Electrical and Chemical Properties of Mica/Epoxy Composite Materials as Affected by Short-Time Aging

Hee-Dong Kim*

Abstract - Electrical properties such as permittivity and tanδ of unaged (control) and aged (72 h at 180 ℃) mica/epoxy composites of 130 ㎛ thickness were measured and their surface conditions were characterized using scanning electron microscopy (SEM), Fourier transform infrared (FTIR), electron spectroscopy for chemical analysis (ESCA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Both permittivity and tanδ of control specimens were higher than those of short-time aged specimens. FTIR results show a new peak at 1710 cm^{-1} for short-time aged specimens, originating from carbonyl group formed by the oxidation reaction during the aging process. ESCA results show that the binding energy at 532.9 eV representing the singlet state of oxygen (O_{1s}) decreases by 13.7%, whereas that at 534.6 eV increases by 13.7%. Glass transition temperatures of control and short-time aged specimens are observed to be 95.4 ℃ and 113.4 ℃, which increase with the increase of aging time. TGA results indicate that the control specimens contain a smaller amount of volatile components than the short-time aged specimens.

Keywords: aged specimen, DSC, ESCA, electrical property, mica/epoxy composite

1. Introduction

In a typical large rotating machine, winding insulation is composed of mica/epoxy composite materials. Since 1892, mica has been used as a key material of high-voltage rotating machine insulation systems. The unique combination of its electrical, mechanical, and thermal properties has yet to be equalled by any synthetic material. Mica paper consists of very small platelets of mica held together by electrostatic forces to form a continuous and self-supporting sheet. The main reason for changing to mica /epoxy composite materials from the large flake material previously used is its uniformity and several properties. Epoxy resins, which remained stable at high temperatures, were used as groundwall insulation bonding material in large turbine and hydrogenerators. Compared to polyesters, epoxy resins were found to have superior mechanical properties and resistance to moisture and chemical attacks. Also, they shrink less after curing. Solventless grades of epoxy, suitable for use in a VPI (vacuum pressure impregnation) process, were developed [1-3].

Insulation in service is exposed to high temperature, high voltage, vibration, and other mechanical forces as well as some adverse environmental conditions [4]. These various factors individually and jointly wear out or age the insulation. Thermal aging occurs when the temperature of the insulation is high enough to degrade the electrical and mechanical properties of insulation. Cycling of the temperature can also induce mechanical stresses causing deterioration, even if the temperature alone is insufficient to cause damage [5]. The mechanism may be treated as a chemical rate phenomenon and includes loss of volatiles, oxidation, depolymerization, shrinkage, embrittlement, and so on [6, 7]. For insulation systems introduced before the mid-1950s, thermal aging was the principal mechanism determining the life of the windings.

In this study, permittivity and tan delta (tanδ) of mica/epoxy composites were measured and the effects of short-time thermal aging (72 h at 180 ℃) were investigated. Both control and short-time aged specimens were further characterized using scanning electron microscopy (SEM), Fourier transform infrared (FTIR), electron spectroscopy for chemical analysis (ESCA), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Measurements on chemical change were conducted using FTIR and ESCA. Other short-time thermal aging aspects of mica/epoxy composites were investigated via DSC and TGA.

2. Experimental Procedures

Test specimens of muscovite mica and epoxy were taken from the B stage cured tape used to construct the insulation system of generator stator windings. The separator tape was removed to produce 0.13 ㎜ thick specimens for testing. The mica tape is composed of about 63.2% by weight

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35.84% of organic materials and 36.8% by weight 35.84% of mica. Two groups of specimens were prepared : one was designated as the control and was not aged, and the other was aged in an air oven at 180 ℃ for 72 hours. These latter specimens were designated as aged-72 h/180 ℃. Specimens from each group were prepared as follows for electrical test. Gold electrodes of 20 ㎜ in diameter were evaporated on both sides of the control and short-time aged specimens. The margin distance between the 20 ㎜ electrode and the edge of the specimen is 6 ㎜. Both permittivity and tan delta measurements of these samples were conducted by Schering bridge (Tettex Instruments, T2818QA). Because creeping discharge occurred in control and short-time aged specimens, these specimens were tested to below 4.5 kV ac. The specimens have been used a mold to prevent adhesion during the cure. The process of the mold removal had no affect on the creeping discharge. To clarify the internal phenomena of mica/epoxy composites, the cross-section of the control and short-time aged specimens was examined using SEM (Philips, 535M). The molecular structure of the surface of mica/epoxy composites was investigated using a FTIR (FTIR Spectrophotometer Bio-Rad Digilab FTS-80) and ESCA (Model ESCALAB 220, VG Scientific). For an ESCA analysis, monochromatic Mg-K_{α} was used as a source X-ray and a base pressure was maintained at 1×10^{-10} Torr. Its binding energy scale was calibrated by a known value (286.2 eV) of CH peak of carbon 1s. The 72hr aging properties of mica/epoxy composites were further analyzed using both DSC (DuPont 9900) and TGA (TA Instrument, TA 2000).

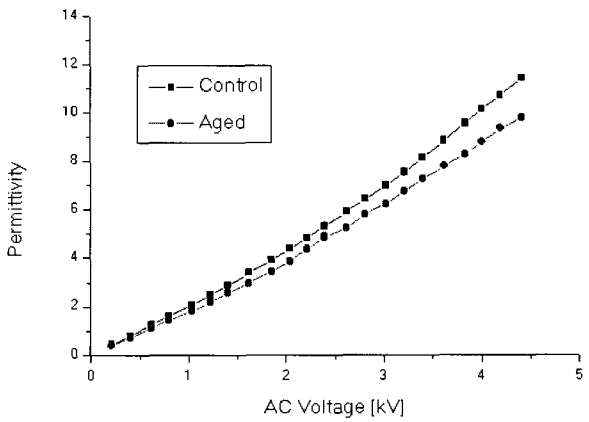


Fig. 1 Permittivity-voltage curves of control and short-time aged specimens

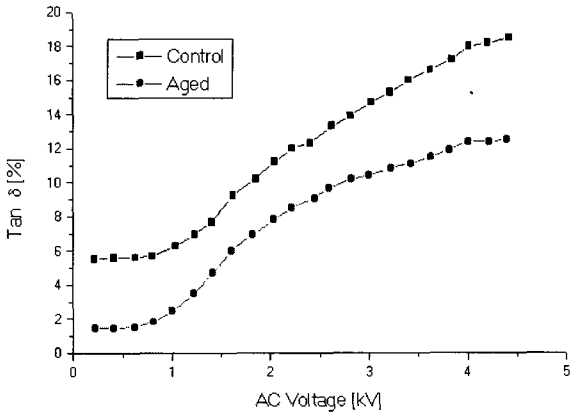


Fig. 2 Tanδ -voltage curves of control and short-time aged specimens

3. Results and Discussion

3.1 Measurements of permittivity and tan delta (tanδ)

Figs 1 and 2 show permittivity and tan delta curves of control and short-time aged specimens in mica/epoxy composites. As shown, permittivity and tan delta increase as the voltage increases. It was found that both the slope of the curve of AC current vs. voltage and the magnitude of the tanδ in the tanδ vs. voltage characteristic decreased with aging. The decrease in current slopes indicated a mix of two properties in unknown ratio, thickness increase, and permittivity loss; about 11%.

A thickness increase would occur if substantial outgassing occurred during the initial stages of aging. Concurrent crosslinking of the epoxy is also expected to increase the density of the epoxy which will decrease the thickness. This crosslinking will also cause a decrease in tanδ during aging. The effect is shown in the bias between the two curves of tanδ vs. voltage, which is 4.2% at low voltage with a definite tendency for magnitude of the bias to increase with increasing voltage (by about 7% tanδ per kV)

This increasing spread between the control and short-time aged dissipation factor with voltage is expected due to internal heating caused by the high tanδ of the poorly cured control specimen which does not occur in service. The effect of the aging on the partial discharges that affect the tanδ is a decrease of the tip-up voltage from 800 V to about 650 V.

Fig. 3 and 4 show typical SEM pictures of control and short-time aged specimens. In these pictures, light gray represents mica flakes and dark gray represents resin matrix. At a given voltage, the values of permittivity and tan delta are expected to increase as the total number of microvoids in discharge increases. Microvoids can result when air, moisture or other low molecular weigh material is trapped in the material during the cure process. Adhesion between epoxy and mica is improved as the density of microvoids decreases, resulting in a decrease of AC current and tan delta. The SEM pictures indicate some cavities about 5 ㎛ thick.

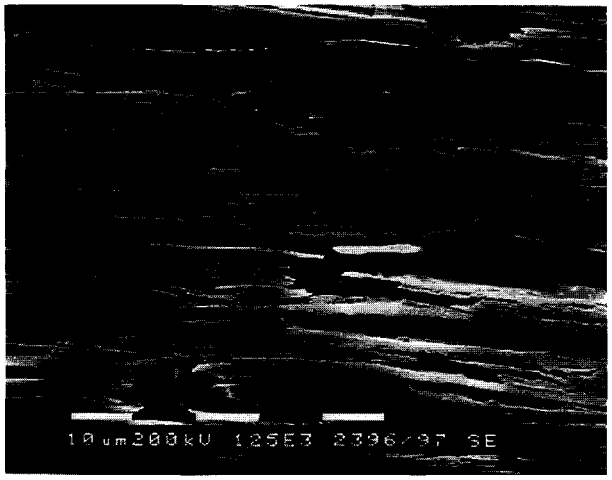


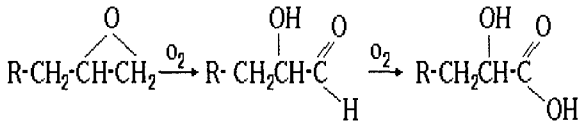
Fig. 3 SEM picture of control specimen

Fig. 4 SEM picture of short-time aged specimen

A Paschen Curve for air indicates that at atmospheric pressure a gap 5 ㎛ thick will ionize with a voltage of 300 volts zero to peak (212 Vrms) across it, and will continue to discharge if the voltage fails to drop below 150 volts zero to peak. The voltage across a 5 ㎛ cavity with a large ratio of area to thickness, as these cavities have, and in a matrix with a permittivity of 6, and a total thickness of 130 ㎛, will be approximately 0.194 times the applied voltage. This leads to an estimate of 155 volt (rms) or (219 volts zero to peak) across the cavity at 800 V applied. The discharge extinction voltage should be 548 V (4.2 kV/mm).

3.2 FTIR analysis

Fig. 5 shows the IR spectra of the control and short-time aged specimens of mica/epoxy composites. In this figure, A shows the FTIR spectrum of control specimens and B shows that of short-time aged specimens. Absorption peaks are found at 3400 cm^{-1}, 2930 cm^{-1}, 1605 cm^{-1}, 1506 cm^{-1}, 1236 cm^{-1}, 962 cm^{-1}, and 830 cm^{-1} in the control specimen. A short-time aged specimen shows another peak at 1710 cm^{-1}, a characteristic peak of the carbonyl group [8-10]. This result indicates that the epoxy has been oxidized during a thermal aging process. Both hydroxyl (OH) and carbonyl (C=O) are known to form by the oxidation reaction of the polymer. Some of the epoxide groups could be oxidized to hydroxyl aldehyde and carboxylic acid groups (1) [11]. These oxidations would also be consistent with our FTIR observations.



Typical characteristic IR absorption bands of both control and short-time aged specimens are shown in Table 1, where the wave number and the bands are presented.

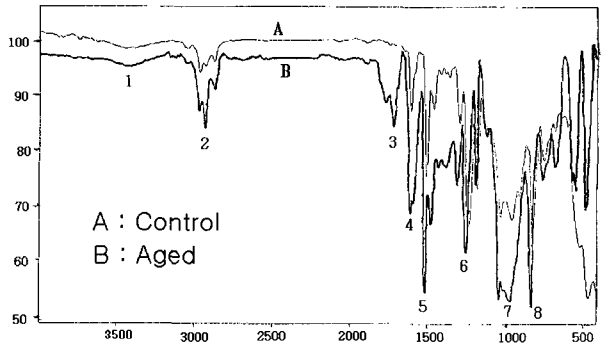


Fig. 5 IR spectrum of control and short-time aged specimens

Table 1 IR absorption bands of control and short-time aged specimens [10, 12]

Absorption Band Number	Wave Number (cm^{-1})	Band
1	3700-3200	OH
2	3000-2800	CH in CH_3
3	1720-1680	C=O
4	1640-1600	C=C
5	1510-1460	CH
6	1270-1255	Si-CH_3
7	870-850	Si-$(CH_3)_3$
8	840-790	Si-$(CH_3)_2$

3.3 ESCA analysis

Fig. 6 and 7 show the typical ESCA spectra as a function of binding energy using a wide scan in the range 0 to 1000 eV for control and short-time aged specimens. Figures 6 and 7 show that the ESCA spectra are comprised of strong peaks at

534 eV and 287 eV which are obtained from direct photoionization of oxygen 1s (O_{1s}) and carbon 1s (C_{1s}), respectively.

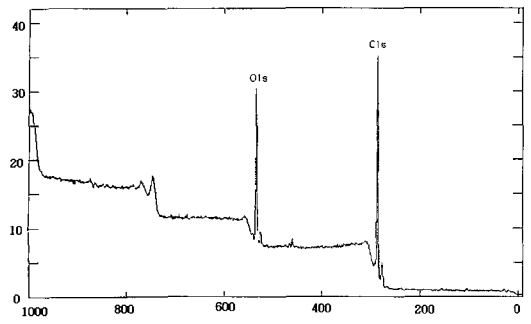


Fig. 6 ESCA spectra of control specimen

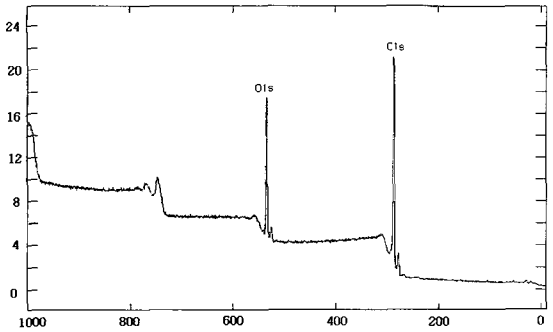


Fig. 7 ESCA spectra of short-time aged specimen

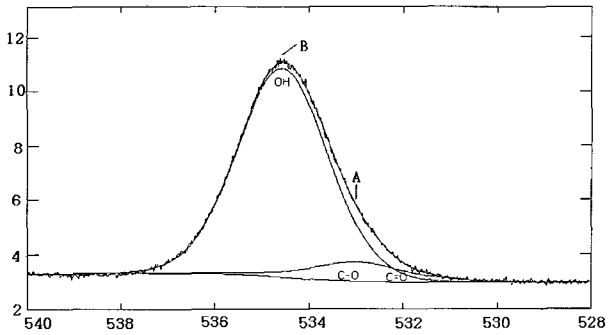


Fig. 8 ESCA spectra of O_{1s} in control specimen

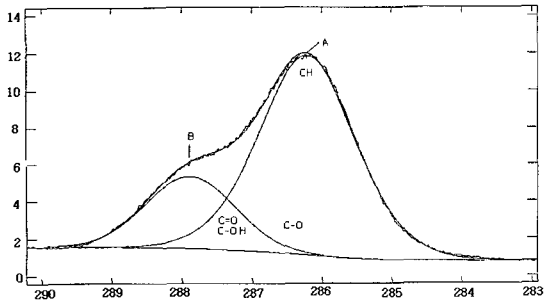


Fig. 9 ESCA spectra of C_{1s} in control specimen

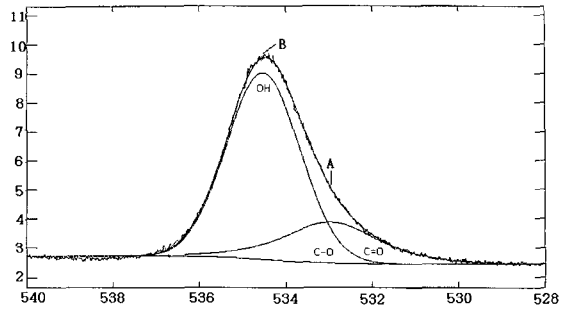


Fig. 10 ESCA spectra of O_{1s} in short-time aged specimen

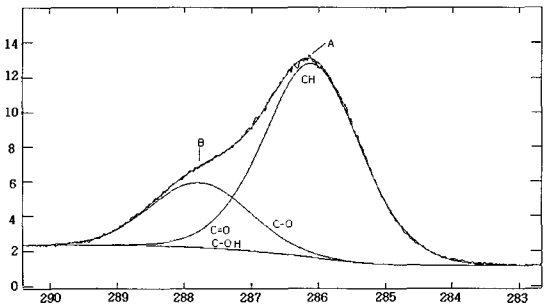


Fig. 11 ESCA spectra of C_{1s} in short-time aged specimen

Fig. 8-11 show ESCA spectra of control and short-time aged mica/epoxy composites. Two major peaks are observed at binding energies of about 534 eV and 287 eV. The peak at 534 eV is due to the photoionization of oxygen 1s (O_{1s}) and the peak at 287 eV is due to that of carbon (C_{1s}). These peaks have asymmetric shapes, suggesting that both O_{1s} and C_{1s} are composed of a few peaks having slightly different binding energies. A curve fitting technique was employed to resolve these peaks. As shown, O_{1s} and C_{1s} peaks are composed of two peaks. ESCA spectra of narrow, high energy resolution scans of the O_{1s} and C_{1s} levels referred to in Figures 6 and 7 are shown in Figures 8, 9, 10, and 11, respectively, in the corresponding energy ranges 532.9 eV to 534.6 eV and 286.1 eV to 287.9 eV. A curve fitting technique using a least square method is employed to obtain a smooth curve. As shown in Figures 8-11, the intensities are defined as the ratios of the area under curves A and B.

Table 2 Measurement of intensity ratios in O and C

Element		O_{1s}		C_{1s}	
		A	B	A	B
Control	BE(eV)	532.99	534.56	286.21	287.88
	Intensity (au)	1851.1	18738.5	18934.9	6164.4
Aged	BE(eV)	532.95	534.52	286.09	287.77
	Intensity (au)	4000.0	13623.0	20379.6	6792.4

Characteristics such as binding energies and intensities of these peaks are summarized in Table 2. It seems that

binding energies remain unaffected by the 72 h/180℃ thermal aging. However, the intensity ratio does change due to the thermal aging. As shown in Table 2, the ratio of two peaks, A/B, of the C_{1s} peaks is 25/75 and remains unchanged after thermal aging. However, the ratio of two peaks, A/B, of the O_{1s} peaks changes from 9/91 to 23/77. This suggests that a major change of chemical structure at the surface of the mica/epoxy composites takes place at hydroxyl (OH) functional groups. It seems that OH dissociates to form C=O. All these results suggest that the surface of mica/epoxy composites was oxidized, due to thermal aging process resulting in carbonyal functional groups at the surface.

A comparison of the present results with reference values of O_{1s} and C_{1s} indicates that 532.9 eV peak is for C-O or C=O, 534.5 eV is for OH, 286.2 eV peak is for C-O, and 287.9 eV peak is for C=O [9, 10, 13]. Figures 8 and 10 show that the curve has an asymmetrical binding energy peak for O_{1s}. This consists of two peaks of curves A and B at the different binding energies. ESCA spectra of O_{1s} indicates ether (C-O) group, carbonyl (C=O) group at the A peak and hydroxyl (OH) group at the B peak. The wave number (1710 cm^{-1}) for short-time aged specimens is confirmed due to the increase of ether (C-O) group and carbonyl (C=O) group at the A peak of O_{1s}. The asymmetry is also found for C_{1s} in Figures 9 and 11, respectively which is separated into symmetrical curves of different binding energies. ESCA spectra of C_{1s} indicate CH group at the A peak, and ether (C-O) group, carbonyl (C=O) group, ester (CO-O) group, C-OH at the B peak. The ratios of C_{1s} leave the relationship between control and short-time aged specimens unchanged.

Table 2 shows the variation of the intensity ratios at 532.9 eV and 534.6 eV for O_{1s}, and 286.1 eV and 287.9 eV for C_{1s}. The binding energy (BE) at 532.95 eV of O_{1s} decreases by 13.7%, whereas the BE at 534.6 eV increases by 13.7%. This is probably due to increased O as C-O, and C=O from the oxidation reaction of epoxy resins. The BE for OH is known to be 534.5 eV [10]. In this paper, the binding energy has been observed at B peak of O_{1s} (Figures 6 and 8). The BE for C=O and C-O are 532.1 eV and 533.6 eV. The BE 286.1 eV and 287.9 eV for C_{1s} decreases by 0.4% and increases by 0.4%, respectively. The BE for CH is known to be 286.2 eV [10]. The binding energy has been observed at A peak of C_{1s} (Figures 9 and 11). The BE for C-O, C=O (C-OH), and CO-O indicates at 286.5 eV, 287.5 eV, and 288.8 eV, respectively.

3.4 DSC and TGA analysis

Fig. 12 shows the cure curve of mica/epoxy composites measured by DSC at a temperature range of 30~350 ℃. The heating rate was at 10 ℃/min. Epoxide consumption takes place primarily at the temperature range 170~310 ℃. The peak temperature of the exothermic reaction representing curing reaction, was 266.7 ℃ and the heat of fusion (Δ H) calculated from the area under this exothermic peak was 33.18 J/g [14].

Fig, 13 and 14 show DSC thermogram of the control and short-time aged specimens. The heating rate for this study was also 10 ℃/min. Glass transition temperature(Tg) of the control specimen was found to be 95.4 ℃ whereas that of short-time aged specimen was found to be 113.4 ℃ The increase of Tg by thermal aging is frequently observed in epoxy systems such as bisphenol-A type epoxy [15]. The increase of Tg indicates that molecules become immo-

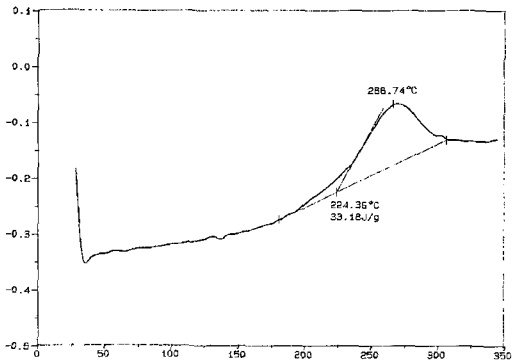


Fig. 12 Cure curve of mica/epoxy composites

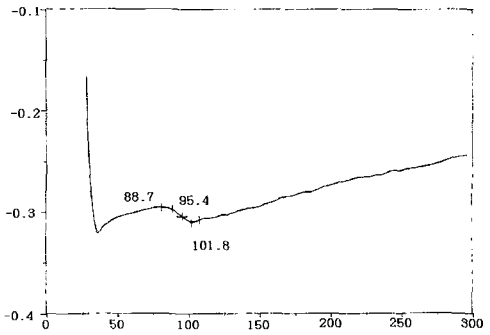


Fig. 13 DSC thermogram of control specimen

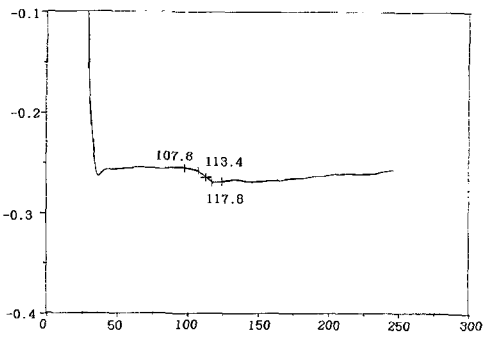


Fig. 14 DSC thermogram of short-time aged specimen

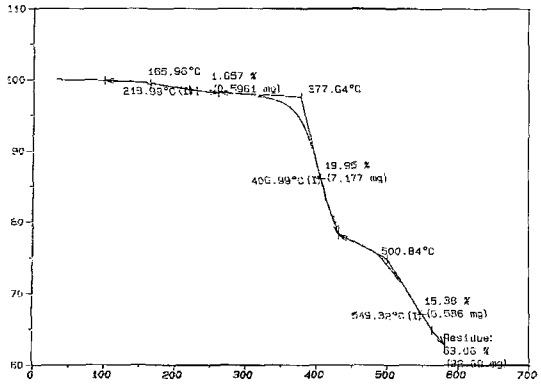


Fig. 15 TGA thermograms of control specimen

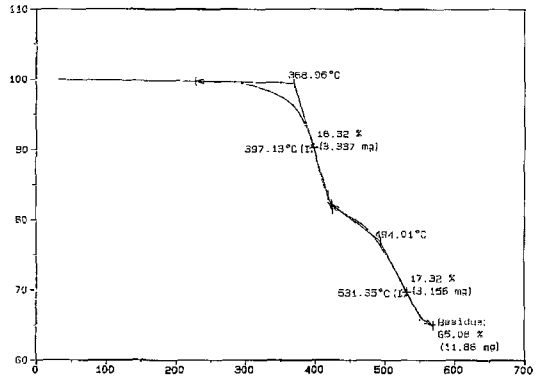


Fig. 16 TGA thermograms of short-time aged specimen

bile, which often is due to increased crosslinking density but in this case may be partly due to an increased adhesion between mica and epoxy. Both phenomena can take place via thermal aging of mica/epoxy composites.

Fig. 15 and 16 compare TGA thermograms of the control and short-time aged specimens. The heating rate was 5 ℃/min for this study. The TGA data indicate that weight loss of control specimen starts at about 165 ℃ and the aging was at 180 ℃. Control specimen shows weight losses at 220 ℃ (1.7%), 407 ℃ (20%) and 549 ℃ (15.3%), whereas the short-time aged specimen shows weight losses at 397 ℃ (18.3%) and 531 ℃ (17.3%). Weight losses at 220 ℃ the control specimen should be due to a volatile component present in the control specimen, possibly. Water molecules associated with mica or epoxy. No weight loss at 220 ℃ is observed in thermally short-time aged specimens perhaps because these water molecules have already disappeared during the thermal aging process. The thermally short-time aged specimen seems to volatize at higher temperatures than the control specimen.

4. Conclusion

Both the permittivity and the magnitude of the tan δ in the tan δ vs. voltage characteristic were found to decrease with aging. The TGA data indicate that weight loss of the control specimen starts at about 165 ℃ and the aging was at 180℃ so this is a reasonable explanation. Concurrent crosslinking of the epoxy is also expected to increase the density of the epoxy, which will decrease the thickness. This crosslinking will also cause a decrease in tan δ during aging. The effect is shown in the bias between the two curves of tan δ vs. voltage, which is 4.2% at low voltage with a definite tendency for magnitude of the decrease to increase with increasing voltage (by about 7% tan δ per kV). The SEM pictures indicate some cavities about 5 μm thick.

Both FTIR and ESCA analysis suggested that the surface of short-time aged specimens should experience chemical structural change, with the major change being the formation of carbonyls. The carbonyl peak at 1710 cm^{-1} was observed from an FTIR analysis, and two peaks at the binding energies of 532.9 eV for the ether (C-O) group and 534.6 eV for the carbonyl (C=O) group were observed in short-time aged specimens from an ESCA analysis. Upon thermal aging, the area under the 532.9 eV peak decreased by 13.7%, whereas that under the 534.6 eV peak increased by 13.7%. Glass transition temperatures measured by DSC were 95.4 ℃ for control specimens and 113.4 ℃ for short-time aged specimens. Weight loss of control specimens was higher than that of short-time aged specimens.

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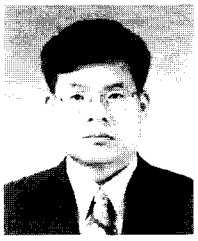

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