Models of Possible Trapping Sites in Homo-Charged PVF

호모로 대전된 PVF박막에서 트랩위치의 제시

김광영* · 김기준** · 황병호*** · 홍진웅* · 이준웅*
(K. Y. Kim · K. J. Kim · B. H. Hwang · J. W. Hong · J. U. Lee)

요 약

두께 30[㎛]의 코로나 대전된 폴리비닐후로라이드 박막에 전압 −3∼−6[kV]를 인가한 후, 온도범위 −100∼200[℃]에서 열자격 전류를 측정하였다.

결과로 β, α 그리고 δ 피크가 온도 −40, 40 그리고 90[℃] 부근에서 각각 나타났다. 이들 피크의 기원으로, 첫째, β 피크는 카보닐기의 기여로, 둘째로 α 피크는 주쇄와 비정질 영역의 측쇄에 트랩된 캐리어의 탈트랩의 기여로 나타났고, 끝으로 δ 피크는 비정질 영역 또는 비정질과 결정질 영역 사이의 경계에 트랩된 캐리어의 탈트랩에 기여로 사료된다.

ABSTRACT

After being formed by applying −3∼−6[kV] to the Polyvinyl Fluoride(PVF) film, 30 micron, corona electrets were experimented to measure thermally stimulated current(TSC) in the temperature range from -100[℃] to 200[℃].

As a result, three peaks of β, α and δ were obtained around −40[℃], 40[℃] and 90[℃], respectively.

Speaking of the origin of these peaks, first of all, β peak is believed to show up by virtue of carbonyl groups.

Second, α peak seems to turn up by the de trapping of the carriers trapped in main chains and side chain in the amorphous regions.

finally, δ peak looks to be ascribed to the detrapping of the carriers trapped in the amorphous regions, or the border between the amorphous regions and the crystalline.

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*광운대학교 전기공학과
**한국원자력 연구소 원격장치 기술실
***충주공업전문대학 전기과

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1. Introduction

Properties of polymers may well be understood to develop the better ones.

In spite of the fact, there remain lots of characters of them to be understood.

The physical properties of PVF have been studied by scholars; for example; J.L.Koening[1] made an infrared study of PVF in 1966, Masamitsi Kosaki[2] studied electrical conduction of PVF in 1970 and Osaki et al.,[3] reported on the dielectric properties of PVF in 1971.

However, despite these studies, the more structual explanation has yet to be made.

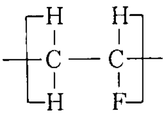
Therefore, a proposal was made to elucidate the origin of corona-charged PVF(homo-charged Polymers) in this paper.

It is based on the proposal that Perlman et al[4] made for corona-charged Polyolefin and electron-bombered Teflon.

2. Experiments.

The specimen used in this study is PVF film of thickness 30[μm] (the commercial name Tedler called by dupont co.).

Its monomer is



$$\left[-\begin{array}{c} H \\ | \\ C \\ | \\ H \end{array} - \begin{array}{c} H \\ | \\ C \\ | \\ F \end{array} - \right]_n$$

It is reported that its melting point, the first glass-rubber transition temperature and the second are around 203[℃], −20[℃] and 40[℃], respectively(The physical properties of the specimen show on the table 1). Figure 1 shows corona-charge controlling apparatus.

Table 1. Physical properties of PVF

Kinds	Numbers	Remarks
Melting point	203[℃].	
Specific Gravity	1044	
Dielectric Constant	10	1[kHz]
Density	1040[g/cm^3]	
Boiling Point	−72[℃]	
Critical temperature	54.7[℃]	
Critical Density	0.320[g/cc]	
Volume Resitibity.	12[Ω.Cm]	50[℃]
Tan δ	0.2	50[℃]

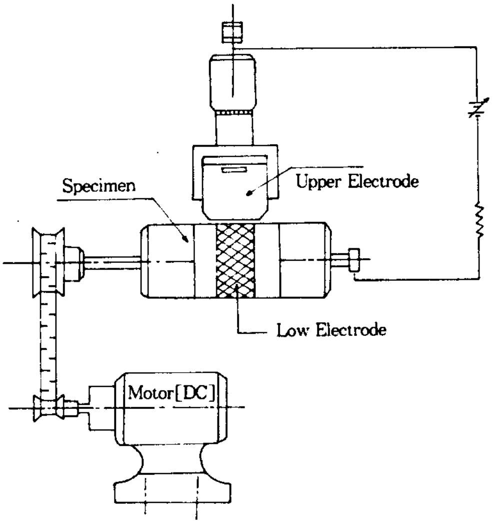


Fig. 1. Corona Charge Controlling apparatus.

Electrets were made by applying −3~−6 [kV] to the specimens in a dark room at rolling speed 3[cm/S] and 0.5[mm] kept the air gap between the knife electrode and the specimen.

After formed, the electrets were discharged in air for 15 minutes.

To measure TSC spectra, the electret was placed in the forced draft oven which was programmed to increase at rates of 0.5[℃/min]~5

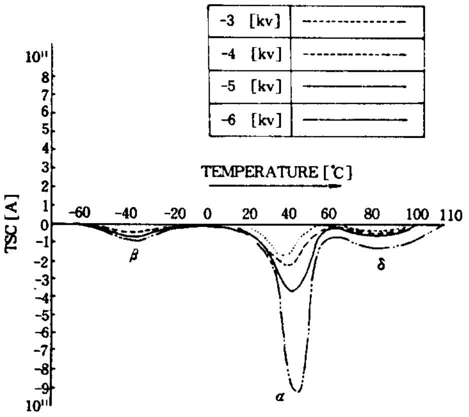


Fig. 2. Dependence of negative corona-electret on voltage(speed of knife-electrode 3[cm/S], discharge time 15 [min], air gap 0.5[mm], heating rate 5[℃/min], negative corona voltage −3∼−6[kV])

[℃/min].

At this time, the charged side of the electret was fixed to be contacted with the upper electrode, so that the direction of TSC spectra might be the same.

The conductive aluminium foil was used for the electrodes.

Fixed in the oven, the electret was rapidly quenched to -150[℃] with liquid nitrogen.

And then, the electret was measured to obtain TSC with increasing temperature at rate of 5 [℃/min].

3. Result and Discussion.

1) Dependence of negative corona-electret on voltage

Figure 2. shows TSC spectra from negative corona-charged PVF from −3[kV] to −6 [kV].

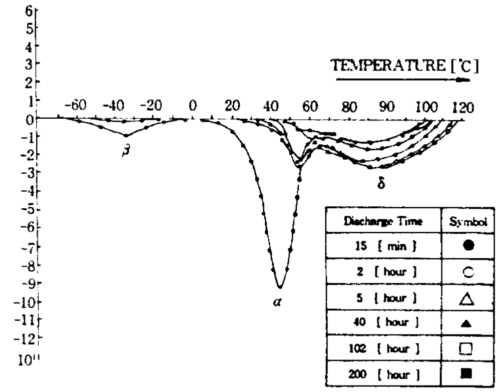


Fig. 3. Dependence of negative corona-electret on discharging time(negative corona voltage −6[kV], heating rate 5[℃/min]

Three peaks turned up around −40[℃], 40 [℃], and 90[℃] respectively.

Also, they were named β, α and δ from one in low temperature for convenience's sake.

2) Dependence of negative corona-electret on discharging time.

Fig. 3 shows TSC spectra from the electrets, which were discharged in a dark room for different time after being formed by applying −6 [kV] to PVF film.

There were three peaks obtained.

β and α peaks have decreased rapidly, but δ peak slowly, with discharging time.

Both β and δ peaks tend to keep the same temperature scale regardless of discharging time.

The α peak, however, have a tendency to go up to a higher temperature scale with discharging time.

Perlman and associates[4] have suggested some possible trapping sites in corona-charged polyolefins.

In this paper, possible changes in chemical structures of corona-charged PVF, which could serve as trap sites, were proposed as follows.

1. Formation of carbonyl groups(C=0)

Oxygen molecule(O_2) in air is impacted and ionized by the electrons from the negative electrode.

After that, ionized oxygen gets to be deposited on the surface of the specimen.

Oxygen atom is hard to penetrate into the specimen because it is heavy and large.

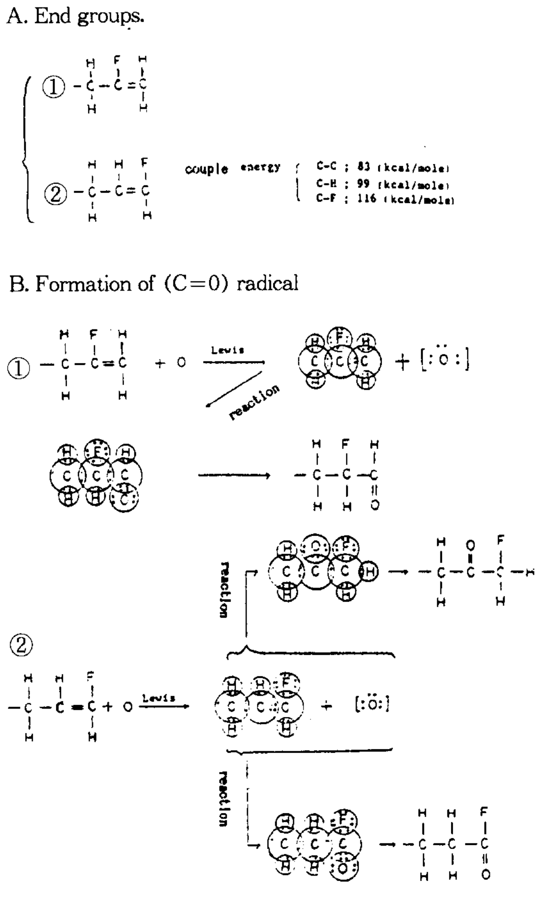


Fig. 4. Possible formation of carbonyl groups.

Carbonyl groups could be produced as the result of the chemical reaction of oxygen with >C=C<, which could exist in PVF's end groups, as in figure 4.

In this case, charge release seems to be initiated by the motion of the end groups, which starts blow −20[℃], the first glass−rubber transition temperature.

Though various models of end groups could be proposed, two ones are presented in this paper as follows.

2. Formation of stable anion, fluorine anion, neutral radical and neutral hydrogen atom.

The second possible changes might occur by the high energy electrons penetrated into the polymer.

Collisions of these electrons with molecules might sever the side chains and the main of molecules, when the decelerated electrons might react on the amputated chains to engender anions, neutral radicals and neutral atoms(Fig 5).

The penetrated electrons would be captured in proportion to the intensity of the electron affinity.

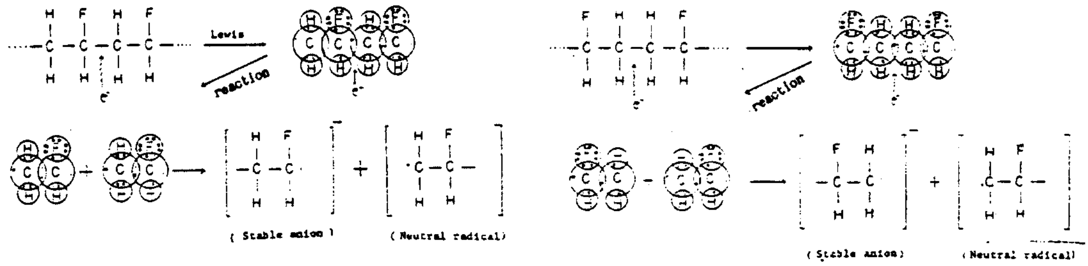
In this case, the reaction should take place farther inside the polymer, for it is what occurs by the penetrated electrons.

The charge release seems to be initiated by motions of the side chains and the main around 40[℃], the second glass-rubber transition temperature, contributing to β peak(Electron affinity on table 2).

3. Trapping of electrons in cavities or defects.

Some slowed electrons would be trapped in cavities(structured defects) within the crystal-

A. Amputation of main chain.



① Type of "head to tail" (or, Type of "Tail to Head")

② Type of "head to tail" (or, Type of "Tail to Head")

Fig. 5. Formation of stable anion, fluorine anion, neutral radical and neutral hydrogen atom.

Table 2. Electron affinity.

H 2.1							He –
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –

line or amorphous regions, or at the crystalline-amorphous interface(Fig 6).

It seems that charge release starts above the glass-rubber transition temperature when the crystalline structure is destroyed.

Meanwhile, K. Schnider et al. and K.Wolf[5] studied dynamic young's modulus of PVF(Fig 7).

β and α dispersions were found about -40[℃] and 40[℃] respectively.

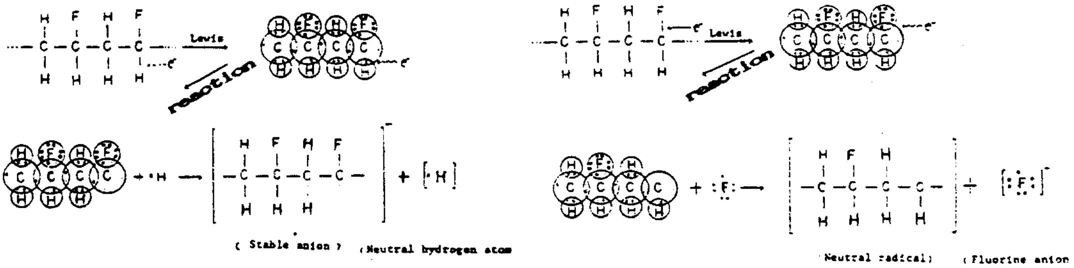
They reported that β dispersion turned up by Micro-Brown Motion of main chains, and α dispersion by molecular chains in the amorphous resions at 40[℃], the second glass-rubber transition temperature.

These two dispersions are in good accord with β and α peaks in TSC spectra.

S. Osaki et al.[3] studied dielectric relaxation of PVF.

Ions are to move because chains. in the crystalline regions, squirm in high temperature.

B. Amputation of side chain.



① Amputation of Hydrogen.

② Amputation of fluorine.

Fig. 6. Possible Trapping of electrons in cavities(or, dielects).

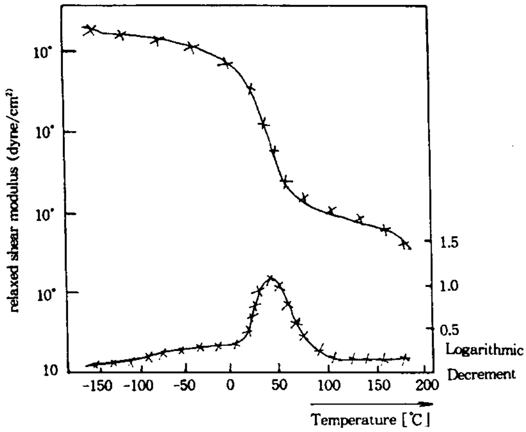


Fig. 7. Temperature dependence of dynamic young's modulus of PVF.

ε'' peak observed at 90[℃] was reported to result from the shifting of ions, which were produced by the impurities in the crystalline regions.

Ions are to move because chains, in the crystalline regions, squirm in high temperature.

ε'' peak is in good agreement with δ peak in TSC specta.

As a general rule, trapped carriers can't be observed by means of dielectric relaxation or dynamic young's modulus study. TSC method, however, makes it possible to discover them.

Taking the fact into consideration, δ peak around 90[℃] seems to show up due to the carriers trapped in the crystalline regions.

4. conclusion.

Three peaks were obtained from the electret formed by applying −3∼−6[kV] to PVF film.

The β, α and δ peaks were observed around −40[℃], 40[℃] and 90[℃], respectively.

To elucidate the origin of these peaks, β peak seems due to carbonyl groups formed on the surface of the specimen.

α peak is believed to result from the detrapping of the penetrated electrons, which were trapped in the side chains and the main.

The penetrated electrons would detrap by virtue of the molecular squirmming around the glass-rubber transition temperature.

δ peak appears by the detrapping of the trapped carriers in defects, which are generally within the crystalline or the amorphous regions, or at the crystalline-amorphous interface.

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