Residual Charge and Filtration Efficiency of Polycarbonate Fibrous Membranes Prepared by Electrospinning

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ABSTRACT: Polycarbonate (PC) ultrafine fiber membranes with benzyl triethylammonium chloride (BTEAC) were prepared by electro-spinning of PC/chloroform solution with different BTEAC contents. In the presence of BTEAC additive, the PC solution showed a better electrospinnability and led to thinner fibers with uniformity than the neat PC solution. The charge retention of the electrospun PC fibrous membranes with BTEAC was investigated in terms of additive content, membrane thickness and storage condition. The residual charge on the PC fibrous membrane was increased to 1 wt % BTEAC content, but thereafter gradually decreased up to 10 wt % BTEAC. In addition, the residual charge on the membrane was increased with increasing the membrane thickness, but was rapidly decreased at a high humidity condition in comparison with a low humidity. The filtration efficiency was examined for the fibrous membranes with or without BTEAC. The PC membrane with BTEAC had higher filtration efficiency than one without BTEAC, not affecting the pressure drop. The filtration efficiency between the PC membranes with or without residual charge was also compared. When the residual charge existed on the membrane, the membrane showed higher filter efficiency because of the enhanced filtration effect by an electrostatic attraction. Therefore, the PC fibrous membranes with BTEAC have a great potential as an electrets filter for air filtration. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41340.

INTRODUCTION

Aerosol filtration is the most widely used technique for air cleaning and sampling in a variety of industries. In particular, fibrous air filters have been widely used to separate solid matter from air flow streams for dust collection and/or environmental protection because of high filtration efficiency and low air resistance.[1,2] Particulate filtration by a fibrous membrane in a gaseous environment is primarily based on depth filtration, namely through the combined effects of diffusion, interception, inertial impaction and electrostatic interaction.[3] Additional filtration using the electrostatic force is desirable in the fibrous air filter in order to obtain the high filtration efficiency without increase of pressure drop. The effect of electrostatic forces on the performance of air filter has been diversely studied for few decades, and the electrets filters are used to clean gas streams with dilute particle concentrations at low pressure drop and high efficiency. The electrets filter is composed of charged fibers which are able to efficiently collect the opposite and neutral charged fine particles. Composed to the uncharged fiber, the aerosol collection efficiency of the electrets fibers can be significantly higher, even if the aerosol particles are uncharged. Therefore, the electrets fibers are often employed to enhance the filtration efficiency of HEPA and ULPA filters.[4]

On the other hand, ultrafine polymer fibers with a high surface area-to-volume ratio can be prepared via electrospinning. The higher specific surface area indicates better efficiency for various advanced applications, such as separation membranes, wound dressing materials, artificial blood vessels, sensors, catalysts, and so on.[5–8] The mechanism of the electrospinning process involves the injection of charge into a polymer fluid. Because the electric charge was injected into a polymer solution, the generated web had a residual charge, whose content is strongly dependent on the polymer nature and solution properties. Some charge still residues on the electrospun polymer fibers, even after some portion of the charge is dissipated during polymer solidification by the evaporation of solvent. The electrospun fibers will dissipate

Additional Supporting Information may be found in the online version of this article.

the excess residual charge by different routes depending on several parameters including dielectric properties of the polymer, solvent, atmospheric humidity, temperature and, specially, the location of the trapped charges in the material. Generally, polymeric materials have a high dielectric property, which retains the electric charge over a long period of time. In other words, the electrical charge in the polymer membrane with high dielectric constant is quasi-permanent. Therefore, the polymer fibrous membrane with high residual electrical charge generated from the electrospinning has a great potential as an electrets filter. Several researchers have investigated to measure the residual charge accumulated on the electrospun fiber membranes.[9–13] Catalani et al. demonstrated that a residual charge in the crystalline poly(butylene terephthalate) nanofibers was trapped within or at the crystalline/amorphous interface and in defects within the crystalline phase.[10]

Polycarbonate (PC) is a promising thermoplastic material with good physical and mechanical properties, such as heat resistance, impact strength, rigidity and toughness.[14–16] Recently, few researches have been reported to employ the electrospinning technique to prepare micro- or nano-porous PC membranes.[17–19] In a previous study,[20] non-woven fibrous structures of PC were produced via electrospinning to develop antimicrobial filtration membranes. For this purpose, the electrospinning of PC was also carried out with quaternary ammonium salt, which was a typical antimicrobial agent and soluble in the organic solvent. The PC is a typical amorphous polymer, and thus may be advantageous in possessing a higher residual charge by electrospinning. The crystallization of PC molecule was inhibited by the chain rigidity originated from both aromatic character of bis-phenol A group and partial double bond character of carbonate group. This chain rigidity does not allow the PC molecule arranged into a crystalline structure, although it can provide a high thermal and mechanical stability.

In this study, the decay of residual charge on the electrospun PC membrane was investigated under various experimental conditions, such as additive content, membrane thickness, and storage condition. In addition, the filtration efficiency of the PC membrane with an organo-soluble salt, benzyl triethylammonium chloride (BTEAC), was also quantitatively examined in terms of residual charge, and compared with numerical simulation values.

EXPERIMENTAL

Materials
PC (M_n = 22,000) was kindly supplied by Samyang, Korea. Chloroform and benzyl triethylammonium chloride (BTEAC) were purchased from Aldrich and used as received.

Electrospinning
The electrospinning setup utilized in this study consisted of a syringe and needle (18G, ID = 0.84 mm), a ground electrode (d = 21.5 cm, stainless steel sheet on a drum whose rotation speed can be varied), and a high voltage supply (Chungpa EMT, CPS-40K03). The needle was connected to the high voltage supply, which can generate positive DC voltages up to 40 kV. For the electrospinning of PC fibers, PC/chloroform solution was prepared at the concentration of 16% (w/v) and different contents of BTEAC (0.25 ~ 10.0% (w/w) based on the weight of PC was added into PC solution, and then delivered by a syringe pump (KD Scientific, Model 100) with the mass flow rate of 2 mL/h. The distance between the needle tip and the ground electrode was 10 cm and positive voltage applied to polymer solutions was 20 kV. All experiments were carried out at room temperature.

Measurement and Characterization
The morphology of electrospun PC ultrafine fibers was observed on a field emission scanning electron microscope (FE-SEM) (JSM-7000F, JEOL, Japan). Samples for SEM were dried under vacuum, mounted on metal stubs, and sputter-coated with platinum for 30–60 s. The average diameter and its distribution of electrospun fibers were obtained by analyzing SEM images with a custom code image analysis program (Scope Eye). The residual voltage of electrospun PC fibers was measured by electrostatic fieldmeter (FMX-003, SIMCO, Japan) at vacuum oven. Twenty times for each sample was measured and averaged. The glass transition temperature (T_g) of PC fibers was measured by differential scanning calorimetry (DSC) with a heating rate of 10°C/min in the temperature range of room temperature to 290°C. The humidity and temperature were controlled by temperature & humidity chamber (TH-ME-025, JEO TECH, Korea) and vacuum oven (VO-10X, JEO TECH, Korea), respectively.

Filtration Performance
The filter testing equipment (TSI 8130, TSI) has a certain kind of conventionally used system which is composed of an atomizer, a charge neutralizer, a filter holder, and a condensation particle counter (CPC).[21] In the atomizer, polystyrene latex (PSL) particles having known sizes are dissolved in distilled water and then the solution is atomized. In order to avoid unwanted electrostatic effects, a charge neutralizer is used. Electrical charges on the aerosols are neutralized by exposing the aerosols to a cloud of bipolar ions produced by a radioactive source. The particles are thus brought to a state of Boltzmann charge equilibrium. The filter to be tested is placed in a filter holder and the particle concentration upstream and downstream of the filter is measured using the CPC. The CPC can measure the number concentration of nano-sized particles to grow to micro-sized droplets in a supersaturated environment. The size of the test filters is 100 cm^2 and the face velocity is fixed at 5.3 cm/s. The filtration efficiency is evaluated using test particles of 0.3 μm in diameter.

RESULTS AND DISCUSSION

Electrospinning of PC/Chloroform with or Without BTEAC
Electrospinning, a new class of fiber spinning, has recently attracted many attentions in material science and engineering community as a potential nanotechnology for various applications, particularly filter application. Ultrafine fiber structure has a high surface-to-volume ratio which is thought to enhance filtration performance.
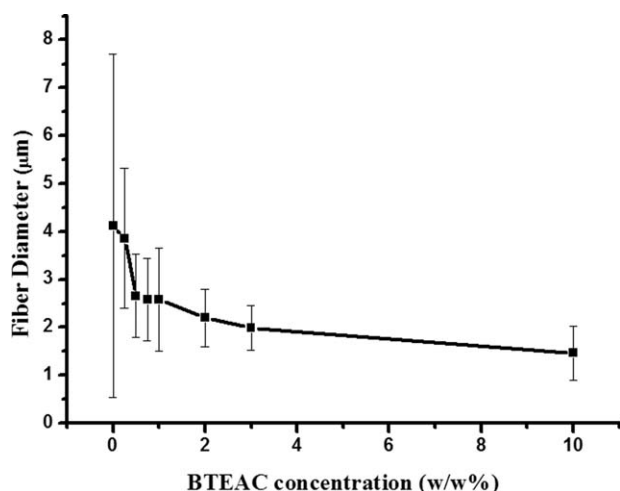
Electrospinning of PC was carried out in the presence of BTEAC, which was chosen as a salt soluble in chloroform. Figure 1 shows SEM micrographs of PC fibers electrospun from the PC solution
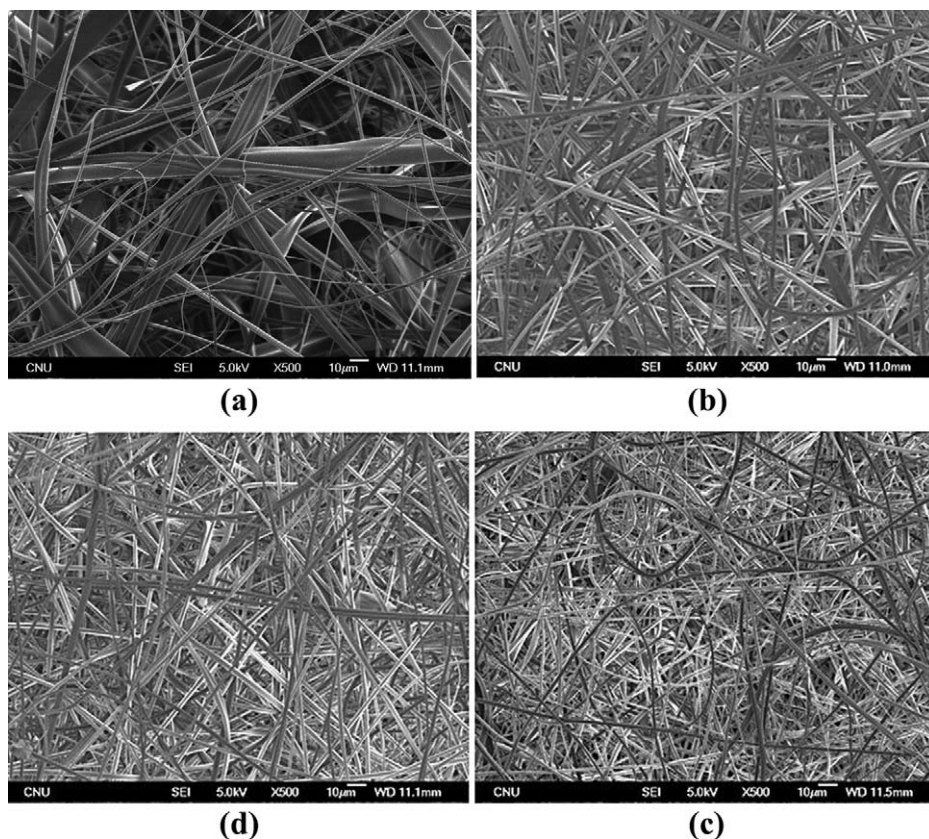
Figure 1. SEM images of PC fibers obtained from PC solution of 16 wt % with different BTEAC contents: (a) 0 wt %, (b) 0.5 wt %, (c) 2.0 wt %, and (d) 10 wt %.

with different BTEAC concentrations. In the neat PC solution, the fiber structure with a wide range of diameter was generated [Figure 1(a)]. The fiber diameters of PC electrospun from a 16 wt % solution were in the broad range 0.7–10.4 μm and the average fiber diameter was 4.1 μm. As the BTEAC concentration increased, the PC fibers were mounted in a straight shape, and more uniform and thinner fiber structure obtained [Figure 1(b–d)]. It is known that the average diameter of electrospun ultrafine

fibers was decreased with the addition of salts, and their morphology was dependent on the type of salts.[22,23] When BTEAC was added, jets appeared to be continuous and thus supported continuous electrospinning and membrane formation. The addition of small amounts of BTEAC to the PC solution caused a significant decrease in the average fiber diameters (4.1 to 1.5 μm at 16 wt % PC solution) as well as increase in fiber uniformity, because the addition of BTEAC caused significant increase in the conductivity of the PC solutions with increasing amounts of BTEAC (Figure 2). Therefore, it was found that the conductivity of the PC solution was a major parameter affecting the morphology and diameter of the electrospun PC fibers.
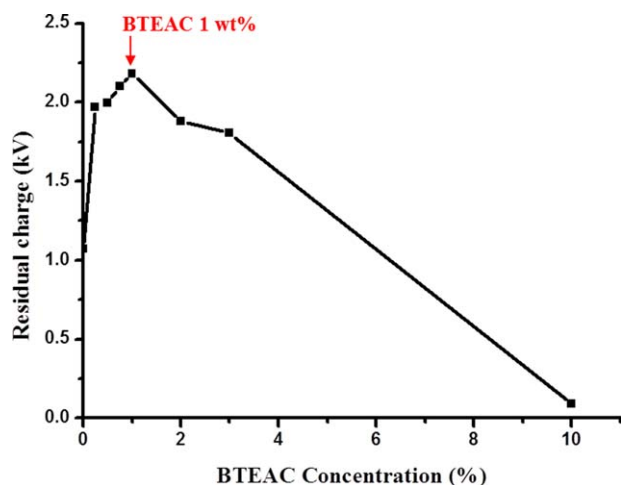
Residual Voltage in the PC Fibrous Membrane with BTEAC

Residual charges, which are embedded within the surface or volume of the solidified fiber structure, still remain in the deposited fibrous membrane after electrospinning. This residual charge was varied depending on the membrane thickness, additive, atmospheric conditions. While there are several techniques for measuring the charge density or charge distribution of electrets, only a relatively small number of researches reported measurements or estimates of stored residual charges in the electrospun fibers.[13] Three methods which have been used to measure the amount of stored charge on electrospun fiber membranes are surface potential measurements, thermally stimulated current (TSC) measurements, and Faraday cup measurements.[13] In this study, the residual voltage of

Figure 2. Average fiber diameter and its distribution of the electrospun PC fibers with different BTEAC contents.
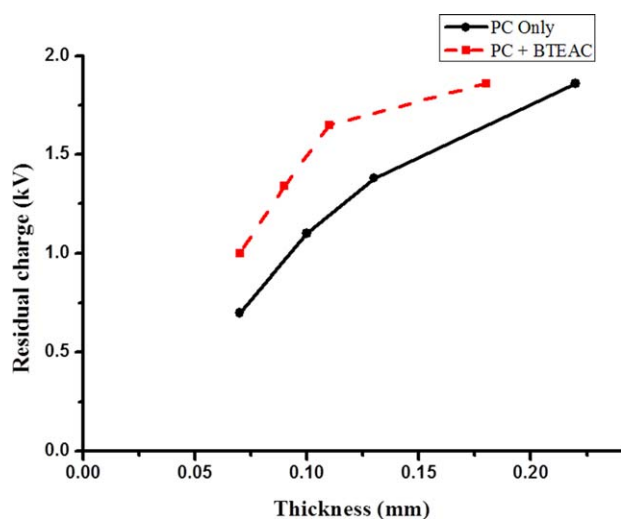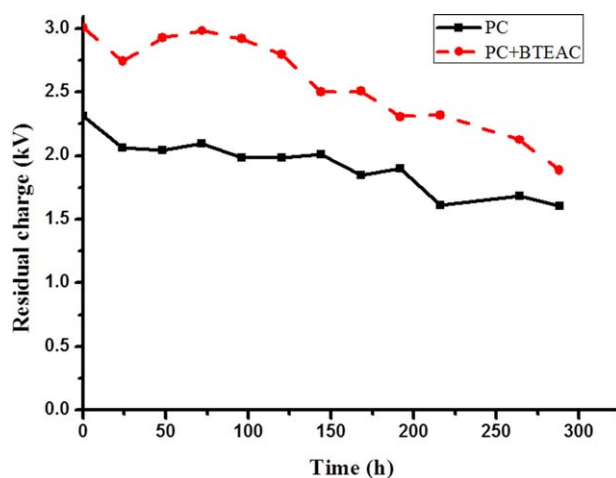
Figure 3. Change in residual charge on the PC fibrous membrane with different BTEAC contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

electrospun PC fibers was measured by electrostatic fieldmeter, which is able to measure the local electric potential near the sample surface.
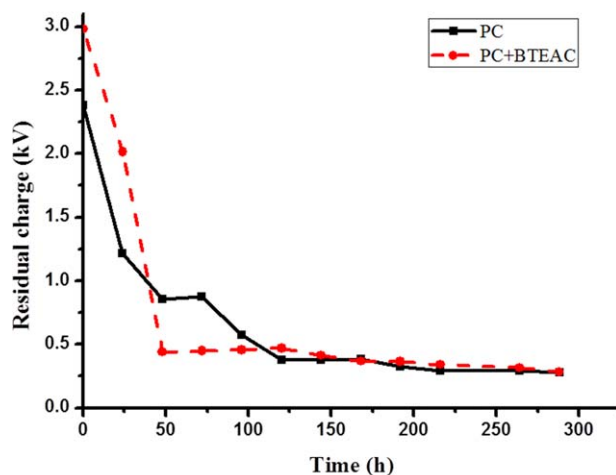
Figure 3 shows the change in residual charge on the PC fibrous membrane with different BTEAC contents. The residual charge was increased to 1 wt % BTEAC, but thereafter gradually decreased up to 10 wt % BTEAC. Residual charges could be generated by entrapment of charge, which was embedded from the electrode during electrospinning, into the PC fiber membrane. The residual charge was increased in the PC membrane by the addition of BTEAC, because the embedded charge was entrapped in the interface between PC and BTEAC as well as PC itself. When BTEAC content was increased, the residual charge was also increased due to the increment of interfaces. However, at higher BTEAC content, the distance between BTEAC molecules became closer, the charge entrapped at the

Figure 4. Change in residual charge on the PC fibrous membrane with different thickness. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
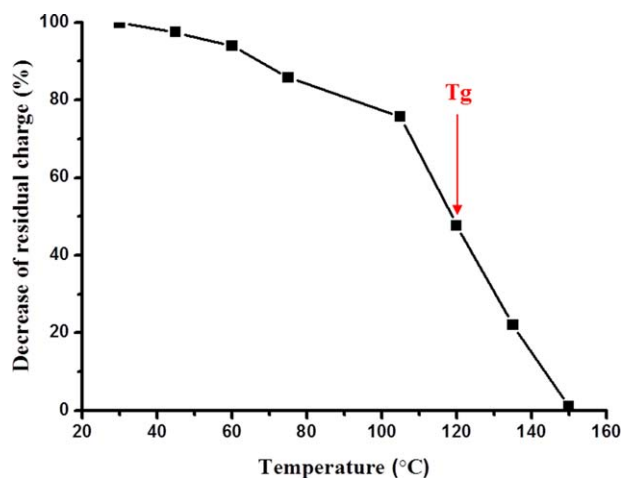

Figure 5. Changes in residual charge on the PC fibrous membrane with storage time (a) in the PE bag and (b) in the constant temperature and humidity chamber. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interfaces can migrate by hopping. Therefore, most of residual charge dissipates to the electrode at high BTEAC content, and thus the residual charge was decreased. The residual charge decay of the electrospun PC membrane is very important in applications such as electrets filter. Therefore, the PC membrane with 1 w/w% BTEAC was used for the following experiments.

Figure 4 shows the change in residual charge on PC membranes with different thickness. The thickness of PC fibrous membrane was varied by changing the deposition time of fibers during electrospinning. The residual charge was increased with membrane thickness because the space (surface and volume) charge was increased with the number of fibers accumulated. Also, the residual charge of PC membrane with 1 wt % BTEAC was higher than that of neat PC one, maybe because the BTEAC can provide an increased space charge in the interface region with the PC.

Figure 6. Change in residual charge on the PC fibrous membrane with temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The residual charge in the membrane can be neutralized by moisture in the air. To investigate the effect of the storage conditions on the residual charge, two storage conditions were employed: the storage in PE bag and the storage in constant temperature and humidity chamber (25°C and 50% RH). Figure 5 shows the change in residual charge on the PC membrane with different storage conditions. The residual charge of membrane stored in PE bag did not changed significantly with time, while the residual charge in the chamber decreased abruptly in 2 days. This decrease in residual charge can be explained by dis-
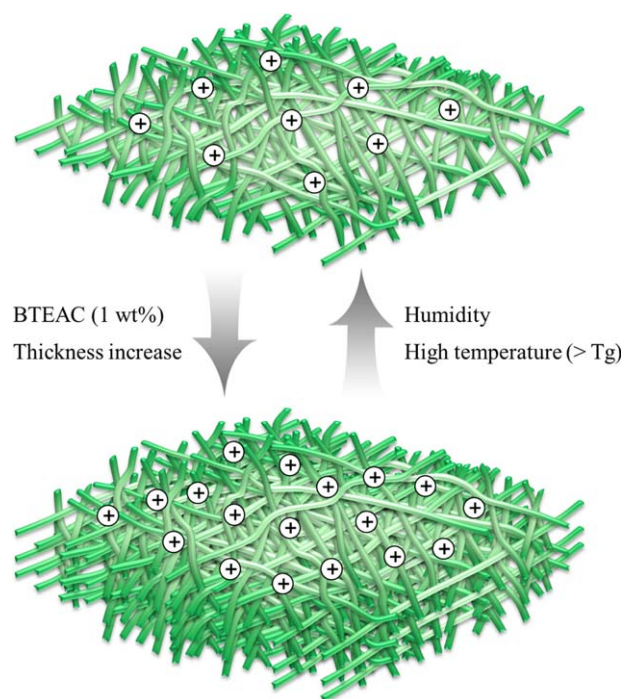

Figure 7. Effect of additive, thickness, humidity, and temperature on residual charge of PC fibrous membrane. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
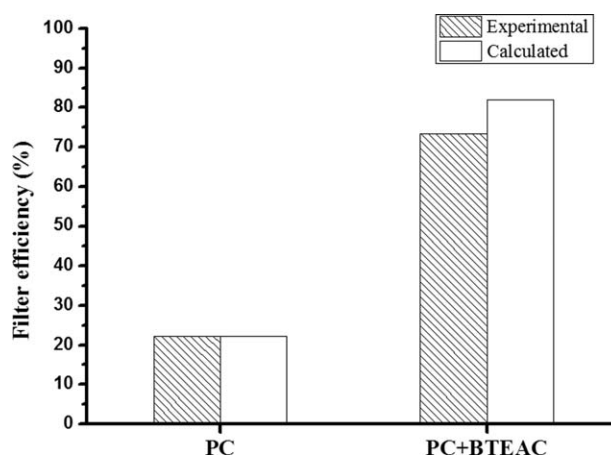
Figure 8. Calculated and experimental filter efficiency of PC fibrous membrane with or without BTEAC.

sipation of surface charge with moisture in the air. The first important effect of adsorbed moisture is to increase the conductivity at surface allowing a fast dissipation pathway through movement of charge. Also, the residual charge of PC membrane with BTEAC was decreased faster than that of neat PC membrane in the chamber [Figure 5(b)]. The ammonium groups in the BTEAC molecule are able to absorb the moisture from the air, resulting in a faster neutralization reaction. Thereafter, the residual charges seemed to remain stable at around 0.5 kV, suggesting that there are two dissipation modes: a fast dissipation (detrapping) mode is presumably from surface trapped charge, and a slow dissipation mode is presumably from volume trapped charge. Therefore, the volume charge maybe remained after above 240 h due to its slower dissipation, although most of surface charge was dissipated by moisture in 96 h [Figure 5(b)].

Figure 6 shows the change in residual charge on the PC membrane with temperature. When temperature was increased, the residual charge was gradually decreased to 100°C, and thereafter decreased abruptly to approach about zero at 150°C. The charge on polymer membrane embedded from an electric field exists, not move freely, in local sites. In the PC molecules, the main sites for embedded charge are interfacial region between PC domain and BTEAC domain. The trapped charge could be dissipated only if the high electric field was applied or polymer chains had some molecular motion. However, polymer chains start to move on heating polymer sample, and then the trapped charge is dissipated to decrease the residual charge. The degree of charge dissipation depends on the segmental motion of polymer chains. From the DSC curves, the glass transition temperature (T_g) of electrospun PC fibrous membrane was approximately 120°C. Therefore, the abrupt decrease in residual charge at above 100°C seemed to be associated with the increase of the segmental motion in glass transition region. At 150°C, the volume charge as well as the surface charge was dissipated by the segmental molecular motion. Conclusively, the effect of additive (BTEAC), thickness, humidity, and temperature on residual charge of eletrospun PC fibrous membrane was summarized in Figure 7.
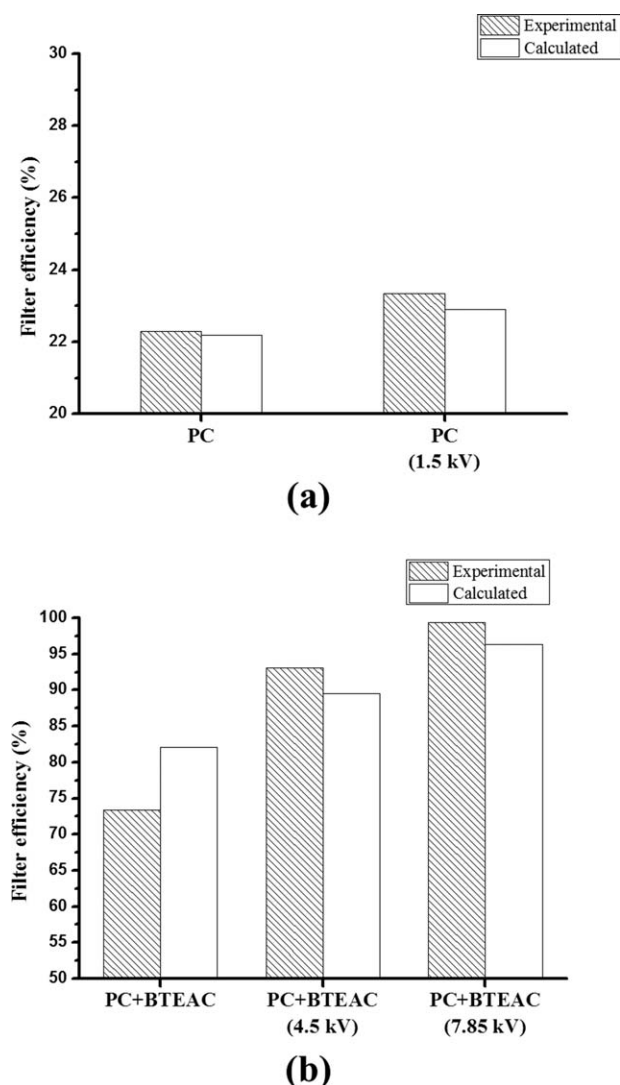
Figure 9. Calculated and experimental filter efficiency of (a) PC fibrous membrane and (b) PC fibrous membrane with BTEAC with or without residual charge.

Filtration Properties of PC Ultrafine Fibrous Membrane with BTEAC

Dielectric materials which exhibit the ability to retain or store electric charges over long periods of time are called electrets.[13] When the electrospun fibrous membrane is applied to ultrafiltration, the degree of electrical charge in the fibers influences the effectiveness of filtration devices. In the application of electrospun fiber membranes as filters, it is expected that the residual charge of the fibers enhances the ability to filter contaminants through an electrostatic attraction to the charged fibers.

The total amount of charge is often correlated to mass concentration of polymer. Depending on the dielectric properties of the substrate to which the eletrospun mat was deposited, the charge dissipates very quickly. The total charge retained is also dependent on thickness of the membrane, hence the mass and total polymer surface.

To evaluate the filtration performance of PC fibrous membrane with BTEAC, the neat PC sample was used as a reference. Figure 8 shows calculated and experimental filtration efficiency of the PC membrane with or without BTEAC (Determination of filtration efficiency by theoretical calculation was described in Supporting Information). The filtration efficiency of test particles can be measured by comparing with the particle number concentration between upstream and downstream of the test filter medium. The PC sample with BTEAC shows higher filtration efficiency than the neat PC sample at 0.3 μm particle size, because, among filtration mechanism, interception effect and diffusion effect was increased due to reduced fiber diameter in the PC fiber membrane with BTEAC. At the face velocity of 5.3 cm/s, the filtration efficiency of the PC sample revealed higher values than that of HEPA filter.

Figure 9 shows calculated and experimental filtration efficiency of (a) PC membrane and (b) PC membrane containing BTEAC, with or without residual charge (Determination of filtration efficiency by theoretical calculation was described in Supporting Information). In the absence of BTEAC, the PC fiber membranes with residual charge showed higher filtration efficiency than the PC one without residual charge, because the residual charge acted a role as static charge in electrets filter [Figure 9(a)]. In the presence of BTEAC, the filter efficiency of PC membrane was increased from 73% to 100% with increasing the residual charge in the membrane [Figure 9(b)]. The filtration by an electric charge was operated additionally in the presence of residual charge, while the particles were filtered by diffusion and interception effect in the absence of residual charge. This electric charge effect provides the enhanced filtration efficiency without increase in pressure drop. Actually the change in pressure drop was not observed in the presence of residual charge.

CONCLUSIONS

The PC fibrous membranes for filtration were obtained by electrospinning of PC/chloroform containing BTEAC, which is an additive to control the electrostatic performance of fibrous membrane. The addition of small amount of BTEAC to the PC solution caused a significant change in the average fiber diameters and in the residual charge on the fiber membrane. Also, the discharging behaviors of the electrospun PC membrane with residual charge were understood in terms of additive content, membrane thickness and atmospheric conditions. The PC fibrous membrane with BTEAC had an excellent filtration performance due to higher residual charge. Therefore, non-woven membranes of PC ultrafine fibers with BTEAC will be applicable to a filter for ultrafiltration.

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