

Three-Terminal Dielectric Cell for Solids

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A dielectric cell for measuring dielectric properties of solid high polymers is described. The cell consists of a three-terminal electrode system housed in a jacket with a hermetic structure. Measurements of capacitance and conductance have been made successfully over the frequency range of dc to 300 kHz at temperatures between -195 and 200°C . The resolutions in capacitance and conductance measurements obtained with this cell by the use of a transformer bridge are demonstrated with the dielectric dispersion and absorption in polytetrafluoroethylene at low temperatures. Some discussions are presented about the dielectric relaxation in polytetrafluoroethylene.

INTRODUCTION

Recent developments of transformer ratio-arm bridge made possible accurate measurements of capacitance and conductance over a wide range of frequency.¹⁾ In dielectric measurements of solid specimens, however, the measuring cell is an important part of the experimental setup. In the course of dielectric investigation of molecular motions in high polymers it became necessary to construct a dielectric cell usable over a wide range of temperature. Although some elaborate dielectric cells are described by Work and co-workers,^{2,3)} in the present work a three-terminal cell with a simple structure was designed for use over a wide temperature range of -195 to 200°C . This temperature range covers relaxation regions to be found for most solid high polymers.

This paper describes the structure of the three-terminal electrode system housed in a hermetic jacket which prevents specimens from moisture and heat deterioration. Test results on dielectric properties of polytetrafluoroethylene (PTFE) are shown to demonstrate the precision measurements of dielectric constant and loss of extremely low loss dielectrics by the use of the new cell.

Construction of three-terminal cell

The construction of the electrode system is illustrated in Fig. 1. The guarded electrode A and the guard electrode C are mounted on the fixed Mycalex plate. The unguarded electrode B is mounted on the moveable Mycalex plate which is lightly loaded with springs J. The outer diameter of the guarded electrode is 37 mm and those of the guard electrode and the unguarded electrode are 50 mm. The gap between the guarded and guard electrodes is 1 mm. These electrodes are made of stainless steel. The electrode surface is ground flat to within 0.005 mm. Teflon-insulated shielded leads are used for connection between the elec-

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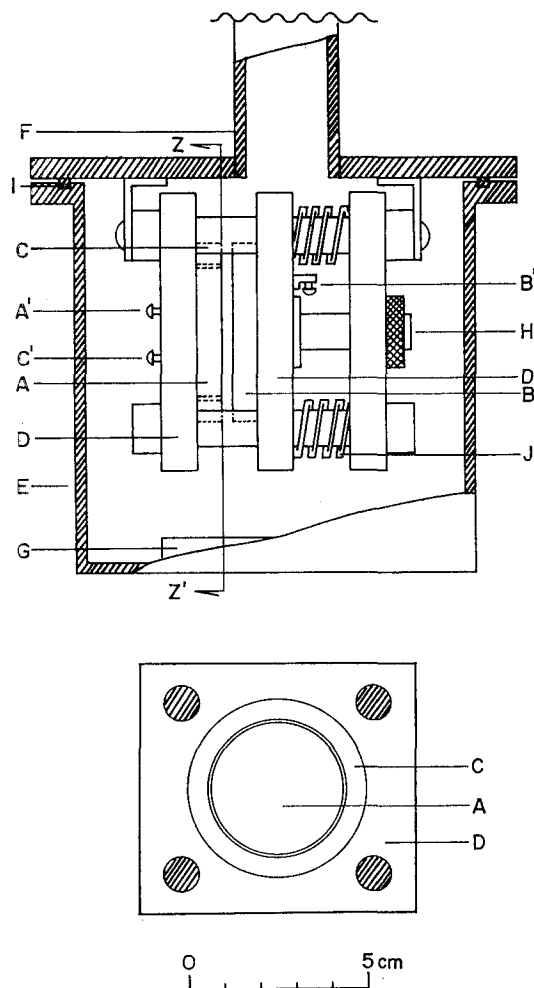


Fig. 1. The construction of three-terminal cell.

A, guarded electrode; B, unguarded electrode; C, guard electrode; A', B', and C' are terminals for respective electrodes; D, Mycalex plate; E, lower part of jacket; F, stainless tubing for housing electrode and thermocouple leads; G, tray for drying agent; H, screw for adjusting electrode separation; I, Teflon gasket; J, spring.

trode terminals A' and B' and modified BNC jacks on top of the jacket. The terminal C' and the jacket wall are grounded. The tip of an Au-Co *vs* copper thermocouple (not shown in Fig. 1) is imbedded in the guard electrode. The Au-Co *vs* copper thermocouple was found very useful at low temperatures for its relatively high thermal emf and for a good linearity of emf with temperature.

The entire arrangement of the cell is shown in Fig. 2. The jacket consists of the upper and the lower parts. The electrode system is housed in the lower part. The upper part is provided with modified BNC jacks for electrode leads, binding posts for thermocouple leads, and inlet and outlet tubings of dry nitrogen. Although the water jacket K was attached to the upper part of jacket, it was

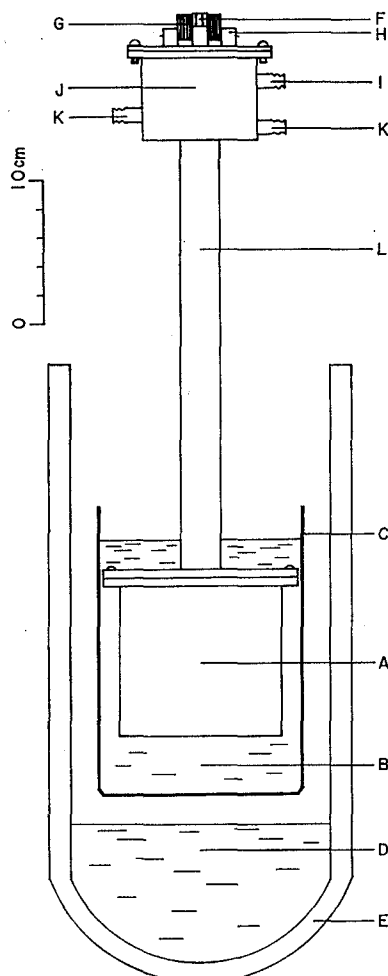


Fig. 2. The arrangement of the cell.

A, lower part of jacket for the electrode system; B, trichloroethylene; C, stainless steel vessel; D, liquid nitrogen; E, Dewar; F, outlet of dry nitrogen; G, binding posts for thermocouple leads; H, BNC jacks for electrode leads; I, inlet of dry nitrogen; J, upper part of jacket; K, inlet and outlet tubings for circulating water.

rarely used because the thermal conductivity of the stainless steel tubing L was low enough to isolate the upper part of jacket thermally in the experimental range of temperature.

In order to keep the specimen from absorption of moisture at low temperature and from heat deterioration at high temperature, the jacket is made a hermetic structure and filled with nitrogen. When a specimen was placed in the cell in actual measurements, the inside of jacket was flashed with nitrogen for a while. Then by closing the nitrogen outlet F, the inside of jacket was pressurized about 10 mm Hg above atmospheric pressure with dry nitrogen fed from a constant pressure nitrogen reservoir. The lower part of the jacket containing the electrode system was immersed in trichloroethylene in the stainless steel vessel C.

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Dry ice was put into the vessel to obtain temperatures between room temperature and -78°C . Further lower temperatures were attained by pouring liquid nitrogen into the Dewar E. Although trichloroethylene freezes below -87°C , the low thermal conductivity of solid trichloroethylene make it easy to control the temperature of the electrode *i.e.* the specimen. There was almost no difference in temperature between the electrode and the jacket well E (Fig. 1) by virtue of the heat conduction of pressurized nitrogen, provided that temperature was varied very slowly. A small electric heater was placed in either the vessel C or the Dewar E. In measurements at higher temperatures than room temperature, the cell was immersed in a thermostatically controlled silicon oil bath, the trichloroethylene vessel C being not used.

No matter how flat the electrode surface is, it may be difficult to make the perfect electrical contact between the electrode and the specimen surfaces, since no perfectly flat surface of a specimen would be realized in many cases of polymer samples as far as the specimens are prepared by molding, casting, or skiving.

Therefore, to ensure the electrical contact between the electrodes and the specimen, metal was evaporated on the particular area to fit the electrode using an appropriate mask. Aluminum was found to be a suitable metal, whereas silver was not always suitable, because silver migrated into the undesired area of the specimen surface by diffusion after evaporation. Aluminum was evaporated three or four times successively on the specimen surfaces to form a metal layer with a high electrical conductivity.

ELECTRICAL MEASUREMENTS

Capacitance and conductance measurements were made over a frequency range of 10 Hz to 300 kHz with a transformer bridge, the Type TR 10 Bridge from Ando Electric Co., Ltd, Tokyo. This bridge was equipped with a guard circuit of the Wagner type to give a higher accuracy in measurements of small capacitance and low conductance. The signal generator was of a conventional type; A high-gain selective amplifier, with a gain of over 110 db, was constructed for the null detector. The accuracy in capacitance measurement was within $\pm 0.01\%$ or ± 0.01 pF, whichever greater, and the lowest limit of dissipation factor to be measured was about 3×10^{-6} between 300 Hz and 100 kHz. Since the new cell was completely shielded and connected to the bridge by coaxial cable, no change in the conductance balance of the bridge was observed when the empty cell with an appropriate electrode separation was connected. The cell also showed a good performance in measurements of the transient current when a dc step voltage was applied.

EXPERIMENTAL RESULTS AND DISCUSSION

In order to test the performance of the new cell, dielectric measurements were made on two samples of polytetrafluoroethylene (PTFE) over the temperature range of -195 to 200°C at frequencies of 10 Hz to 100 kHz. Sample 1 is Polyflon M-12 from Daikin Kogyo Co., Ltd. and Sample 2 is Teflon 7 from E. I.

du Pont de Nemours and Company, Inc. The degrees of crystallinity for samples 1 and 2 determined with the x-ray diffraction were 49 and 52 % respectively. Specimens are skived films of 50 diam. and about 0.2 mm thick. Aluminum was evaporated onto the specimen surface.

The dielectric constant ϵ' and dissipation factor $\tan \delta = \epsilon''/\epsilon'$ for sample 1 are plotted against temperature in Fig. 3 (a) and (b), respectively. The drop in ϵ' near 20°C shows the crystalline transition of PTFE.⁴⁻⁶⁾ The dissipation factor exhibits only one peak (the r relaxation) near -70°C and remains almost constant above 0°C, being $\approx 2 \times 10^{-5}$ at 100 kHz. It has been accepted that the r relaxation is associated with limited movements of short segments of the molecular chains in amorphous regions.⁷⁾ Below -120°C $\tan \delta$ shows higher values than those at room temperature, no peak being observed. Figure 4 illustrates

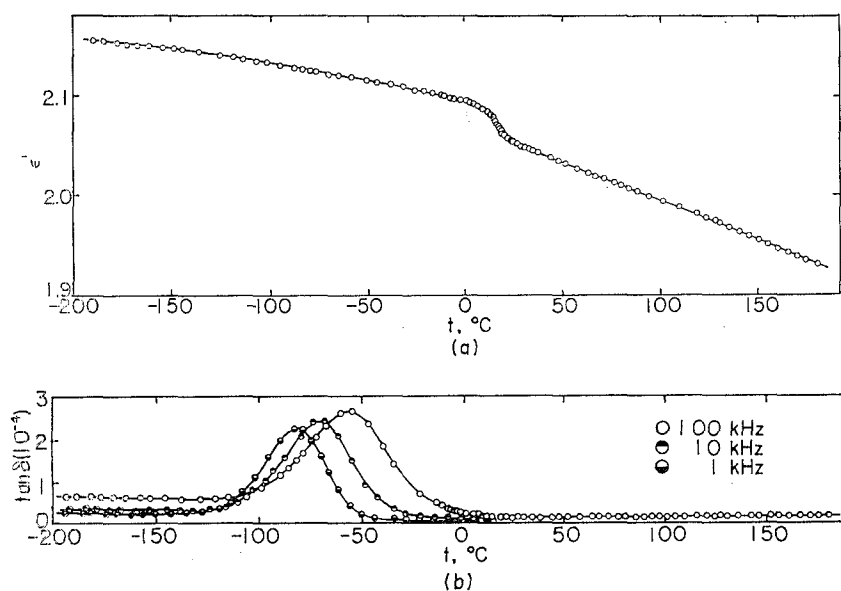


Fig. 3. Dielectric constant ϵ' (a) and dissipation factor $\tan \delta$ (b) vs temperature for PTFE, sample 1, at different frequencies.

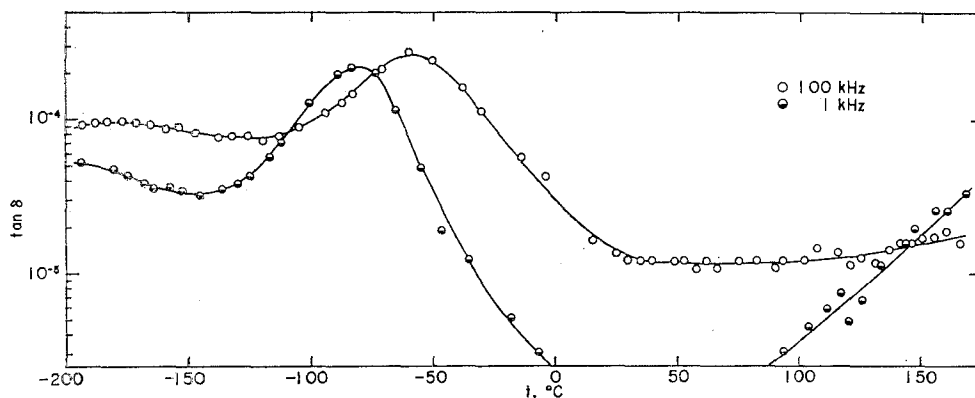


Fig. 4. Logarithmic plots of $\tan \delta$ vs temperature for PTFE, sample 2, at 1 and 100 kHz.

variation of $\log \tan \delta$ vs temperature for sample 2. No significant difference was found in the size of the τ peak between sample 1 in Fig. 3 (b) and sample 2 in Fig. 4. The difference of $\tan \delta$ regarding frequency, however, is clearly seen from the logarithmic plots in Fig. 4. The dissipation factor of sample 2 was too low to be measured between 0 and 85°C at 1 kHz, since the lowest measurable limit of $\tan \delta$ with the bridge used was about 3×10^{-6} .

The gradual increase in $\tan \delta$ at high temperatures would be due to the dc conductance (Fig. 4). Below -120°C $\tan \delta$ for sample 2 was greater than that for sample 1 and increased slightly with decreasing temperature. This indicates the existence of a small and broad peak at a temperature below -200°C . The mechanism of this low temperature loss is likely associated with motions of the end groups of molecular chain, as have been suggested for copolymers of tetrafluoroethylene and hexafluoropropylene,⁸⁾ and thus the magnitude of the loss would be connected with the molecular weight or the degree of polymerization.

The resolutions in capacitance and conductance measurements are demonstrated with the frequency dependence of ϵ' and ϵ'' in the τ relaxation of sample 2 at -78°C in Fig. 5. The precision in measurements of ϵ' was $\pm 0.01\%$. The frequency dependence of ϵ' and ϵ'' in the τ relaxation was well fitted to the Cole-Cole equation⁹⁾ with the distribution parameter α of 0.50. Some deviation of ϵ'' from the calculated curve at high frequencies would be related to the low-temperature loss due to the motions of the end groups. The static dielectric constant and the limiting dielectric constant at high frequency ϵ_∞ in the relaxation were calculated to be 2.1462 and 2.1436 respectively. Thus the magnitude of dielectric dispersion $\Delta\epsilon$ is 0.0026. The effective dipole moment associated with the relaxation was calculated to be 0.03 D from the value of $\Delta\epsilon$ by the use of the

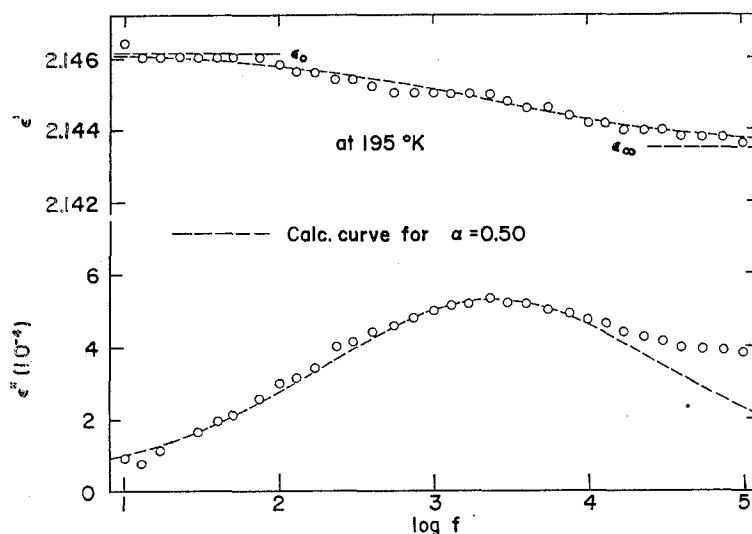


Fig. 5. Frequency dependence of dielectric constant and loss, ϵ' and ϵ'' , in the τ relaxation of PTFE, sample 2, at -78°C .

Broken lines are drawn for the Cole-Cole equation with a distribution parameter α of 0.50.

Onsager-Kirkwood equation.¹⁰⁾ These results show that the performance of the cell is stable and accurate enough to make measurements of the relaxation of extremely low loss dielectrics such as PTFE.

REFERENCES

- (1) R. H. Cole and P. M. Gross Jr., *Rev. Sci. Instr.*, **20**, 252 (1949).
- (2) R. N. Work, *Rev. Sci. Instr.*, **26**, 1171 (1955).
- (3) R. D. McCammon and R. N. Work, *ibid.*, **36**, 1169 (1965).
- (4) P. Ehrlich, *J. Res. Natl. Bur. Stand. (U.S.)*, **51**, 185 (1953).
- (5) S. Saito, H. Tanno, T. Nakajima, and T. Kashimura, *Denki Shikensho Iho*, **22**, 654 (1958).
- (6) N. Koizumi, S. Yano, and F. Tsuji, *J. Polym. Sci., Part C*, **23**, 499 (1968).
- (7) See, *e. g.*, N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids", Wiley, New York, (1967) p. 458.
- (8) N. Koizumi, S. Yano, K. Tsunashima, and F. Tsuji, *Bull. Inst. Chem. Res. Kyoto Univ.*, **46**, 30 (1968).
- (9) K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 314 (1941).
- (10) See, *e. g.* H. Fröhlich, "Theory of Dielectrics", Oxford University Press, (1958) Chapter III.