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Fabrication of Biopolymer-Based Piezoelectric Thin Film From Chitosan Using Solvent Casting Method

Nadia Syauqi Syahid Mohammed[1], Maziati Akmal Mat Harttar[2,*], Farah Ahmad[1]

[1] Department of Biotechnology Engineering, Kulliyyah of Engineering, International Islamic University Malaysia (IIUM), 53100 Kuala Lumpur, Malaysia
[2] Department of Science in Engineering, Kulliyyah of Engineering, International Islamic University Malaysia (IIUM), 53100 Kuala Lumpur, Malaysia

ABSTRACT

The application of biopolymer in piezoelectric application provides a great potential to replace traditional piezoelectric substances like polyvinylidene fluoride (PVDF) and lead zirconate titanium (PZT), because of their biodegradability, biocompatibility, low toxicity properties and sustainable production. Chitosan, a natural polysaccharide has been found to fulfil all the characteristics and can be used safely for piezoelectric applications in agricultural, food industries and biomedical fields. This study aims to assess how piezoelectric characteristics are affected by different acid solvents and solvent casting volumes during chitosan thin film production. Chitosan thin film prepared using acetic acid and formic acid were fabricated using solvent casting method on petri dish at different volume of acids solvent. Chitosan thin films produced using acetic acid and 25 mL solvent loading provided the most significant mechanical quality factor (2.8). Moreover, the dissipation factor (0.80) was the lowest, indicating comparability to traditional thin PVDF film piezopolymer. Hence, thin chitosan films produced using acetic acid is proven to have the potential in piezoelectric application.

Keywords:
Biopolymer, chitosan, piezoelectric,
thin film, solvent casting

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1. Introduction

The piezoelectric effect is a mechanical stress to electrical energy transformation based on the non-centrosymmetric presence in piezoelectric substances [1]. The mechanical stress applied on the piezoelectric material causes the balance of the ions in the crystal structure to shifts, hence creating dipole moment [2-3].

Polyvinylidene fluoride (PVDF) and lead zirconate-titanate (PZT) from synthetic polymer and piezoceramics are widely known piezoelectric materials. Irrespective of PZT's excellent piezoelectric properties as it demonstrates potent piezoelectric ability (200-350 pC/N) [4], the application of PZT in biomedical field is very limited [2] because of its brittleness, rigidity, lack of design flexibility and

**Corresponding Author*
E-mail address: maziatiakmal@iium.edu.my

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toxicity [5- 6]. In addition, the limitation of PVDF in the application of tissue engineering is due to its non-biodegradability [5].

Thus, recent advancement in technology has found new biomaterial that is biodegradable, biocompatible and lead-free piezoelectric material, which can be utilized in biomedical field. Chitosan, a renewable source of natural biodegradable polymers can be produced from crustacean exoskeletons commercially and from fungal cell wall [7-9]. Furthermore, chitosan for piezoelectric application particularly for biomedical sensor devices can be promising because of its biodegradability, biocompatibility, and low toxicity. Yet, the studies of chitosan-based piezoelectric material are very limited.

Hence, this study intends to assess how formic and acetic acids affect the fabrication of thin chitosan films, including solvent casting volume and its effects on the film's electrical properties during production. Chitosan thin films fabricated using solvent casting method were analyzed for its piezoelectric properties, namely, dissipation factor (*tan δ*) and mechanical quality (Q_m) factors, as well as physical, chemical, and structural characteristics of fabricated thin chitosan films.

2. Methodology

2.1 Chitosan thin film production

1 g of chitosan powder were dissolved in diluted 0.25 M of acetic acid and formic acid, separately to obtain 1% (w/v) of final chitosan solution concentration. After 3 hours of heating and stirring on a hot plate at 600 rpm, the solvent was casted on petri dishes at volume 20 mL, 25 mL, and 30 mL before left dried in the dryer for 4-5 hours at 60 °C.

2.2 Piezoelectric characteristics of thin chitosan films

A thin film specimen was attached to a handheld LCR apparatus (Keysight U1730C); a copper wire was used for conduction. Dissipation (*tan δ*) and mechanical quality (Q_m) factors were measured and recorded at a constant frequency of 10 kHz.

2.3 Chitosan thin film characterization

2.3.1 Chemical characteristics

The Fourier transform infrared spectroscopy (FTIR) analysis confirmed the functional groups of chitosan present in the chitosan thin films produced from acetic and formic acids. The absorbance spectra belonged to the $\lambda = 4000$ cm^{-1} to 400 cm^{-1} spectral range at 2 cm^{-1} resolution and 16 scans at room temperature. X-ray diffraction (XRD) was also performed on chitosan powder and chitosan thin films produced from acetic and formic acids. X-Ray Diffractometer comprising $\lambda = 1.5406$ Å Cu-Kα radiation and angular scan of 2θ between 5° to 55° was used for analysis.

2.3.2 Physical and structural properties.

The average thickness of chitosan thin film prepared at different volume were measured using digital micrometre gauge. The structure and morphology of the thin chitosan film surface were visualized using scanning electron microscopy (SEM) and ICON ANALYTICAL, FEI (QUANTA 200 systems) configured to 2000x magnification. Porosity test of chitosan thin films were conducted using liquid displacement method by Grabska-Zielińska *et al.*, [10]. Isopropanol was used as the solvent for the porosity test as it could not dissolve the specimens. Chitosan thin films were placed inside a

cylinder having a fixed volume (V_1) of isopropanol for 3 minutes, followed by isopropanol volume measurement for the immersed sample (V_2) and after film removal (V_3). Thin film porosity (ε) was determined as specified in Equation 1.

$$Porosity, \varepsilon\ (\%) = \frac{V_1 - V_3}{V_2 - V_3} \times 100\% \quad (1)$$

3. Results

3.1 Chitosan thin film preparation from different organic acids

The prepared chitosan solutions were casted on petri dishes and thin film formed after drying are shown in Figure 1, where the chitosan thin films produced through both acetic and formic acids exhibited transparency and flexibility. At solvent casting volume of 25 mL and 30 mL for both acetate and formate chitosan thin films, the films appeared slightly yellowish. However, the films prepared at volume of 20 mL were almost colourless. The thin films prepared using formic acid were naturally peeled off while the films prepared using acetic acid were manually peeled as they attached to the petri dish. The ability of the films to peel-off is a good indicator on the binding and interfacial strength.

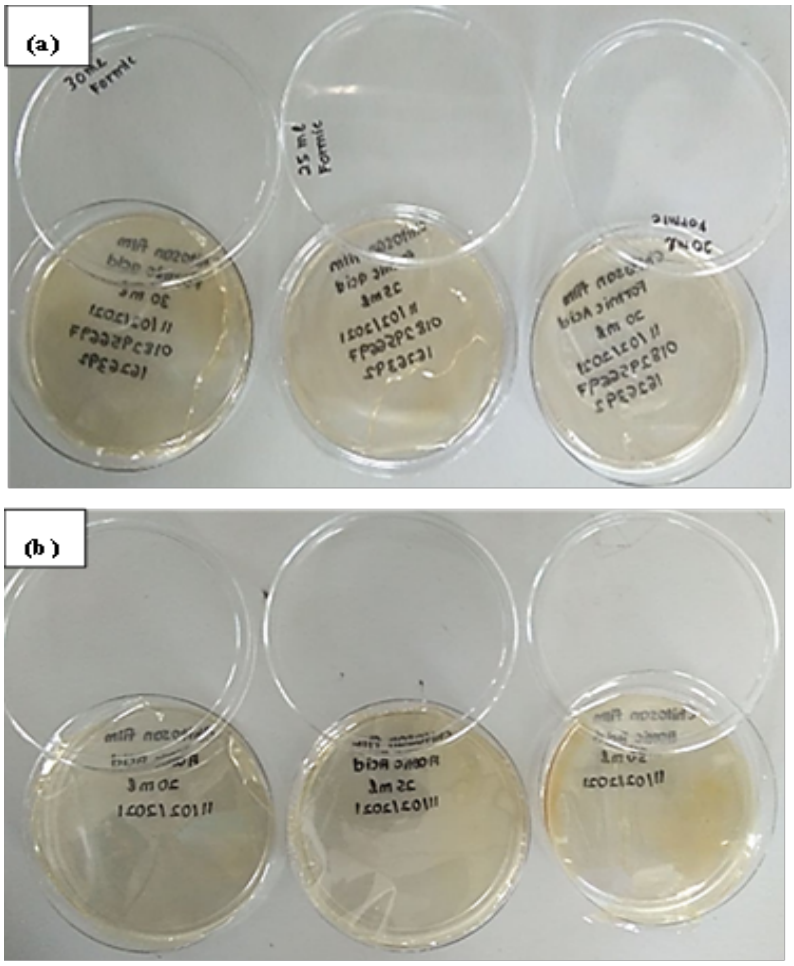

Fig. 1. Thin chitosan films produced through varying solvents volumes of 20, 25 and 30 mL of (a) formic acid, (b) acetic acid

The two carboxylic acids used in this study, formic acid (CHOOH) and acetic acid (CH_3COOH), differs in the length of carbon chain. A study conducted by Praveen et al., (2017) on chitosan thin film prepared using different weak acids for piezoelectric applications showed that chitosan thin film prepared using formic acid is more flexible [11]. Furthermore, the study also found that chitosan thin film prepared using formic acid provided good sensitivity for vibration sensor in comparison to chitosan thin film prepared from other weak acids [9].

3.2 Piezoelectric properties of acetate and formate chitosan thin films

The mechanical quality factor (Q_m) is a measure of the stored energy ratio per energy dissipated [12], which is related to the mechanical losses. Meanwhile, the dissipation factor (*tan δ*) assesses how much energy is lost during a mechanical, electrical, or electromechanical oscillation in a dissipative system [12]. The dissipation factor is the inverse of quality factor, which stands for mechanical's "quality" or durability [13]. A good piezoelectric material is expected to exhibit high Q_m value (around 10-100 for biopolymer) as it indicates the less damping and heat generation during energy conversion [13-15]. The results of Q_m and *tan δ* of chitosan thin films are presented in Figure 2 and 3, respectively. The highest average reading for mechanical quality factor (Q_m) was recorded by chitosan film prepared from acetic acid at 25 mL, followed by acetic acid at 20 mL and acetic acid at 30 mL. The chitosan films prepared from formic acid at 3 different volumes also shows similar trends with chitosan films prepared from acetic acid, where the highest average reading for Q_m were recorded by chitosan films prepared at volume of 25 mL, followed by 20 mL and 30 mL. In comparison with chitosan thin film prepared by acetic acid and formic acid, the films prepared by acetic acid shows the highest average reading of Q_m. The lowest average reading of dissipation factor was recorded by chitosan prepared by acetic acid than that of formic acid.

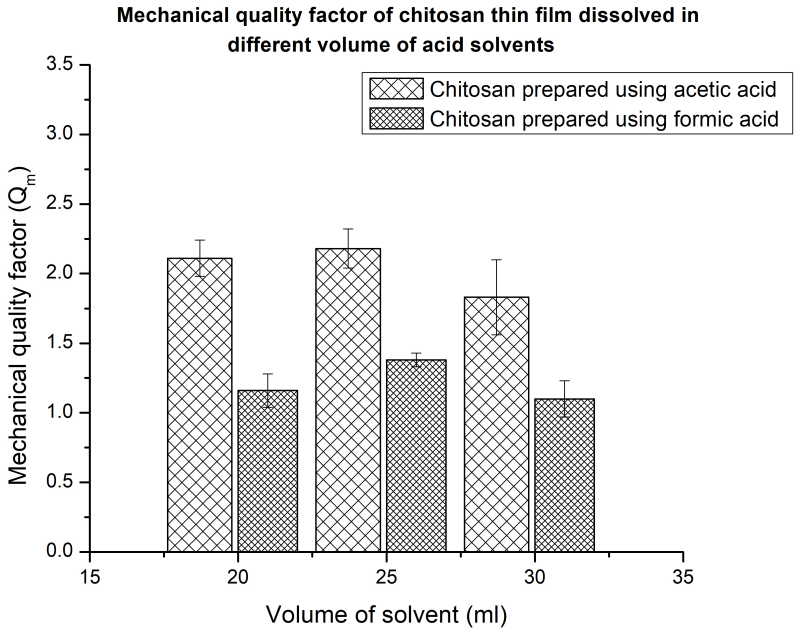

Fig. 2. Mechanical quality factor (*Qm*) of chitosan thin film prepared using acetic acid and formic acid at different solvent-casting volume

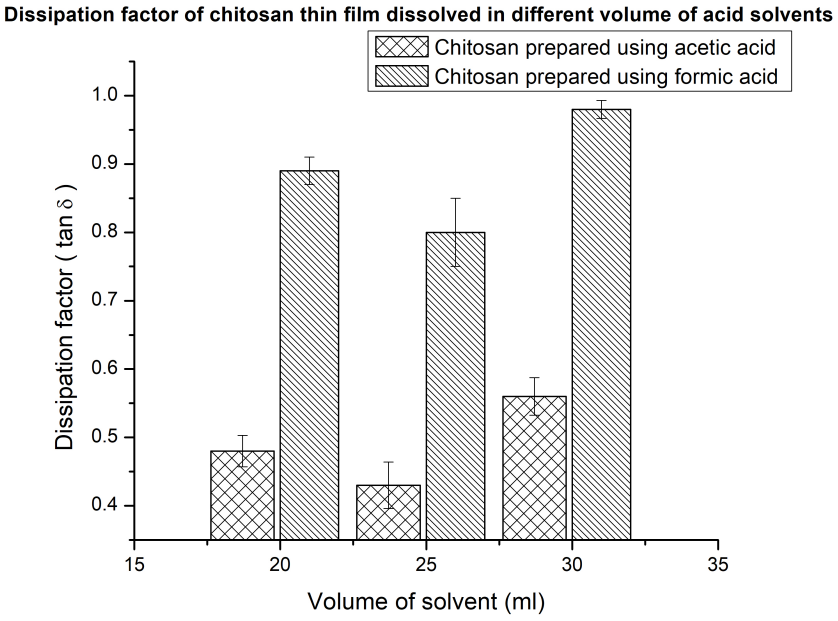

Fig. 3. Dissipation factor *(tan δ*) of thin chitosan film produced using acetic and formic acids at different solvent-casting volumes

Dissipation factor is a measure of energy lost during the reversal of electric polarization and expressed as a fractional energy loss [17]. The lower the dielectric constant (*κ*) and dissipation factor, the less energy is absorbed from an electric field [18]. Therefore, for excellent piezoelectric application, the value of dissipation factor should be low.

Chitosan thin film prepared from acetic acid at volume of 25 mL recorded the highest reading of Q_m (2.89) and the lowest reading of *tan δ* (0.8) (Table 1). The resulting trend in the mechanical quality factor and dissipation factor of the chitosan film is likely the result of the generation of conduction electrons, which increases the localised charge carriers and improves the efficiency of energy conversion while decreasing dielectric loss [19]. On the contrary, low mechanical quality factor of the synthetic polymer is attributed to the diminish in charge carriers within the polymeric structure of PVDF, which caused an abrupt increase the dissipation factor. Intriguingly, the quality factor and dissipation factor obtained in this study is slightly higher than the reported value of commercial synthetic polymer (PVDF). Hence, biopolymer chitosan thin film has a great potential to substitute synthetic polymer for piezoelectric application.

Table 1
Dissipation (tan *δ*) and mechanical quality (Q_m) factors for the thin chitosan film obtained in this study in comparison to PVDF film as conventional piezoelectric polymer

Thin film	Mechanical quality factor (*Qm*)	Dissipation factor (tan *δ)*	Reference
Chitosan	2.81	0.43	Current study
PVDF	0.018	-	[14]
PVDF	-	0.05	[15]
PVDF	10	-	[16]

3.3 Chemical properties of acetate and formate chitosan thin films

Fourier transform infrared spectroscopy (FTIR) evaluation of thin chitosan film prepared from acetic acid and formic acid were presented in Figure 4. Based on the FTIR spectra, acetate chitosan film had peak bands at 3278 cm^{-1}, while formate chitosan film exhibited peaks at 3251.47 cm^{-1}. These peaks indicate intermolecular hydrogen bonding of chitosan molecules. The 1584 cm^{-1} peak for formic, and 1635 cm^{-1} peak for acetic acid-based thin chitosan films exhibited C=C stretching corresponding to Amide I area. Amide III area exhibited aromatic C=C stretching for formic and acetic acid-based chitosan films, as depicted by the 1380 cm^{-1} and 1410 cm^{-1} band peaks.

The peak shifts to a lower frequency range in chitosan films prepared using acetic and formic acid, which could be attributed to varying matrix interactions like the interaction of the acid proton with the nitrogen atom of the amine group of chitosan, inter-molecular reorganisation, and changes in primary chain configuration [20].

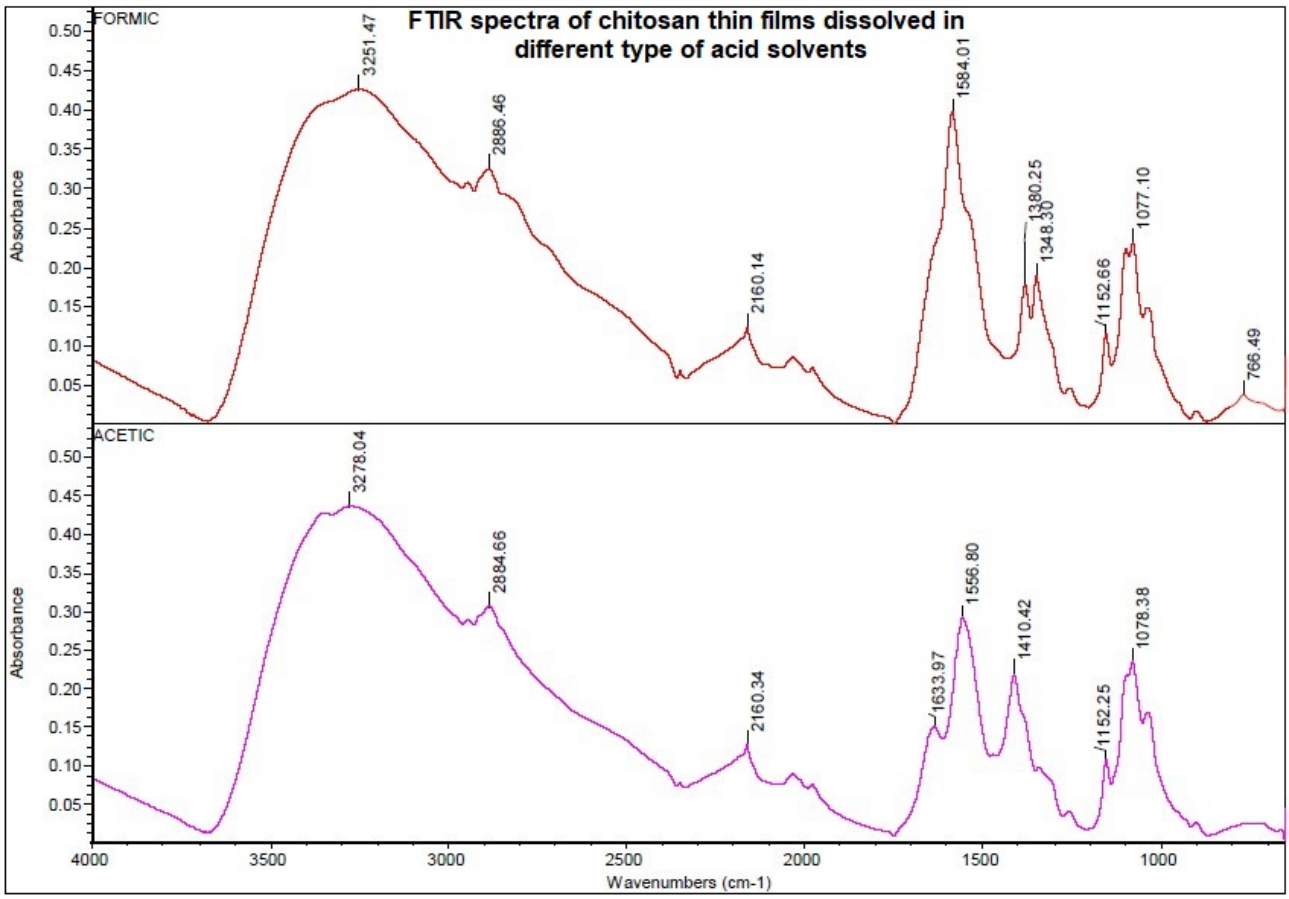

Fig. 4. FTIR spectra of chitosan thin film produced based on (a) acetic and (b) formic acid

Figure 5 depicts the crystallinity of chitosan in a form of powder (before dissolution in acid solvents) and thin film (after dissolution in acid solvents). XRD analysis conducted on chitosan powder showed a quite sharp and narrow diffraction peaks around 20° indicating semi crystallinity of chitosan powder. The similar result was obtained for chitosan thin films prepared from acetic acid and formic acid solutions. According to El Zawawi et al., hydroxyl and -$NH3^{+}$ groups have intermolecular interactions in chitosan, reducing chitosan chain molecular movement ability [20]. Moreover, the development of intra- and intermolecular hydrogen bonds might have been inhibited by the presence of the acid counter-ions that caused difficulty to obtain the closed-packed arrangement required for

crystallization hence leads to the semicrystalline structure of chitosan [20]. Furthermore, the presence of excess acid might also contribute to the decreased of the crystallinity of films [18].

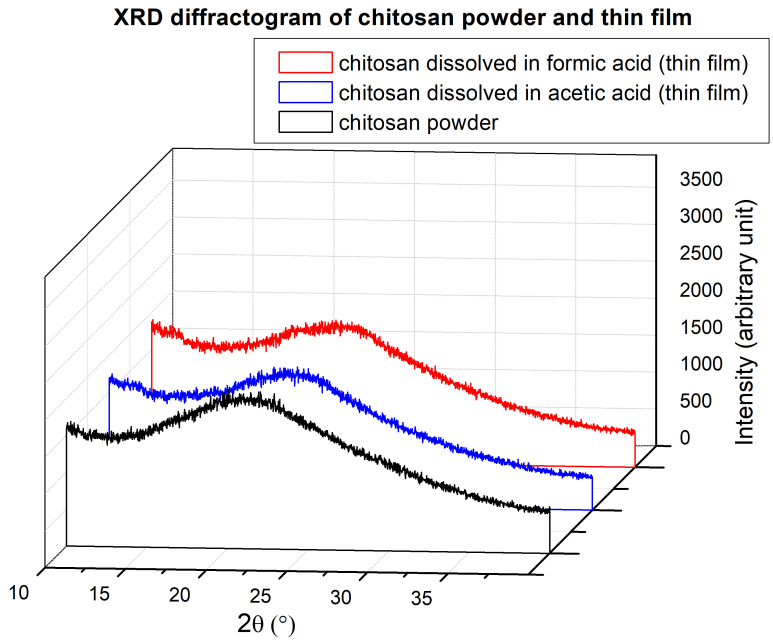

Fig. 5. XRD analysis of (a) chitosan powder and chitosan thin film prepared from (b) acetic acid and (c) formic acid

3.4 Physical and structural properties of acetate and formate chitosan thin films

The average thickness of thin chitosan film produced using acetic acid and formic acid at volume of 20 mL, 25 mL and 30 mL is showed in Figure 6. A similar trend was exhibited for both acetate and formate chitosan films, whereby the thickness was increased as the volume of chitosan was increased. Thin-film thickness is a key parameter that could enhance the crystallinity and enhance the film's piezoelectric characteristics [21].

Figure 7 shows the results of SEM analysis conducted for assessing chitosan films' morphology. SEM micrographs of chitosan thin films revealed homogeneous structure with no pores or cracks on the surface regardless of the acid solvents used. The result of SEM analysis for formic and acetic acid-based chitosan thin films in this study were comparable to the result obtained in the previous study conducted by [22], where the author concluded the result obtained show acid-based thin chitosan films exhibit a smooth and homogenous surface. Besides, the similar structure also can be found for other chitosan thin films dissolved in hydroxylated acid films such as lactic acid, citric acid and tartaric acid [23-24]. This occurrence can be explained by the strong intermolecular interaction between chitosan molecules and hydroxylated acid counter anions, which promoted the densification of the chitosan matrix and, as a result, could improve the homogeneity of the chitosan structure [25]. It is worth noting that the uniform chitosan matrix is an indicator of the structural integrity of the observed films, resulting in sufficient piezoelectric characteristics.

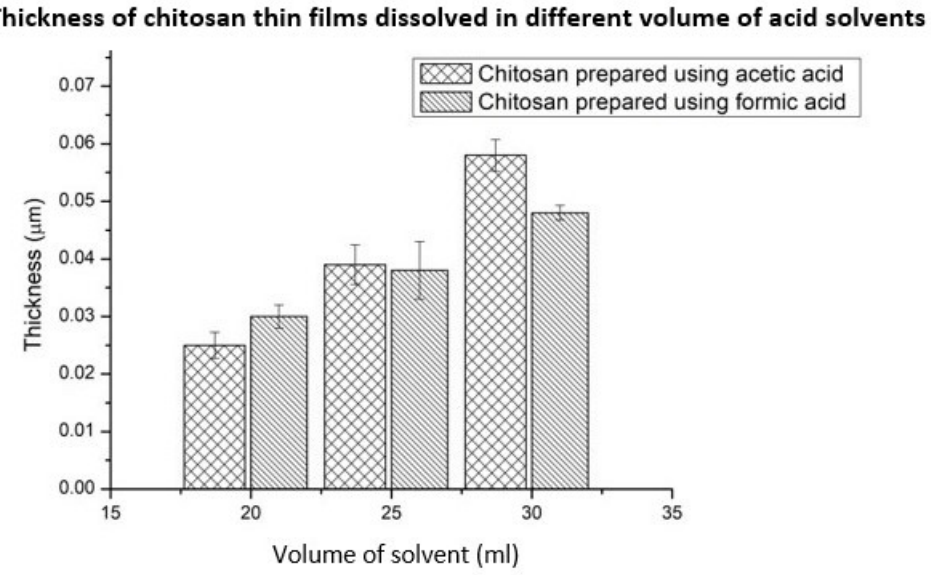

Fig. 6. Average thickness of thin chitosan films produced using acetic and formic acid

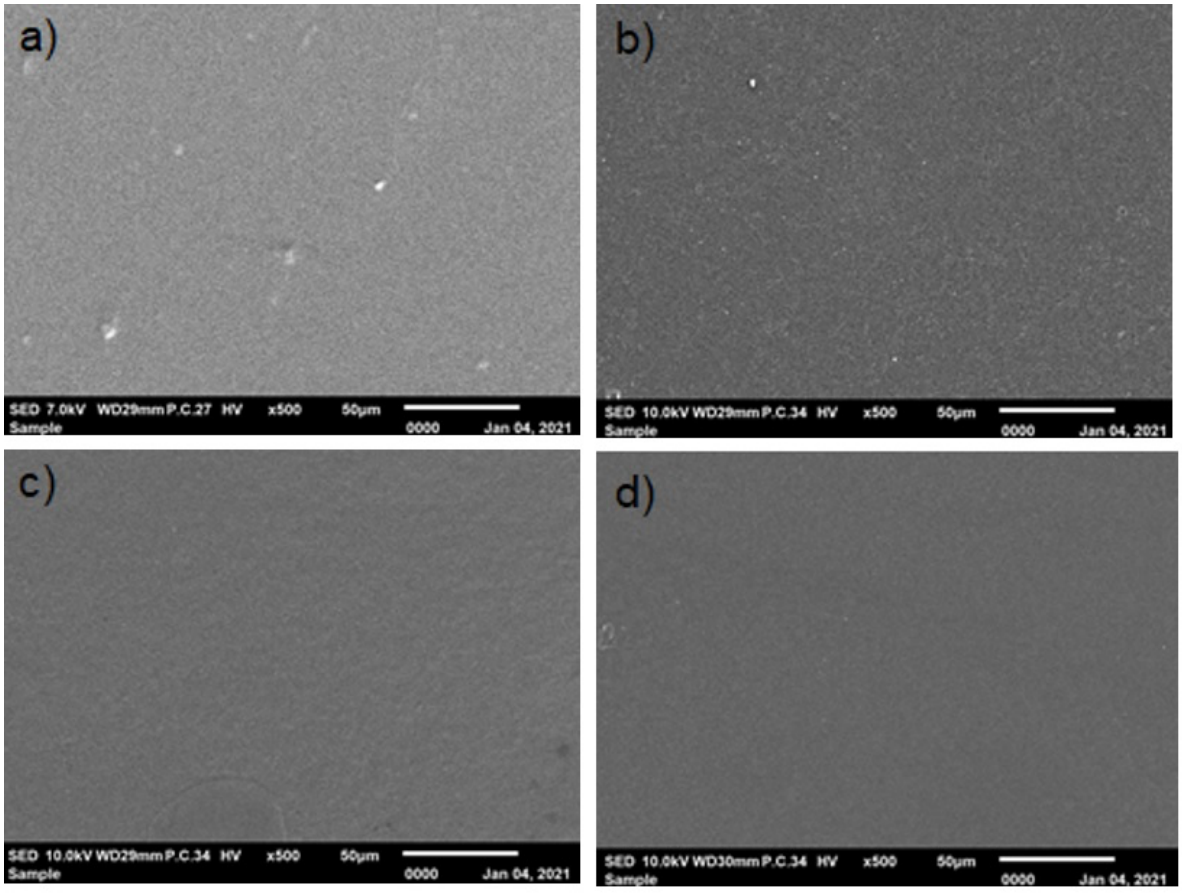

Fig. 7. SEM images of surface morphology of thin chitosan film produced using acetic acid at (a) 25 mL and (b) 30 mL and formic acid at (c) 25 mL and (d) 30

The result of porosity test conducted on thin chitosan films produced using acetic and formic acids at volume of 25 mL (Table 2) shows that acetic acid produces a less porous (80%) film than

formic acid (90%). The more porous the film will result in more current leakage [10][17]. Since the result of Q_m for the thin chitosan film produced by acetic acid is more than that produced using formic acid, thus it is expected to have less porous structure as the result obtained.

Table 2
Porosity assessment of chitosan thin film produced using acetic and formic acids at 25 mL of solvent-casting volumes

Type of thin film	Porosity (%)
Acetate chitosan film	80
Formate chitosan film	96

4. Conclusions

Acetic acid-based chitosan film prepared using a volume of 25 mL can be said to have a potential application for piezoelectric biomaterial due to high Q_m and low *tan δ*. Further characterization of chitosan thin films using XRD reveals semicrystalline diffraction patterns for both thin films prepared with acetic and formic acids, while SEM analysis revealed homogeneous and smooth surfaces with no abnormalities and defects detected. The outcomes of porosity assessment demonstrated that chitosan film produced using formic acid has more porosity than acetic acid-based film.

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