Improvement of heat resistance of silica-agglomerate electret using electrostatic spraying

Chenye WU*, Kensuke KAGEYAMA* and Tatenobu SAKAI*
* Graduate School of Science and Engineering, Saitama University
Shimo-Okubo 255, Sakura-ku, Saitama-shi, 338-8570 JAPAN
E-mail: wuchenye@yeah.net

Received 26 January 2015

Abstract
The silica-agglomerate electret could be obtained after spraying negatively charged solution of colloidal silica on a fluororesin film using an electrostatic spraying technique. The surface electric potential was measured after spraying to investigate which method was suitable for preparing the electret. As a result, the method in which a spray gun was installed to a conventional corona-charging setup delivered the electret with the amplitude of the electric surface potential over 0.8 kV. The silica agglomerates using an electrostatic spraying technique (ES electret) showed larger diameter $D$ and lower point density $N$ than those using conventional technique (corona-charging after spraying, CC electret). Furthermore, the prepared electrets were heated to examine the improvement of the heat resistivity by the electrostatic spraying. Then, the obtained silica-agglomerate electret showed better heat resistivity than the conventional silica-agglomerate electret. Then, the charge retention at $250^\circ C$ $R_{250}$ of ES electrets prepared in this study was higher than 57 % when the electrets suffered high temperature from 200 to 250 $^\circ C$ for 12.5 min at the heating test. Consequently, it can be concluded that the electrostatic spraying was excellent technique to obtain the silica-agglomerates electret with high heat resistance.

Key words : Electret, Silica agglomerates, Electrostatic spraying, Fluorine resin, Heat resistance

1. Introduction

Electret (Fig. 1) is an electrified insulation film, i.e. surface charges are attached on the film (Kestelman, et al., 2000) (Sessler and West, 1966). The surface charges induce a polarization of the film in thickness direction followed by the emission of the electric field out of the film. The electret is generally obtained by embedding negative charges on the polymer film using corona-charging (Giacometti, et al., 1999). In addition, electret can be achieved using pyroelectric effect of a ferroelectric ceramic (Kageyama and Nagashima, et al., 2011). The fluororesin, e.g. PTFE (Poly tetra fluoroethylene), PFA (Poly tetra fluoroethylene perfluoroalkyl vinyl ether copolymer), FEP (Fluorinated ethylene propylene) are widely used for the electret because of its excellent insulation properties.

Electret is widely used for a electret condenser microphone (ECM) (Sessler and West, 1966) (Yasuno and Ohga, 2006) (Miura and Yasuno, 1997). In general, ECM is mounted on printed-circuit board. The ECM, therefore, suffers high temperature over 250 $^\circ C$ at reflow process for lead-free soldering. Such a heat treatment at high temperature induces the degradation of the charge retention of the electret, i.e. the charges diffuse through the electret (Zhongfu, 1991). To improve the charge retention at reflow process, a silica electret has attracted many researchers and the excellent heat resistance of the silica electret has been reported (Olthuis and Bergveld, 1992). The improvement of humidity resistance for silica electret, however, has been required because water molecule diffuses along the surface of the hydrophilic silica electret (Olthuis and Bergveld, 1992). Kageyama, et.al prepared the silica-agglomerate electret to improve the humidity resistance of the electret as well as the heat resistance as shown in Fig. 2 (Kageyama, et al., 2014). They prepared the silica agglomerates by spraying and drying colloidal silica on PFA film to obtain the isolated agglomerates. The silica agglomerates were isolated each other on the hydrophobic PFA film to prevent the diffusion of water molecule along the surface of the electret. The prepared electret thereby showed the higher charge retention at
reflow process while the humidity resistance was not degraded. This technique, however, charges the PFA film as well as the silica agglomerates. Negative charges reached the PFA film as well as the silica agglomerates when a corona-charging was done to obtain the electret. Eventually, part of negative charges were embedded to the PFA film between the silica agglomerate as shown in Fig. 2.

In this study, we used an electrostatic spraying to apply negatively-charged colloidal silica on fluororesin film. Electrostatic spraying is one of the methods to coat film with fine, uniform, and self-dispersive droplets (Hakberg, et al., 1983) (Cloupeau and Prunet-Foch, 1990). On the metal nozzle of the front end of the solution filled plastic syringe, the high voltage is applied to the spraying solution. The solution is charged positively and electrostatic force is used to spray the droplets. As all the droplets contain positive electricity, the drops are repulsively interacted. Consequently, the droplets are dispersed uniformly in the air. In this study, the colloidal silica solution was charged negatively to prepare the negatively charged electret. The droplets of colloidal silica should be deposited and isolated due to Coulomb repulsion after the solution is sprayed on the fluororesin film. Eventually the silica-agglomerate electret could be obtained after drying the solution as shown in Fig. 3. Three spraying methods were used to prepare the silica-agglomerate electret. The surface electric potential was measured after spraying to investigate which method was suitable for preparing the electret. Furthermore, the prepared electrets were heated to examine the improvement of the heat resistivity by the electrostatic spraying.

2. Experimental procedures

2.1 Preparation of silica-agglomerate electret by static spraying

PFA film (Poly tetra fluoroethylene perfluoroalkyl vinyl ether copolymer, Junkosha) with 12.5μm of thickness was used. A PFA film was welded to an aluminum plate (40 × 40mm) with thickness of 0.1mm. Three spraying methods were selected to apply colloidal silica droplets on a PFA film as shown in Fig. 4. Commercial colloidal silica (20L, Nissan Chemical Industry) was used for the spraying solution.

For method A, a comb-shaped electrode was used to deposit negative charges on the droplets (Fig. 4(a)). The comb-shaped electrode was set in front of an air spray gun (HG-WT, Tamiya Corp.). A high voltage of -20 kV was supplied to the comb-shaped electrode to induce corona discharge. The solution was sprayed on a PFA film through corona-discharge space below the comb-shaped electrode. Negative charges should be deposited to the droplets of the sprayed solution when they passed through the corona discharge space. The applied droplets on the PFA film was dried under atmospheric condition and thus negatively charged silica agglomerates (silica-agglomerate electret) were obtained.

For method B, a ring electrode was set in front of the spray gun as shown in Fig. 4 (b). A high voltage of -20 kV was supplied to the spray gun to charge negatively the solution inside the nozzle. The sprayed solution was atomized due to Coulomb repulsion. The atomized droplets were collected electrostatically to a PFA film using the cage because a negative voltage of -2 kV was applied to the cage.
For method C, the spray gun was installed to a conventional corona-charging setup as shown in Fig. 4(c). The setup consisted of a needle, grid and plate electrode. Such a setup is widely used for the preparation of an electret polymer film (Kageyama, et al., 2014). Corona discharge is induced at the needle electrode and negative charges are deposited on a polymer film on the plate electrode while the grid electrode control the surface electric potential of the sample. In this study, spraying the solution was started before corona discharge. Then corona-charging was done immediately after the beginning of the spraying. The voltage of the needle and grid electrode was set to -20 and -1 kV, respectively. The negative charges from the needle electrode are trapped in the sprayed droplets because the dielectric constant of the solution was much higher than the air. Eventually, selectively charged silica agglomerates were obtained after drying the charged droplets on the PFA film.

The spraying conditions of each method were listed in Table 1. We used an ESD (Electro-Static Discharge sensor, ZJ-SD Omron) to measure the surface electric potential of electret $V_s$. Furthermore, the amount of silica agglomerates on PFA film $m_s$ was calculated from the difference in the weight of the PFA film before and after the application. Furthermore, stereomicroscope observation was performed for the electret samples. Then an image analysis was performed using ImageJ from the captured images to measure area fraction $f_a$, average diameter $D$ and point density $N$ of silica agglomerates on a PFA film.

Table 1. Spaying parameters of silica-agglomerate electret

<table>
<thead>
<tr>
<th>Spraying method</th>
<th>$D$ [cm]</th>
<th>$T_s$ [s]</th>
<th>$m_s$ [mg/m²]</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>10–35</td>
<td>60–300</td>
<td>2–20</td>
<td>10</td>
</tr>
<tr>
<td>B</td>
<td>9–18</td>
<td>30–60</td>
<td>2–15</td>
<td>12</td>
</tr>
<tr>
<td>C</td>
<td>12–20</td>
<td>10</td>
<td>2–15</td>
<td>12</td>
</tr>
</tbody>
</table>

Fig. 4 Experimental setup for preparation of silica-agglomerate electret using electrostatic spraying. The $d$ is a distance in horizontal direction from a spray nozzle to a center of a sample. Three methods, (a) A, (b) B and (c) C were selected.
2.2 Measurement of charge retention of silica-agglomerate electret at heating test

Heating test was carried out on a hot plate, as shown in Fig. 5. An electret sample was set on a hot plate and the upper space on the sample was sealed using aluminum plates and a glass dish. A sheath thermocouple was set between the surface of the hot plate and the sample to measure temperature. A temperature curve of the heating test was shown in Fig. 6. Heating rate above 100 °C was approximately 4 °C / min. An electrostatic electrometer (ZJ-SD, Omron) was used to measure a surface electric potential of the electret sample. The electric potential was measured at the interval of 5 min during the heating test by removing the glass dish temporarily. The charge retention $R_e$ was derived by the ratio of the measured value of the surface electric potential to the initial value before heating.

3. Results and discussion

3.1 Influence of spraying methods on surface electric potential of silica-agglomerate electret

Amount of applied silica agglomerates, $m$, depended on the distance between the spray gun and the sample, $d$ when colloidal silica was sprayed by method A or B. The biggest $m$, was obtained when $d$ was 23 and 15 cm for method A and B, respectively. The amount of applied solution is usually increased with the decrease in $d$ at spraying. The smaller $d$, therefore, resulted in the bigger $m$, for method C. The spraying direction, however, was parallel to the surface of the sample in method A and B to attract only the charged droplets as shown in Fig. 4 (a) and (b). Eventually, the relatively heavy droplet could not reach to the sample when $d$ was so short that the electrostatic force was not strong enough to attract the droplet to the sample.

Fig. 7 shows the behavior of the amplitude of $V_s$, $|V_s|$ against $m$, when the samples were prepared by each spraying method. The $|V_s|$ did not depend on $m$, whatever method was used. These results reveals that most of the droplets were not charged because even the sample with smallest $m$, showed comparable value of $|V_s|$. Hence, the surface electric potential might be rapidly increased by charged droplets just after the beginning of spraying. Further study, however, must be required to estimate the minimum $m$, to obtain silica-agglomerates electret using electrostatic spraying. The samples using method A showed the smaller value of $|V_s|$ than those using the other methods as shown in Fig. 7.
in Fig. 7. Once the samples was negatively charged, the electrostatic repulsion should occur between the charged droplets on the sample and an additional charged droplet from a spray gun. Eventually, the charged droplet was no longer attracted to the sample at method A when the surface electric potential of the sample reached a certain level. On the other hand, \(|V_s|\) was enhanced by method B because more charged droplets were attracted to the sample by the cage electrode to which -2 kV was applied. The samples using method B, however, indicated large scattering of \(V_s\) because the value of \(V_s\) was not controlled. The method C can control \(V_s\) using the gate electrode. Eventually, the samples with \(|V_s| > 0.9 \text{kV}\) was stably obtained by method C.

Fig. 8 shows the observation of silica agglomerates on samples using method A, B and C by stereomicroscope. The tiny silica agglomerates were distributed around the agglomerates larger than 100 µm on the samples using method A and B. The number of tiny agglomerates was significantly decreased on the samples using method C. The charged droplets travelled in much longer distance in method A and B than in method C (\(d\) in Fig. 4 (a) and (b) for method A and B, \(dg\) in Fig. 4 (c) for method C). Thereby, the Coulomb repulsion force of the droplets was developed by water evaporation during the flight. Eventually, the charged droplets were often divided into tiny fragments due to Coulomb explosions in method A and B (Bringa, 2003) (Zohra, et al., 1998). On the other hand, the silica agglomerates on the samples using method C showed the desirable distribution for the purpose of this study because they were perfectly isolated each other.

![Fig. 8 Stereomicroscopic observation of the prepared samples.](image)

Fig. 8 Stereomicroscopic observation of the prepared samples. The \(m_s\) and \(V_s\) were (a) 6.43 mg/m² and \(V_s = -0.74\text{kV}\) of method A, (b) 6.38 mg/m² and \(V_s = -0.85\text{kV}\) of method B, (a) 6.35 mg/m² and \(V_s = -1.03\text{kV}\) of method C, respectively.

### 3.2 Charge retention of silica-agglomerate electret at heating test

Fig. 9 indicates the influence of the spraying methods on the behavior of the charge retention \(R_e\) of the samples at heating test. The samples using method B revealed that \(R_e\) began to decrease from 150 °C. This behavior was similar with the silica-agglomerate electret obtained by corona-charging after spraying. On the other hand, the samples using method A and C showed that \(R_e\) was maintained over 95 % until temperature reached 190 °C. Consequently, the heat resistance of the charge retention of the silica-agglomerate electret was apparently improved by method A and C. The \(|V_s|\), however, was smaller than 0.8 kV for the samples using method A while it was bigger than 0.8kV for the samples using method C. Furthermore, Fig. 10 showed the dependency of \(R_{250}\) on \(|V_s|\). The degradation of \(R_{250}\) with the increase of \(|V_s|\) is reasonable because the heat resistance of the electret is generally degraded with the increase of the surface electric potential, i.e. the electric field in the bulk. (Thielemann and Hess, 1997) The samples using method C, however, revealed the comparable value of \(R_{250}\) to those using method A although \(|V_s|\) at method C was much higher than that at method A. Hence, the silica-agglomerate electret prepared by the method C demonstrated the highest performance of three methods used in this study. Fig. 11 shows the relationship between \(m_s\) and \(R_{250}\) of the samples using method C. The \(R_{250}\) was the value of \(R_e\) at 250 °C. The \(R_{250}\) was derived from linear approximation using experimental data of \(R_e\) behavior as shown in Fig. 9. The \(R_{250}\) apparently did not depend on the amount of silica agglomerates \(m_s\). This result was similar with the relationship between \(|V_s|\) and \(m_s\) as shown in Fig.7.

Fig. 12 shows \(R_{250}\) behavior of the silica-agglomerate electrets against area fraction \(f_e\). The samples using method C represent the silica-agglomerate electret using electrostatic spraying (ES). The silica-agglomerate electret using corona-charging after spraying (CC) was referred from prior work (Kageyama, et al., 2014). The value of \(V_s\) was -1.0 kV for all CC electrets while it varied from -1 to -1.2 kV for ES electrets. The CC electrets demonstrated that \(R_{250}\)
was initially increased with the increase of $f_a$. No correlation, however, was recognized between $f_a$ and $R250$ when $f_a$ was higher than 0.15. On the other hand, ES electrets always showed that $f_a$ was higher than 0.15. Then, no correlation was recognized between $f_a$ and $R250$ for ES electrets. These results, therefore, suggest that most of negative charges might be embedded in the silica agglomerates on CC electrets as well as ES electrets when the value of $f_a$ reached 0.15. The $R250$ of the ES electret, however, was apparently higher than that of the CC electret, although the value of $|V_s|$ was same or higher as shown in Table 2 when $f_a > 0.15$. Fig. 13 and table 2 indicates that the average diameter $D$ and point density $N$ of ES electret was much different from those of CC electret. The silica agglomerates of ES electret apparently showed larger $D$ and smaller $N$ than those of CC electret. Hence, such a difference of $D$ and $N$ might cause the improvement in $R250$ by ES electret as shown in Fig. 12. Fig. 14 and 15 show the influence of $D$ and $N$ on $R250$. ES and CC electret showed similar behavior of $R250$, i.e. $R250$ was increased with the decrease in $N$ and the increase in $D$. The specific surface area of silica agglomerate becomes higher when $D$ is small. Eventually, the possibility that negative charge is captured on the surface should be increased. The diffusion rate of charges trapped on surface of insulation material is generally higher than that in the bulk. (Vanderbilt and King-Smith, 1993) (Thielemann and Hess, 1997) Hence, a possible model concluded from these results was that larger $D$ causes smaller specific surface area followed by more enhancement of charges’ trapping in the bulk of the silica agglomerate.

We also tried to deliver the dependency of $R250$ on $D$ and $N$ of the samples using method A and B. No correlation between $R250$ and $D$ or $N$ was obtained when the silica agglomerates with over 70 µm of diameter were analyzed for the measurement (stereomicroscopic observation could not measure the size of tiny silica agglomerates). Thus, tiny silica agglomerates around large agglomerates as shown in Fig. 8 might significantly influence on $R250$. In addition, further enhancement of $R250$ of the samples using method C could be expected if $|V_s|$ is reduced to the same level as those using method A in this study. Further study, therefore, is needed for the dependency of $R250$ on $|V_s|$ using method C as well as verification of the model mentioned above.

![Fig. 9 The $R_e$ behavior with temperature at heating test. Depicted samples were same as those observed in Fig 8.](image)

![Fig. 10 Relationship of $R250$, and $|V_s|$ for the prepared samples using method A, B and C.](image)

![Fig. 11 The $R250$ behavior with $m_s$ of the samples obtained by method C.](image)
Table 2. Mean values and standard deviation for \( f_a \), \( D \), \( N \) and \( R_{250} \) of ES and CC electrets when \( f_a > 0.15 \).

<table>
<thead>
<tr>
<th>Electret</th>
<th>Statistical values</th>
<th>( f_a )</th>
<th>( D ) [cm]</th>
<th>( N ) [1/mm(^2)]</th>
<th>( R_{250} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ES</td>
<td>mean ( = 0.22 )</td>
<td>0.22</td>
<td>59</td>
<td>91</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>standard deviation</td>
<td>0.04</td>
<td>0.05</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>CC</td>
<td>mean ( = 0.22 )</td>
<td>0.22</td>
<td>29</td>
<td>176</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>standard deviation</td>
<td>0.05</td>
<td>1</td>
<td>46</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The \( R_{250} \) of ES electrets prepared in this study was higher than 57%. The samples suffered high temperature from 200 to 250 °C for 12.5 min at the heating test in this study. The heating time under this temperature zone is generally designed to be less than 120 sec for reflow treatment of ECMs. The \( R_{250} \) of ES electrets must be higher than 90% at reflow treatment if the \( R_{250} \) is proportional to exponential heating time. Consequently, it can be concluded that the electrostatic spraying was excellent technique to obtain the silica-agglomerate electret with high heat resistance. The excessive size of silica agglomerates, however, was not preferable for ECM application because the silica agglomerates must be smaller than the gap in the ECM. The optimal size of silica agglomerate for ES electrets, therefore, must be investigated in future study.

4. Conclusion

The silica-agglomerate electret was obtained using an electrostatic spraying technique. The surface electric potential was measured after spraying to investigate. Furthermore, the prepared electrets were heated to examine the heat resistivity.

The method in which the spray gun was installed to a conventional corona-charging setup delivered the silica-agglomerate electret of which the amplitude of the electric surface potential, \( |V_s| \) was higher than 0.8 kV. The obtained silica-agglomerate electret showed the \( |V_s| \) did not depend on the amount of silica agglomerates, \( m_e \). On the
other hand, the silica agglomerates on ES electret showed larger diameter $D$ and lower point density $N$ than those on conventional silica-agglomerate electret (corona-charging after spraying, CC electret).

The obtained silica-agglomerate electret by electrostatic spraying method (ES electret) showed higher charge retention than CC electret when the electret was heated to 300 °C. In consequence, the charge retention at 250 °C $R_{250}$ of ES electrets prepared in this study was higher than 57 % when the electrets suffered high temperature from 200 to 250 °C for 12.5 min at the heating test. The increase of $D$ and the decrease of $N$ might cause the improvement in $R_{250}$ by ES electret. The charge retention at 250 °C $R_{250}$, however, did not depend on $m$. Hence, further study must be required to optimize $m$, $D$ and $N$ of silica-agglomerate electret for excellent $|V_s|$ and $R_{250}$ using electrostatic spraying.

References