論 文
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필름 Capacitor의 전기적 Damage에 관한 연구

Electrical Damage of Metallized Film Capacitors

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Abstract - Damage in film capacitors has been investigated, using FTIR and ESCA, aiming to elucidate the nature of electrode removal and the possibility of base films to be damaged. Also, tests were conducted to investigate the effect of a long-term thermal aging at elevated temperatures. Unsuccessful clearing or grape-clustering processes can induce a long-term degradation which involves the chemical and morphological changes. Major changes are the oxidation and the decrease in surface crystallinity possibly arising from the corona discharge. An immediate deterioration of BOPP film may occur when the air entrapped between the film layers induces an extensive autocatalytic oxidative degradation. This type of immediate damage may result in a premature failure at an early stage of qualification test. As far as the nature of electrode removal is concerned, a permanent removal of electrode materials was observed in the main erosion area.

1. Introduction

Medium and high voltage power capacitors are composed of thin biaxially oriented polypropylene (BOPP) film the one side of which is coated with a thin layer of metallization. Due to this thin metallized layer, the power capacitors can be self-healed when the faulty condition creates the breakdown in BOPP film. Frequently, however, an unacceptable loss in capacitance was experienced during the qualification tests at an elevated temperature typically for 2000 hrs.

It has been previously reported[1] that the grape-clusters responsible for a large loss in capacitance can be reproduced by a lab scale test equipment and that the grape-cluster is a sequential cascade event resulting from an unsuccessful clear. Grape-clusters grow into a large area by dispensing the stored electrostatic energy laterally. Microscopical investigation have also revealed that the base BOPP film is considerably damaged, the most important one being a physical removal of certain amount of polymer by electrical stresses. Lots of mechanical pits belong to this damage. The observation of pits was speculated to form as a result of corona discharge. Since the previous

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report concerned only the microscopical study on the polymer damages related to the grape-clustering process, it would be necessary to conduct the investigation on what other types of damage are involved on both metallization and polymer sides. It is also necessary to confirm the speculation that the corona discharge occurs over the test period. All these information would provide the clues for a better understanding of the degradation mechanisms and possibly the ways to improve the reliability of film capacitors.

The present work, a continued investigation on polymer damages by grape-clustering process, was centered at the changes in the eroded area and the overall structural changes in the base polymer.

2. Experimental

The test equipment used in the present study is basically the same as the one reported elsewhere [1]. It is composed of power supply, graded electrode which can prevent the premature breakdown of the film and the buffer layers which can hold the film specimen without wrinkling.

Structural or chemical changes by the electrical activity were studied using FTIR-ATR and ESCA. Film specimen was placed in the test system and the electric stress was applied until current pulsing ceases. By doing this, we could confirm that most electrode was eroded. Then two films with grape-clusters all over the electrode area were installed on both sides of KRS crystal through which the IR beam was irradiated. For an ESCA analysis, a circular mask of 1mm diameter was overlapped in order to ensure the data collection only at the eroded area.

To help establish that thermal aging and pro-breakdown electrical activity can damage the film, tests were used to evaluate changes caused by thermal aging and prebreakdown partial (corona) discharges. 8 μm thick plain BOPP film was partial (corona) discharged under the AC stress. AC voltage of 4 kV_{rms} was applied across about 1.5 mm gap distance. A needle electrode was used to generate the corona. For aging tests, fresh metallized films were placed in an air-blowing oven typically at 90-120℃ for up to 1000 hrs.

3. Results and Discussion

3.1 Surface morphology and elemental analysis

The nature of electrode removal was further analysed using a microscopic method. Figure 1 shows a typical surface morphology by a light microscope (a) and a SEM (b) for a single clearing site. (c) shows EDX results on four spots in a single clearings site, where the ratio of the concentration of Al used for metallization to that of Au layer (about 60 Å) used for the SEM/EDX experiment. The location of these spots are seen in (b). As shown in (c), the main erosion area (# 1-#3) has very low Al concentration, only about 10~20% compared to nondamaged area (#4). Besides, there observed very fine particles which were proved to be residual Al particles. A close

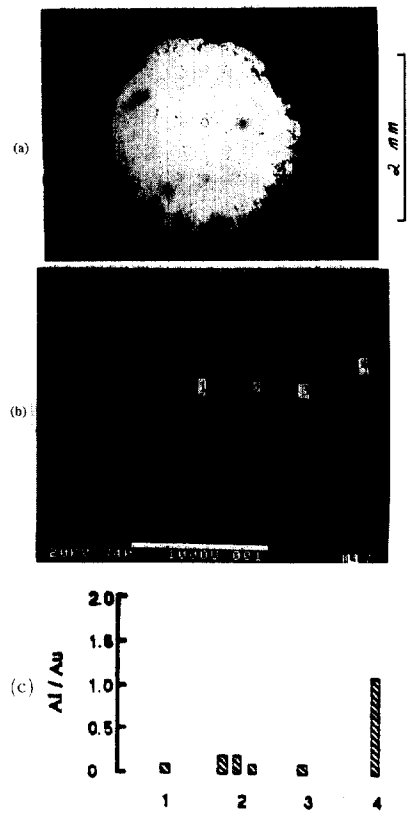

Fig. 1 Photos and EDX results of a single cleared site: (a) optical microscope, (b) SEM, (c) EDX result

examination at higher magnifications has revealed that the metallized layer looks peeled off, leaving many Al patches behind in the interface region. While the main eroded area shows a very rough surface, the interface region shows somewhat clean surface.

The present analysis on the nature of electrode erosion indicateds that a permanent removal of electrode(metallization) may be one possibility for a capacitance loss during the qualification test. Major portion of electrode is physically removed by the discharging activity, so that the main erosion area becomes an insulator and correspondingly a capacitance loss resulted in by reducing an effective electrode area. It is questionable, however, whether this type of electrode damage occurs in film capacitors or not. It may depend on the level of applied voltage. If high voltages are applied,then permanent removal of electrode may occur. In film capacitors, however, the applied voltage is much lower than about 100V/μm. In film capacitors, therefore, the permanent removal of electrode may not occur or at least much less, if any, than the one observed in the present work. In that case, the electrochemical conversion of the metal to the metal oxide may be dominant, as pointed out by Shaw et al.[2, 3] and Taylor[4], and the damage will be more cumulative. Nevertheless, once the discharging event occurs the possibility of such permanent removal of electrode material may not be excluded.

3.2 Chemical changes by electrical activity

FTIR-ATR spectra of plain and electrically damaged films(6μm thick and 2.2 ohms/square) were collected. A comparison at an expanded scale shows a systematic change depending on the duration in an electric field, as shown in Figure 2. Two or more peaks are identified in the range of 1600~1800cm^{-1}. Peaks are at 1637, 1703, and 1747cm^{-1}. It seems that as the duration in an eleectric field increases, the absorbance of the peaks at 1700~1750cm^{-1} increases. This result indicates that the electrical activity can impose the chemical change. However, the absorbance of these peaks is still very small, so that similarily treated films were subjected to a chemical elemental analysis using an ESCA facility.

Figure 3 is the overall ESCA spectra of the plain(a) and electrically damaged(b and c) BOPP films. As shown in Figure 3, the plain BOPP film contains mainly carbon and a trace amount of oxygen in its surface. On the other hand, both metallization and polymer sides show large oxygen peaks. In particular, the ratio of oxygen to carbon peaks is very large compared to that of the plain BOPP, which indicates that the oxygen is one of the major species at both metallization and polymer surfaces. In addition to the oxygen and carbon peaks, the metallization side has Al peaks possibly from the Al metallization and the polymer side Cu Auger peaks coming from the copper electrode. Figure 4 is the curve fitting of C-ls peaks of the plain and electrically damaged BOPP films. Figure 4 shows that the carbon of the plain film(a) is composed of only one peak at −286eV, whereas that of the electrically damaged film(b and c) is composed of three

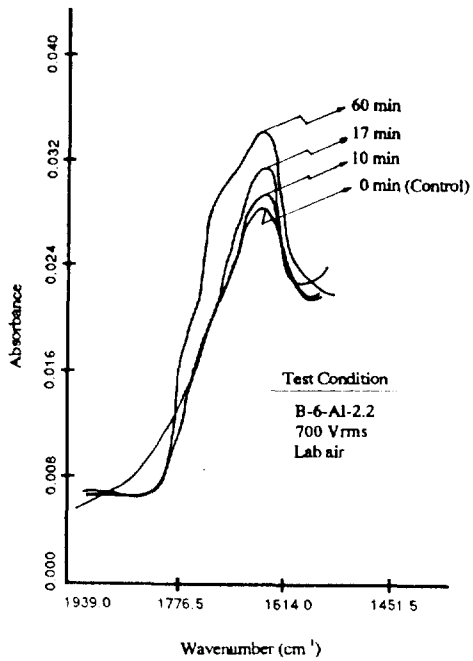

Fig. 2 FTIR-ATR spectrum of electrically damaged BOPP films: Test conditions: 700 V_{rms}, Lab air, film thickness: 6 μm, metallization: Al, 2.2 ohms/square.

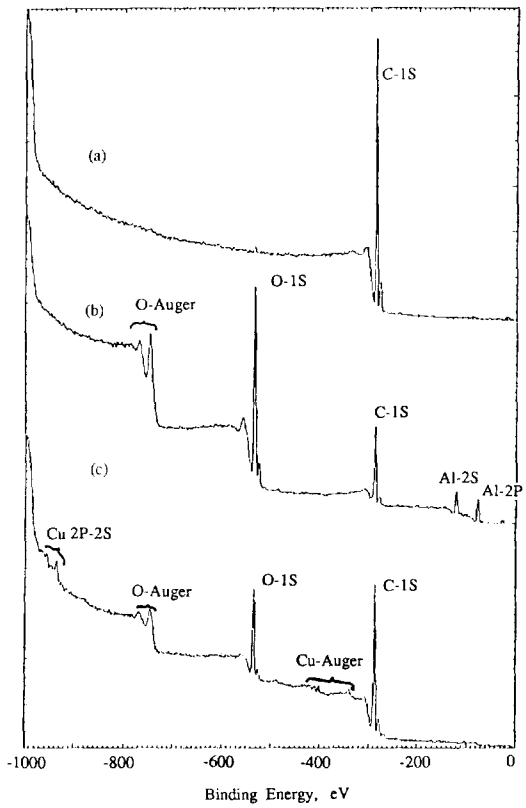

Fig. 3 ESCA response of electrically damaged BOPP films: (a) control, (b) metallization side, (c) polymer side. Test conditions & films: same as in Figure 2.

peaks at −286, −287 and −298 eV, respectively. The fact that the C-ls peak can be resolved into three peaks implies that the environment around the main chain carbon has changed.

Besides, the metallized BOPP films once subjected to the AC stresses showed the hazy (opaque) color and the polymer side of tested films were stuck to the fresh plain BOPP film surface, i.e., the autoadhesive characteristic was observed.

Instrumental analysis using FTIR and ESCA facilities indicates that the chemical nature at the surface of electrically damaged films has changed by the electrical activity. FTIR-ATR analysis shows new peaks at 1637, 1703, and 1747cm^{-1}. With the assistance of literature information[5-7], these peaks have been identified as unsaturated double bonds for the peak at 1637cm^{-1} and carbonyl group for the peaks at 1703 and 1747cm^{-1}.

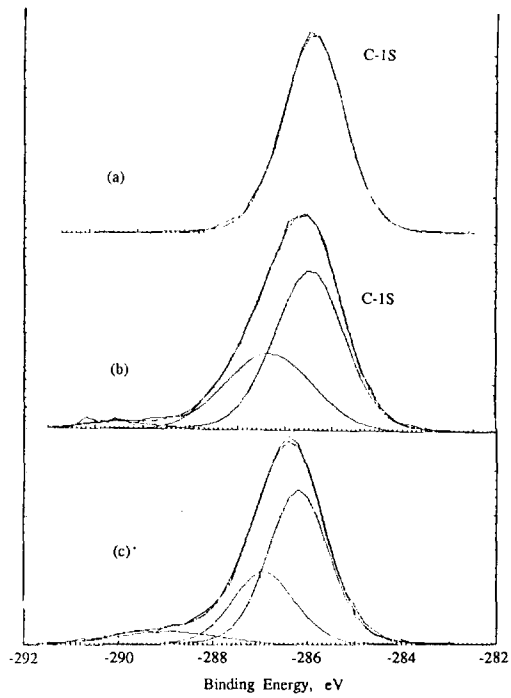

Fig. 4 Curve fitting for C-I_s peak: (a) control, (b) metallization side, (c) polymer side. Test conditions & films: same as in Figure 2.

The peaks in an ESCA analysis have not been carefully characterized. Along with the results from a FTIR analysis, however, it seems that the peak with the largest area in Figure 4 must be the C-C bond and the other two the C=O and C=C bonds. These results suggest that the BOPP films are oxidized by the electrical activities. This suggestion can be supported by the observation of hazy (opaque) color and autoadhesive characteristic of the tested films. All observed features, i.e., carbonyl and unsaturation groups, polar groups and low molecular weight waxy layer, are well known to form at a result of the oxidation and subsequent chain scission reaction[5-8].

3.3 Corona discharged BOPP film

To ensure that prebreakdown electrical activity can damage the OPP film, tests were used to investigate changes by prebreakdown partial discharges. The films was 8 μm thick nonmetallized plain OPP film.

Figure 5 shows three FTIR spectra: (a) is the

FTIR-ATR spectrum of non-treated BOPP film, (b) that of corona treated one, and (c) the FTIR -transmittance spectrum of corona treated BOPP film. FTIR-ATR spectra were taken at the incident angle of 45° and the corona was generated at 4 kV_{rms} at a gap distance of 1.5 mm. FTIR-ATR spectrum of the corona treated BOPP film (Figure 5-b) shows a considerable difference compared to that of the non-treated one (Figure 5-a). A major apperciable difference is the formation of broad new peaks, one at 1750 and the other at 1640cm^{-1}. A broad peak at around 3220cm^{-1} was also observed. Appearance of these peaks indicates that the chemical nature of the surface of BOPP film has changed considerably due to the corona treatment. A broad peak at 3220cm^{-1} is associated with the hydroxyl (-OH) group, and the peaks around 1750 and 1640cm^{-1} can be assigned as the carbonyl and unsaturated double bond groups, respectively [5-7], as already mentioned. Such changes of BOPP films can be attributed to the chemical nature of polypropylene. Chemically, polypropylene has a weakness in the sense that the polypropylene is prone to the chain degradation, although the orientation can suppresss degradation a lot. The reason for this is that polypropylene has a high population of tertiary hydrogen atoms which induces the degradation very easily [8].

Peak positions corresponding to the carbonyl and unsaturation groups are the same for both grape-clustered and corona treated films. For this, compare Figure 2 and 5-b. In addition, the absorbances at many peaks changed by the corona treatment. In particular, three peaks at 841, 998, and 1167 cm^{-1} decrease considerably. These peaks are known to originate from the crystalline part of polypropylene [9-12]. Of these, two peaks at 841 and 998 cm^{-1} are usuallys used for the estimation of the surface crystallinity. The crystallinity estimated from the ratio of these peaks decreased from 71.7% for non-treated film to 56.6% for corona treated film. Note that these values are different from the ones which will appear in the next section. Remember that specimens are different.

Figure 5-c, a FTIR-transmittance spectrum of the corona treated film shows no peaks at

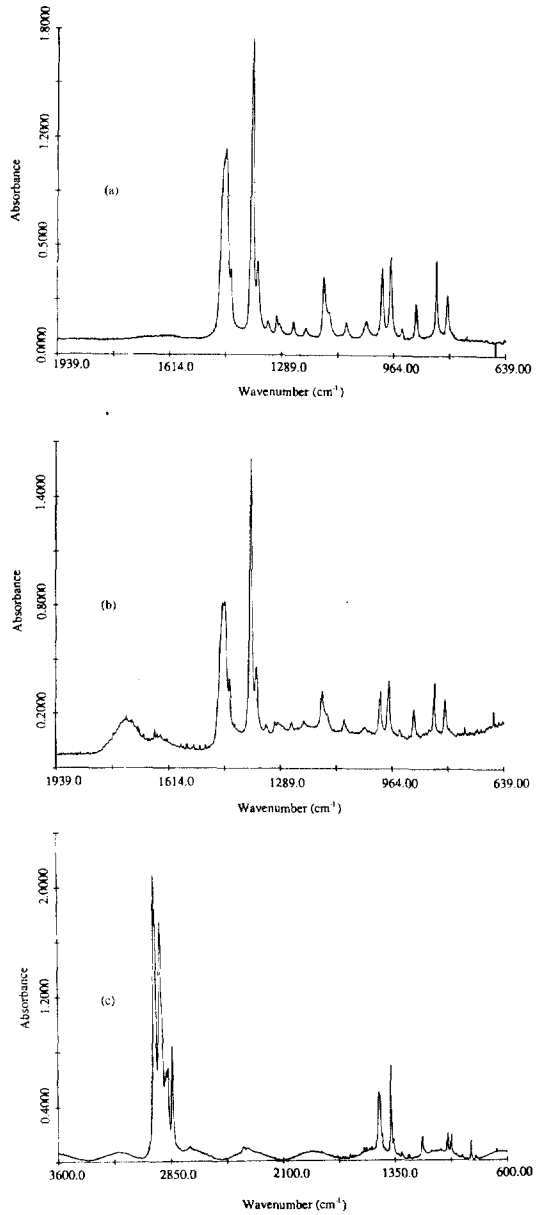

Fig. 5 FTIR-ATR spectrum of non-treated BOPP film (a), FTIR-ATR spectrum of corona treated BOPP film (b), and FTIR-transmittance spectrum of corona treated BOPP film (c). $\theta = 45°$ for FTIR-ATR spectra, film thickness : 8 μm, corona : 4 k V_{rms} at 1.5 mm gap distance.

wavenumbers around 3220, 1700cm^{-1}, which implies that no appreciable oxidation can be detected when a transmittance technique is em-

ployed even though the film surface is considerably oxidized. Considering that no differences were found from the transmittance method while appreciable differences were found from the FTIR-ATR method, one can notice that chemical and morphological modifications in BOPP films by the corona discharge are confined only to the surface region.

3.4 Thermal aging effect

Film capactiors have to pass the qualification test lasting up to 2000 hrs at an elevated temperature, which suggests that the themal aging effect might become important as the test time goes on. Therefore, in order to isolate the thermal effect, fresh non-metallized films were thermally aged typically at 90 and 120℃ for up to 1000hrs and then changes in physical properties were evaluated. The aging temperature of 90℃ was chosen such that the temperature does not impose a great damage such as shrinkage and other physical properties[13]. Also, 120℃ was chosen for an extensive thermal stressing.

Figure 6, in which the surface crystallinity was plotted against the aging time, shows that the surface crystallinity changes as a function of aging time at 90℃. In the figure, 38 and 45° indicate the angle of the incident IR beam and can be used as a measure of the penetration depth of IR beam [9]. In the case of 45°, the IR beam penetrates into the deeper region of the film than 38°. At the very surface(38°) the degree of crystallinity increases first and then decreases, whereas at a little deeper surface(45°) it decreases monotonically. The crystallinity of the fresh film has less than 50% at the very surface and higher than 70% in the bulk. Therefore, the surface region has a higher amorphocity than the bulk region. In this region, the crystallinity may get increased at an early stage of thermal aging due to the "annealing" effect, but eventually will decrease as the surface degradation starts developed. On the other hand, deeper region can be considered as a highly oriented state, so that the chains will be relaxed immediately upon thermal aging. Also, the results indicate that the film is more oriented to the machine direction that to the transverse direction.

As far as the evolution of carbonyl and unsaturation groups is concerned, only small peaks for the oxidation were observed by thermal aging and no consistent changes in peak absorbances were found as a function of aging time. Of couse, this does not mean automatically that there is no oxidation. Rather, the level of oxidation is low below the detecting limit of FTIR-ATR. Further analysis using more sensitive instruments is required for a full characterization.

A very interesting feature was obseved when the metallized film was thermally aged at 120℃ in the same oven. That is, most aged films(metallized ones) were completely destroyed, as shown in Figure 7. These pictures were taken after about 100-hour aging. A bottom picture shows how the destruction looks like when a small piece is rubbed by fingers. On the other hand, non-metallized films did not show such destruction at comparable aging

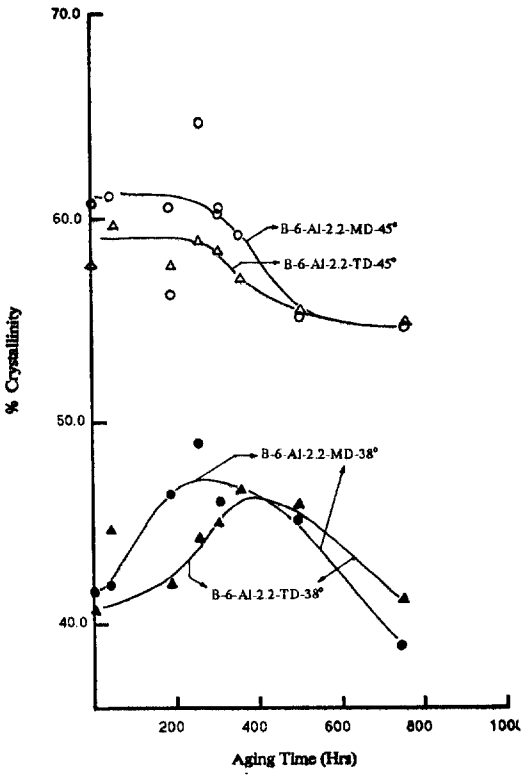

Fig. 6 Surface crystallinity of thermally aged BOPP film : Temp : 90℃, film thickness : 6 μm, metallization : Al, 2.2 ohms/square, oven : air-blowing oven

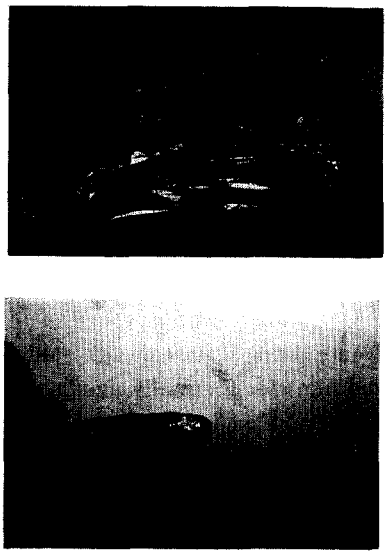

Fig. 7 Appearance of metallized BOPP films thermally aged for about 100 hours : Temp : 120℃, oven : air-blowing oven, film thickness : 6 μm, metallization : Al, 2.2 ohms/square

time. This destruction might be due to the autocatalytic oxidation and subsequent degradation reaction. The thin metal layer enhances the oxidation reaction, so that the extensive oxidation occurs at the interface between the metal layer and the base BOPP film. This type of oxidation will become significant as the thickness of BOPP film decreases.

For grape-clustered and corona treated films, many observed features are the same. These are (1) the introduction of carbonyl and unsaturation groups at the same wavenumbers, (2) the autoadhesive characteristic, and (3) the confinement of modifications only at the surface region. From these, therefore, one can conclude that the BOPP films are oxidized during the test period to generate the lab grape-clusters and the corona discharge may be one of the major causes for the oxidation.

An oxidative degradation of metallized BOPP films becomes considerable as the thermal aging temperature increases. In particular, aging at 120℃ seems detrimental to metallized BOPP films since thus aged films have shown a complete destruction. This phenomenon might be one of the reasons for a premature failure of film capacitors at an early stage of qualification test. The air entrapped by improper wrapping procedure may cause such detrimental damage in BOPP films under the faulty conditions resulting in a local heating.

4. Conclusion

Unsuccessful clearing or grape-clustering processes can induce a long-term degradation which involves the chemical and morphological changes. These changes were attributed to the oxidation possibly from the corona discharge. An immediate deterioration of BOPP film may occur when the air entrapped between the film layers induces an extensive autocatalytic oxidative degradation. This type of immediated damage may result in a premature failure at an early stage of qualification test. As far as the nature of electrode removal is concerned, a permanent removal of electrode materials was observed in the main erosion area.

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