

Effects of Absorbed Benzene on Relaxation Behavior of Polytrifluoroethylene

Yukinobu MURATA

*Osaka Prefectural Technical College, 26-12 Saiwai-cho,
Neyagawa, Osaka 572, Japan*

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ABSTRACT: Relaxation behavior in polytrifluoroethylene (PTrFE) with varied crystallinity and swollen with benzene was investigated by mechanical and dielectric measurements. PTrFE showed the α , β , and β' relaxation in decreasing order of temperature. The β relaxation observed around -20°C at 100 Hz was considered to consist of two components assigned to the amorphous and crystalline regions. The β' relaxation found in a lower temperature region below -50°C was related to molecular motions around the defects of anomalous linkages such as head-to-head and tail-to-tail. In swollen PTrFE, the α relaxation due to the micro-Brownian motions of main chains shifted from 50°C to -10 – 0°C in mechanical measurements. The β relaxation for swollen samples decreased in intensity or vanished. This was interpreted by considering that the component assigned to the amorphous regions did not occur or was concealed by the α relaxation shifted to lower temperature. Relaxation behavior of the component assigned to the crystalline regions was revealed in swollen samples and related to reorientation of chains adjacent to the row vacancy defects at chain end.

KEY WORDS Polytrifluoroethylene / Swelling / Dielectric Relaxation / Overlapped Relaxation / Component / Defects / Chain End / Anomalous Linkage /

In polytrifluoroethylene (PTrFE) two relaxations, designated as α and β in decreasing order of temperature, were found by some authors.¹⁻⁴ The α relaxation was attributed to the micro-Brownian motions of the main chains. The β relaxation shifted to low temperature and increased in magnitude with increasing crystallinity.^{1,2,4} The similar shift to the β relaxation was observed for the γ relaxation of polychlorotrifluoroethylene (PCTFE) and ascribed to overlapping of two components, γ_a and γ_c , in the amorphous and crystalline regions, respectively.⁵ Thus the β relaxation of PTrFE was considered to consist of two components in the amorphous and crystalline regions.^{1,2} It was inferred that the crystalline relaxation was likely related to row vacancy defects at the chain end in crystals as considered in the γ_c relaxation of PCTFE. Yagi

observed the same behavior of the β relaxation in mechanical measurements and ascribed the β relaxation partly to local molecular motions around defects of anomalous linkages of head-to-head and tail-to-tail.⁴ Furukawa *et al.*⁶ studied the dielectric properties of PTrFE and vinylidene fluoride-trifluoroethylene (VDF-TrFE) copolymer with entire range of comonomer content. They ascribed the relaxation found at -20°C and 1 kHz in the copolymers to the rotational molecular motions of the all *trans* segments to *gauche* in the amorphous regions similar to those of the ferroelectric relaxation in crystalline regions. In contrast to this assignment, it was considered in the mechanical study¹ that the relaxation for copolymers with 48 to 71 mol% TrFE was related to the micro-Brownian motions of VDF rich sequences and that the

relaxation for copolymer with 87 mol% TrFE was connected with the local molecular motions in the amorphous and crystalline regions similar to those of the β relaxation in PTrFE.

Further investigation of the relaxation mechanism for PTrFE should contribute to revealing the relaxation mechanisms of VDF-TrFE copolymers with high TrFE content and ferroelectric properties of the copolymers which have been studied by the present author.^{7,8} This work was undertaken to find additional evidence for the assignment of the α relaxation to the micro-Brownian motions, to resolve the β relaxation into two components, and to clarify the relaxation mechanisms of these components. For these purposes, mechanical and dielectric properties were examined for PTrFE with varied crystallinity and swollen with benzene.

EXPERIMENTAL

PTrFE powder supplied by Daikin Kogyo Co., Ltd. was heat-pressed into films at 250°C. To obtain the films with different crystallinity, two cooling conditions were used: quenching a specimen in cold water and cooling slowly from 250 to 50°C. The sample with the highest crystallinity was prepared by annealing the slowly cooled specimen at 180°C for 22 h. The crystallinity estimated by the X-ray diffraction method¹ and the density obtained by the floating method are listed for samples prepared under different conditions in Table I. These samples were immersed in benzene for two weeks and the uptake of benzene was 3.5, 2.1, and 1.0 wt% for samples 1, 2, and 3 with different degrees of crystallinity, respectively. The samples with and without benzene are designated as "wet" and "dry", respectively. Dielectric measurements were made by an Ando-Denki Model TR-1C transformer bridge and an operational amplifier bridge using a three terminal electrode in a temperature range from -140 to 25°C and over a

Table I. List of samples

Sample No.	Crystallinity	Density
	%	10 ³ kg m ⁻³
1	26	1.967
2	42	1.998
3	52	2.021

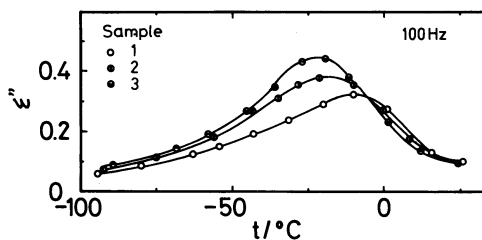


Figure 1. Temperature dependence of dielectric loss ϵ'' at 100 Hz in the β relaxation for dry samples 1, 2, and 3.

frequency range from 1 Hz to 1 MHz. Mechanical measurements were performed by Toyo Baldwin Model DDV-II-C Rheovibron at a frequency of 3.5 Hz in a temperature range from -100 to 90°C. The weight loss of wet samples in measurements of mechanical and dielectric properties was negligible.

RESULTS AND DISCUSSION

The temperature dependence of dielectric loss ϵ'' at 100 Hz in the β relaxation is shown for samples 1 to 3 with different degrees of crystallinity in Figure 1. The β loss peak shifts to low temperature side and increases in magnitude with increasing degree of crystallinity as observed by mechanical measurements in the previous studies.^{1,2} The details of the β relaxation are shown as a contour diagram of ϵ'' for sample 3 in Figure 2 where the β relaxation is seen as a mountain ridge. The maximum loss frequency (relaxation frequency) f_M in frequency dispersion is shown by a dotted line and maximum loss temperature T_M in temperature dispersion is by a dotted dashed line. As seen clearly in Figure 2, another relaxation, designated as β' , is found in

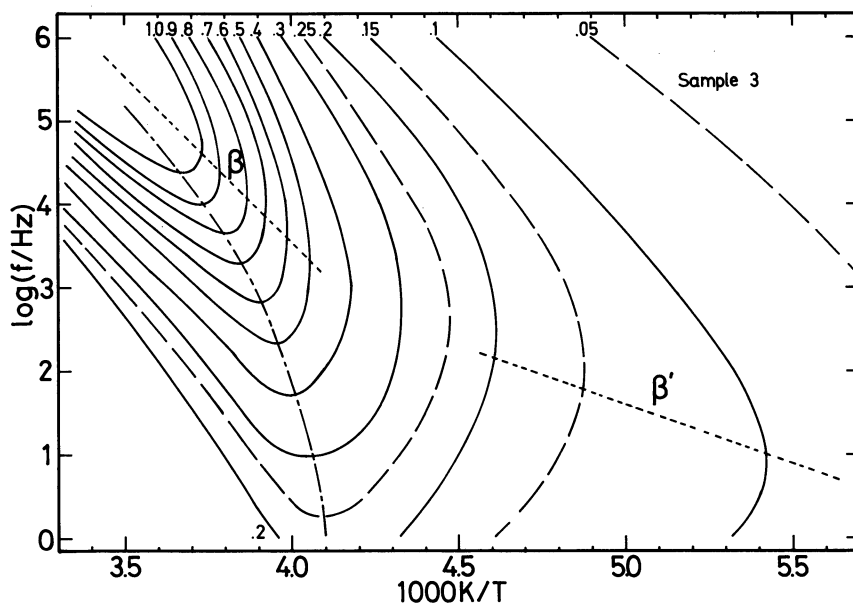


Figure 2. Contour diagram of ϵ'' in the β relaxation for dry sample 3.

the low temperature region. The β and β' relaxations take place mainly in temperature ranges above -35°C ($=4.2 \times 10^{-3}\text{K}^{-1}$) and below -50°C ($=4.48 \times 10^{-3}\text{K}^{-1}$), respectively. The activation energy for the β and β' relaxations was 70 and 32 kJ mol^{-1} , respectively. The β' relaxation does not appear in the temperature dispersion of ϵ'' so that it was not found by dielectric and mechanical measurements in the previous studies.^{1,2}

The frequency dependence of ϵ' and ϵ'' was fitted by the Cole-Cole equation by which the relaxation strength $\Delta\epsilon$ was obtained for dry samples. The value of $\Delta\epsilon$ was examined also from the ϵ'' vs. frequency curve by use of the empirical formula⁹ for evaluating $\Delta\epsilon$. The accuracy in value of $\Delta\epsilon$ was thus confirmed using two methods. Figure 3 shows plots of $\Delta\epsilon$ as a function of the crystallinity X_c at various temperatures. These values increased with increasing crystallinity in a temperature range of the β relaxation above -40°C . Thus it is apparent that the β relaxation is related to the crystalline regions. However, the temperature of the β loss peak shifted to low temperature

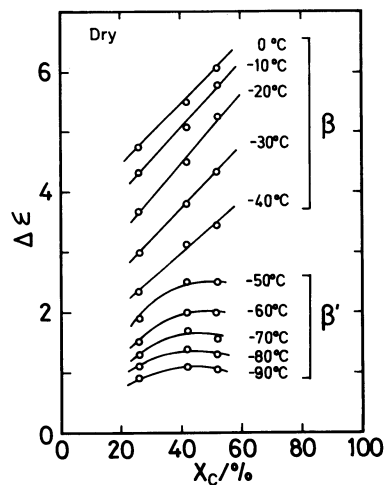


Figure 3. Dependence $\Delta\epsilon$ (overall) on crystallinity at various temperatures for dry samples 1, 2, and 3.

with increasing crystallinity as seen in Figure 1. The peak shift similar to that of the β relaxation was observed for the γ relaxation in PCTFE which was attributed to overlapping of two components.⁵ Therefore it was considered that the β relaxation is attributable to the two components due to amorphous and

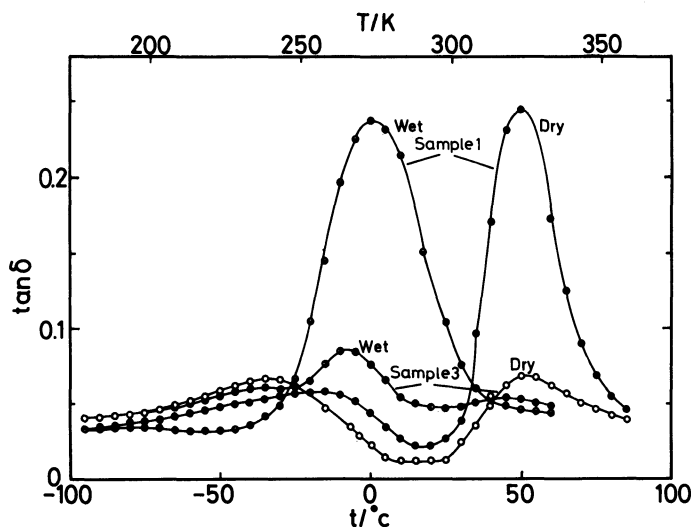


Figure 4. Temperature dependence of mechanical loss tangent $\tan \delta$ for dry and wet samples 1 and 3.

crystalline regions. In a temperature range of the β' relaxation below -50°C , the values of $\Delta\epsilon$ showed the maximum at 42% of crystallinity. The increase in $\Delta\epsilon$ with increase of crystallinity from 26 to 42% indicates that the β' relaxation is related to crystalline regions although $\Delta\epsilon$ decreases at higher crystallinity.

Figure 4 shows mechanical loss tangent $\tan \delta$ as a function of temperature for dry and wet samples 1 and 3. For dry samples, two relaxations α and β were observed at 50°C and about -25°C . The α relaxation shifted to lower temperature for wet samples. This supports the conclusion in the previous study² that the α relaxation is due to the micro-Brownian motions of the main chains, because the absorbed benzene plasticizes PTrFE and lowers the glass transition. In the dielectric study,² the α loss peak was very weak in magnitude and concealed by dc conductance due to ionic impurity so that the details of the α -relaxation were not made clear.

Effects of the absorbed benzene on the β relaxation were investigated by dielectric measurements. The temperature dependence of ϵ'' for wet and dry samples 1 and 3 is shown

in Figure 5. In wet sample 1, no loss peak takes place at -10°C but a dull peak appears at -50°C . Since benzene would enter the amorphous regions, the component β_a assigned to the amorphous regions of the β relaxation was affected by the absorption of benzene. In poly(vinyl chloride), by adding a small amount of plasticizer such as tricresyl phosphate, butylbenzyl phthalate or dioctyl phthalate, the local mode relaxation in the amorphous regions below glass transition was depressed or disappeared and an increase in the elastic modulus was also observed at lower temperature below glass transition.^{10,11} These effects of plasticizers were termed "antiplasticization".¹² For polyamide and polyurethane, the local mode relaxation was affected by absorbed water and a new local mode relaxation took place at higher temperature.¹⁰ Additives that entered interchain regions may depress the local mode molecular motions or shift the temperature for these motions to higher temperature. In PTrFE the α relaxation shifted to low temperature by plastization so that it presumably concealed the local mode relaxation. The variation of f_M with the reciprocal of temperature T^{-1} is shown for wet samples 1 and 3 in

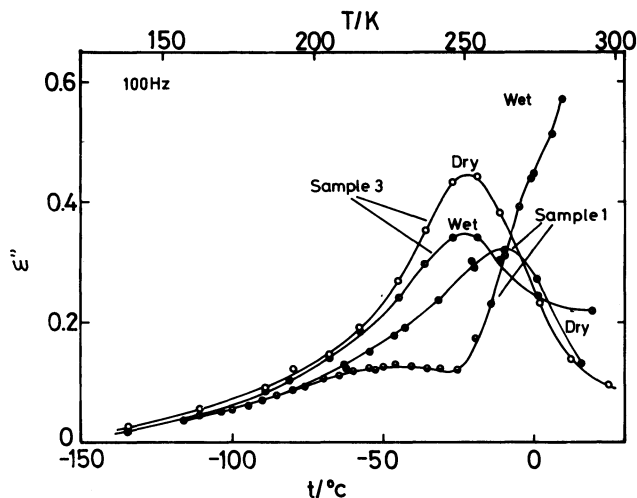


Figure 5. Temperature dependence of ϵ'' for dry and wet samples 1 and 3.

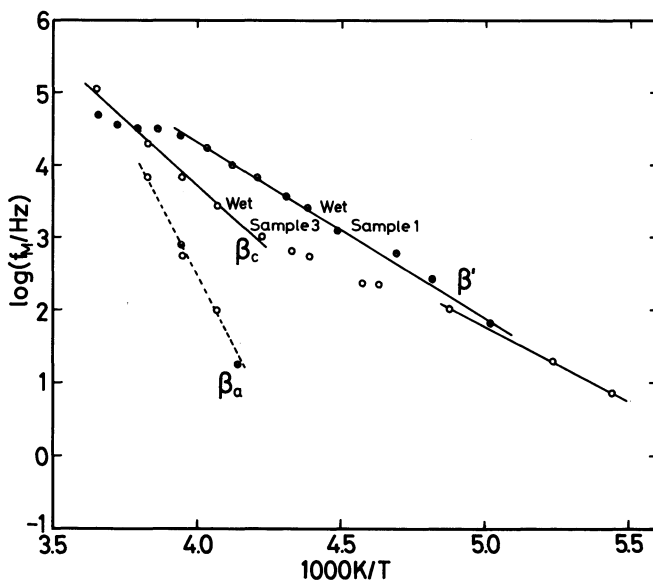


Figure 6. Plots of relaxation frequency f_M vs. reciprocal of temperature T^{-1} for wet samples 1 and 3 and for the separated β_a relaxation. \ominus , sample 1; \circ , sample 3.

Figure 6. In sample 1, the β_a relaxation disappeared or was concealed by the α relaxation shift to lower temperature and furthermore the β_c relaxation may be small because of low crystallinity. Thus wet sample 1 shows only the β' relaxation with activation energy of 46 kJ mol^{-1} . For wet sample 3, two relaxations in crystalline regions, β_c and β' , are

observed above and below -50°C ($=4.48 \times 10^{-3} \text{ K}^{-1}$) in Figure 6. Activation energies were estimated as 70 and 42 kJ mol^{-1} for the β_c and β' relaxations, respectively. On comparing wet and dry samples, the activation energy of the β' relaxation was slightly higher for wet sample. The overlapping of the β_a and β' relaxations may shift the relaxa-

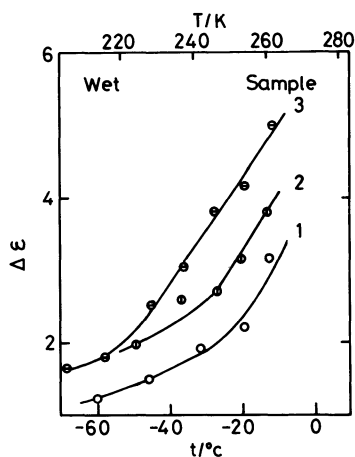


Figure 7. Temperature dependence of $\Delta\epsilon$ (overall) for wet samples 1, 2, and 3.

tion frequency f_M in overall frequency dispersion of the dry sample to lower frequency than that of wet sample. The values of $\Delta\epsilon$ obtained by the Cole-Cole equation for wet samples are plotted against temperature in Figure 7 where a steep rise of $\Delta\epsilon$ takes place at temperatures of -55 to -20°C , depending on crystallinity. The β_c relaxation may take place at temperatures above the break in $\Delta\epsilon$ vs. temperature curves and $\Delta\epsilon$ became large with increasing crystallinity. At lower temperatures for the β' relaxation below the break, $\Delta\epsilon$ gradually changed with temperature. The β' relaxation was complicated in the dependence on the crystallinity, as seen in Figure 3. This feature for the β' relaxation seems to be related to the condition of sample preparation. Yagi observed that anomalous linkages such as head-to-head or tail-to-tail are contained considerably in PTrFE.⁴ These linkages possibly yield defects in crystals, and annealing may decrease the disorder or irregular conformations around this type of defects. The β' relaxation is likely related to this type of defect. Yagi did not find the resolved β' relaxation so that he ascribed the β relaxation partly to local molecular motions around this type of defect in crystals.⁴

As considered in some crystalline polymers,

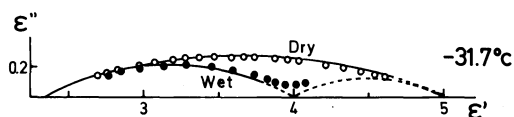


Figure 8. Estimation of $\Delta\epsilon$ for the separated β_a relaxation from dry and wet data. Open circles, dry; filled circles, wet.

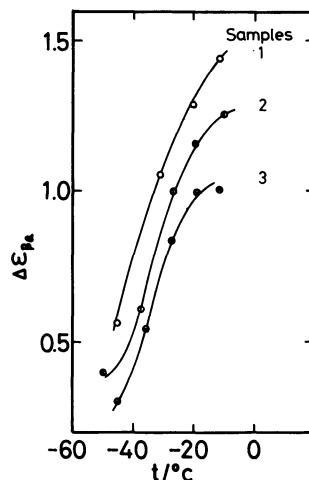


Figure 9. Temperature dependence of $\Delta\epsilon_{\beta_a}$ for the separated β_a relaxation.

row vacancy defects at chain ends are also present in crystals.⁵ The activation energy for the β_c relaxation in PTrFE was similar to those for the chain end defects in crystals of polyethylene and PCTFE.⁵ Thus, the β_c relaxation seems to be related to the row vacancy defects at the chain end. The values of $\Delta\epsilon$ for the β_c relaxation were larger for annealed sample 3 than those for sample 2. The row vacancy defects may grow with increasing lamella thickness in annealing.⁵

The Cole-Cole plots of ϵ' and ϵ'' for the dry and wet sample 1 at -31.7°C are shown in Figure 8. Subtracting $\Delta\epsilon$ for wet sample from that for dry sample, we obtained $\Delta\epsilon$ for the β_a relaxation assigned to the amorphous region. The temperature dependence of $\Delta\epsilon$ for the β_a relaxation is shown for samples 1, 2, and 3 in Figure 9, where values of $\Delta\epsilon_{\beta_a}$ increase with decreasing crystallinity and increasing tem-

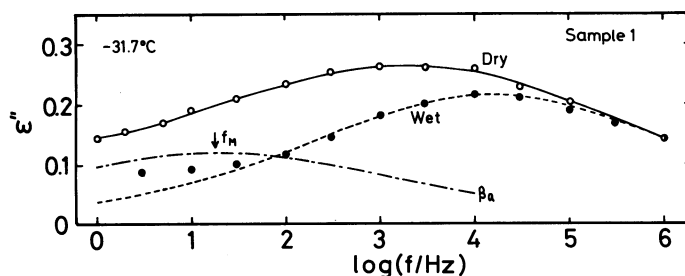


Figure 10. An example of separation of frequency dispersion for the β_a relaxation. Broken line denotes the best fit by the Cole-Cole equation ($\beta=0.31$).

perature. The increase in $\Delta\epsilon$ for the β_a relaxation with temperature was characteristic of the local mode relaxation. The frequency dependence of ϵ'' for the β_a relaxation was obtained by subtracting the values of ϵ'' estimated by the Cole-Cole equation for the wet sample from those for the dry sample, as shown for sample 1 at -31.7°C in Figure 10. Variation of $\log f_M$ with temperature for the β_a relaxation was the Arrhenius type as shown in Figure 6. The activation energy estimated for this relaxation was 147kJ mol^{-1} . This value is about two times larger than that for the local mode relaxation for some polymers¹³ and thus indicates that a fairly large size of molecular chain is involved in the β_a relaxation process. In Figure 2, the variation of T_M with T^{-1} for the overall β relaxation curved similarly to that for WLF type of relaxation. This may be attributable to the overlapping of the β_c and β_a relaxations. PTrFE having a pure head-to-tail sequence was recently synthesized by Cais *et al.*¹⁴ Dielectric measurements on such a sample would make the molecular mechanism of the β' relaxation clearer.

CONCLUSIONS

Three relaxations, α , β , and β' , were observed for PTrFE with various crystallinity and swollen with benzene in decreasing order of temperature. The α relaxation shifted to lower temperature by absorption of benzene and was confirmed to be due to the micro-

Brownian motions of the main chains. The β relaxation consisted of two components, β_a and β_c , attributed to the local mode molecular motions in amorphous regions and molecular motions around the row vacancy defects at the chain end in crystals, respectively. The β' relaxation was found below -50°C and inferred to be due to molecular motion around the defects of anomalous linkages such as head-to-head or tail-to-tail in crystals.

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