{12 13}. The interlayer distance is larger in the solubilization-method samples than in the organo-method samples for both curing agents. Moreover, the average size of aggregates is smaller in the solubilization-method samples than in the organo-method samples^{14 15}. Therefore, the solubilization method seems superior to the organo method.

3 EXPERIMENTAL METHOD

For both dielectric permittivity and electrical conductivity measurements, electrodes made of Sn foil with a diameter of 20 mm were attached on each side of the sample. While permittivity was measured in a frequency range from 10-1 to 105 Hz with an impedance analyzer (Solartron 1296), electric current was measured for about 17 min under applied electric field of 10kV/mm, and conductivity was calculated from the value of nearly steady state current about 17 min after the start of voltage application. Space charge distribution was measured using a pulsed electroacoustic (PEA) system for 90 min while dc electric field of 80 kV/mm was applied and for 150 min after having been short-circuited. These experiments were carried out at room temperature. Moreover, spectra of ultraviolet photon (UV) absorption, photoluminescence (PL), and photoluminescence excitation (PLE) were measured at 10 K using synchrotron radiation under multibunch operation as a photon source at the BL1B line of UVSOR Facility

11 M. Tomoi, Y. Nakamura, I. Hara, and K. Kamagata [Ed.], *Epoxy Resins*, Japan Society of Epoxy Resin Technology, p. 120, 2003 [in Japanese].

12 M. Tomoi, Y. Nakamura, I. Hara, and K. Kamagata [Ed.], *Epoxy Resins*, Japan Society of Epoxy Resin Technology, p. 120, 2003 [in Japanese].

13 M. Harada, M. Aoki, T. Miyamoto, and M. Ochi, "Clay dispersibility and mechanical property of epoxy/clay nanocomposite cured with acid anhydride", *Proc. 45th Sympos, Adhesion Society of Japan*, pp. 77-78, 2007 [in Japanese].

14 M. Harada, T. Miyamoto, M. Ochi, T. Tanaka, Y. Ohki, and T. Imai, "Dispersibility, mechanical, and electrical insulation properties of Epoxy/Clay nanocomposites", *Polymer Preprints, Japan*, Vol. 56, No. 1, p. 1306, 2007 [in Japanese].

15 M. Harada, M. Aoki, T. Miyamoto, and M. Ochi, "Clay dispersibility and mechanical property of epoxy/clay nanocomposite cured with acid anhydride", *Proc. 45th Sympos, Adhesion Society of Japan*, pp. 77-78, 2007 [in Japanese].

(beam energy: 750 MeV) in the National Institutes of Natural Sciences, Okazaki, Japan.

4 EXPERIMENTAL RESULTS

4.1 PERMITTIVITY

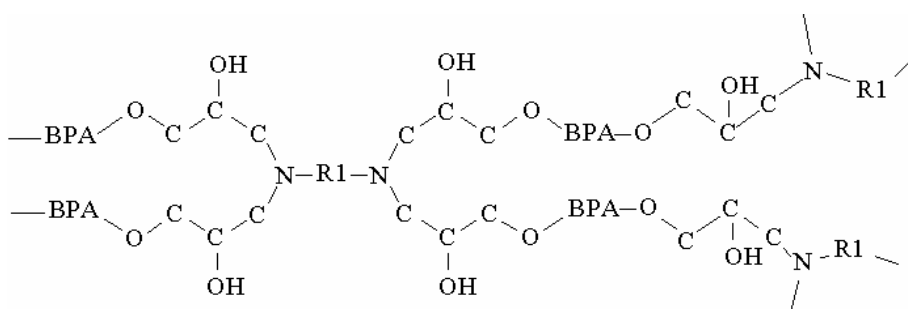
Relative permittivity of each sample is shown in Figure 2. The relative permittivity values of the amine-cured samples are higher than those of the acid anhydride-cured samples. Among the amine-cured samples, the permittivity is lower in the NC samples than in the base resin, whereas all the acid anhydride-cured samples have similar values.

Table 1. Sample codes.

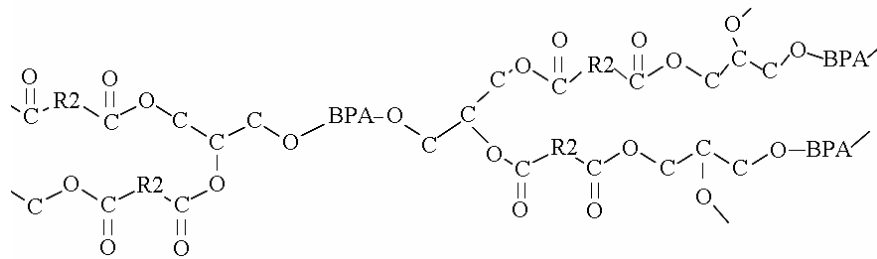
Curing agent	Unmodified epoxy	Solubilization method	Organo method
Amine	E(U)AM	C(S)AM	C(O)AM
Acid anhydride	E(U)AH	C(S)AH	C(O)AH

Table 2. Average clay interlayer distance in each sample [12, 13].

Clay condition	Clay interlayer distance [nm]
Unmodified clay	1.5
Organo clay	2.2
Clay in C(O)AM	5-15
Clay in C(S)AM	8-30
Clay in C(O)AH	5-15
Clay in C(S)AH	100



(a) Amine-cured epoxy.



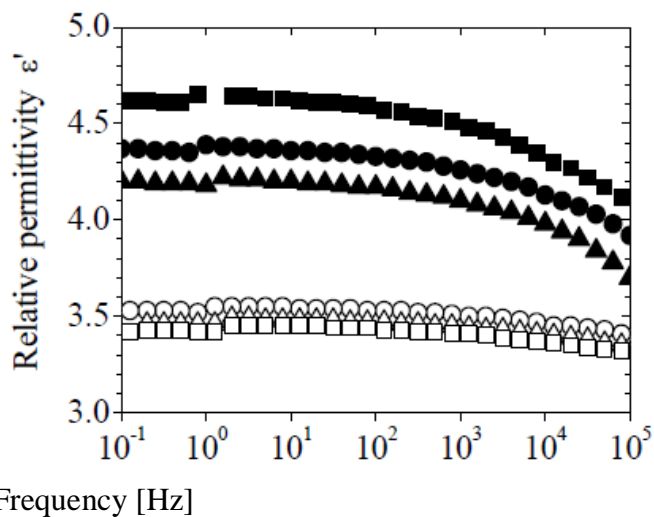
(b) Acid anhydride-cured epoxy.

BPA: Pre-polymer-unit of bisphenol A

R1: Amine curing agent

R2: Acid anhydride curing agent

Figure 1. Chemical structures of cured epoxy resins.



Frequency [Hz]

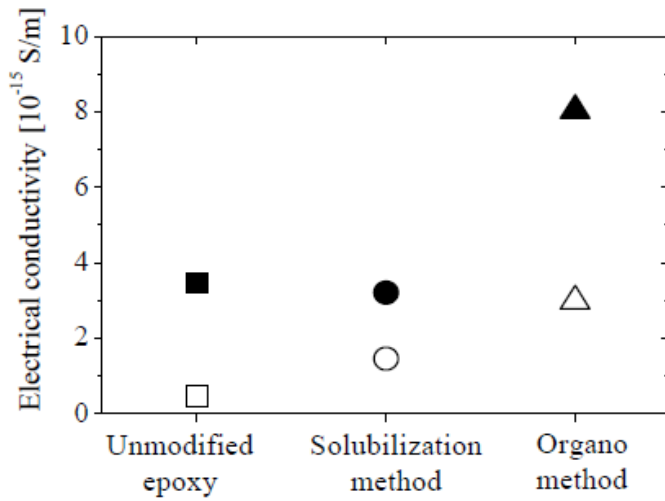
V: E(U)AM, i: C(S)AM, x : C(O)AM

ë: E(U)AH, I: C(S)AH, Δ : C(O)AH

Figure 2. Relative permittivity at room temperature as a function of frequency.

4.2 CONDUCTIVITY

The electrical conductivity calculated from the conduction current is shown in Figure 3. Focusing on its dependence on the curing agent, the conductivity shows the same tendency as the relative permittivity shown in Figure 2. Namely, both the relative permittivity and the electrical conductivity are higher in the amine-cured samples than in the acid anhydride-cured samples.



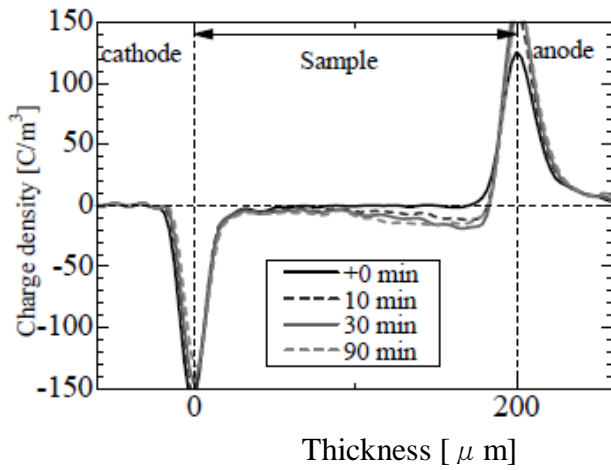
V, i, x: Amine-cured samples

ë, I, Δ: Acid anhydride-cured samples

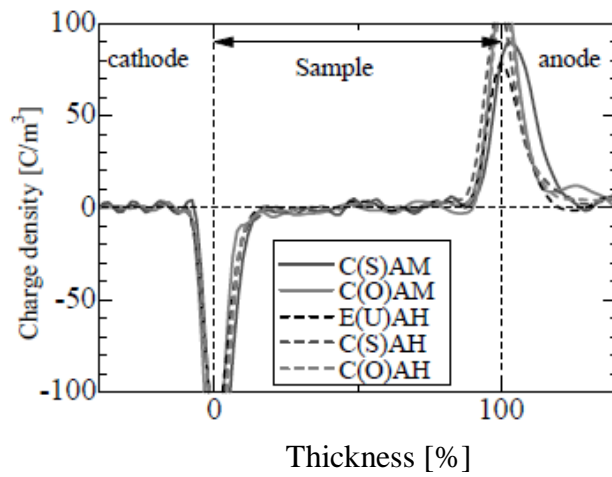
Figure 3. Comparison of electrical conductivity among six kinds of samples tested.

4.3 SPACE CHARGE DISTRIBUTION

Figure 4a shows typical examples of temporal change in space charge distribution observed in E(U)AM with time during the application of dc electric field of 80 kV/mm, while Figure 4b shows the space charge distributions observed 90 min after the start of voltage application for all the other samples. Here, in Figure 4b, the sample thickness is represented by % on the abscissa, since it differs among the five samples within the range from 165 μ m to 200 μ m. In Figure 4a, accumulation of negative heterocharge is observed in E(U)AM near the anode from 10 min after the start of voltage application. In Figure 4b, charge accumulation is not seen in the bulk of the samples except E(U)AM and only the charge induced on the electrodes is seen. The electric field strength applied to the sample was 80 kV/mm, which is comparatively high. This high electric field should have induced large signals on the electrodes. Such a signal may hide the space charge near the anode if the charge is a small amount, even though it really exists. Thus, it is difficult to observe a small amount of charge during the voltage application using the present experimental equipment. Figure 5 shows the space charge distribution in each sample observed right after the short-circuit that followed the voltage application for 90 min. After the sample was short-circuited, the negative heterocharge observed in E(U)AM near the anode is also seen as shown in Figure 5a. Irrespective of the clay dispersion method, negative heterocharge is seen near the

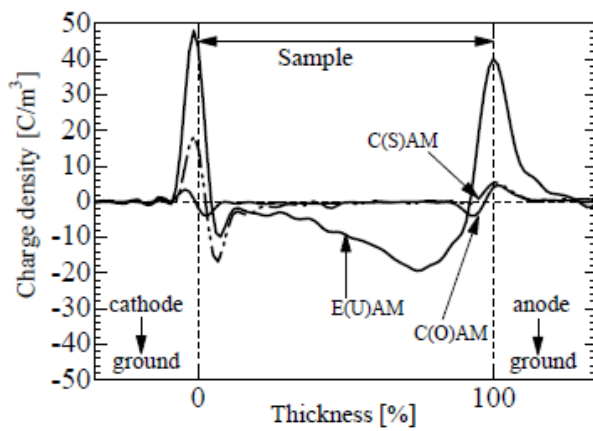


(a) Charge observed in E(U)AM with time.



(b) 90 min after the start of voltage application for each sample other than E(U)AM.

Figure 4. Space charge distributions during the application of dc electric field of 80 kV/mm.



(a) Amine-cured samples.

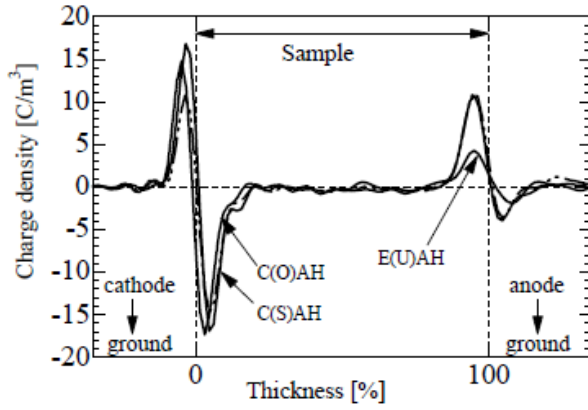


Figure 5. Space charge distributions right after the short-circuit following the dc voltage application for 90 min.

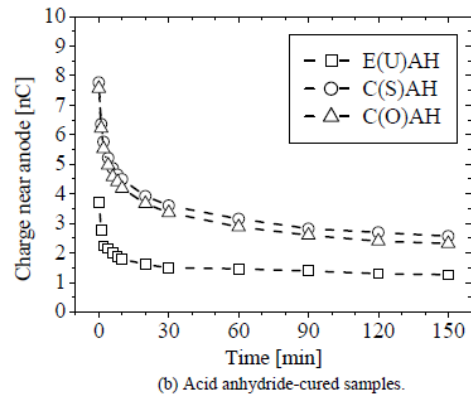
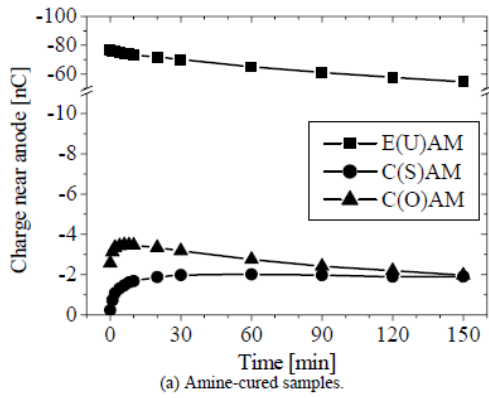


Figure 6. Change in accumulated charge quantity near anode with time.

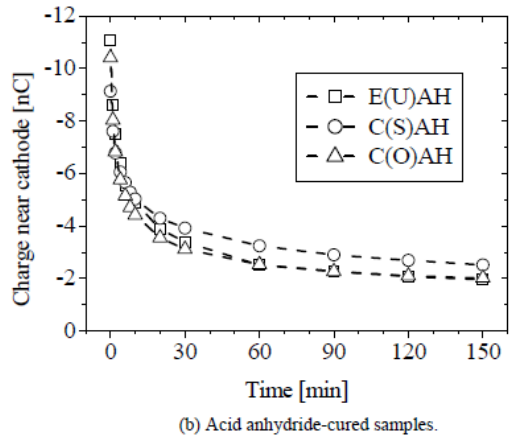
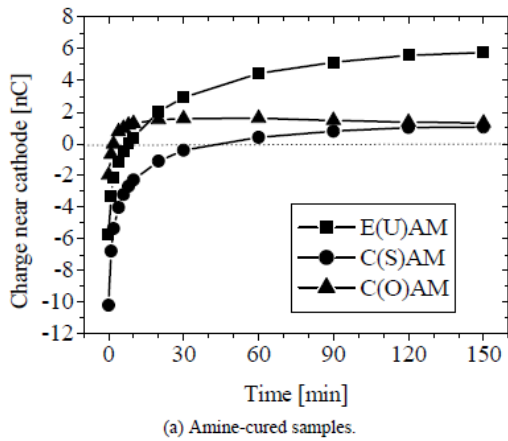


Figure 7. Change in accumulated charge quantity near the cathode with time.

anode in both C(S)AM and C(O)AM. Focusing on the effect of nano-structuration or the effect of the resin having been properly structured by the addition of nanofillers, the heterocharge near the anode decreases significantly in the amine-cured samples by adding the nanofillers as shown in Figure 5a. In Figure 5b, positive homocharge is seen near the anode of the acid anhydride-cured samples. Focusing on the effect of nano-structuration, the positive homocharge accumulated near the anode in the acid anhydride-cured samples is larger in the two NCs than in the epoxy resin without nanofillers as shown in Figure 5b. Figure 6a shows the temporal change in the negative heterocharge remaining in the vicinity of the anode in the amine-cured samples with the time after the short-circuit, which is calculated by multiplying the PEA signal area shown in Figure 5 and the surface area of the electrode.

Figure 6b shows similar change for the positive homocharge near the anode in the case of acid anhydride-cured samples. As shown in Figure 6b, the positive homocharge drastically decreases in the acid anhydride-cured samples for initial 10 min after the start of the short-circuit and then gradually decreases. In Figure 6a, the quantity of accumulated charge constantly decreases in the amine-cured epoxy resin without fillers, whereas it drastically increases for 10 min after the start of the short-circuit and then gradually decreases in the NC samples.

Figures 7a and 7b show temporal changes in the accumulated charge quantity near the cathode in the amine-cured and acid anhydride-cured samples. As for the charge distribution near the cathode in the amine-cured samples, it might appear from Figure 5a that positive heterocharge does not accumulate and that only negative homocharge is present right after the short-circuit. However, it is apparent from Figure 7a that the space charge polarity near the cathode becomes opposite from negative (homo) seen right after the short-circuit to positive (hetero). This tendency of the heterocharge accumulation near the cathode is similar to the negative heterocharge accumulation near the anode in the amine-cured samples shown in Figure 6a. Figures 6a and 7a clearly show that heterocharge accumulation occurs for both the anode and cathode in the amine-cured samples. Focusing on the effect of nano-structuration, the quantity of the heterocharge near the cathode more than 20 min after the short-circuit is smaller in the two NCs as shown in negative heterocharge near the anode shown in Figure 6a. In the case of the acid anhydride-cured samples, the decay of the negative homocharge near the cathode shown in Figure 7b, consisting of a fast decay right after the shortcircuit and

a subsequent slow decay, is also similar to the decay of the positive homocharge near the anode shown in Figure 6b. The absolute quantity value of the negative homocharge near the cathode after the short-circuit in C(S)AH shown in Figure 7b is larger than in E(U)AH, although the difference is small. Namely, the effect of nano-structuration on the accumulated charge has a similar tendency both near the cathode and near the anode. Namely, the accumulated homocharge is less in the base sample than in the NC samples for the acid anhydride-cured samples.

In Figures 5, 6, and 7, no significant difference is seen between the two NC samples cured with the same curing agent, namely, between C(S)AM and C(O)AM and between C(S)AH and C(O)AH, indicating that the filler dispersion method has a very weak effect. To conclude, it is indicated that the curing agent gives the strongest effect on space charge behavior. Compared to the curing agent, the presence of nanofillers affects secondly, and the filler dispersion method gives the weakest effect.

4.4 PHOTO-ABSORPTION AND LUMINESCENCE

Figure 8 shows UV absorption spectra observed for the six kinds of samples tested. The energy at which the photon absorption starts to increase is somewhere around 3.4 eV in the three amine-cured samples and 4.0 eV in the three acid anhydride-cured samples. These values of energy depend on neither the presence of clay nor the clay dispersion method. In Figure 8, the photo-absorption seems saturated at energy values higher than 3.6 eV or 4.2 eV. This is probably because the samples were too thick and the light intensity passing through the sample was too weak for the present experimental equipment to measure the absorption. Figure 9 shows PL spectra excited by 4.5-eV photons for both the amine-cured and the acid anhydride-cured samples. It is clearly shown that the three amine-cured samples have a PL band with its peak at around 3.5 eV, while the three acid anhydride-cured samples have a PL band at around 4.1 eV. These PL peak energy values are very near the energy values at which the absorption increases drastically. Figure 10 shows PLE spectra observed at 3.2 eV in the amine-cured samples and those observed at 4.0 eV in the acid anhydride-cured samples. The PLE spectra show how the intensities of PLs detected at the designated energy, either 3.2 eV or 4.0 eV, change as a function of the energy of the excitation photons. The energy at which the PLE spectrum starts to rise is around 3.5 eV for the amine-cured samples, while it is around 4.1 eV for the acid anhydride-cured samples. These values of energy are in fairly good agreement with respective PL peak energy values and those at which each UV absorption starts to increase.

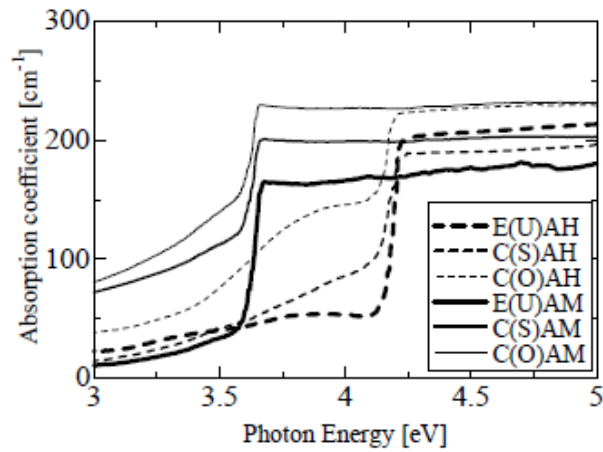


Figure 8. Comparison of ultraviolet absorption spectra among six kinds of samples tested.

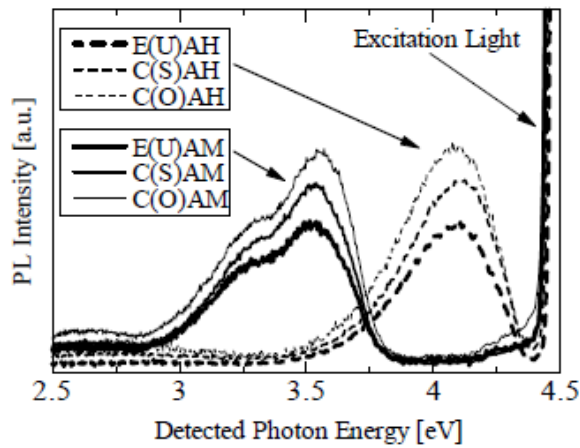
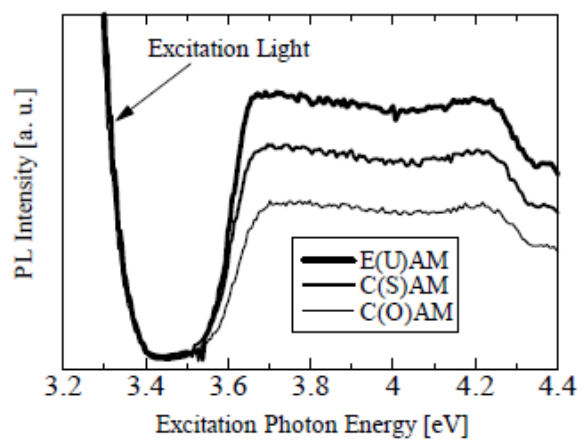
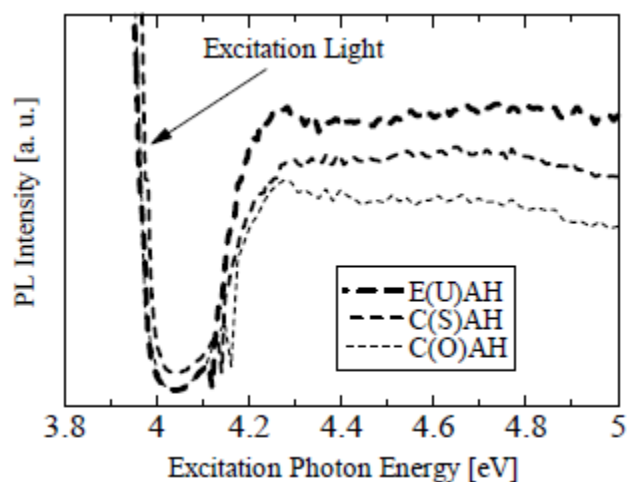


Figure 9. PL spectra as a function of PL photon energy, excited by 4.5 eV photons from SR.



(a) PLE spectra detected at 3.2 eV in the amine-cured samples.



(b) PLE spectra detected at 4.0 eV in the acid anhydride-cured samples.

Figure 10. PLE spectra of six samples as a function of photon energy of excitation light.

5 DISCUSSION

5.1 PERMITTIVITY

As mentioned above, permittivity is much higher in the amine-cured samples than in the acid anhydride-cured samples. One of the main reasons for this is the presence of polar OH groups in the amine-cured samples as shown in Figure 1. The polar OH groups cause dipole polarization, thus resulting in high permittivity.

The effect of nano-structuration on permittivity is also more significant in the amine-cured samples than in the acid anhydride-cured samples. Namely, the permittivity decreases significantly from a high value in E(U)AM to lower values by the nano-structuration. It is assumed that OH bonds present in the clay form strong hydrogen bonds with OH bonds in the amine-cured samples. For this reason, clays in the amine-cured samples exist steadily. According to the ‘multicore model’ we proposed^{16 17}, molecular motion of the resin is restricted in the vicinity of the clay because of this strong interaction. Therefore, the orientation of polar groups such as OH bonds would be restricted and the permittivity becomes lower in the amine-cured NC samples.

16 T. Tanaka, M. Kozako, N. Fuse, and Y. Ohki, “Proposal of a multi-core model for polymer nanocomposite dielectrics”, IEEE Trans. Dielectr. Electr. Insul., Vol. 12, No. 4, pp. 669-681, 2005.

17 T. Tanaka, “Dielectric nanocomposites with insulating properties”, IEEE Trans. Dielectr. Electr. Insul., Vol. 12, No. 5, pp. 914-928, 2005.

On the other hand, the acid anhydride-cured samples do not have OH bonds as shown in Figure 1b. Therefore, the interaction between the clay and epoxy matrix is weak. For this reason, rather than the restriction of molecular motion, the intercalation of clay into the epoxy matrix would break the physical structure of the resin, leading to an increase in free volume^{18 19 20}. Since the permittivity in free volume is low, this should result in the decrease in the permittivity of the sample^{21 22 23 24}. However, the permittivity would increase if the free volume makes dipolar orientation toward the direction of the electric field easier. The fact shown in Figure 2 that the relative permittivity increases by the addition of fillers in the case of the acid anhydride-cured samples is assumed to be due to this effect.

5.2 CONDUCTIVITY

It is generally assumed that ionic conduction is dominant in epoxy resin²⁵. Since the amine-cured samples have hydrophilic OH bonds that should attract impurities such as water, ions or substances that are easily dissociated into ions would be introduced into the resin of the amine-cured samples. Moreover, the Coulombic attractive force between two charge carriers with opposite polarities, which holds mobile ions in the vicinity of their parent atoms, is inversely proportional to the permittivity. Ions can, therefore, be released easily in a high permittivity material and they move easily in the bulk. Since the amine-cured samples have high permittivities, dissociation and transport of ions occur easily, which results in their high electrical conductivities. Therefore, the electrical conductivity can be explained by the ionic character of the samples and the permittivities.

5.3 SPACE CHARGE DISTRIBUTION

18 J. K. Nelson and Y. Hu, "The impact of nanocomposite formulations on electrical voltage endurance", IEEE Intl. Conf. Solid Dielectrics, pp. 832-835, Toulouse, France, 2004.

19 T. Tanaka, M. Kozako, N. Fuse, and Y. Ohki, "Proposal of a multi-core model for polymer nanocomposite dielectrics", IEEE Trans. Dielectr. Electr. Insul., Vol. 12, No. 4, pp. 669-681, 2005.

20 T. Tanaka, "Dielectric nanocomposites with insulating properties", IEEE Trans. Dielectr. Electr. Insul., Vol. 12, No. 5, pp. 914-928, 2005.

21 J. K. Nelson and Y. Hu, "The impact of nanocomposite formulations on electrical voltage endurance", IEEE Intl. Conf. Solid Dielectrics, pp. 832-835, Toulouse, France, 2004.

22 J. C. Fothergill, J. K. Nelson, and M. Fu, "Dielectric properties of epoxy nanocomposites containing TiO₂, Al₂O₃ and ZnO fillers", IEEE Conf. Electr. Insul. Dielectr. Phenom., Boulder, Colorado, USA, pp. 406-409, 2004.

23 T. Tanaka, M. Kozako, N. Fuse, and Y. Ohki, "Proposal of a multi-core model for polymer nanocomposite dielectrics", IEEE Trans. Dielectr. Electr. Insul., Vol. 12, No. 4, pp. 669-681, 2005.

24 T. Tanaka, "Dielectric nanocomposites with insulating properties", IEEE Trans. Dielectr. Electr. Insul., Vol. 12, No. 5, pp. 914-928, 2005.

25 M. Shimbo [Ed.], Epokishi-jushi Handobukku (Epoxy Resin Handbook), Nikkan Kogyo Shinbun, p. 338, 1987 [in Japanese].

As described in Section 4.3, the temporal changing behavior of the accumulated charge near the electrodes in the amine-cured samples is similar between the anode and cathode shown in Figures 6a and 7a. This is also the case for the acid anhydride-cured samples shown in Figures 6b and 7b. Therefore, discussion can be focused only on the charge behavior near the anode, namely, only on the negative heterocharge near the anode shown in Figure 6a and the positive homocharge near the anode shown in Figure 6b as representatives for the amine-cured and the acid anhydride-cured samples, respectively.

Discussion will proceed based on the assumption that the negative heterocharge near the anode in the amine-cured samples shown in Figure 5 are ions came from impurities. In Figures 4a and 5a, negative heterocharge is seen near the anode. As mentioned in the preceding two sections, the amine-cured samples easily take impurities such as water in their bulk, and ions in the samples can move easily. Therefore, the negative heterocharge near the anode in the amine-cured samples shown in Figure 5a is assumed to be due to negative ions that had originated from impurities and moved toward the electrode with the opposite polarity as shown in Figure 11a. Assuming that the accumulated negative charge is due to ions came from impurities, the fact that the heterocharge near the anode decreases significantly by nano-structuration in Figure 5a indicates either of the following two possibilities or both; the number of mobile ions becomes less and the ion migration is restricted by the filler addition. The latter factor can be

assumed based on the multicore model²⁶.

Generally homocharge formation is assumed to be due to injection of charge carriers. The acid anhydride-cured samples have no OH bonds and the pre-polymer and the curing agent are mainly ester-bonded. Considering these facts, it is reasonable to assume that ions do not play a significant role in space charge formation in the acid anhydride-cured samples. Therefore, the positive homocharge near the anode might be injected charge from the anode. In this case, however, a question arises on the following point; why did the positive charge injection occur only in the acid anhydride-cured samples and not in the amine-cured ones despite the same applied electric field of 80 kV/mm between the two kinds of the samples? In addition to the injection of electronic charge carriers, homocharge formation near the electrode can be also realized by ionic charge carriers. Namely, if ions move to a nearby electrode with the opposite polarity and they lose their charge on the electrode by charge exchange, a homocharge layer would be formed in the bulk close to the electrode, unless charge carriers that should

26 T. Tanaka, M. Kozako, N. Fuse, and Y. Ohki, "Proposal of a multi-core model for polymer nanocomposite dielectrics", *IEEE Trans. Dielectr. Electr. Insul.*, Vol. 12, No. 4, pp. 669-681, 2005.

cancel the homocharge are transported as shown in Figure 11b. When charge carriers (negative in the present case) are extracted from the place which was originally electrically neutral, the opposite-polarity charge carriers (positive in this case) are left behind. If the conductivity of the bulk is high, the opposite-polarity charge carriers will migrate to cancel the space charge. However, if the conductivity is low, the migration of charge carriers in the bulk is difficult and the space charge remains. Thus, homocharge can be formed by the sweep of ions from the bulk to a nearby electrode. It is indeed very difficult to identify the charge species responsible for the conduction in a dielectric solid, not limited to the case of epoxy resin. However,

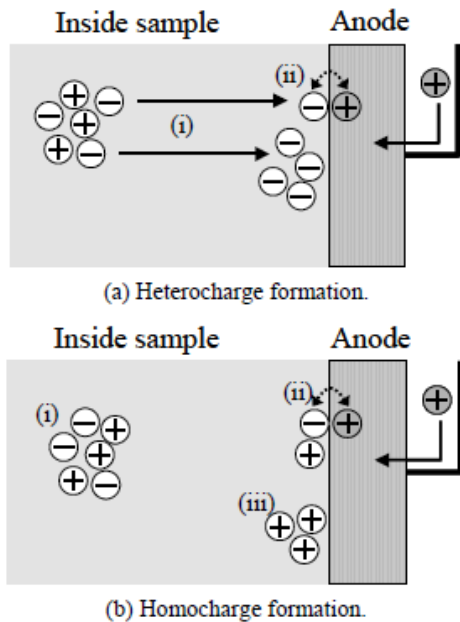


Figure 11. Mechanism of the space charge formation near the anode.

(a): (i) Negative charge carriers migrate to the anode. (ii) While some carriers will be neutralized by transferring electrons to the anode (= occurrence of charge exchange), some will remain charged, forming negative heterocharge.

(b): (i) Charge carriers inside the sample are difficult to migrate to electrodes, which maintains electrical neutrality in the bulk. (ii) Negative charge carriers in the vicinity of the anode are swept out to the anode, where charge exchange occurs. (iii) Positive charge carriers left behind are difficult to be neutralized by the migration of negative charge carriers, since the conductivity is low.

reactions bring about large differences in electrical properties, it is natural to assume that ions are dominant charge carriers in epoxy resin.

As shown in Figure 5b, the positive homocharge accumulated near the anode in the acid anhydride-cured samples is larger in the two NCs than in the epoxy resin without nanofillers. If the carriers responsible for the homocharge are positive holes, the increase in the accumulated homocharge can be explained by assuming that the injected carriers are easily trapped. However, the same phenomenon can be also explained by assuming that the homocharge formation is due to ions, if we focus on the effect of nano-structuration. Namely, if the responsible carriers are ions, the increase in homocharge can be understood by assuming that the transport of negative ions from the bulk, which should cancel the already existing positive homocharge, was retarded by the nano-structuration, as expected by the multicore model²⁷.

As shown in Figure 6b, the positive homocharge drastically decreases in the acid anhydride-cured samples for initial 10 min after the start of the short-circuit and then gradually decreases. It has been reported that accumulated space charge in epoxy resin shows two decay speeds, fast and slow²⁸. Assuming that the accumulated homocharge is electronic such as holes, this phenomenon can be explained by assuming the presence of two traps with different depths; one is shallow from which carriers can be detrapped fast and the other is deep with a longer detrapping time. On the other hand, assuming that accumulated homocharge is ionic, it can be explained by assuming two types of ions with different mobility.

The heterocharge in the amine-cured samples shown in Figure 6a drastically increases for 10 min after the start of the short-circuit and then gradually decreases in the NC samples. This is explained by assuming the presence of the following two types of space charge. Near the anode, there is a possibility that both negative heterocharge due to negative ions migrated from the bulk and positive homocharge due to remaining positive ions left behind after the charge exchange on the anode are present as shown in Figure 11. Note that the PEA system shows only the net charge quantity. Namely, only their difference can be seen. If the positive homocharge decays quickly upon the short-circuit as shown in Figure 6b, the negative heterocharge should be observed as if it increased for the following 10 min.

Near the cathode in the amine-cured samples right after the short-circuit, negative homocharge accumulates more than positive heterocharge as shown in Figure 7a. The negative homocharge decays much faster than does the positive heterocharge, which

27 T. Tanaka, M. Kozako, N. Fuse, and Y. Ohki, "Proposal of a multi-core model for polymer nanocomposite dielectrics", *IEEE Trans. Dielectr. Electr. Insul.*, Vol. 12, No. 4, pp. 669-681, 2005.

28 L. A. Dissado, V. Griseri, W. Peasgood, E. S. Cooper, K. Fukunaga, and J. C. Fothergill, "Decay of space charge in a glassy epoxy resin following voltage removal", *IEEE Trans. Dielectr. Electr. Insul.*, Vol.13, No. 4, pp. 903-916, 2006.

results in the appearance of positive heterocharge in about 10 min after the short-circuit in E(U)AM and C(O)AM and in about 50 min in C(S)AM. Similarly to this case, the assumption that two kinds of charge species with opposite polarities have different decay profiles can explain all the experimentally obtained space charge distribution measurement results shown in Figures 4-7.

5.4 PHOTO-ABSORPTION AND LUMINESCENCE

Through Sessions 5.1 to 5.3, the obtained results on permittivity, conductivity, and space charge distribution have been explained by assuming ionic conduction. This is because there is some doubt, as we already mentioned in Session 5.3, as to whether electrons and holes can play significant roles in the electrical conduction in practical polymeric insulators like epoxy resin, especially when ordinary voltages (= not extremely short-duration pulsive high voltages) are applied at temperatures higher than room temperature. As is typically shown by the fact that the Fermi level of a metal determines its ionization tendency, the band structure of a solid matter governs its ionic behavior. From this viewpoint, the band structures of the present samples are discussed in this session.

As shown in Figures 8, 9, and 10, the energy at which the absorption starts to increase is very similar to the PL peak energy and the energy at which the PLE spectrum starts to increase, for all the six samples tested. This strongly indicates that these energy values correspond to the bandgap energy (E_g) of each sample. This means that E_g is 3.4 eV for the amine-cured samples and 4.0 eV for the acid anhydride-cured samples. Considering the fact that the E_g is 3.0 eV for TiO_2 ²⁹, 4.4 eV for Ta_2O_5 , and 1.1 eV for undoped Si³⁰, these E_g values seem convincing, although we could not find reference data in literature. Even if these energy values are not directly related to E_g , it is quite certain that a band with a high density of electronic states lies 3.4 eV or 4.0 eV above the top band. If we refer to this energy difference as E_g' , the abovementioned results indicate that E_g or E_g' is smaller in the amine-cured samples than in the acid anhydride-cured samples.

Namely, E_g or E_g' depends on the curing agent. When two materials A and B are mixed together, localized electronic states associated with B are introduced in the energy band structure of A if B is incorporated in A as an impurity, whereas a totally different new

29 K. Hashimoto, A. Fujishima [Ed.], Sankachitanhikarisyokubai-nokenkyudoko (TiO₂ Photocatalysis ; its application to self-cleaning, antibacterial and air purifying materials), CMC Publishing, pp. 30-31, 2005 [in Japanese].

30 J. Robertson : "High dielectric constant gate oxides for metal oxide Si transistors", Report. Prog. Phys., Vol. 69, pp. 327-396, 2006.

band structure is formed if A and B form an alloy or compound^{31 32}. Judging from chemical structures shown in Figure 1, it is reasonable that the epoxy resins cured with different curing agents have different energy band structures.

The amine-cured samples, in which E_g or E_g' is smaller, have higher relative permittivity and higher electrical conductivity than the acid anhydride-cured samples as shown in Figures 2 and 3. If the conduction process is governed by electronic carriers, the relationship among E_g (or E_g'), permittivity, and conductivity is reasonable and easily understood. Even if the conduction is dominated by ionic carriers, this relationship is also understandable. In the case of a battery consisting of two different metals and electrolyte, ions are conduction carriers in the electrolyte, while electrons are in an outside conductor connecting the two metals. In this case, positive ions move from the metal with a higher ionization tendency to the one with a lower tendency, while electrons move from the metal with a higher Fermi level to the one with a lower level. Therefore, as we already mentioned, the Fermi level has the same physical meaning as the ionization tendency. For this reason, it is highly possible that the energy band structure and ionization tendency are closely related. Thus it is reasonable that the sample with a smaller E_g (or E_g') shows a higher conductivity, even if the conduction is governed by ionic carriers.

In a battery, the current transported by ions in electrolyte and the electronic current in the outside circuit become continuous by charge exchange at the electrodes. A similar process is assumed to occur in the present experiment, which passes electric current through the outside ammeter.

6 CONCLUSION

We investigated the effects of curing agent and clay dispersion method on the dielectric properties of epoxy/clay nanocomposites.

[1] The experimental results indicate that the curing agent gives the strongest effect on the properties of epoxy/clay NC. The presence of nanofillers affects secondly, and the filler dispersion method gives the weakest effect.

[2] Permittivity and conductivity are higher in the aminecured samples than in the acid anhydride-cured samples. From the space charge distribution measurement, after the sample was short-circuited following the voltage application, irrespective of the clay

31 Y. Ohki [Ed.], Yudentaibussei (Properties of dielectrics), Baifukan, pp. 73-76, 2002 [in Japanese].

32 N. Tanaka [Ed.], Amorufasuhandoutainokiso (Basics of amorphous semiconductors), Ohmsha, pp. 77-79, 1982 [in Japanese].

dispersion method, accumulation of negative heterocharge is observed near the anode in the amine-cured samples, while positive homocharge is seen near the anode in the acid anhydride-cured samples. From UV absorption, PL, and PLE measurements, the bandgap or the energy difference between localized electronic state and extended state is 3.4 eV for the amine-cured samples and 4.0 eV in the acid anhydride-cured samples. For epoxy resin in which ions are supposed to be dominant charge carriers, the influence of ions on the dielectric properties is more significant in the amine-cured samples than in the acid anhydride-cured samples, since the amine-cured samples contain more impurities such as water.

[3] Among the amine-cured samples, permittivity is lower in the NC samples than in the base resin, whereas all the acid anhydride-cured samples have similar permittivity values. This means that the effect of nano-structuration is significant in the amine-cured samples. This is because the amine-cured samples have OH bonds that cause a strong interaction with clays, resulting in the restriction of the movement of polar groups.