

유전완화와 열자격전류법에 의한 폴리테트라후로루에틸렌의 유전특성 평가

Estimate of Dielectric Characteristics on Polytetrafluoroethylene by
the Dielectric Relaxation and Thermally Stimulated Current Method

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요 약

폴리테트라후로루에틸렌의 유전특성을 규명하기 위해 두께 100[μm]를 시료로 선택하여 온도범위 30~150[$^{\circ}\text{C}$], 주파수범위 30~ 3×10^5 [Hz]에서 유전특성과 열자격전류를 측정하였다.

유전정점은 유리전이온도 부근에서 긴 체인의 마이크로 브라운 운동에 의한 손실로 이때 활성화 에너지는 15.18[kcal/mole]를 얻었으며, 열자격전류방법에서 얻은 β 피크의 활성화에너지와 거의 일치함을 확인하였다. 또한 열자격전류방법으로 계산된 유전정점의 크기도 유전특성의 초저주파에서 나타나는 값과 잘 일치됨을 확인하였다.

ABSTRACT

In this study, dielectric properties and Thermally Stimulated Current were measured in Polytetrafluoroethylene, thickness of 100[μm], the temperature range from 30 [$^{\circ}\text{C}$] to 150[$^{\circ}\text{C}$] and frequency range 30~ 3×10^5 [Hz] for searching the dielectric characteristics.

As a result, activation energy at 15.18 [kcal/mole] by micro Brownian motion's loss of long chain is obtained of glass transition temperature. It is almost confirmed that activation energy of β peak obtained at thermally stimulated current method.

Also it is affirmed that the amplitude of dielectric loss factor calculated by thermally stimulated current method, concurred with the value appeared in infrasonic region of dielectric characteristics.

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1. Introduction

The recent advances in petrochemical industries as well as organic chemical engineering paved a way for polymeric materials to replace dielectric and other materials used in electric components. Such usages of polymeric materials have expanded into diverse purposes such as composing materials for electric conductors, insulators, semiconductors and other-functional components.^{1~3)} Such circumstances necessitates more research activities devoted on analysing electrical properties of polymeric materials and, consequently, developing new polymeric materials with superior electrical properties⁴⁾.

Recently, the ever increasing demand for electricity also accompanies the increasing demand for high voltage and large capacity of electric power machinery, equipments as well as high density integrated electric components, and to cope with such technological demand for better and reliable electric materials, many formidable technological problems should be resolved. Especially, the molecular structures of polymers are complex, so it is difficult to accurately predict their material properties by analytical means. Furthermore, the method of analysis should vary according to the application field.^{3,5)}

In this study, the material properties specifically dielectric properties, of Polytetrafluoroethylene which is known to exhibit superior dielectric characteristics among Polytetrafluoroethylene (PTFE) is experimentally analysed. Specifically a combination of two experimental methods are used : One is the thermally stimulated current(TSC) method which facilitates the measurement of the dielectric properties during prolonged relaxation period and the other is the dielectric relaxation method to directly measure the time and chronological of dielectric dispersion and absorption. Finally the material properties founded in this study is compared with other reported results and its validity is discussed in detail^{1,6,7)}.

2. Experiments

2.1 Sample Preparation

The sample in this study is PTFE of thermo plastic resin, melting point (known) is 327[°C] in general. It becomes gel type above the range of melting point, but not liquidity.

The value of dielectric constant and loss is similar to low density polyethylene or less than that, these properties shows that there is close relation of chemical structure and molecular weight of PTFE. It is monomer structure of PTFE as —
[CF 2 —

CF_2], since it has not chain and high crystal degree.

The specific gravity of PTFE powder, which is not pass through disposition process, obtained at common polymerization is 2.28—2.295, it is applicable to the degree of crystallinity of 93—98[%].

In this study, it was used as a sample of PTFE film, thickness of 100[μm], main electrode of 38 [mm] and guardring electrode, having inner and outer diameter 40 [mm] and 80[mm], respectively. And then surface was attached using pure vaseline. As it is mentioned above, PTFE is a good insulator, and exhibits excellent chemical resistance and incohesive properties as well as good mechanical manufacturability. The material is bonded with strong C-F bonding whose bonding strength is 114.76[kcal/mole]. Also, since it's molecules compact structured in such a way that the F molecules are compactly fills the spaces around the C-C bonding (79—79.8[kcal/mole]), it exhibits strong anti-permeation characteristics.

(1) X-Ray Diffraction

For the first time Bunn reported on the structure and specific gravity of PTFE to analysis with X-Ray diffraction test, after that many workers have studied their atom arrangement and model of element, and so on. According to results

of the study by Bunn, the molecule chain of PTFE takes a coiled shapes titled from planar zizag shape, and the volume of fluoride molecules are compactly arranged around C-C bonds. Also according to Machio Iwasaki's report⁸⁾, the crystal structure of PTFE takes tetrahedral structure at the rang of temperature below 19[$^{\circ}\text{C}$] where every 13th CF_2 molecule is rotated by 180 $^{\circ}$ to result in coiles shape and such rotation is repeated at every 16.9[\AA].

Besides, it reported on lattice distance of 5.46[\AA] and the around of 2.38[\AA] obtained X-Ray diffraction of PTFE by Krim dispersed at amorphous and the distance of 4.92[\AA] dispersed at crystalline region⁹⁾.

It reported on the contribution of amorphous region and dispersion of crystalline region appeared in $2\theta=16^{\circ}$ and $2\theta=18^{\circ}$ respectively, as shown in Fig2-1. part of the crystal and amorphous region overlapped. Therefore, crystallinity of PTFE can be obtained from area ratio.

$$\% \text{ Crystallinity} = 100I_c / (I_c + KI_a)$$

I_c : crystal region area

I_a : amorphous region area

So measured XRD from used sample shown in Fig. 2-1, dispersion at $2\theta=16.7$, at the same time it confirmed that lattice distance had appeared in dispersion of crystalline, it's numerical value was 4.

834[Å], and it were observed that it were very similar to the results by Krim. Also in this figure obtained crystallinity which applied area of 3.15[cm²] calculated by Planimeter with Ia and Ic using equation (1) was about 81[%].

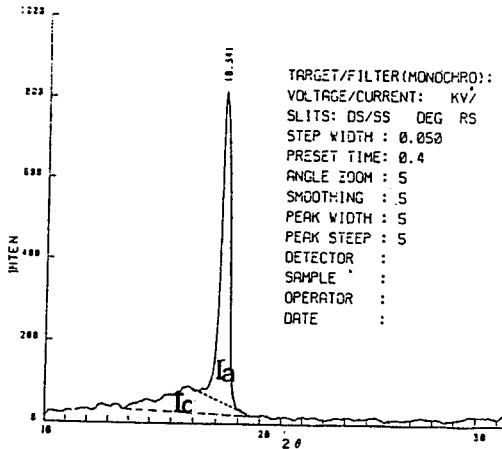


Fig. 2-1 X-Ray Diffraction of PTFE

2.2 Experimental Devices

Dielectric loss test equipment used in this experiment was Ando Electric (Japan) Products, it consists of an oscillator WBG-9 (30-3×10⁶[Hz]), balance detector BDA-9, dielectric loss detector TR-10C(Tan δ: 1×10⁻¹~1×10⁻⁵), oven TO-9B(-70~200[°C]).

3. Results and Discussion

Fig. 3-1 shows the dielectric characteristics obtained with varying temperature range of 30~150[°C] in 100 [μm] thickness of PTFE.

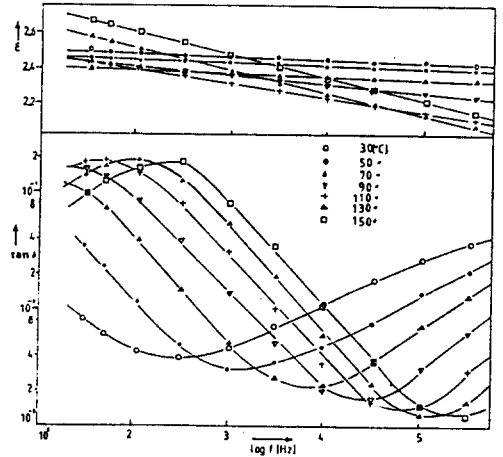


Fig. 3-1 Frequency characteristics with varying temperature

Dielectric ratio divided three division in measurement area, it is not appeared dispersion in low and high frequency region under the temperature range of 70[°C], the amplitude of dielectric ratio was about 2.45 among the temperature range from 70 to 110[°C]. But among the temperature, it took dielectric distribution because of dielectric ratio of 2.2~2.45, the more increased division of dielectric distribution above 110 [°C], the more changed almost straight line with 2.2~2.65. And dielectric absorption appeared low frequency range than measured frequency range under the temperature of 90[°C], in the measured frequency range it observed dielectric loss curve over the measured temperature of 110[°C], the amplitude of loss curve of 10⁻¹~10⁻⁴ had very large absorption width. When

maximum loss energy was 30, 50 and 110[Hz], dielectric absorption appeared at 100, 110 and 125[°C] respectively, also if measurement frequency raised above 1[kHz], maximum temperature of dielectric absorption appeared at high temperature region.

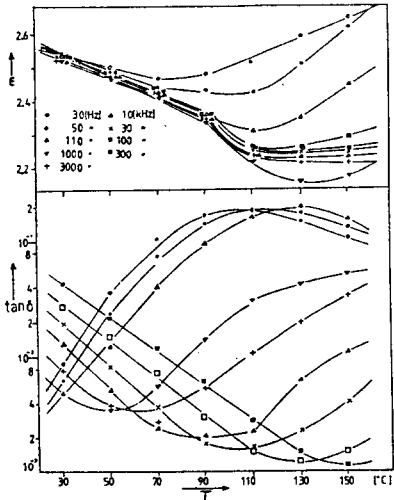


Fig. 3-2 Temperature characteristics with varying frequency

Fig. 3-3 shows TSC curves which obtained with the forming temperature of PTFE film 120[°C] and the temperature increment 5[°C/min] between the applied voltage 200 to 2000[V], during the observation time 1200[sec]. The similar TSC spectra were obtained in the reported experiments.

There were 4 peaks, already reported. Only β peaks between the temperature range of 0 to 150[°C] were shown to investigate the correlation with the dielectric characteristics, and the maximum

temperature(T_m) of the peaks was uniform in accordance with the forming field.

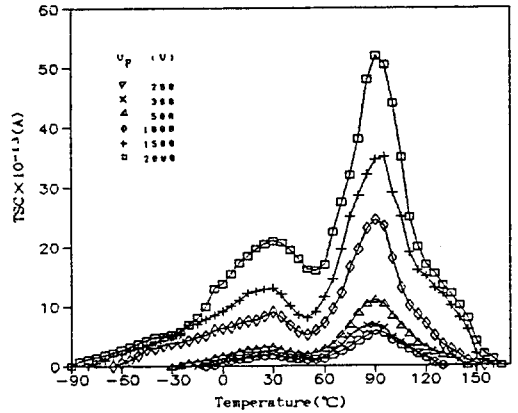


Fig. 3-3 TSC spectra vs. forming field

PTFE is usually known as non-polarized polymer. But Berry and Bro reported that PTFE has been polar groups at the tip when using acidity sulfite as initiator include SO₃H or using persulfate as initiator include COOH, and many researchers (Muller, etc) have studied and reported the dielectric dispersion⁹.

The algebraic reduction ratio of distortion vibration observed from the dielectric relaxation phenomena and TSC characteristics in the experiment was applicable to the α peak reported by McCrum. Fig. 3-1 and 3-2 show that few dielectric dispersion arises under 90[°C] and very large dispersion arise above 110[°C] within the measurement frequency range. On the other hand, when density (D) is acquired by various methods dielectric ratio can be obtained from the equation, $\epsilon = (1 + 0.238D)/(1 - 0.119D)$,

with D : density.

Obtained dielectric ratio using this equation to the measured value. And within the measuring temperature range 110–150[°C] and the frequency 10 [Hz]. Many researchers have reported that there exists changing point near 130[°C] in the case of measurement of linear expansion, and because the bending point of specific volumetric change is high at the side of the low degree of crystallinity.

It is known that this transition occurs in amorphous region.

In the study on biscoelastic or dielectric characteristics by Iller, Eby, McCrum, Becker, Machio, Iwasaki, Krum, Etc, it was reported that there existed the dispersion near 130[°C], but McCrum reported that this transition was principally caused by comparatively long CF₂ chains¹⁰⁾.

Because this phenomenon is the microscopic loss by long chains at high temperature, it is observed that dielectric absorption arised in the infrasonic range (10⁻²~10²[Hz]). And if the frequency, at which tan δ has maximum value, is f_m, f_m moves to the side of high temperature low frequency depending on the measuring temperature.

Applying relaxation process of Eyring, when R is gas constant and T is absolute temperature, freuency at which tanδ has

maximum value is $f_m = A \exp(-\Delta H/RT)$

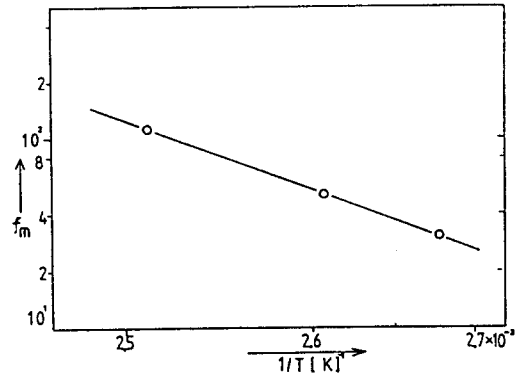


Fig. 3-4. Activation energy of dielectric relaxation

Figure 3-4 illustrates the relation of $\ln f_m$ versus $1/T$ and activation energy by polarized group is calculated 15.18[kcal/mole].

Beside PTFE hold at the end of two carboxyl group or sulfon group per one polymer molecule, in accordance with kind of initiator and because specimen sintered at high temperature have strong possibility of being $-CF=CF_2$ group it is supposed that this group can be contributed to TSC forming polarization.

Typical COOH group shows an strong absorption at wave length of 1811 and 1780[cm⁻¹](5.52 and 5.62[μ]).

It is possible to observe that a large amount of absorption at band of 1780 [cm⁻¹](5.62μ) exists in the IR spectra¹¹⁾.

It is supposed that β₁ peak is generated by polarized group of a COOH radical.

Moreover β₂ peak at low temperature of 30[°C] presents TSC by contributing of electric charge trapped in the high

electric field and depolarization current of ohmic type.

The meaning of the dielectric characteristics of β peak in the TSC spectra is the absorption at infrasonic region in TSC case. So, from the measurement of TSC to obtain the dielectric characteristics through searching activation energy, elevating speed and relaxation time it is easy to measure the value of dielectric dissipation factor in infrasonic region.

Using these values, the amplitude of calculated dielectric loss factor was 4.5×10^{-3} , and it confirmed the value in the infrasonic region as shown in Fig. 3-1.

4. Conclusion

The results show measurement of dielectric characteristics by dielectrics relaxation and TSC method in the PTFE film.

1) Dielectric loss which was appeared in infrasonic contribute long chain by micro Brownian motion in the vicinity of glass transition temperature, at that time we obtained activation energy of 15.18 [kcal/mole].

2) Dielectric loss factor which was calculated by dielectric characteristics and TSC method was 4.5×10^{-3} , and it confirmed the value at infrasonic of dielectric characteristics.

3) Among the physical characteristics of this sample, dielectric constant which was calculated by density method was 2.

15 and the degree of crystallinity was 81 [%].

4) Activation energy of β peak in TSC was similiar to dielectric characteristics.

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