# Superposition of Electrical Properties in Temperature-Sensing Wire Composed of Thermosensitive Polyamide–Phenol Compounds at Various Temperatures and Humidities

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## Synopsis

The relationship between the DC conductance ($G$) and the capacitance ($C$) in temperature-sensing wire composed of thermosensitive polyamide–phenol compounds has been studied. The $G$–$C$ characteristics at various temperatures and humidities are approximately plotted on a same line, and the log $G$–log $C$ plots draw a straight line with time. This implies that when the temperature-sensing wire is in equilibrium under the constant temperature and humidity, if either one of them has been known, the other value is determined from the characteristics. These characteristics will be available properties, e.g., for the temperature and humidity sensing material. These also show that the electrical behaviors due to an absorbed water cannot be distinguished from that due to the amide and phenol groups. This is because that both of them constitute the similar dielectric segments composed of hydrogen bonds, and proton carriers for conduction also generate from them. It also shows that the behaviors of protons from amide, phenol group, and absorbed water cannot be electrically distinguished from one another. It is deduced that the absorbed water mainly contributes to the number of proton carriers and the increase in moisture content contributes more to the DC conductance instead of less than the increase of mobility due to thermal activation of the proton carriers generating from amide, phenol, and absorbed water.

## INTRODUCTION

The electrically thermosensitive properties can be utilized for temperature-sensing devices in electronics. The excellent flexibility and moldability of the thermosensitive polymers make possible the fabrication of flexible thermosensing cable devices useful for temperature detection in wide or flexible areas. The electrically thermosensitive properties, that is, the temperature dependence of admittance, conductance or capacitance is used as temperature signals.[1] As the material which changes capacitance as the temperature signal, polyamide compounds have been studied.[1] The authors have already reported the thermosensitive dielectric properties in polyamide–phenol hybrid compounds, "New Plastic Thermistor," and their application to the temperature-sensing wire in the previous paper.[2] In this paper, it is reported that the superposition properties of electrical characteristics in the polyamide–phenol compounds at various temperatures and humidities draw a master line.

With respect to the superposition properties of polyamide, the time–humidity superposition and the time–temperature superposition have been studied

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on the viscoelastic properties such as the relaxation modulus,[3] the extension,[4] and the compliance curve.[5] These studies show that a master curve is given, e.g., by shifting the viscoelastic curves in the horizontal direction by proper distance. On the other hand, in the dielectric properties, the study of the time–temperature superpositions have been reported for nylon 66[6] and nylon 6.[7] In this paper, it is described below that the superposition of the relationship between the DC conductance and the capacitance at various temperatures and humidities approximately shows a master line, and it is discussed in relation with their hydrogen bond behaviors.

## EXPERIMENTAL

A sensing material: polyamide–phenol compound (Material A in the previous paper[2]) consists of *p*-hydroxybenzoate–formaldehyde condensation oligomer (called phenol compound below) and antioxidants molecularly dispersed in nylon 12 homopolymer. This compound was pelletized after blending each raw material by extruder, and the pellets were applied to thermosensitive dielectric layer in a flexible thermosensing heater (TSH) wire as described in the previous paper.[2] The TSH wire was cut in the length of 20.5 m, and two terminals were attached to both ends of it.

The TSH wire showed ohmic characteristics in the current–voltage plots in a wide range of AC and DC fields. Admittance at 60 Hz and DC conductance were measured under the voltage of 50 V by the potential-fall method. Capacitance was measured at 120 Hz and 1 kHz by a digital LCR meter Type-2581 (Yokogawa Electric Works Ltd.). These electrical properties were measured with time by setting moisture-absorbed wires in an oven of constant temperature. The temperatures were set at 50, 60, 70, 80, 90, 100, and 110°C. The moisture-absorbed wire was prepared in advance by placement for a week in an oven of 45°C, 95% RH.

## RESULTS AND DISCUSSION

**Superposition of Electrical Characteristics at Various Temperatures and Humidities.** The moisture absorption of the polyamide–phenol compounds shows the Fickian type diffusion in which the quantities of absorbed water are proportional to the square root of time as shown in the previous paper.[2] The variations of the admittance ($Y$) and the DC conductance ($G$) due to the moisture desorption under a constant temperature are shown in Figures 1 and 2, respectively, where the moisture-absorbed samples previously prepared in an oven of 45°C, 95% RH for a week were set in an oven of each constant temperature. All plots in the moisture-desorbing states show straight lines in the $\log Y$–$t^{1/2}$ plots or the $\log G$–$t^{1/2}$ plots at various temperatures. The moisture-absorbed TSH wire standing in the oven of 60°C desorbes moisture with time, decreases the values of $G$ and $Y$ thereby, and shows a straight line in the $\log G$–$\log Y$ plots as shown in Figure 3. The $\log G$–$\log Y$ characteristics are, as shown in Figure 4, plotted on the same line in wide temperature range, that is, in various temperatures of 50, 60, 70, 80, 90, 100, and 110°C. The $\log G$–$\log Y$ characteristics are asymptotic with increasing temperature to the straight line of $G = Y$. This is because that the admittance is the value including the DC conductance, and shows that the value of $Y$ is the near value to the $G$ at high temperature region. We have shown the

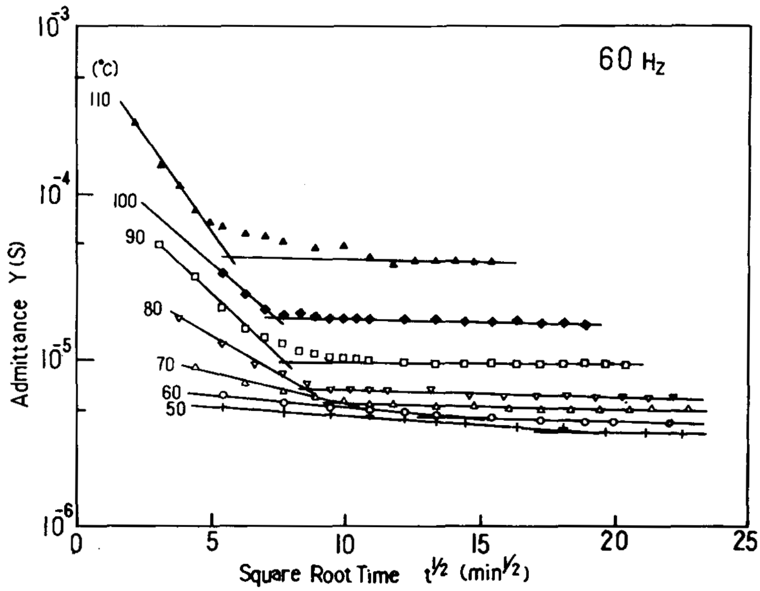


Fig. 1. Dependence of admittance of 60 Hz on the square root time for the moisture-absorbed TSH wire at each temperature.

equivalent circuit of the thermosensitive dielectrics in form of series and parallel connections of capacitance and resistance in the previous paper.[2] The relationship between the capacitance and the DC conductance at various constant temperatures approximately shows a straight line in the whole temperature range of 50–110°C as shown in Figure 5. This shows that the log $G$–log $C$ characteristics at various temperatures and humidities overlap one another. This fact indicates that when the TSH wire has the same capacitance in some states, its conductances approximately show the same value in spite of

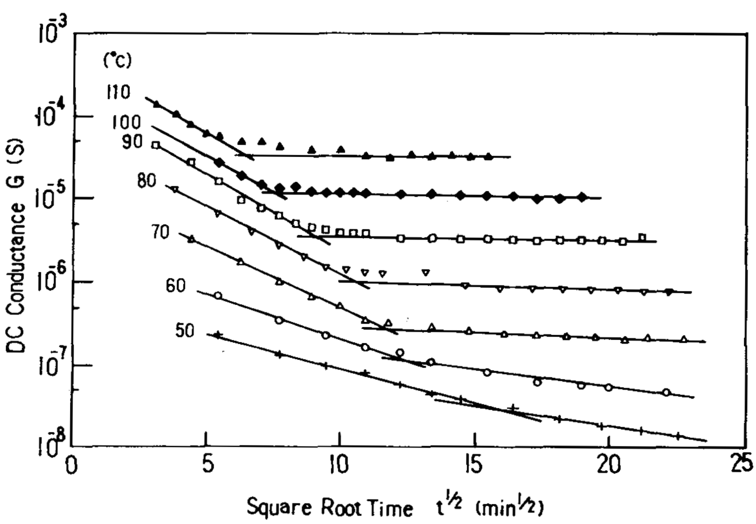


Fig. 2. Dependence of DC conductance on the square root time for the moisture-absorbed TSH wire at each temperature.

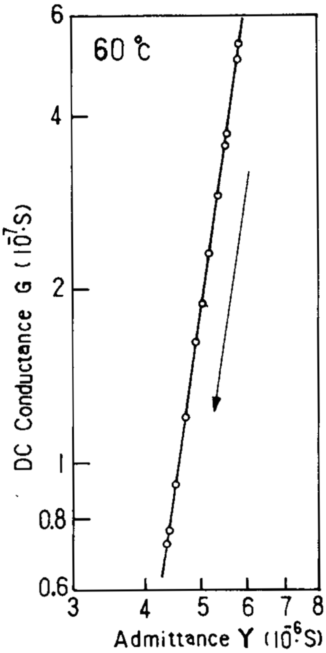


Fig. 3. Relationship between the DC conductance and admittance of 60 Hz for the TSH wire desorbing the moisture with time in the 60°C oven.

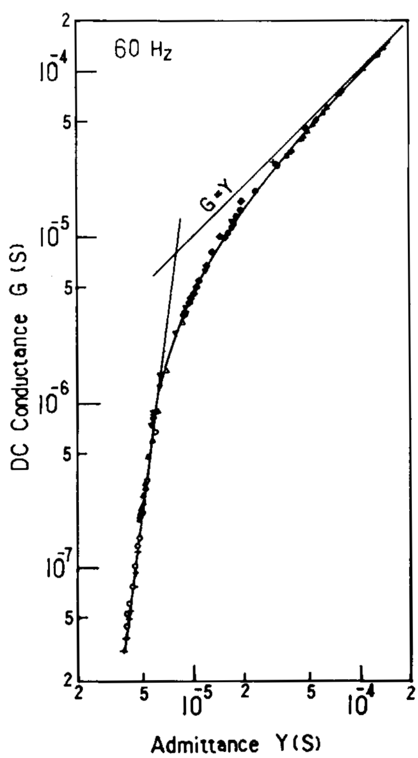


Fig. 4. Relationship between the DC conductance and admittance of 60 Hz for the desorbing TSH wire at various temperatures (°C): (▲) 110; (●) 100; (◆) 90; (▽) 80; (△) 70; (○) 60; (+) 50.

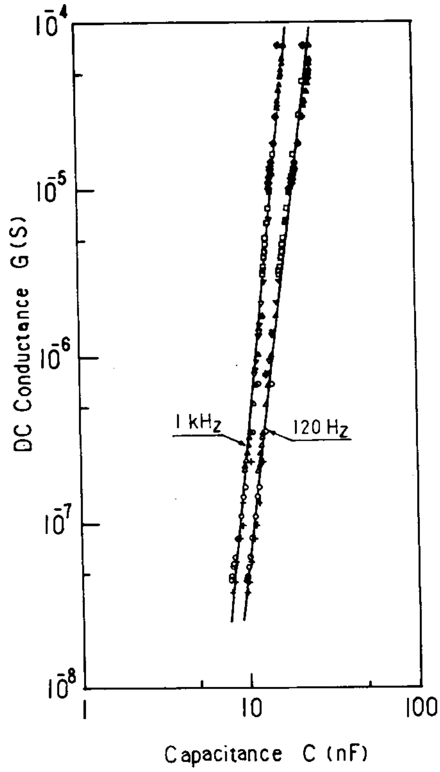


Fig. 5. Relationship between the DC conductance and the capacitance for the desorbing TSH wire at various temperatures (°C): (▲) 110; (◆) 100; (□) 90; (▽) 80; (△) 70; (○) 60; (+) 50.

the temperatures and humidities. This implies that the dielectric constant ($\epsilon$) and DC conductivity ($\sigma$) of the thermosensitive dielectric material are represented by the relation of $\sigma = A \times \epsilon^m$ in spite of the temperature and the humidity ($A$ and $m$ = constants). That is, the increase of $\epsilon$ due to the thermal activation and that due to the moisture absorption cause the same quantities of increase of the conductivities, and these states cannot be distinguished from one another by means of the electrical characteristics.

However, exactly considering the log $G$–log $C$ characteristics, it is found that the characteristics at each temperature are slightly split as shown in Figure 6 plotted by log $G$ vs. log $C^5$. The DC conductance in the case of showing the same value of capitance is slightly high at the higher temperature. That is, it indicates that the increase of capacitance due to increase of temperature gives slightly more increase of the DC conductance than the same quantity of that due to the moisture absorption. In Figure 6, some irregularities of plots at 100 and 110°C will depend on a slight oxidation in the surface of copper electrodes, which is caused by placement in the high temperature oven.

**Mechanism of the Superposed Electrical Characteristics and the Molecular Behaviors.** Electrical properties of the polyamide–phenol compound mainly depend on the hydrogen bond behaviors of amide, phenol, and absorbed water in the material. The results in the previous section show that the relationship between $G$ and $C$ is roughly constant in spite of the tempera-

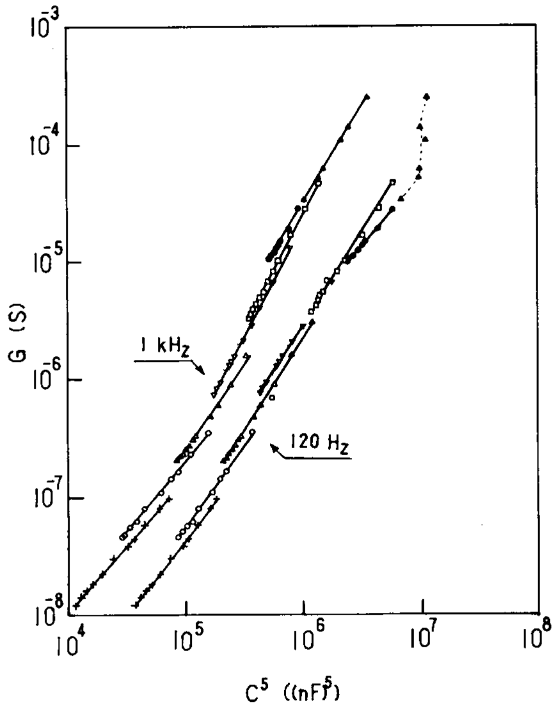


Fig. 6. log $G$–log $C^5$ plots for the desorbing TSH wire at various temperatures (°C): (▲) 110; (●) 100; (□) 90; (▽) 80; (△) 70; (○) 60; (+) 50.

tures and humidities. Generally, the dielectric constant depends on the number and polarizability of the hydrogen-bonded dielectric segments, while the conductivity depends on the number and mobility of carrier. The moisture-absorbed sample includes more protons which exist in the form of the bound or free ion than the dry sample. Therefore, the moisture-absorbed sample should be considered to have more carriers than the dry sample. The dry sample which shows the same conductivity under the higher temperature will be considered to have the higher mobility of protons. In any event, all protons which generate from amide, phenol, and absorbed water function in a similar manner in the electrical properties. The linearity of the log $G$–log $C$ plots was observed also in the nylon 12 homopolymer, which supports that all hydrogen bonds constituted of amide, phenol, and absorbed water behave in the same way under the electric field. The polarizability of hydrogen-bonded segments will be proportional to the degree of dissociation of them which contribute to the conductivity.

These behaviors are understood from the following consideration; the temperature dependence of the DC conductance for dry sample shows a straight line in the log $G$–$1/T$ plots as shown in Figure 7, and the value of the $Y$ curves so as to be asymptotic to them. The value of $Y$ at the low temperature region ($10^3/T > 2.7$) is nearly equal to the value of $\omega C$ and the log $\omega C$–$1/T$ plots also show a straight line, where $\omega$ is the angular frequency. Thus, from Figure 7, it is understood that the log $G$–log $\omega C$ plots show a straight line in the dry sample. From the relation between this fact and Figure

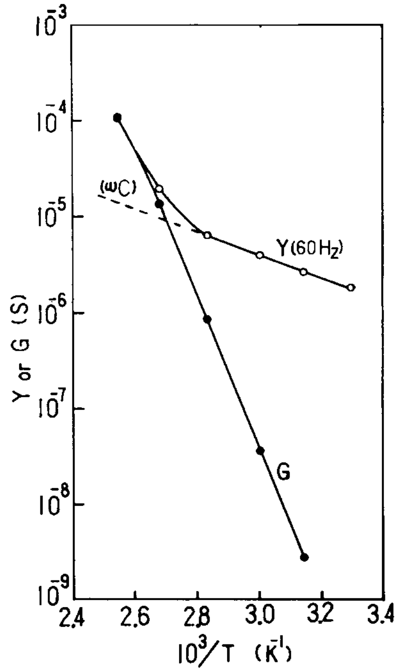


Fig. 7. Temperature dependence of admittance and DC conductance for the dry TSH wire.

5, it is deduced that the log $G$–$1/T$ plots of the moisture-absorbed sample set in a humidity-controlled oven also show the similar linearity. These results show that the polyamide–phenol compounds themselves have approximately a linearity in the relation of log $G$–log $C$, and the moisture-absorbed ones will be also similar to them.

On the other hand, "exactly" considering the log $G$–log $C$ characteristics, as shown in Figure 6, it is observed that the log $G$–log $C$ characteristics at higher temperature slightly shift to the direction of the higher DC conductance. That is, the value of $A$ in the previous equation is slightly high at the higher temperature, and the values of $m$ are nearly equal. This indicates that the increment of the conductance due to the increase of temperature is slightly more than that due to the moisture absorption in the case of the same capacitance. The increase of temperature will generally increase the polarizability and the mobility of carrier, while its moisture absorption will mainly increase the number of carriers due to the dissociation of the absorbed water and also the mobility due to the plasticization effect thereby. The behaviors in Figure 6 show that the influence of the moisture absorption contributes to the capacitance slightly more than the thermal activation due to the increase of temperature in the case of having the same DC conductance. From this result, it is considered that the absorbed water forms more multipoles in the hydrogen-bonded sites, and the protons which generate from the water, although increasing the number and mobility of the carrier, contribute to the DC conductance slightly less than the increase of mobility due to the thermal activation. That is, the proton transport through the hydrogen-bonded network constituted of the amide and the phenol segments contributes to the DC conductance slightly more than that through the network constituted of them and the absorbed water when each shows the same capacitance. The capacitance which reflects the polarizability corresponds to the short-range movement of bound proton, while the DC conductance reflects the long-distance movement of the proton carrier. These molecular behaviors will contribute to the above-mentioned electrical characteristics. Detailed consideration for this mechanism will need to be supported by the detailed investigation in future.

In conclusion, these characteristics described here imply that when the TSH wire is in equilibrium under the constant temperature and humidity, if either one of them has been known, the other value is determined from the characteristics. These characteristics will be available properties for the sensing material shown in the previous paper,[2] and their applications to the another practical use such as, e.g., a temperature and humidity hybrid sensor will also be devised.

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