Extraction of microbial chitosan for piezoelectric application

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Abstract. Chitosan is a natural polysaccharide derived from chitin which is found in the fungus cell walls and crustacean shells. Chitosan has generated a great interest in piezoelectric application because of its interesting properties such as biodegradability, biocompatibility, and low toxicity. The purpose of this study is to focus on the cultivation, fabrication and characterization of chitosan thin film from fungal strain, Aspergillus oryzae cell walls. The fungi was cultivated in bioreactor. Fabrication of chitosan thin film via solvent casting method was optimized via one-factor-at-a-time (OFAT) with 2 parameters (drop-casting volume of solution and drying temperature). Pure chitosan dissolved in formic acid at 0.25 M concentration, dried at 60˚C with 35 mL of solution volume gave the highest mechanical quality factor (3.22) and the lowest dissipation factor (0.327) for thin film fabrication. The optimized fabricate thin film was validated using fungal chitosan and shows the results of mechanical quality factor (3.68) and dissipation factor (0.248) which is comparable to conventional piezopolymer thin film. Therefore, fungal chitosan thin film obtained in this study has the potential to be used in piezoelectric application.

1. Introduction

Recently, chitosan has also been used as a natural substance for the application of piezoelectric in sensor devices [2]. Piezoelectric materials have the ability to convert the mechanical stress into electrical charge. The existence of non-centrosymmetric in chitosan’s crystalline structure exert piezoelectricity [11, 13]. Crystalline structure of piezoelectric crystals consists of ions that are compacted to occupy positions in a specific repeating relationship to each other, thus exhibit piezoelectricity [17]. The conventional piezoelectric materials include piezocermics such as lead zirconium titanate (PZT) and piezoelectric polymer such as poly (vinylidene fluoride) (PVDF), exhibit large piezoelectric effects [7]. These materials are widely used as commercialized actuators and sensors in intelligent systems and smart structures [7]. However, the high lead content in PZT has become a concern which can affect the health of humans, especially in the application of implantable biomedical devices, such as piezoelectric-based pacemakers. Piezoelectric polymers (e.g., PVDF) are more flexible, non-toxic and produce high piezoelectricity [15]. However, PVDF is also considered as a non-biodegradable polymer, the raw material is expensive and its synthesis releases toxic gases.

Bio-based functional materials have been studied for its piezoelectric behaviour [4]. Chitosan is also a biomaterial and a renewable source of natural biodegradable polymers which are also second most abundant polymers after cellulose. Commercially, it is produced from waste crustacean exoskeletons such as crabs and shrimps, as well as fungal cell wall [9].This study focused on the optimization the thin film fabrication by observing the piezoelectric coefficient, electromechanical coupling factor and
tensile strength. The thin film fabricated could be further used in piezoelectric application either in energy harvesting or sensing.

2. Materials and method

2.1. Fungal cultivation and chitosan extraction

The fungi strain *Aspergillus oryzae* was grown on potato dextrose agar (PDA) in a petri dish and was incubated at 25°C for 5 days. The pre-inoculum was cultured in the mixture of media that consist of 30 g/L glucose, 3 g/L peptone and 300 mL of distilled water [1]. The prepared media was transferred into a 2 L bioreactor with controlled parameters [14]. Extraction of chitosan from *Aspergillus oryzae* via alkaline treatment (sodium hydroxide (NaOH)) and acidic treatment (acetic acid) using method Abdel-Gawad et al. [1]. The extracted chitosan yield was calculated from the following Eq. (1):

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\text{Chitosan yield (\%)} = \frac{\text{dry weight of extracted chitosan}}{\text{dry weight of sample}} \times 100\%
\] (1)

2.2. Optimization of thin film fabrication

Chitosan thin film fabrication via solvent casting method using formic acid (2.5 M) was optimized via OFAT. The parameters of OFAT were (1) drop-cast volume of chitosan solution and (2) drying temperature. The response factors analysed in this study were (1) mechanical quality factor \((Q_m)\) and (2) dissipation factor \((\tan \delta)\). The range for volume of chitosan solution, drying temperature and acid solvent concentration were chosen based on the previous study [12].

1 g of pure chitosan was dissolved into 99 mL formic acid solution (1% v/v) followed by solvent casting onto petri dish at different volumes of chitosan solution. The drying temperature and acid solvent concentration were kept constant at 60°C and 0.25 M respectively [12]. After the volume of solution was chosen based on the best results, the drying temperature was varied (50°C, 60°C and 70°C). The thin film was peeled off naturally after 3-4 hours of drying. The optimum parameters were used in the fabrication of fungal chitosan thin film.

2.3. Characterization of pure and fungal chitosan thin film

2.3.1. Chemical properties. A Fourier-transform infrared spectroscopy (FTIR) was performed in the middle infrared region (4000 cm\(^{-1}\) to 400 cm\(^{-1}\)) with a resolution of 4 cm\(^{-1}\) in the transmittance and absorbance mode for 16 scans at room temperature [8].

2.3.2. Electrical properties. Thin film sample was connected to the Keysight U1730C Series handheld LCR meter via copper wire as conductance and charged with a constant frequency (10 kHz). Mechanical quality factor \((Q_m)\), dielectric constant (relative permittivity) and dissipation factor \((\tan \delta)\) can be measured using a Keysight U1730C Series handheld LCR meter with the frequency at 10 kHz.

3. Results and discussion

3.1. Optimization of solvent-casting techniques for thin film fabrication via one-factor-at-a-time method (OFAT)

The production of chitosan thin film via solvent-casting technique was optimized via OFAT with two parameters which were (1) drop-casting volume of chitosan solution and (2) temperature of oven drying; and two responses which are (1) mechanical quality factor \((Q_m)\) and (2) dissipation factor \((\tan \delta)\). The thickness of thin film was optimized by controlling the drop casting volume of chitosan solution.
The result (Figure 1 (a) and (b)) of chitosan dissolved in formic acid with 35 mL showed the highest mechanical quality factor (3.22) and the lowest dissipation factor (0.327). Superior piezoelectric materials, such as PZT and PVDF, are expected to possess high mechanical quality factor owing to the ability to increase dipole moments orientation which leads to the improvement of piezoelectric response within the crystal unit in thin-film [3]. The highest mechanical quality factor ($Q_m$) obtained was 3.22. The increasing trend in $Q_m$ value might be related to the thickness of chitosan thin film, which was linearly increased and eventually, improved the densification and crystallinity of the chitosan thin film. The increment in crystallinity of the thin film can facilitate dipole-dipole movement. Therefore, it can lead to enhancement of piezoelectric response [15]. The reduction in the dissipation factor with increasing the chitosan thickness is likely due to the increment of localized charge carriers hence reducing the dissipation factor within the chitosan’s crystalline structure [17].

The drying temperature thin film was optimized by controlling the temperature of thin film drying treatment. Figure 1 ((c) and (d)) showed that the drying temperature of chitosan thin film at 60˚C showed the highest mechanical quality factor (3.22) and the lowest dissipation factor (0.327). Increasing the temperature can increase the dissipation factor that may give rise to the vibrations of the lattice and some phonons that are created which interact with the charge carriers, subsequently, giving
rise to electron-phonon scattering [6]. Therefore, the optimum parameters were drying temperature at 60˚C with 35 mL of drop-casting chitosan solution volume.

3.2. Characterization of fungal chitosan for piezoelectric application

3.2.1. Functional group via FTIR. Based on the FTIR spectra, the distinctive functional group for amide were observed at vibration bending peaks of 1587 cm\(^{-1}\) for fungal chitosan (Figure 2) which indicated the stretching vibrations of C=O group (Amide II). The presence of bands at the peak of 3366 cm\(^{-1}\) in fungal chitosan indicate the presence of intense dimeric OH stretch. The presence of bands at peak 1587 cm\(^{-1}\) in fungal chitosan can be attributed to the C=C stretching in Amide I region. The bands at peak 1419 cm\(^{-1}\) in fungal chitosan is due to the presence of aromatic C=C stretch in Amide III region.

![Figure 2. FTIR spectrum of fungal chitosan extracted from this study.](image)

3.2.2. Mechanical quality factor (Qm). Q\(_m\) values obtained for pure chitosan and fungal chitosan were 3.22 and 3.68, respectively (Table 1). The fungal chitosan showed slightly higher Q\(_m\) value compared to pure chitosan. This phenomenon could mean that fungal chitosan film has slightly higher efficiency to convert mechanical force into electrical force. The difference in Q\(_m\) reading for both films can be ascribed by the surface morphology’s factor that causes an abrupt decrease/increase in mechanical quality factor [5].

3.2.3. Dissipation factor (tan δ). The dissipation factor measurement was undertaken on pure chitosan and fungal chitosan thin films. The dissipation factor is a measure of loss-rate energy during the reversal of electric polarization. Table 1 showed the dissipation factor (tan δ) of pure chitosan and fungal chitosan was 0.327 and 0.248, respectively. Higher tan δ value for pure chitosan likely occurred to the increment of dipole moment interaction in the pure chitosan crystalline structure. In addition, less interaction of the phonons in the lattice structure due to some factors like surface inhomogeneity will result in low electron phonon scattering, thus increasing the dissipation factor of fungal chitosan [13].
Table 1. Mechanical quality factor and dissipation factor values of fungal chitosan compared film with pure chitosan from this study and benchmarked with polyvinylidene fluoride (PVDF) film [10, 16], which has been widely used in piezoelectric application.

| Piezoelectric film | Fungal chitosan | Pure chitosan | PVDF |
|--------------------|-----------------|---------------|------|
| Type of piezoelectric films | Biopolymer | Biopolymer | Synthetic polymer (conventional piezoelectric material) |
| Mechanical quality factor ($Q_m$) | 3.68 | 3.22 | ~4 – 10 |
| Dissipation factor ($\tan \delta$) | 0.248 | 0.327 | ~0.05 – 0.3 |

Fungal chitosan film obtained in this study was also benchmarked with polyvinylidene fluoride (PVDF) film (Table 1), which is a conventional piezoelectric polymer [16]. The results of $Q_m$ and $\tan \delta$ of chitosan thin films were comparable to conventional piezopolymer thin film. Therefore, fungal chitosan thin film obtained in this study has the potential to be used in piezoelectric application.

4. Conclusion

Fungal biomass of A. oryzae fungi that was cultivated in bioreactor was used for extraction and deacetylation via alkaline-weak acid treatment for the production of fungal chitosan. Chitosan thin film fabrication via solvent casting method was further optimized for maximum mechanical quality factor ($Q_m$), in which the optimum parameters selected were drying temperature at 60˚C with 35 mL of drop-casting chitosan solution volume. The characterization of chitosan thin films showed that the films were comparable with the commercial PVDF thin film. Therefore, this study revealed the potential of using fungal chitosan thin film as good biomaterial for piezoelectric application.

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