Charge storage and mechanical properties of porous PTFE and composite PTFE/COC electrets

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Abstract: Recent futuristic applications of flexible electret loudspeakers have garnered much interest for these novel loudspeakers. To increase the loudspeaker properties, a processing method was developed to improve the electret and mechanical properties of porous PTFE film. Taking a thin porous PTFE film as the base material, a cyclic olefin copolymer (COC) was coated to a base material to form a PTFE/COC composite film. Results show that the composite material improves the advantageous characteristics when used as an electret diaphragm for loudspeakers. By measuring the surface potential decay and the elastic modulus, properties of a standard porous PTFE film were compared to an improved composite PTFE/COC film. Experimental results showed that the composite PTFE/COC possess the following advantages: (1) 80% higher surface potential after 10 days at room temperature, (2) a better thermal resistance of charge storage, and (3) a 643% higher elastic modulus. Therefore, our novel composite material can be used to create a much improved electret diaphragm for flexible electret loudspeakers.

Introduction

An electret is a dielectric material that traps quasi-permanent space charges which are induced by an external charging process [1]. Current commercially available electret polymers which include polypropylene (PP), polyethylene terephthalate (PET), cyclic olefin copolymers (COC), polytetrafluoroethylene (PTFE) and fluoroethylene propylene (FEP), exhibit good charge storage capacity [1-3]. In particular, a thick porous PTFE exhibits excellent dielectric properties including high charge storage stability at high temperatures [4-7]. Widely used PTFE electret related applications include such items as electret condenser microphones (ECM), soft ferro-electret transducers and transdermal drug delivery (TDD) systems [5, 8-11].

Recently, novel flexible loudspeakers in futuristic applications have generated much interest [12-15]. Applications in areas such as 3C (computer, communication and consumer electronics), smart windows, smart curtains, automobile audio and children’s toys have been actively discussed. Traditional type electret actuators have been studied since the 1970s [15, 16]. Taking a typical structure, an electret-based diaphragm was placed beside perforated electrodes and separated by a set of spacers. Interaction between the externally applied voltage and space charge of an electret induced vibration on the diaphragm was done by varying the electrostatic force which in turn induced acoustic waves to be radiated. Results show that inherent advantages include a simple and compact construction, higher efficiency,
and an excellent high-frequency response. In recent years, electret actuators have been perfected to complete the idea of its use as a flexible loudspeaker [17-20].

To obtain a high performance electret loudspeaker, the electret diaphragm should possess good charge storage capability and a light mass. By effectively enhancing the charge density, we can obtain an efficient device. However, despite the advantages and benefits of porous PTFE, its disadvantages including characteristics such as difficulty to adhere to an electrode layer, medium charge storage stability for high porosity thin-film [4], a low elastic modulus, and an easy plastic deformation at low stress, have hindered the further development of flexible electret loudspeakers. Some studies have attempted to improve the properties of porous PTFE which adopt coating and lamination methods to form a composite material [10, 11, 21, & 22]. However, the resulting composite material becomes less conformable than desired. Therefore, although difficult to achieve, the ideal properties for a good electret diaphragm include features such as low cost, good adhesion between the aluminum layer and the PTFE, and a light mass.

In this study, taking a thin porous PTFE film as the base material, a COC was coated to the base material to form a PTFE/COC composite film. In addition, to improve the typically low adhesion found between the aluminum layer and the composite film, an ethylene-ethyl acrylate copolymer (EEA) was used as the bonding layer. All charges to the electrets were prepared using a corona charge method. Characteristics such as surface potential decay, adhesion strength and elastic modulus were investigated.

Results and discussion

SEM morphology of composite PTFE/COC films

To investigate and compare the cause of a COC addition on morphology of the composite material, the surface of the specimens were studied using a scanning electron microscope (SEM). In Figure 1(a), the SEM images of the standard porous PTFE clearly show a porous structure at the outer surfaces. It is clear that a standard porous PTFE has an open-porous structure and possesses high porosity under high SEM magnification (see Figure 1(c).) The morphology of the composite PTFE/COC film was obtained as shown in Figures 1(b) and 1(d). Results show that the COC penetrated the cavities of the porous PTFE and filled in some of the spaces in-between. In Figure 1(d), the composite material shows good mechanical adhesion between the fibrous PTFE and the COC. Comparing the porosity of a standard porous PTFE to a composite PTFE/COC film, we found that the porosity of the composite films was reduced significantly when compared to standard porous PTFE.

Electret properties of composite films

The charge storage capacity of electret samples was determined by measuring the remaining surface potential. Both the standard porous PTFE and the composite PTFE/COC film were first charged in a point-to-plane corona discharge without a grid voltage in order to achieve high surface potentials [4]. A small region near the surface was then charged by the corona ions. The surface charges are called homocharges or real charges. The internal electric field in the air void of the material began to exceed the Paschen breakdown limit when the surface potential exceeded the critical threshold. Local discharging was initiated under this condition as well. When the charges were separated and then trapped at the top and bottom surfaces
of the air void, macroscopic dipoles were induced. These porous materials coexist in the presence of both homocharges and heterocharges [24]. The electret properties of these specimens were then measured and recorded over time at room temperature (e.g. 25 deg. C & 30% RH). For each kind of specimen, at least 3 samples were taken and measured. Experimental results (Figure 2) indicate that the standard porous PTFE and the composite PTFE/COC films exist at -530 V and -920 of the initial surface potential. The remaining surface potential of the standard porous PTFE and the composite PTFE/COC films then decayed to a stable value at around -410 V and -740 V after 10 days, respectively. That is, under the above charging conditions, the composite film was characterized by a better charge storage capacity than that of standard porous PTFE at room temperature. It appears that the composite PTFE/COC can effectively enhance the surface potential by about 80% due to its increased initial potential. Furthermore, the slight increase in the surface potential was observed during the early stage of the experimental results as shown in Figure 2. The early increase in the net homocharge can be attributed to the drain of the unstable heterocharges [25].

![Fig. 1. (a,c) SEM images of porous PTFE and (b,d) SEM images of composite PTFE/COC.](image)

For future automobile applications, electret diaphragms with good temperature resistance are necessary. Aging has also been known to improve the charge stability of electret materials. Several thermal treatments of the charging are referenced (see Refs [1, 7]). In this paper, we investigated the charge storage properties with temperature resistance. First, both the standard porous PTFE and the composite PTFE/COC films were charged using corona discharging at room temperature without a grid voltage in order to achieve a high surface potential. When the porous
materials reached a saturated charge state, increased instability of the charges appeared within the dielectric. After charging, all samples were placed in an oven at 100 °C and the surface potentials were measured over time. From the experimental data (Figure 3), the charges were found to be quickly discharged due to the influence of the high temperature during the early stage. Five hours later, the surface potential was found to be at a stable condition. Results showed that standard porous PTFE with 24 μm thickness had poor charge storage at high temperatures. However, we found that the surface potential of the composite film with 25 μm thickness possessed excellent charge storage when compared to that of standard porous PTFE. Therefore, it appears that a composite PTFE/COC can effectively improve the surface potential to about -170 V with good temperature resistance. In addition, the charge storage stability of electrets is one of the most important indicators of quality. We further studied the relationship between the thermal treatment of charging and charge storage stability. Comparisons were done such that all samples were charged to the same initial surface potential in order to ensure that the internal electric fields remain nearly identical. The standard porous PTFE and the composite PTFE/COC films were both heated to 100 °C and corona discharge performed (e.g. heating during charging process) at -800 V and -400 V of the grid voltage in order to limit the surface potential [1, 7]. Experimental results (Figure 4) indicate that the standard porous PTFE (24 μm) and the composite PTFE/COC (25 μm) films exist at -328 V and -343 V of the initial surface potential. Both samples possessed a similar internal electric field. The surface potential of the standard porous PTFE and the composite PTFE/COC films then decayed to a stable value of around -140 V and -265 V after 70 hours, respectively. The remaining surface potential decayed to 43% and 77% when compared to that of the initial values. Furthermore, the slight increase in the surface potential was observed during the early stage (0 to 0.5 hours) of the decay curve as shown in Figure 4. The increase in the surface potential can be attributed to the coexistence of both homocharges and heterocharges. These results can be easily reproduced. However, the effect of the increased potential at the early stage of the experimental data (Figure 3) was not observed due to a fast drain of the unstable homocharges and heterocharges [25].

![Graph](image)

**Fig. 2.** Decay of measured static surface potential for porous PTFE and composite PTFE/COC at room temperature (25 deg. C & 30%RH).
Fig. 3. Decay of measured static surface potential for porous PTFE and composite PTFE/COC at 100 °C.

In our sample preparation, the embryo sample was annealed in an oven at 100 °C for one hour twice in order to evaporate the solvent completely and to solidify the immiscible polymers further. Then, the aluminum layer was evaporated onto the composite sample. The COC was an amorphous copolymer which had a glass transition temperature higher than 140 °C. Since the porous PTFE is a highly-crystalline polymer with a wide operating temperature (-200 °C to +260 °C), we thus assume that the 100 °C aging step will not significantly affect the physical properties (e.g. crystalline grain size or degree of polymer crystallinity). The annealing process was thus identified as not the main cause of the increased charge storage capacity.

Fig. 4. Decay of measured static surface potential for porous PTFE and composite PTFE/COC at 100 °C. The electret films were charged using corona discharging with a specific grid voltage at 100 °C (e.g. heating during charging) in order to limit the same surface potential.
At present, the mechanism of a storage charge remains unclear. Several possible reasons include the following: (1) the COC is an amorphous copolymer which has a glass transition temperature higher than 140 °C. The COC also possesses good electret properties and has a higher thermal resistance than PP [2]. When COC and porous PTFE come together to form the composite film, more interfaces are formed which lead to a higher storage capability [23]. In other words, the improvement of a higher surface potential is the result of the aggregation of COC and the interfaces of the composite. (2) The appropriate ratio of COC and porous PTFE was investigated. The COC appears to penetrate the cavities of the porous PTFE and fill in some of the spaces in-between, resulting in an original open structure of porous PTFE which is transformed into a semi-open structure that has reduced porosity. Possible reasons for the increased charge storage stability of the composite film include the generation of a barrier by the semi-open porous structure within the membrane thickness, which prevented the charge from drifting [24]. In addition, COC may be a bound variant of the thermal expansion of PTFE that has reduced molecular chain movement at 100 °C, which in turn reduces the charge loss.

**Mechanical properties of the composite films**

The elastic modulus of the sample is the ratio of stress to strain within the range of the elastic limit. The elastic modulus of standard porous PTFE was calculated to be within the range of 0 to 0.02 mm/mm for strain and with an average value of 30.79 Mpa.

![Engineering stress-strain curve of porous PTFE and composite PTFE/COC film.](image)

Comparing the elastic modulus between a standard porous PTFE and composite PTFE/COC samples (Figure 5), it is clear that the composite PTFE/COC possesses a higher elastic modulus. The elastic modulus of composite films was found to be 228.86 Mpa, which is 643.3% higher than that of the standard porous PTFE material.
In Figure 5, the porous PTFE film generated a large tensile deformation at low stress which can create problems when applied to electret loudspeakers. In Table 1, we found that by adding a COC amount of 0.2204 mg/cm², it is possible to effectively enhance the mechanical strength and overcome the low stress deformation found with standard porous PTFE.

To achieve low cost and ease of production, an aluminum layer was used to serve as the electrode for this newly developed composite electret diaphragm. To solve the problem of the low adhesion between the aluminum layer and the PTFE, a polymer EEA was used as the bonding layer. Figure 6 shows the optical Imaging of the specimens after adhesion and cross-cut tests (e.g. ASTM D3359 standards). According to the results, the EEA can effectively improve the adhesive strength of the aluminum layer and the composite film. We obtained a surface measurement value of 3B (5-15% damage) which shows it to be far more effective than that of the original material with value at 0B (100% damage).

**Fig. 6.** The optical Imaging of the specimens after adhesion and cross-cut tests (based on ASTM D3359 standards): (a) porous PTFE film with aluminum layer and (b) composite PTFE/COC film with aluminium layer after adhesion.

**Tab. 1.** Specimen Properties.

<table>
<thead>
<tr>
<th>Polymer Film Type</th>
<th>Mass Per Unit Area (mg/cm²)</th>
<th>Thickness (μm)</th>
</tr>
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<tbody>
<tr>
<td>Porous PTFE</td>
<td>1.1314-1.15501</td>
<td>24±2</td>
</tr>
<tr>
<td>Composite PTFE/COC</td>
<td>1.3182-1.44</td>
<td>25±2</td>
</tr>
</tbody>
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**Conclusions**

A composite material processing technology for a flexible electret loudspeaker was presented in this paper. Our results show that the addition of a thin composite PTFE/COC electret film improves the surface potential and increases the charge storage stability when compared to a standard porous PTFE material. In addition, this newly developed composite PTFE/COC electret can also improve the elastic modulus and create a better adhesion to the aluminum layer. All these advantages can lead to a much improved electret diaphragm for flexible electret loudspeaker applications.
Experimental

Materials
A COC pellet called Topas® 6013 was purchased from Topas Advanced Polymers GmbH in Germany. The porous PTFE membrane, 24 μm thickness with porosity of 80 percent was purchased from Yeu Ming Tai Chemical Industrial Co., Ltd. in Taiwan. The EEA copolymer pellet and toluene (99%, density=0.866 g/mL) solvent were purchased from Sigma-Aldrich (USA).

Sample preparation
The COC with 7.5 wt % concentration was dissolved in toluene to form a COC solution which was measured to have a 12.1cp viscosity using a viscosity meter (SV-10, A&D Scientech, Taiwan). The EEA with a 0.5 wt% concentration was also dissolved in toluene to form an EEA solution. The COC solution was spun-coated (2000 rpm, 20 s) into the porous PTFE to form a PTFE/COC composite film. Then, the embryo sample was annealed in an oven at 100 °C for 1 hour. Repeating the above steps, the coating of the embryo sample with the EEA solution was spun-coated again. Finally, an e-beam evaporator was used to evaporate 100 nm of the aluminum layer onto the composite film.

Microstructural examination
The morphology of samples was obtained using a SEM (Hitachi S-4800, Japan) operating at 10 kV. The composite films were metalized with a thin gold layer prior to SEM observation with an ion beam sputtering device (Hitachi E-1030).

Mechanical properties examination
The elastic modulus of the samples was the ratio of the stress to strain within the range of the elastic limit. The extension experiment was performed using a Nano Bionix® universal testing system from the Industrial Technology Research Institute (ITRI), Taiwan. This system possessed a load range from 0 to 500 mN and was conducted at a strain rate of 0.01 mm/mm/s following ASTM D882 standards [25].

The adhesive strength between a composite PTFE/COC film and an aluminum layer was measured using a cross-cut method based on ASTM D3359 standards.

Evaluation electret properties
All the samples were charged using a corona discharging process without a grid in order to achieve high surface potential for 1 minute at room temperature. The negative needle voltage corona of 18 kV was supplied by a high voltage power supply (FX-20R15, Glassman, USA). After charging, all samples were then placed in humidity cabinets (25 °C & 30% RH) and the surface potential of all samples were measured over time using a voltmeter (Trek 344, USA) and a non-contacting probe (Trek 6300-7). In addition, the evaluation of the charge storage capacity at high temperature was further examined. After the above charging condition at room temperature, all specimens were placed in an oven at 100 °C and measured over time using a high temperature probe (Trek 6300-7) to measure the surface potential decay. To evaluate the charge storage stability, all specimens were heated to 100 °C and corona discharge was performed (e.g. heating during charging process) at -800 V and -400 V of the grid voltage in order to limit the surface potential. All specimens
were placed in an oven at 100 °C and measured over time to evaluate the decay rate of the surface potential.

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References