Highly Flexible Mechanical Energy Harvester Based on Nylon 11 Ferroelectric Nanocomposites

Farsa Ram,1,2 Sithara Radhakrishnan,1 Tushar Ambone,1 Kadhiravan Shanmuganathan1,2*

1Polymer Science and Engineering Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra-411008, India.

2Academy of Scientific and Innovative Research, CSIR- National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra-411008, India.

*email: k.shanmuganathan@ncl.res.in
**Experimental:**

*Determination of carboxylate content:* Conductometric titration was used to determine the carboxylic acid density of CNCs.\(^1\) Briefly, 6 mg/mL CNC dispersion was prepared in DI water by stirring and sonication. When the dispersion was stable, 10 mL was withdrawn and diluted to 100 mL with addition of deionized water. Conductivity meter was calibrated with standard buffer solutions. 50 µL of 11.65N HCl was added to the diluted CNC dispersion which resulted in agglomeration of CNCs due to protonation of carboxylic groups. Under continuous stirring this dispersion was titrated against 0.5M NaOH. The titration was repeated three times and the carboxylic acid charge density calculated as follows:

\[
\text{Charge density (mmol/kg)} = \frac{\text{Volume of NaOH} \times \text{molarity of NaOH}}{(1000 \times \text{mg of CNCs} \times 10^{-6})}
\]

The average carboxylic acid charge density was found to be ~600 mmol/kg

---

**Figure S1:** Calculation of carboxyl content on CNCs.
Preparation of NY and NYC via solution casting approach:

**Scheme S1:** Preparation of brittle nylon 11 and nylon 11/CNC film.
Fabrication of flexible piezoelectric nanogenerators:

**Scheme S2:** Fabrication of piezoelectric nanogenerators.

**Figure S2:** FTIR of cellulose nanocrystals.
**Figure S3:** Transmission electron microscopic image of CNC.

**Figure S4:** WAXD and FTIR of 8 NYC films.
Figure S5: DSC analysis of solution casted NY and NYC films (first heating cycle, scan rate - 10º C/min).
Field Emission- Scanning Electron Microscopic (FE-SEM) images: NYG and 5NYCG films and their cross sections mounted on stub using conductive carbon tape. The samples were gold coated prior to FE-SEM analysis. Morphology of the films and their cross sections were imaged using the Nova Nano FE-SEM 450 microscope operating at an accelerating voltage of 5-30 kV.

Figure S6: FESEM images of top surfaces, a) NYG and b) 5NYCG; cross-section of, c) NYG and d) 5NYCG and their zoomed in part shown in inset of d).
Figure S7: DSC analysis of solution drawn flexible films (first heating cycle, scan rate- 10º C/min).

500 – 800 cm\(^{-1}\) - Amide V and VI band
1000- 1400 cm\(^{-1}\) - Methylene segments
1500 -1700 cm\(^{-1}\) - NH stretching and C=O bonds

<table>
<thead>
<tr>
<th>Vibration</th>
<th>(\alpha) phase (cm(^{-1}))</th>
<th>(\alpha') phase (cm(^{-1}))</th>
<th>(\gamma) phase (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amide V band</td>
<td>686</td>
<td>582</td>
<td>709</td>
</tr>
<tr>
<td>Amide VI band</td>
<td>686</td>
<td>581</td>
<td>627</td>
</tr>
<tr>
<td>Methylene segments</td>
<td>1126, 1159, 1190, 1223, 1240, 1279, and 1373</td>
<td>1126, 1159, 1190, 1223, 1240, 1279, and 1373</td>
<td>1123, 1160, 1198, 1225, 1250, 1279, and 1371</td>
</tr>
<tr>
<td>Amide I band</td>
<td>1640</td>
<td>1637</td>
<td>1640</td>
</tr>
<tr>
<td>Amide II band</td>
<td>1537</td>
<td>1544</td>
<td>1552</td>
</tr>
<tr>
<td>Amide A band</td>
<td>3309</td>
<td>3310</td>
<td>3297</td>
</tr>
</tbody>
</table>
Figure S8: Power output of NYG and 5NYCG PENGs across different resistors.

Reference:


(S2) Nair, S. S.; Ramesh, C.; Tashiro, K.; Polymorphism in Nylon-11: Characterization using HTWAXS and HTFTIR. Macromolecular symposia 2016, 242, 216-226

(S3) Nair, S. S.; Ramesh, C.; Tashiro, K. Crystalline phases in nylon-11: studies using HTWAXS and HTFTIR. Macromolecules 2006, 39, 2841-2848.