Enhancement of composite polymer piezoelectric materials and their potential engineering applications
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DOI:
10.33612/diss.1036422684

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2024

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Chapter 7

Conclusions and future work

7.1 Conclusions

Currently, flexible and wearable electronics have become an emerging technology with a strong impact in different engineering fields. Motion monitoring (tactile sensing), health monitoring, wearable energy harvesting, energy storage systems, and electronic skin are some of the examples of the potential applications for this technology. According to the report of IDTecEX [206], an independent market research company, the market size for printed, flexible electronics will reach $12 Billion by 2033, with the CAGR (Compound Annual Growth Rate) of 10%. Also, wearable technology devices’ market size has tripled between the years 2014 to 2022, and it is predicted to reach $161 billion by 2033 [207]. Reports of MarketsandMarkets website [208, 209] also corroborate this information, predicting CAGR of 8.8% and 18.0% respectively for the mentioned fields.

In this regard, piezoelectric transducers proved to be reliable, precise, and with fast response in comparison to other sensors. Therefore, flexible piezoelectric materials, such as Polyvinylidene fluoride (PVDF) and its copolymers, have a huge potential in this growing market. Flexibility and high piezoelectric response in comparison to other polymer piezoelectric materials are some of the advantages of PVDF. However, lack of large-scale fabrication methods and high piezoelectric properties, and the difficulty of obtaining β polar phase in PVDF is an obstacle on the way of industrialization of piezoelectric polymer materials [210]. Moreover, a comprehensive study of the composite properties and the impact of the fabrication process and doping agents within the system is missing. In this work, we aim to resolve these issues by introducing novel fabrication methods and presenting a deep study of the piezoelectric composites’ properties with higher sensing performance.

In chapter three, utilizing ultrasonic nozzle-less spray coating method for fabrication of PVDF films with high uniformity and performance is presented. This method offers the potential for easy scalability and large-scale fabrication. It is shown that by choosing proper parameters, PVDF films in polar phase and with high piezoelectric coefficient are produced, with no post processing required. The
reason for alignment of dipoles during the process of deposition is:
1. The shear effect of radial outward capillary force and the interaction between the polar solvent and PVDF chain that causes local conformation changes and the nucleation of polar phase.
2. High sound energy of the sonication in ultrasonic methods causes formation of the $\beta$ polar phase.

Later in this work, the observation that deposition of piezoelectric composite solutions using the spray coating method has limited benefits reinforces the validity of the initial argument. However, more experiments and studies are required to be performed in this regard. Moreover, for future study, the effect of environmental parameters, like temperature and humidity on the quality of produced films using ultrasonic spray coating method has to be investigated.

In chapter four, five, and six, the effect of adding nanofillers to the P(VDF-TrFE) piezoelectric polymer is studied. P(VDF-TrFE) is a copolymer of PVDF, with an easier polar phase formation. In these chapters, nanofillers of barium titanate, zinc oxide and hafnium zirconium oxide are added in different concentrations to the P(VDF-TrFE), using casting method. Afterwards, their piezoelectric properties and performance as sensors in different applications by focusing on wearable devices is presented and compared.

First, Barium titanate, one of the well-known and old piezoelectric ceramics with two different crystal structure (cubic and tetragonal) is added to P(VDF-TrFE). The optimal concentration of 10 wt% BaTiO$_3$ after applying surface modification methods is added to the P(VDF-TrFE) polymer. Considering the fact that ceramics piezoelectric materials possess positive piezoelectric coefficient, it is interesting to compare the performance of two composites that are made with tetragonal (piezoelectric) and cubic (dielectric) BaTiO$_3$ nanofillers. Tetragonal BaTiO$_3$ composites have a better performance in comparison to cubic one, and they show ferroelectric behavior at lower electric field. Since the composite samples are not poled, it is concluded that the better performance of these composites is attributed to better distribution of the nano fillers and therefore better mechanical properties such as less loss tangent, higher quality factor, hardness, and young’s modulus. The higher performance of tetragonal BaTiO$_3$ composites is further confirmed by performing an energy harvesting test on the human finger joint.

In chapter five, zinc oxide nanoparticles are used in P(VDF-TrFE). Zinc oxide is generally not considered as a ferroelectric material. However, the non-centro symmetric wurtzite structure of this material provides piezoelectric properties. For this reason, common electrical poling methods can be less effective for this material. In this work, after finding the optimal concentration of ZnO nanofiller (20 wt%) in P(VDF-TrFE), flexible piezoelectric sensors are made using casting and spray coat-
7.1. Conclusions

ing method. Addition of this filler disrupts polymer polar crystalline chain formation, but introduces stress at the interface that eventually results in some improvement in the final fabricated tactile sensors. Moreover, our studies present a high repeatability, and linearity of such sensors. The composites are successfully applied to the gripper of the robotic arm as a feedback sensor. Finally, we show that deposition of such sensors on a copper fabric makes it more comfortable to be used as a wearable sensor on a human body.

Another recently discovered piezoelectric material that got the attention of many researchers is hafnium. Due to difficulty of stabilizing this material in ferroelectric phase, it is used here as a dielectric nanoparticle. In chapter 6, the process of synthesizing the HZO particles is explained and the piezoelectric composites made by such nanofillers are used as a cantilever energy harvester. In this work, it is shown that the piezoelectric polymers can produce higher electric field in response to vibrations at lower frequencies. Such high-performance cantilever energy harvesters are promising for novel applications, particularly in IoT and biomedical technology realms. Piezoelectric hafnium has a negative piezoelectricity, similar to piezoelectric polymers. Therefore, we predict enhanced piezoelectric properties, when both are used. However, thus far, ferroelectric HZO has been observed only at nanoscale thin films. In the table below, the properties of different piezoelectric films made in this work are presented for the sake of comparison.

Table 7.1: Piezoelectric properties of PVDF, P(VDF-TrFE) and its composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (µm/m)</th>
<th>Pr (µC/cm²)</th>
<th>Ps (µC/cm²)</th>
<th>Ec (kV/cm)</th>
<th>d33 (pm/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF (sprayed)</td>
<td>9</td>
<td>15.2</td>
<td>16.97</td>
<td>1272</td>
<td>38.0</td>
</tr>
<tr>
<td>P(VDF-TrFE)</td>
<td>15</td>
<td>6.16</td>
<td>8.34</td>
<td>546</td>
<td>44.2</td>
</tr>
<tr>
<td>P(VDF-TrFE) 10 wt% BaTiO₃</td>
<td>19</td>
<td>6.18</td>
<td>7.81</td>
<td>537</td>
<td>47.4</td>
</tr>
<tr>
<td>P(VDF-TrFE) 20 wt% ZnO</td>
<td>17</td>
<td>5.98</td>
<td>7.65</td>
<td>567</td>
<td>48.9</td>
</tr>
<tr>
<td>P(VDF-TrFE) 5 wt% HZO</td>
<td>17.5</td>
<td>4.33</td>
<td>6.11</td>
<td>535</td>
<td>52.0</td>
</tr>
</tbody>
</table>

Despite improvement of piezoelectric properties in PVDF films fabricated by spray coating, the piezoelectric coefficient (d33) is lower than casted P(VDF-TrFE). This is due to better piezoelectric properties of P(VDF-TrFE). Though, the thickness can also play a role. By comparing the other composites with pure P(VDF-TrFE), it is evident that BaTiO₃ and HZO cause a decrease in coercive field, which can have