Thermally stimulated current spectra of binder resin powders for copiers:
Correction for thermal shrinkage of the sample powder compactions

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Abstract. Thermally stimulated current (TSC) spectra observed under open- circuit condition for styrene- acrylic binder resin powder compactions for toners are corrected for their thermal shrinkage during TSC observation. For this binder resin, extrinsic current from motion of powder compactions with charges due to their thermal shrinkage was found to be much more effective than the sensitivity coefficient of a TSC measuring apparatus used. Particle size dependence of charge retention power of the resin powders was also examined by using this correction method and found that it decreased with decreasing their particle size.

1. Introduction

For powders of toner for copiers or paint for electrostatic powder coating, charge retention power of these polymeric powders is one of the most important factors directly controlling their efficiencies. For evaluation of charge retention power of insulating materials, the thermally stimulated current (TSC) method is the most powerful tool. However, only a few papers [1] have been published concerning about TSC spectra of polymeric powder systems such as toners and powder paints. The most serious problem of this method when applied to powder systems is change in their sample thickness during TSC measurement. Therefore, some correction is necessary to obtain intrinsic TSC spectra of powder samples. As for this correction, a trial was previously made for polymeric powders [2]. However, this correction method only predicts that the intrinsic TSC spectrum for a given material appears between two extreme TSC spectra. Recently, we proposed a general method to obtain uniquely the intrinsic TSC spectrum for a given polymeric powder system [3]. This method utilizes a current signal or a voltage signal observed under open- circuit condition.

In this paper, we applied this method to obtain intrinsic TSC spectra $I_{TSC}(T)$ from current signal $I_{obs}(T)$ experimentally observed in open circuit for a styrene- acrylic binder resin for toners and examined particle size dependence of the TSC spectra for the resin powders.

2. Principle of the method

The principle of the correction method [3] is briefly described here. Supposing a surface charge $Q$ for a powder compaction of a thickness $d$, then induced charge $Q_{ind}$ in the upper electrode located $l- d$ above the sample compaction ($l$ is the distance between the upper electrode for TSC measurement and the lower earthed electrode on which the sample compaction is placed), is expressed in the following equation,

$$Q_{ind} = -\gamma Q \quad (1).$$

Here, $\gamma$ is a sensitivity coefficient of our open-circuit TSC measurement apparatus used in this study and expressed as follows using $\epsilon_k$, a relative dielectric constant of the sample compaction.

$$\gamma = \frac{1}{1 + [(l/d) - 1] \epsilon_k} \quad (2).$$

Under a constant heating velocity $\beta$, the intrinsic TSC of the sample compaction at temperature $T$, $I_{TSC}(T)$, and observed TSC signal at $T$, $I_{obs}(T)$, are expressed in the following equations, respectively,

$$I_{TSC}(T) = -\frac{dQ}{dt} = -\beta \frac{dQ}{dT} \quad (3),$$

$$I_{obs}(T) = -\frac{dQ_{ind}}{dt} = -\beta \frac{dQ_{ind}}{dT} \quad (4).$$

Considering $Q(T)$, the residual charge in the sample compaction at $T$, is expressed as follows,
\[
Q(T) = \frac{1}{\beta} \left[ \int_{T_0}^{T_f} I_{TSC}(T) dT - \int_{T_0}^{T_f} I_{TSC}(T) dT \right] 
\]

(5),

where, \(T_0\) and \(T_f\) are the TSC starting temperature and the final temperature where the TSC ceases, respectively, the intrinsic TSC \(I_{TSC}(T)\) can be derived from eqs. (1) - (5) as follows,

\[
I_{TSC}(T) = \frac{I_{obs}(T)}{\gamma} + \left[ \int_{T_0}^{T_f} I_{TSC}(T) dT - \int_{T_0}^{T_f} I_{TSC}(T) dT \right] \frac{d \ln \gamma}{dT} 
\]

(6).

To obtain the intrinsic TSC spectrum \(I_{TSC}(T)\) from the integral equation of eq.(6), we used the iterative approximation method: as the first step, using \(-I_{obs}(T)/\gamma\) as an initial value we substitute it for integrand \(I_{TSC}(T)\) in the right side of eq.(6) and calculate the right side. Then, the calculated result is replaced for \(I_{TSC}(T)\) in the left side of eq.(6) and written as \(I_{TSC}^{(1)}(T)\). Next, this \(I_{TSC}^{(1)}(T)\) is substituted in turn for the integrand in the right side of eq.(6) to obtain \(I_{TSC}^{(2)}(T)\) in the same way as the case of obtaining \(I_{TSC}^{(1)}(T)\). Repeating these processes \(n\) times, the following recurrence relation is obtained,

\[
I_{TSC}^{(n)}(T) = -I_{obs}(T)/\gamma + I_{C}^{(n-1)}(T) \quad (n \geq 1) 
\]

(7),

where,

\[
I_{C}^{(n-1)}(T) = \left[ \int_{T_0}^{T_f} I_{TSC}^{(n-1)}(T) dT - \int_{T_0}^{T_f} I_{TSC}^{(n-1)}(T) dT \right] \frac{d \ln \gamma}{dT} 
\]

(8)

\[
I_{TSC}^{(0)}(T) = -I_{obs}(T)/\gamma 
\]

(9).

By repeating iterative calculation of eq.(7) till it fulfills the following convergence condition,

\[
I_{TSC}^{(n)}(T) \approx I_{TSC}^{(n-1)}(T) 
\]

(10),

the intrinsic TSC spectrum \(I_{TSC}(T)\) can be approximately obtained.

3. Application to a toner binder resin for copiers

3.1. Experimental

We applied this method to powders of a styrene-acrylic binder resin for toners and examined its particle size dependence of charge retention power. For this aim, the resin powders were sieved through multistage screens and classified into three fractions according to their particle size: Sample I (< 38 \(\mu\)m), Sample II (38-75 \(\mu\)m), Sample III (75-180 \(\mu\)m). The sample powders of 120 mg of this resin were put into a shallow pan-shaped Al holder with 1.0 mm in depth and 20 mm in diameter and pressed at 5.4 MPa. This Al sample holder was used also as an earthed electrode for corona-charging and TSC observation. After sample compactions were corona-charged to -500 V, their TSC spectra were observed under open-circuit condition at a heating rate of 3.5 \(^\circ\)C/min from room temperature to about 150 \(^\circ\)C. Thickness of powder compactions \(d(T)\) were also measured with a laser displacement sensor under the same heating condition as that of TSC observation.

![Figure 1](image1.png)  
Figure 1: Temperature dependence of \(d(T)\) for sample powder compactions.

![Figure 2](image2.png)  
Figure 2: Experimentally obtained TSC spectra for sample powder compactions.
Experimentally obtained \( d(T) \) and \( I_{obs}(T) \) are shown in figure 1 and figure 2, respectively. Calculated TSC band areas for \( I_{obs}(T) \), which correspond to the total charge in the sample powder compactions, depended on their particle sizes: The TSC band area of Sample I is smaller by 12 - 13 % than those of Samples II and III. The main cause for this fact is difference in spatial charge distribution in the sample compactions, because charging level of the sample is only controlled by surface voltage of the sample compactions. Therefore, TSC spectra presented hereafter are normalized in such a way that the band areas for the corrected TSC spectra have the same value. As shown in figure 2, peak position of the main band with large intensities shifts to the lower temperature side with decreasing particle size. This fact seems apparently to show that charge retension power of this binder resin drastically decreases with decreasing particle size. On comparison of figure 2 with figure 1, however, temperature ranges of the TSC main bands are found to overlap with those of rapidly decreasing parts of \( d(T) \). Therefore, TSC correction due to thermal shrinkage of sample compactions is expected to be large.

3.2. TSC correction by iterative calculation
To execute iterative calculation of eq.(7), \( \varepsilon_r(T) \) is assumed to be expressed by the following equation,

\[
\varepsilon_r(T) = 1 + (\varepsilon_r - 1)\nu(T)
\]

(11).

Here, \( \varepsilon_r \) is the relative dielectric constant of the base polymer of the sample powders and \( \nu(T) \) is the packing fraction of the sample compaction. For the binder resin used in this study, we suppose that \( \varepsilon_r \) is temperature independent. This supposition of temperature independence of \( \varepsilon_r \) for the binder resin is based on the following consideration: Generally, the dielectric constant for nonpolar polymers is temperature independent because the main factor of their polarization is electronic. However, the actual dielectric constant of nonpolar materials has a tendency to decrease with increasing temperature because of their density decrease due to thermal expansion [4].

While, polar materials are expected to decrease in inverse proportion to the absolute temperature in the temperature region above their glass transition. Contrary to this expectation, the dielectric constant of them can actually increase with temperature because of their temperature dependence of a dipole-dipole interaction or interactions of the dipole with its surrounding molecules. As a result, the mixture of nonpolar and polar polymers with a suitable mixing ratio can be said to even become temperature independent in some temperature range [5].

The temperature dependence of \( \nu(T) \) is directly derived from \( d(T) \) by the following equation because the sample compaction is put in a metal sample holder and its dimensional change due to temperature rise is allowed only in a direction of the sample thickness.

\[
\nu(T) = d^*/d(T)
\]

(12)

Here, \( d^* \) is the thickness of the sample compaction when it melts and has no void in it. For this iterative calculation, we also used the values of 4mm for \( l \) in eq.(2) and 3 for \( \varepsilon_r \) in eq.(11).

The results of iterative calculations of eq.(7) for Sample I are shown with \( I_{obs}(T) \) in figure 3. In this figure, polarity of \( I_{obs}(T) \) is reversed and its intensity is also normalized in such a way that its spectral area has the same value as that of \( I_{TSC}^{(0)}(T) \) for convenience to compare these spectra with each other. As shown in figure 3, difference in graphics of \( I_{TSC}^{(n)}(T) \) can be hardly found for \( n > 3 \). To make sure of the convergence condition of eq.(10), the following values were calculated.

\[
\delta (n, T) = \left| I_{TSC}^{(n-1)}(T) - I_{TSC}^{(n)}(T) \right|/I_{TSC}^{(n)}(T)
\]

(13)

For the case of Sample I shown in figure 3, absolute values of \( \delta (n, T) \) were less than \( 7 \times 10^{-4} \) for \( n = 6 \) in the whole temperature range from room temperature to 150 °C. Therefore, we regarded \( I_{TSC}^{(6)}(T) \) as the convergent intrinsic TSC spectra. Figure 3 also shows that correction due to the second term in the right side of eq.(6) is much more important than that due to the sensitivity coefficient of the TSC measuring apparatus used in this study. The second term in the right side of eq.(6) is a product of the amount of the residual charge in the sample at \( T \) and the derivative of \( \gamma \) with respect to \( T \), that is, to time \( t \). Therefore, this second term is qualitatively considered as charge movement due to change in the sample thickness \( d \) because \( \gamma \) is a function of \( d \). This apparent TSC attributes to fairly large extent to the experimentally observed TSC for the resin used in this study because large charges are still left in the sample at temperatures where the thickness of the sample compaction decreases rapidly.
Previously, we reported that only a small correction was needed for TSC spectra of a powder paint which lost almost all of their charges below the temperature range where \( d(T) \) rapidly decreased \([2, 3]\). This fact shows, as is previously described \([3]\), that the singular behavior observed for the binder resin comes from a bimodal molecular weight distribution with two peaks around \( 3 \times 10^3 \) and \( 3 \times 10^5 \) which is designed for good fixing and anti-offset properties for the resin. In this case, the low molecular weight component brings about thermal shrinkage of the sample compactions at low temperatures despite of the large residual charge in the higher molecular weight component of the resin.

For Samples II and III, we can also recognize \( I^{(6)}_{TSC} (T) \) as the convergent intrinsic TSC spectra for them because their calculated absolute values of \( \delta(6,T) \) are less than \( 7 \times 10^{-5} \). These convergent TSC spectra are shown in figure 4. From figure 4, we can also conclude that charge retention power of the resin powders decreases with decreasing their particle size. During size reduction process of polymer particles, extraction, disentanglement and scission of molecular chains are brought about in the skin parts of these particles. These changes in molecular aggregation state of the particle skin are considered to be a cause for decrease in charge retention power of the resin powders with smaller particle sizes.

4. Conclusions
For open-circuit TSC spectra of polymeric powders, two main spectral correction factors are the sensitivity efficiency of a TSC measuring apparatus used and an apparent TSC due to thermal shrinkage of charged samples during their TSC observation. The latter factor was much more effective for the styrene-acrylic binder resin used in this study because of its bimodal molecular weight distribution. Charge retention power of the resin powders was found to decrease with decreasing their particle size.

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