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Processing and Properties of PTFE-FEP-PTFE Ferroelectret Films

M. GERARD, C. R. BOWEN,* AND F. H. OSMAN

Department of Mechanical Engineering, University of Bath, Bath, UK, BA2 7AY

This paper describes the manufacture of porous polytetrafluoroethylene (PTFE) and fluoroethylenepropylene (FEP) films by pressing PTFE-FEP-PTFE films between metallic meshes to produce a porous ferroelectret material. The influence of uniaxial pressing force and processing conditions (temperature and presence of a vacuum between the polymer films) on the as-formed ferroelectret film are assessed in terms on pore (void) height, distribution of pore height and film quality. The piezoelectric d_{33} coefficient (charge per unit force) of polarised films is measured and related to pore height and film quality.

Keywords Ferroelectret; piezoelectric; polymer; processing

Introduction

Ferroelectrets [1–9] are polymeric materials that contain microscopic voids or pores which are polarised by the application of a potential difference across the sample thickness. Polarisation is achieved by the direct application of an electric field to an electroded film or via corona poling [1] and leads to the generation of electrical charges of opposite polarity on the upper and lower surfaces of the voids. The presence of charged voids results in the material exhibiting piezoelectric behaviour, i.e. the development of a charge under a force or a strain under an applied electric field. Potential applications include flexible pressure sensors, acoustic sensors and ultrasonic transducers [3]. One of the most widely researched ferroelectret is cellular polypropylene fabricated by biaxial stretching and foaming of a polymer pre-form [2]. The poor thermal stability of this material has led to interest in other materials, such as porous polytetrafluoroethylene (PTFE) [3] and fluoroethylene-propylene (FEP) [4, 5] along with the development of new processing methods to produce a suitable pore size and morphology. Altafim et al. [4, 5] formed FEP films with millimetre sized voids with two FEP films stacked on a metallic mesh grid. A vacuum was used to draw the polymer into the metallic mesh and create the appropriate sized voids. Zhang et al. [6–8] proposed a simple method of creating fused fluorocarbon layers with gas voids at the interface of the layers. A three layer PTFE-FEP-PTFE was manufactured by placing a metal mesh on top of the film stack and applying a 20 N force at 280°C. The polarised material was thermally stable up to 90°C but exhibited some variability in

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*Corresponding author. E-mail: c.r.bowen@bath.ac.uk

piezoelectric coefficients, indicating a need to improve the reproducibility of the as-formed films.

This paper examines the processing conditions to form PTFE-FEP-PTFE ferroelectret films, with an emphasis on the influence of processing parameters such as pressing force, temperature and the presence of a vacuum on void height and the distribution of void heights (film quality). The as-formed PTFE-FEP-PTFE ferroelectret films are polarised and characterised to assess the influence of void height and film quality on the measured piezoelectric properties (d_{33}).

Experimental

Ferroelectret films were manufactured using the process of Zhang et al. [6]. Polymer films of 25 μm thick PTFE (RS Components) and 50 μm thick FEP (Adtech Polymers) were arranged in a three layer stack to form a PTFE-FEP-PTFE film. The 45 $\times$ 45 mm films were sandwiched between two steel perforated mesh plates ($\sim$1 mm thick) as in Fig. 1 which contained holes 1.2 mm diameter with a 1.7 mm spacing. Alignment pins ensured the holes of the upper and lower mesh plates were in the same position. A compressive force was applied to both the metal mesh and polymer films in a screw press and the sample heated to 255–260°C. This temperature was based on initial peel testing of the films; the bond strength was zero below 200°C and increased to 3 N at 260°C. Temperatures above 280°C damaged the polymer film. Samples were prepared at forces of 175–1575 N to evaluate the influence of applied force on pore (void) height and film quality (variability of void height). The 175–1575 N range was based on initial observations that no voids were formed below 175 N and that large voids were damaged above 1575 N. To facilitate void formation, a vacuum system was used in some cases to draw the outer PTFE layers into the holes of the mesh.

Once formed, gold electrodes were applied to the porous PTFE-FEP-PTFE films using chemical vapour deposition. Electroded films were corona poled at 25°C with a potential of 28 kV and a tip height of 7 cm. The d_{33} coefficients were measured via a Berlincourt Piezometer which applies a $\sim$0.1 N oscillating force to the film and measures the charge produced. A circular loading head with a diameter of 5 mm was used with the piezometer so that a relatively large region (and large number of voids) was tested and ten measurements

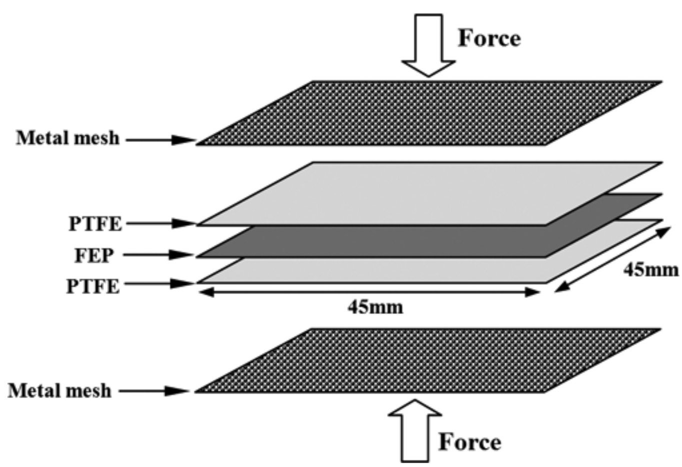

Figure 1. PTFE-FEP-PTFE lay-up and pressing configuration.

were made for each sample. Void height was measured using a non-contact profilometer. Cut and sectioned bubbles were examined using Scanning Electron Microscopy (SEM).

Results and Discussion

Figures 2a–d show cross section SEM images of the PTFE-FEP-PTFE layer films formed with no vacuum applied at applied loads of 175 N, 525 N, 875 and 1225 N. Figs. 2e–f shown cross sections of films produced using a combined load and vacuum at applied loads of 525 N and 1225 N. The loads necessary to form voids in this work are significantly higher than the load of ∼20 N reported by Zhang [6–8]. Since the sample areas are 45 mm^2 in both cases the need for higher pressing loads in this work may be due to the thinner PTFE (3 μm) and FEP (12.7 μm) films used by Zhang [6–8]. While the void diameter is purely dependent on mesh hole diameter, the SEM images in Fig. 2 show, qualitatively, that there is an increase in the void height as the processing load is increased. Although the ferroelectrets consist of three polymer layers (PTFE-FEP-PTFE) it is clear that most

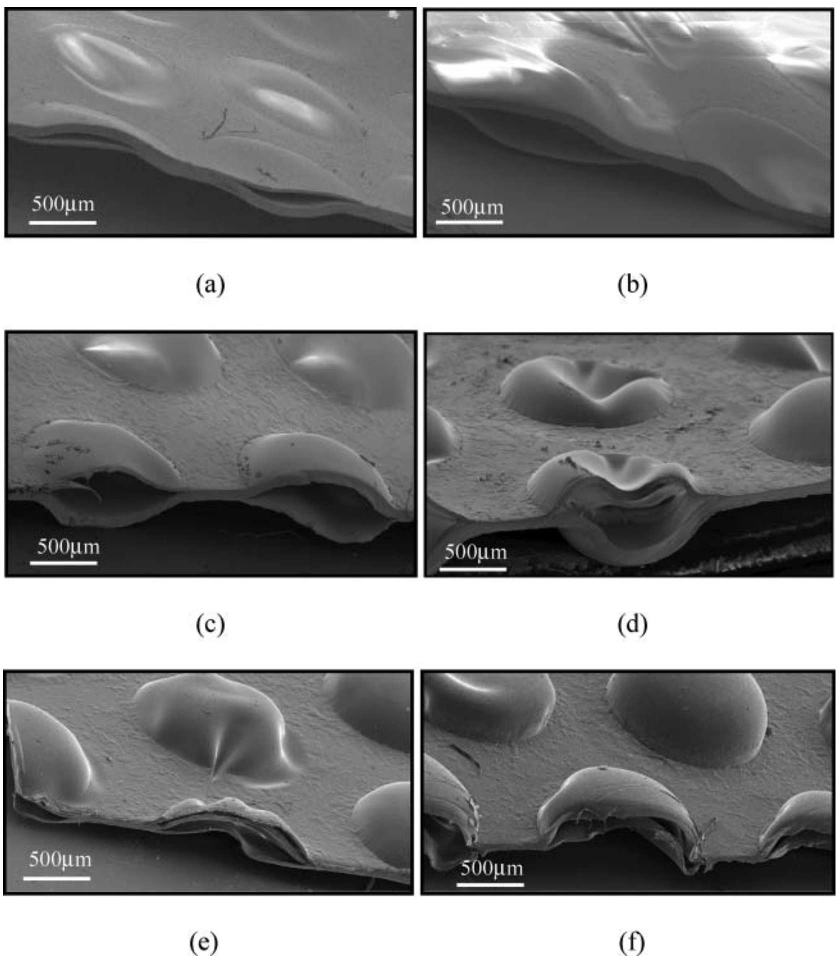

Figure 2. SEM images (a) 175 N (b) 525 N (c) 875 N (d) 1225 N (e) 525 N (vacuum) (f) 875 N (vacuum).

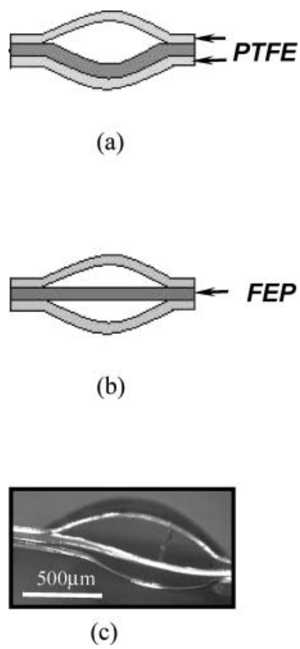

Figure 3. (a) Single bubble, (b) double bubble, (c) optical of double void (525 N/vacuum).

of the voids in Fig. 2 are single voids due the central FEP layer adhering to the top or bottom layer of the PTFE, as in Fig. 3a. Two voids, formed around a central FEP layer, as in Fig. 3b, could only be observed in the samples prepared using a vacuum at 525 N (Figs. 2e and 3c). Measurements of void height and piezoelectric d_{33} coefficient are summarised in Fig. 4 (error bars represent the standard deviation). As observed by SEM, void height increases with applied force. The application of a vacuum to draw the outer PTFE films into the metallic mesh leads to larger mean void heights compared to the non-vacuum samples formed at the same force. For vacuum formed pores the variability of void heights was also generally smaller, although some asymmetry of the voids can be observed which may be the result of an uneven vacuum pressure between upper and lower mesh plates. Generally larger voids lead to high piezoelectric d_{33} coefficients, although the d_{33} exhibited relatively large standard deviations. The variability of piezoelectric coefficient may be related to the distribution of void heights since it leads to the force being unevenly distributed between voids during the d_{33} measurement. The vacuum formed films exhibited smaller, but more consistent, d_{33} coefficients compared to the non-vacuum formed films and is thought to be due the applied load being more evenly distributed between voids during d_{33} testing. The vacuum formed PTFE-FEP-PTFE at 525 N produced the most regular void height and a piezoelectric d_{33} coefficient with the smallest standard deviation (Fig. 4). This was also the sample that produced the two void structures (see Figs. 2e and 3c).

Conclusions

This paper has examined the influence of processing conditions on the formation of PTFE-FEP-PTFE polymer films for ferroelectret applications. Void height increased with increasing pressing force and the use of a vacuum to draw the polymer film into the mesh

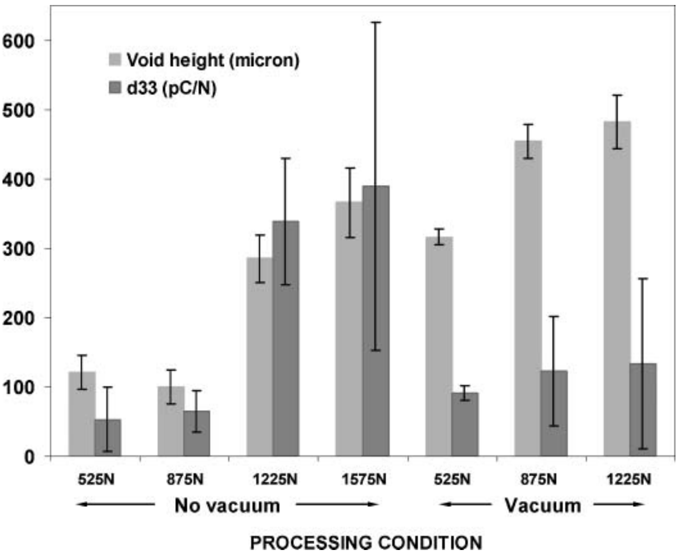

Figure 4. Void height and d_{33} for different processing conditions. Error bars represent standard deviation.

facilitated the formation of more regular void dimensions. The variability in piezoelectric d_{33} coefficient was thought to be due to the variability in void dimensions and non-uniform distribution of force in the charged voids during the measurement of the d_{33} coefficient. Single voids were often formed with the FEP film adhering to the top or bottom layer of the PTFE (Fig. 3a), although two voids (Fig. 3b) were formed under the application of a vacuum at 525 N. This particular sample also exhibited the smallest standard deviation of void height and most consistent d_{33} coefficient. Optimisation of processing conditions (pressure, temperature and application of a vacuum) to develop a homogeneous structure and void shape is therefore vital for the fabrication of PTFE-FEP-PTFE ferroelectrets with consistent piezoelectric properties.

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