Anomalous Behavior of the Current from PVA Films in the Glass Transition Region

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Synopsis

Measurements of the current from PVA films prepared by casting solution method were carried out on an isothermal and a non-isothermal processes by changing a previous history of each specimen. The current produced by applying a constant field to an undisturbed specimen exhibits a peak in the glass transition region (75–110°C) on the non-isothermal process. Its peak temperature is about 20°C higher than that of TSC from PVA electrets. There are probably no effects of variation in the crystallinity and removal of the sorbed water upon the growth of such peak. It is suggested that the counteraction of thermal agitation due to the glass transition plays an important role in this anomaly.

1. Introduction

For the commonly used plastic insulating materials, their temperature dependent currents with a direct field may be represented by the Arrhenius type. When experimental data are plotted with logarithm current (log I), against reciprocal absolute temperature (1/T), an almost linear relation will be observed and the apparent activation energy may be calculated from its slope. A change in slope usually appears in the glass transition region of amorphous polymers. In fact an apparent glass transition point Tg may be determined experimentally by the intersection of extrapolated linear portions of log I-1/T plots.

However, nonconformity of the current to the Arrhenius type has been pointed out by a few investigators[1]~[5] for some polymers in a certain temperature region. Furthermore, recent studies of many kinds of polymer electrets[6]~[8] have shown that the thermally stimulated current (TSC) from polarized polymers exhibits several peaks at various temperatures, but their nature and mechanisms are not yet well understood.

On the basis of the experimental results described above, it is interesting to note that a sudden application or removal of field across some kinds of polymer materials seems to cause nonconformity to the Arrhenius type. In fact during our recent studies of polyvinyl alcohol[9], we have found some systems demonstrated very anomalous behavior of the current in its glass transition region (75–110°C). These results have also shown

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that this anomaly strongly depends on a short-term history of the specimen as a function of an applied field.

A first purpose in this paper will be experimentally to reveal the conditions determining whether a current peak occurs or not in log I-1/T curves by changing the previous history of each specimen. Another purpose will be to suggest possible mechanisms dominated the growth of the current peak, where the effects of crystallization, glass transition, and sorbed water will be discussed.

The polymer samples used are films of polyvinyl alcohol (PVA), which were prepared by casting solution method. In most cases the specimen was progressively heated or cooled down at a constant rate during measurements. For comparison a few measurements were made on an isothermal process.

In this paper the anomalous behavior in which the magnitude of current from PVA films occurs a pronounced maximum in a certain temperature region is called "current peak phenomenon", irrespective of the polarity of measured currents.

2.　Preparation of samples

The polymer materials used were powdered polyvinyl alcohol (PVA) which were made by Wako Pure Chemical Industries as ♯ 1500. PVA is known to have the glass transition of 65–85°C[10] and the prominent dipoles of hydroxyl grope. It is said[11] that the usual situation for PVA may be partly amorphous and partly crystalline, and that the crystallinity of PVA films is capable of being controlled in accordance with the temperature of heat-tratment.

The samples were prepared by casting solution method[12] since PVA is solved in water. In order to speed up the rate of evaporation, solvent mixtures such as water-alcohol were used. The procedure was similar to the one already referred to in a previous report[13]. The casting film obtained was subjected to a heat-treatment above 130°C under 10^{-5} torr in order to remove the solvent further. Moreover, this treatment will prevent variation in the crystallinity of samples while measuring below 130°C. The film, after heat-treated, had a thickness of several hundreds of microns.

Then alminum was evaporated on the surfaces of the film to form a three electrode system for current measurements. The collecting electrode was 40 mm in diameter. Finally the specimens to be measured were stored in a desiccator containing Silica gel.

3.　Experimental Method

The setup for measuring current is indicated schematically in Fig. 1, which used a Takeda Riken TR-8651 electrometer and a recorder. In some experiments, the current was detected by deflection method[14] with a Shimazu R-A galvanometer. For no appreciable differences were found in results between the two devices, the resistance of the electrometer and the time constant of the measuring circuit can be neglected. The voltage
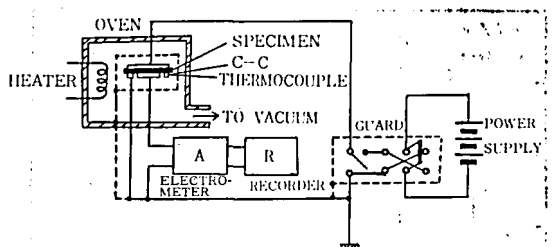
Fig. 1. Diagram of experimental apparatus for
current measurements.

up to 500 volt was furnished across the specimen by a regulated power supply or by many butteries. The specimen-cell was enclosed in a grounded copper screen bath and all leads were of coaxial shielded cables in order to reduce external noise during test.

The temperature of the specimen-cell was controlled by two methods. One will be expressed as progressive method in which the specimen-cell was heated or cooled down continiously at a constant rate of about 1°C/min during test. The other, hereafter expressed as step method, was employed for comparison in which it was held at various temperatures for a certain period before each test. The specimen should be attained an isothermal state in the latter; not yet in the former. The thermometry was made with a copper-constantan thermocuple attached to the guard-ring which was in contact with the specimen. Measuremens were limited to maximum temperature of about 120°C.

In some cases experiments on the effect under vacuum were carried out in a sealed oven which can be evacuated to better than 10^{-5} torr. Since PVA is a hygroscopic polymer in air, this precaution was also taken.

4. Experimental Results

4-1. Effect of Short-Term History

The anomalous behavior of the current looks like very sensitive to a short-term history of the specimen. At first the manifestation of its history used for this investigation such as "off $\nearrow$ on", "on $\nearrow$ off", and "on $\searrow$ on" currents means as follows : The symbols "on" and "off", respectively, indicate a state in the presence and the absence of an applied field. In front of a slanting line with an arrow, "on" and "off" represent previous histories, that is, the specimen has been already disturbed by an applied field prior to each test in the former and not yet, in the latter. In the rear of the slanting line, "on" or "off" represents a voltage condition in measuring currents. The "on" current is produced by the application of voltage in Fig. 1. On the other hand, the "off" current flows back in the short-circuit by the removal of voltage. The upward or the downward arrows, respectively, indicates an increase or a decrease in the temperature of the specimen at a constant rate during measurements.
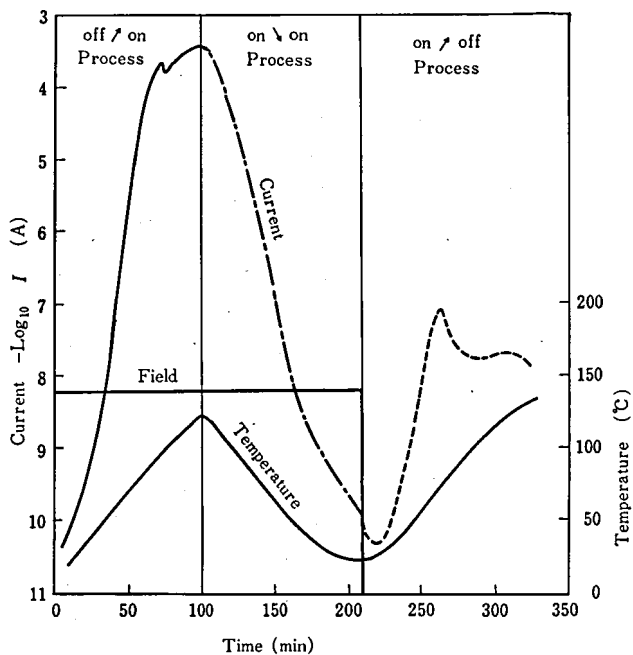
Fig. 2. Illustration of the field-temperature superposition in the progressive method for various histories of the specimen. The applied field was *ca.* 1.88×10^5 v/m in "on" state.
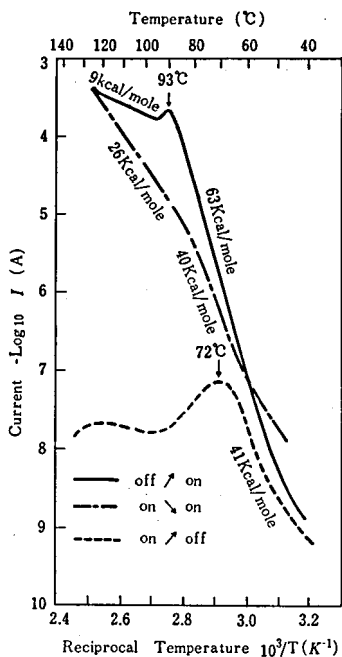

Fig. 3. Temperature dependence of current on previous history. These data were obtained from Fig. 2. The applied field was *ca.* 1.88×10^5 v/m.
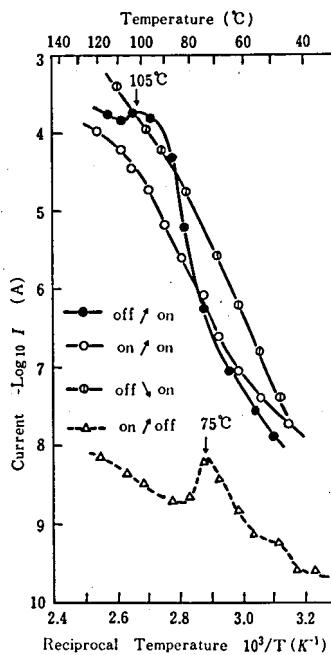
Fig. 4. Temperature dependence of current, measured with galvanometer, on previous history. The applied field was *ca.* 1.06×10^5 v/m.

Some typical experimental results are recorded in Fig. 2, where temperature, field, and log I against time elapsed are shown. In this paper our interest attaches to the absolute magnitudes of measuring currents. In order to express distinctly the anomaly in the current-temperature relationship, the log I in Fig. 2 are plotted against 1/T as seen in Fig. 3. For various types of histories another typical results are shown in Fig. 4. From these and other similar curves certain general observation can be made as follows :

(1) The "off $\nearrow$ on" current with temperature increases first with a steep slope, goes up a peak in the glass transition region, then decreases, and finally increases again with a slow slope. The position of the peak current in temperature is somewhat scattered. The apparent activation energy decreases, as the temperature rises, from 63 to 9 Kcal per mole across the peak position in Fig. 3.

(2) The "on $\nearrow$ off" current also reaches a peak in the region of 75°C. With further increase in temperature a differential peak can be observed near the maximum temperature at which the specimen was charged, and the current eventually drops to zero. This "on $\nearrow$ off" current seems to be referred as TSC from polymer electrets. The details of its behavior will be described later.

(3) For the "on $\nearrow$ on", "on $\searrow$ on", and "off $\searrow$ on" currents, their log I-1/T curves could be represented by the Arrhenius expression. Each change in slope of their
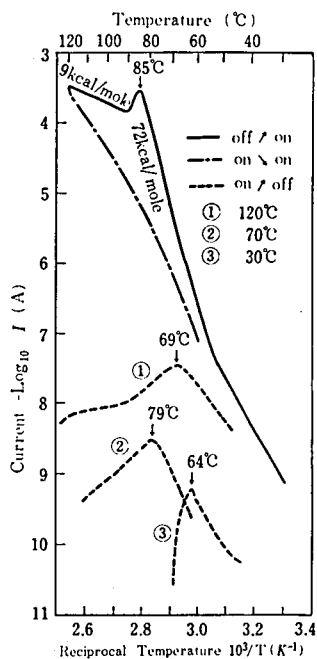

Fig. 5. Effect of removal of sorbed water in 10^{-5} torr. The applied field was ca. 7.69 $\times 10^5$ v/m. Each polarization temperature before measuring "on$\nearrow$off" currents is 120°C above Tg, 70°C near Tg, and 30°C well below Tg.
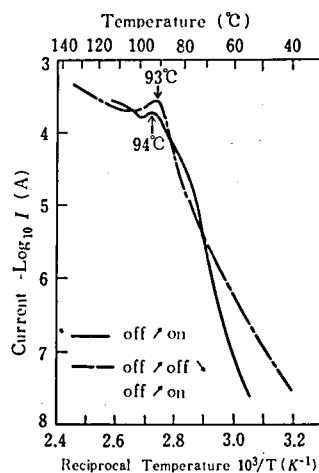
Fig. 6. Effect of heating from outside on the current peak. The applied field was ca. 2.07×10^5 v/m for first run (solid curve) ; ca. 5.85×10^5 v/m, for second run (broken curve.)

curves exhibits in the glass transition region, though it is somewhat affected by each experimental condition.

4-2 Effect of Removal of Sorbed Water

PVA films in air cannot avoid containing sorbed water. Fig. 5 shows the effect of removal of the sorbed water as much as possible under vacuum. After a specimen, as short-circuited, had been subjected to a drying treatment at 120°C under 10^{-5} torr, measurements were carried out in 10^{-5} torr for various types of histories. These results are similar, in qualitative aspects, to those observed in air as shown in Figs. 3, and 4.

Furthermore, Fig. 5 illustrates three types of the "on ↗ off" currents for the same specimen, where their maximum charging temperatures have reached, respectively, at 30°C in the glass state, at 70°C near Tg, and at 120°C in the rubbery state. The three curves reveal each individual peak, the temperature of which depends on their charging conditions and does not always exist in the glass transition region.

4-3 Effect of Heating from Outside

There is a possibility of variation in crystallinity of PVA films due to heating accompanied with the measurements of the "off ↗ on" current. Fig. 6 shows to have tested this effect on the growth of the peak current. Two specimens were prepared under the same conditions. In the first warming up process one was used for the measurements of the "off ↗ on" current, whereas the other was placed with no applied field under the same temperature conditions. In the second warming up process the "off ↗ off ↘ off ↗ on" current in the latter also exhibits a similar peak at almost the same temperature, as compared with the "off ↗ on" current in the former. No effects of heating from outside could be found in the peak current phenomena.

4-4 Anomalous Behavior of the Transient-Charging Current

The temperature dependences of the transient-charging currents, which are referred to as so-called absorption currents were measured by means of step method. After a previously undisturbed specimen, held at 17°C for about 2 hour was suddenly applied to a constant voltage, its transient current was recorded for 60 min in an isothermal state. Then the same procedures were repeated in the diretion of higher temperatures and after a waiting period each charging current was observed for 60 min. Care was taken not to remain a trace of the previously applied field and to establish thermal equilibrium prior to
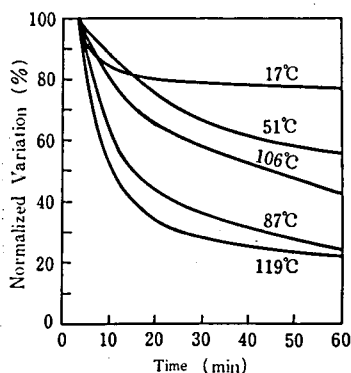
Fig. 7. Normalized variation of so-called absorption currents in 10^{-5} torr, expressed in values relative to each 200 sec curren in the step methed. The applied field was $ca.$ 3.92×10^5 v/m for 17, 87, 106°C; $ca.$ 2.88×10^5 v/m for 51, 119°C.

each test.

Fig. 7 represents a normalized vari-
ation of the transient currents in 10^{-5}
torr, where these data were almost the
same as those observed in air (unpublished
in this paper). The transient current at
higher temperatures is apt to be sensitive to
the duration of charging time, in contradic-
tion to the experimental results obtained
from polyvinyl chloride films[13].

Fig. 8 represents a temperature de-
pendence of such currents in air, where
parameters used are the time elapsed. The
"off ↗ on" current in the progressive
method is illustrated, for comparison, by
broken line. The transient currents also
show the anomalous behavior in the region
of 100°C, the near temperature at which
the anomaly in the "off ↗ on" current
appears. All the transient currents almost

Fig. 8. Temperature dependence of so-
called absorption currents with ca.
2.67×10^4 v/m (solid curves), in order to
compare with the data in the progres-
sive method for the same specimen
(broken curve).

coincide below 80°C, giving the same straight line. With further increase in temperature,
the shape of the peak current is shallower as the charging time goes and the current at
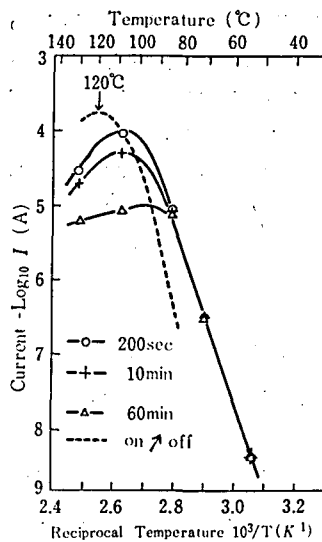200 sec is most similar to the "off ↗ on" current.

5. Discussion

For some polymers a few investigators[1]~[5] have pointed out an anomalous current
with a constant field in a certain temperature region, which they have attributed to
dielectric absorptions[1]~[4] or crystallization[6]. Moreover, from recent studies of some
polymer electrets[6]~[8] TSC exhibits multiple peaks at various temperatures, measurements
of which are becoming a new method for thermal analysis of polymer properties.

In our investigation measurements were almost carried out on the non-isothermal
process unlike their data[1]~[4]. Then the current to consider does not follow the superpo-
sition principle[15], that is, PVA specimens have not a linear dilectric property under our
experimental conditions. Therefore, the anomaly discussed in this paper may not be
immediately correlated to the dielectric behavior, in contradiction to their studies[1]~[4].
The effect of crystallization will be discussed later. Our "on ↗ off" current under some
conditions is considered to be TSC from PVA electrets. The peak in the "off ↗ on"
current flowing from non-isothermal specimens appears to be unique.

5-1 ON ↗ OFF Current

PVA films should be made into electrets by heating above Tg and subsequent cooling as subjected to a high field. The peak of "on $\nearrow$ off" current from PVA electrets occurs in the region of 75°C, which may be considered to be Tg of PVA specimens.

Integration of the "on $\nearrow$ off" current from PVA electret which has been polarized at 119°C as in Fig. 5 yields an effective surface hetero-charge density of about 1.00×10^{-1} coulomb/m². Assumption is made that the dipole alignment is a predominant mechanism involved in the "on $\nearrow$ off" current from PVA does possess prominent dipoles. The dipole concentration may be calculated according to the Debye formation[16] by use of a reasonable moment of 3.6 D[17]. In Fig. 5 it takes values of about 1.4×10^{31}/m³, which appears to be enormously higher than that one might expected. It would indicate that the dipole alignment alone is not sufficient to form PVA electrets.

5-2 OFF $\nearrow$ ON Current

The absorption current in this paper has a broader definition than usual, including the case in non-isothermal state. The "off $\nearrow$ on" current is thought to be mainly made up of such absorption current, which will receive a support from the following experimental results. First there are no peaks in both the "on $\searrow$ on" and "on $\nearrow$ on" currents since a trace of previously applied fields persists in the specimen. Next the shape of the so-called absorption current is more pronounced as the charging time shortens as in Fig. 8. Then no peaks in the "off $\searrow$ on" current may be understood to be attributable to little contribution of the absorption current for the polarization of the specimen has already finished at elevated temperatures.

The growth of the current peak may be, phenomenally, explained in terms of a sudden increase in electric resistivity of the specimen or the presence of some apparent negative current. Variation in the crystallinity and removal of the sorbed water may be possible in the former; structural variation due to the glass transition, in the latter.

(1) *Crystallization* It is said[18] that, due to polymer crystallization, current carriers are reduced in number or in mobility or possibly in both.

Two possibilities to be considered are that heating from inside by passing current through the specimen and from outside may cause an increase in its crystallinity. A density of the specimen was measured by use of benzene and carbon tetrachloride in order to check such increase. The density takes values from 1.28 to 1.29 at 30°C before measurements of the "off $\nearrow$ on" current and after that it shows a slight increase by about 0.05. After all it can be considered that heating from outside and inside do not result in crystallization, in so far as measurements are carried out below the treating temperature. Hence the crystallization does not affect the growth of the peak.

(2) *Sorbed water* As often pointed out[19] even a little water can have an important effect on the conductivity and the removal of one leads to an increase in resistivity. In our case it is probably impossible to remove all of the sorbed water from PVA films. However, the "off $\nearrow$ on" current from the specimen which has been dried out at about

120°C under 10^{-5} torr as much as possible reveals still the peak in vacuum. Therefore sorbed water has possibly no direct effects on the current peak phenomena.

(3) *Morecular reorientation* Finally it is satisfactory to consider that the peak phenomena in the "off ↗ on" and the "on ↗ off" currents, in qualitative aspects, are both due to the same kind of process. This is because the peak temperature of the "off ↗ on" current exists in the region of the glass transition which has been determined by the peak temperature of the "on ↗ off" current from PVA electrets. In the glass transition region it appears that the counteraction of thermal agitation may maintain a disordered state in spite of the presence of an applied field. Consequently an apparent negative current should be induced and the current peak should be grown. (A similar effect has been observed in a material which is known to be capable of acting as a true ferroelectrics[20]. Then for PVA films to possess prominent dipoles of hydroxyl group indicates a possibility of such ferroelectric behabior.) The fact that the reductive rate of the so-called absorption current becomes rapid with time elapsed at temperatures above Tg as seen in Fig. 7 may be successfully explained in terms of this idea.

With further increase in temperature PVA films are transformed into their rubbery state and become thermostable in their structure. As a result the polarization against the randomizing action of the Brownian movement should be produced with the help of an external field. Then in this region the "off ↗ on" current increases again with temperature.

Between the "off ↗ on" and the "on ↗ off" currents, however, there are significant differences over a range of 20°C in each peak temperature. The applied field of the magnitude used in this paper should be expected to have any measurable effect, but the precise answer to this cause cannot be obtained.

5–3 The Rest Currents

No peaks can be found in the "on ↘ on" and "on ↗ on" currents. Because the specimen to be measured contains still a trace of the previously applied field above Tg, the randomizing effect of the temperature is likely to be overcome. No peaks of the "off ↘ on" current have been discussed already.

6. Conclusion

Our experiments in this paper have been designed to reveal some systems demonstrated the current peak phenomena by altering the previous history of PVA specimen. The following results are obtained:

(1) It is found that the peak phenomena on the non-isothermal process are limited to both the "off ↗ on" and "on ↗ off" currents in the glass transition region (75–110°C). The others such as the "on ↗ on", "on ↗ on", and "off ↘ on" currents exhibit the Arrhenius plots. The so-called absorption current from the isothermal specimen also shows a similar peak near 100°C.

(2) For the specimen polarized above Tg, its "on ↗ off" current is probably refer-red as TSC from PVA electrets. The peak of such current presents at about 75°C, which closely corresponds to Tg of PVA specimens.

(3) The "off ↗ on" current may be understood to be mainly made up of the absorption current. Its peak presents at about 20°C higher than the peak temperature of the "on ↗ off" current from PVA electrets.

(4) For the "off ↗ on" current there are probably no effects of variation in the crystallinity and removal of the sorbed water on the growth of the peak. Such peak may be explained by the interaction of two mechanisms; one being the polarization effect depending on the applied field, the other being the randomizing action of thermal agitation due to the glass transition.

The current behavior, depending on the previous history of non-isothermal polymers, seems to provide a new field as to conduction mechanisms of polymer materials.

Further study should be aimed at a better understanding of significant differences between the "on ↗ off" and the "off ↗ on" currents. Furthemore, it remains to be seen in the future whether or not an anomaly may take place when the same techniques used in this paper are applied to other polymers.

Acknowledgement

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