

Electronic Supporting Information

**Nanocomposites with Tunable Dielectric Properties: BaTiO₃ loaded Cellulose Nanocrystal-
Liquid Crystalline Polymers**

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METHODS

Fourier Transform-Infrared (FT-IR)

An infrared study is performed on a Nicolet Magna-IR 560 spectrometer with a Specac Quest single reflection ATR accessory containing a diamond crystal sample plate. It has a resolution of 2 cm^{-1} and 32 scans in micro-ATR mode.

^1H NMR spectroscopy

^1H NMR spectroscopy is recorded on Bruker AVANCE500 MHz NMR spectrometer with CDCl_3 and DMSO-d_6 as solvents. Results are retrieved using FileZilla and analyzed using MestreNova software with residual chemical shifts of CDCl_3 and DMSO-d_6 reported at 7.26 ppm and 2.50 ppm respectively as the internal standards.

X-Ray Diffraction (XRD)

We perform WAXS studies on an Oxford Diffraction XCalibur PX Ultra (transmission mode) diffractometer with an Onyx detector ($\text{Cu-K}\alpha$ radiation 1.542 \AA , double mirror focusing, 45 kV and 45 mA). The crystallinity index is calculated using the ratio of the area under the crystalline region and the total area obtained from peak fitting. The Scherrer equation determines crystallite size, and the peak is centered at $\sim 23^\circ$ (2θ).

Small Angle X-ray Analysis (SAXS)

Small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) measurements were conducted using a XENOCS Xeuss 2.0 system at the University of Pennsylvania. The system features a GeniX3D $\text{Cu-K}\alpha$ source with a wavelength of $\lambda = 1.54\text{ \AA}$. Silver behenate and lanthanum hexaboride were employed to calibrate the distance between the detectors and the samples for SAXS and WAXS, respectively. Temperature-resolved measurements were conducted on a Linkam hot stage mounted in the instrument's sample chamber.

Broadband dielectric spectroscopy

The dielectric spectroscopy is measured by Solartron SI 1260 frequency response analyzer, and the temperatures are controlled by the Delta Design 9015 temperature controller using liquid nitrogen for cooling.

Sample Thickness

The thickness of the samples is determined by the LE 1000-2 linear displacement sensor.

EXPERIMENTAL

Materials

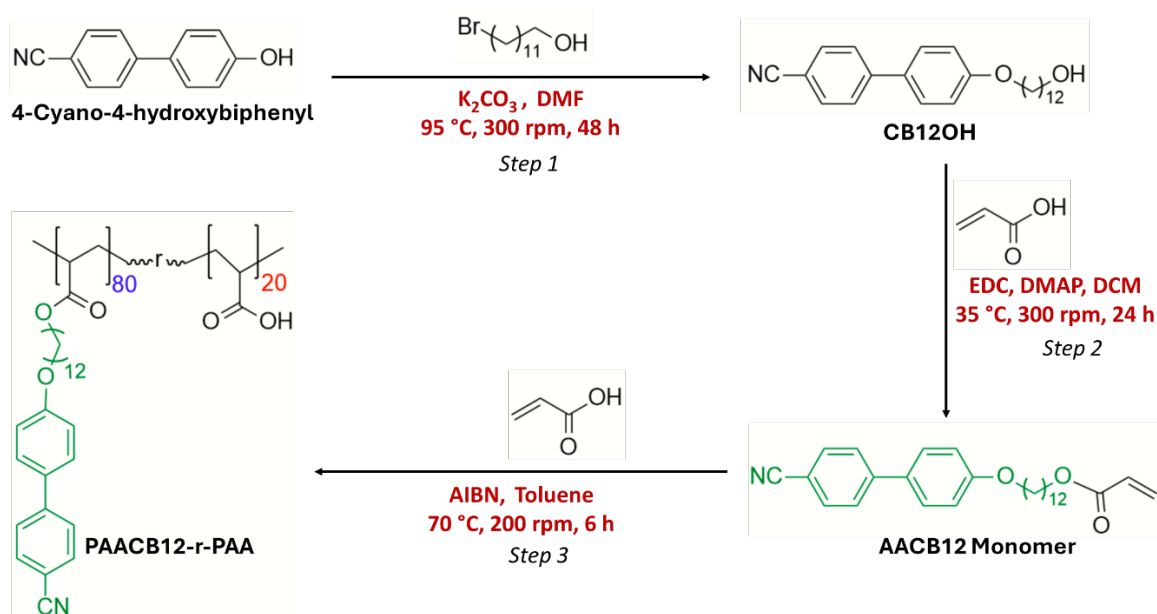
Acrylic acid (99%), 4-dimethylamino pyridine (99.0%), azobisisobutyronitrile, AIBN (98%), potassium carbonate (99%) are purchased from Sigma Aldrich, 4-cyano-4-hydroxyphenyl is purchased from TCI America, 12-Bromo-1-dodecanol (95%) is purchased from lab seeker chemicals, 3500kDa MWCO dialysis membrane is obtained from Cole-Parmer, dichloromethane (98%), Toluene (98%), dimethyl sulfoxide (99.0%) are purchased from thermo fisher scientific, dimethylformamide (99%) is purchased from across organics, 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide hydrochloride, EDC.HCl (98.0%) and 1-butyl-3-methylimidazolium acetate (>95%) are purchased from Oakwood Chemicals. Standard-grade quality filter paper is obtained from Cytiva Life Sciences.

Synthesis of liquid crystal grafted acrylate monomer.

The synthesis of CB12OH and AACB12 is adapted from previous work.^{1,2} The synthesis of AACB12 is adopted from previous work. Transfer acrylic acid (1.0 g, 13.9 mmol), EDC (2.4 g, 15.3 mmol), and 30 mL DCM in a clean, oven-dried 300 mL round-bottom flask equipped with a magnetic stir bar. Seal with a rubber septum, and purge using nitrogen for 3 min under constant stirring using 300 rpm in an oil bath at 25 °C. DMAP (0.3 g, 2.1 mmol) dissolved in 5 mL DCM is then added, and the reaction is purged for a further 2 min. The temperature is increased to 35 °C and then allowed to proceed in an inert environment for 3 hrs. After 3 hours, CB12OH (5.3 g, 13.9 mmol) dissolved in 25 mL of DCM is added dropwise, under nitrogen, and allowed to proceed at the same temperature for 24 hrs. The sample is then opened to air to terminate the reaction and carefully transferred to a clean, dry separatory funnel. 10 mL DCM is used to rinse all the remaining samples from the round-bottom flask. The crude sample is washed using 50 mL 0.5 M NaOH, where the organic layer is separated and the aqueous layer is washed two more times using 20 mL DCM. The combined organic extracts are rinsed with 50 mL of saturated NaCl solution, then dried using Na₂SO₄ and vacuum filtered. The filtrate is concentrated by rotary evaporation and then crystallized using ethanol. The final product, 12((-4'-cyano-[1,1'-biphenyl]-4-yl)oxy)dodecyl acrylate, AACB12, is vacuum filtered, rinsed with more cold ethanol, and dried in the vacuum oven overnight before characterization and polymerization. This material was prepared exclusively for this platform.

Synthesis of PAACB12-r-PAA copolymer

The synthesis of cyanobiphenyl-containing polyacrylate is adopted from a previous study. In a clean, dry 250 mL round bottom flask equipped with a magnetic stir bar, 12((4'-cyano[1,1'-biphenyl]4yl)oxy)dodecyl acrylate, AACB12 (2 g 4.6mmol), acrylic acid (500 mg 6.9 mmol), azobisisobutyronitrile, AIBN (12.7 mg 0.07 mmol), and 10 mL of dry toluene are charged and purged with argon for 2min. The reaction mixture is then allowed to proceed for 5 h. in that inert environment at 70 °C and 200 rpm. This material was synthesized previously, as shown in Scheme S1.



Scheme S1: Synthesis of PAACB12-r-PAA copolymer.

Broadband dielectric spectroscopy

To conduct broadband dielectric spectroscopy measurement, all samples are vacuum-dried for over 24 hours and heated at 50 °C for 10 minutes immediately before the experiments to minimize the effects of moisture. For good electrical contact, Pb/Pt electrode deposited on both sides of the samples using Cressington sputter coater 6002-8. The thickness of the samples is determined by LE 1000-2 linear displacement sensor. The dielectric spectroscopy is measured by Solartron SI 1260 frequency response analyzer, and the temperatures are controlled by the Delta Design 9015 temperature controller using liquid nitrogen for cooling.

RESULTS

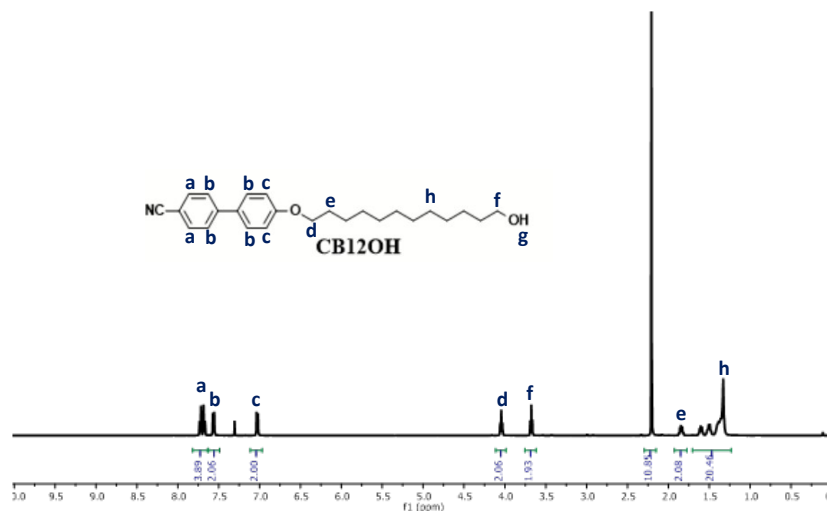


Fig. S1: ¹H NMR for CB12OH in CDCl₃ at room temperature.

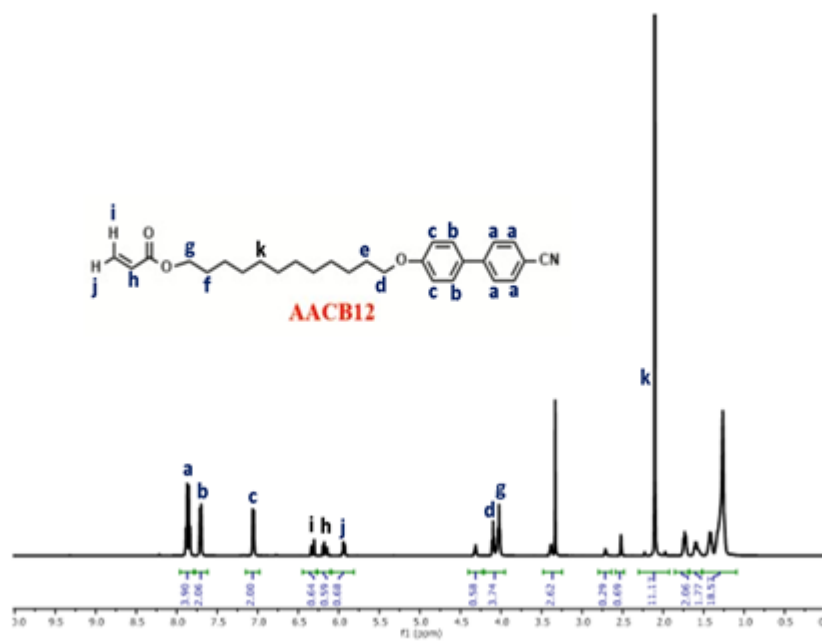


Fig. S2: ¹H NMR for AACB12 monomer in CDCl₃ at room temperature.

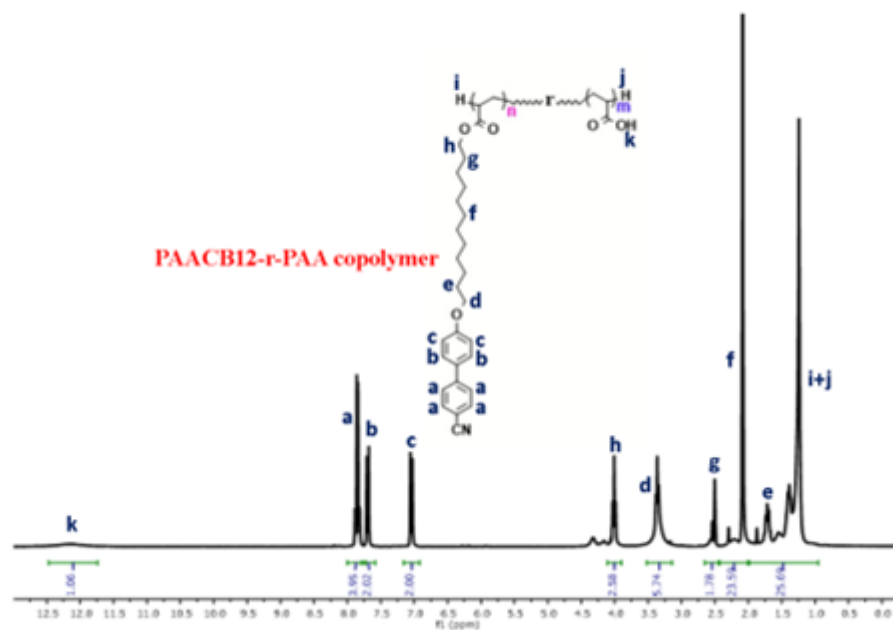


Fig. S3: ^1H NMR for PAACB12-r-PAA copolymer in CDCl_3 at room temperature.

Table 1: Thermogravimetric analysis results showing the decomposition temperature (Td) for the copolymer, hybrid LCP, and BaTiO₃ (10, 20,40 wt.%)/CNC-i-(PAACB12-r-PAA) nanocomposites.

| Sample | T _d (°C) | Residue (%) |
|---|---------------------|-------------|
| PAACB12-r-PAA | 279.83 | 0.000 |
| CNC-i-PAACB12-r-PAA | 286.71 | 1.832 |
| BaTiO ₃ _{10wt.%} /CNC-i-PAACB12-r-PAA | 292.61 | 12.760 |
| BaTiO ₃ _{20wt.%} /CNC-i-PAACB12-r-PAA | 300.54 | 22.432 |
| BaTiO ₃ _{40wt.%} /CNC-i-PAACB12-r-PAA | 305.49 | 33.670 |

Table 2: 1st cooling and 2nd heating cycles DSC results for the copolymer, hybrid LCP and BaTiO₃ (20 wt.%)/CNC-i-PAACB12-r-PAA nanocomposite.

| 1 st Cooling cycle | | | |
|--|------------------|------------------|----------------|
| Nanocomposite | Transition | Temperature (°C) | Enthalpy (J/g) |
| PAACB12-r-PAA | T _{LC} | 84.34 | 18.16 |
| CNC-i-PAACB12-r-PAA | T _{LC1} | 40.75 | 3.79 |
| | T _{LC2} | 81.13 | 19.19 |
| BaTiO ₃ (20 wt.%)/CNC-i-PAACB12-r-PAA | T _{LC1} | 42.46 | 6.81 |
| | T _{LC2} | 78.53 | 20.18 |
| 2 nd Heating cycle | | | |
| PAACB12-r-PAA | T _{LC} | 97.99 | 19.16 |
| CNC-i-PAACB12-r-PAA | T _{LC1} | 48.59 | 4.86 |
| | T _{LC2} | 94.75 | 12.86 |
| BaTiO ₃ (20 wt.%)/CNC-i-PAACB12-r-PAA | T _{LC1} | 50.39 | 8.59 |
| | T _{LC2} | 95.63 | 22.18 |

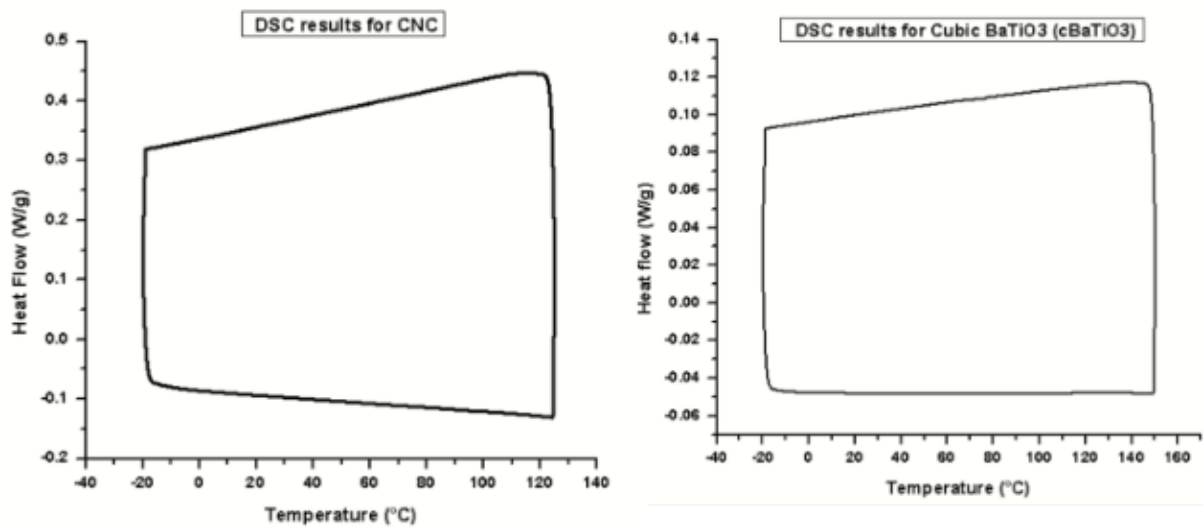


Fig. S4: 1st cooling and 2nd heating cycles DSC thermograms for CNC and BaTiO₃

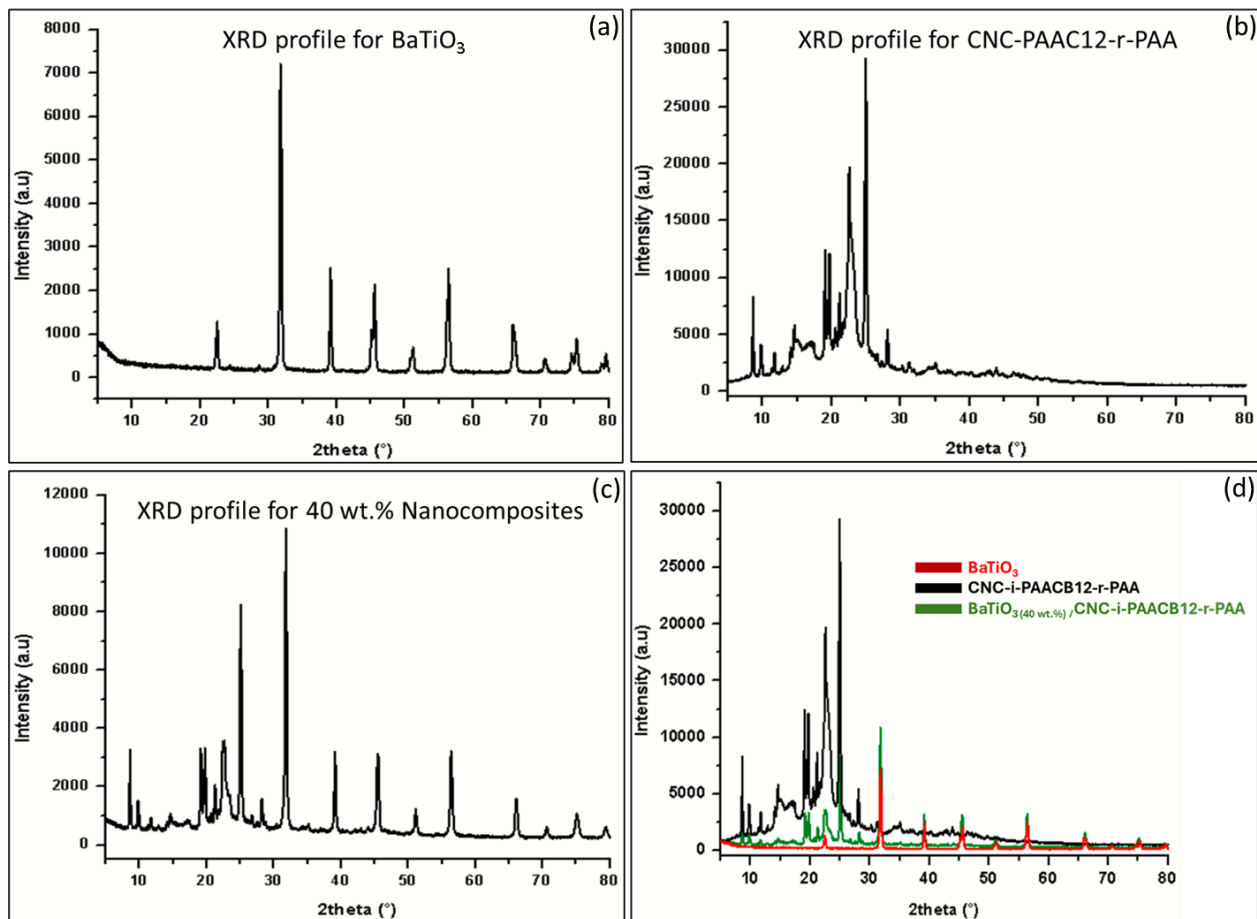


Fig. S5: XRD results for (a) BaTiO_3 (b) CNC-i-(PAACB12-r-PAA) hybrid LCP, (c) BaTiO_3 (40 wt.%)/CNC-i-(PAACB12-r-PAA) nanocomposite (d) overlaid XRD results for cubic BaTiO_3 , CNC-i-PAACB12-r-PAA hybrid LCP and BaTiO_3 (40 wt.%)/CNC-i-PAACB12-r-PAA nanocomposites.

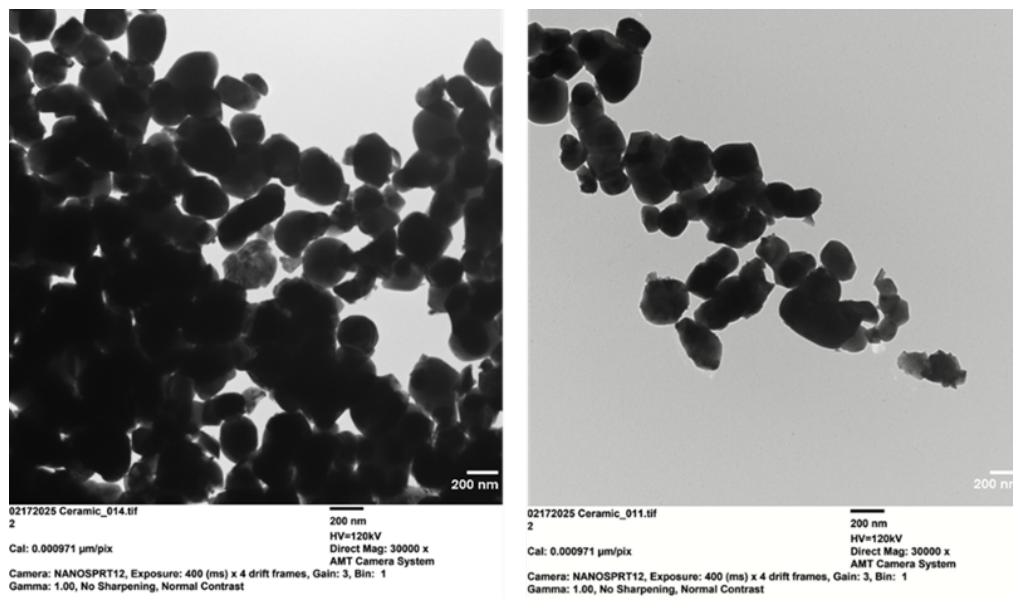


Fig. S6: TEM micrograph of pure cubic BaTiO₃ showing a quasi-spherical shape and size (200 nm)

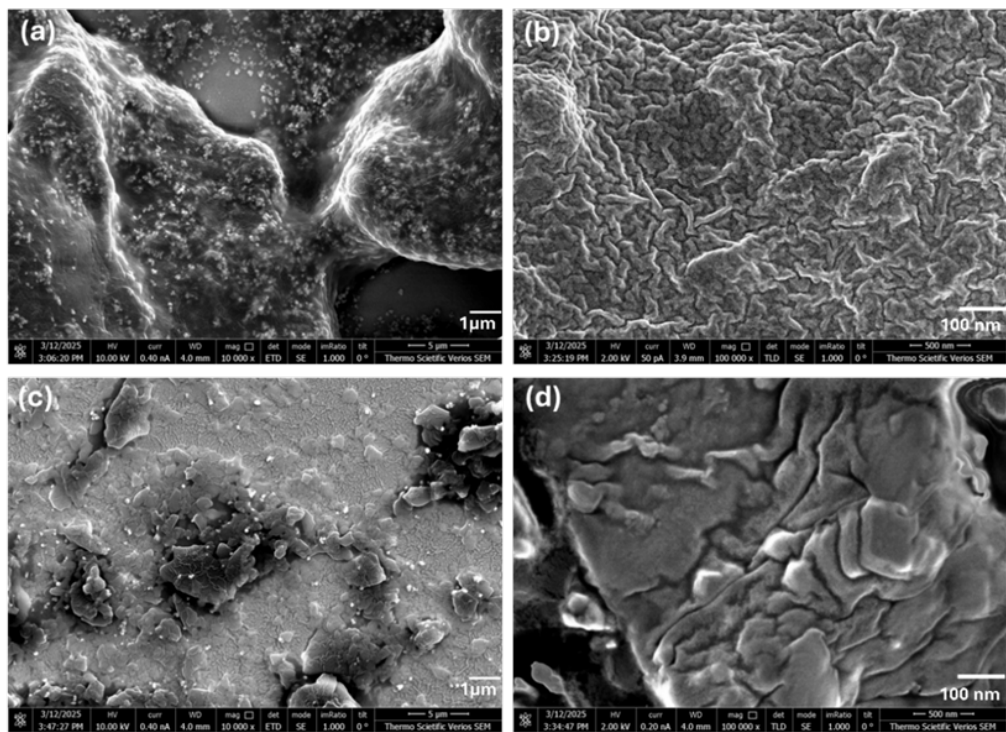
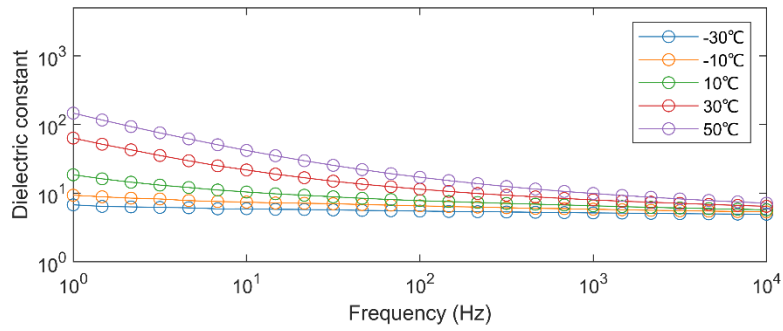
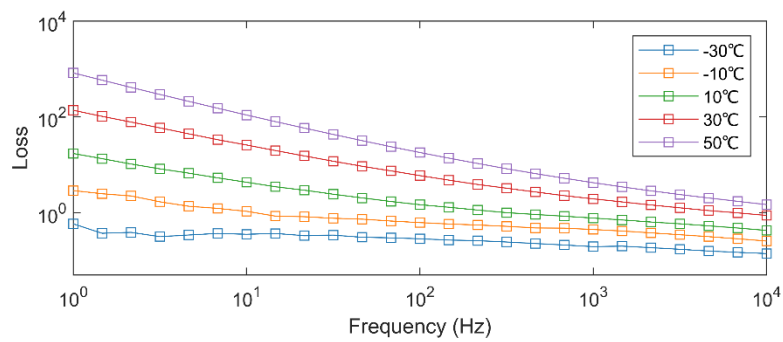


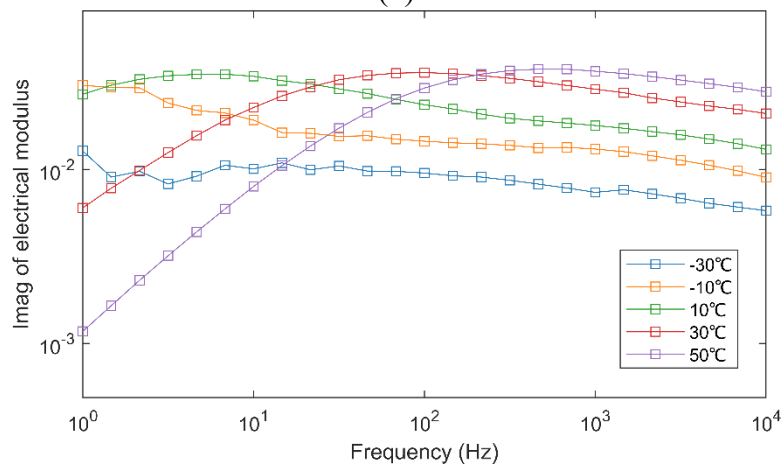
Fig. S7: SEM micrograph for BaTiO₃ (20 wt.%)/CNC-i-PAACB12-r-PAA nanocomposites annealed at 90 °C showing morphological texture and dispersion behavior of the BaTiO₃ in the polymer matrix at (a) and (c) 10K magnification, (c) and (d) 100K magnification.



(a)



(b)



(c)

Fig. S8. Board dielectric spectroscopy of PAACB12-r-PAA. **(a)** Dielectric constant **(b)** Loss and **(c)** Imaginary component of electrical modulus.

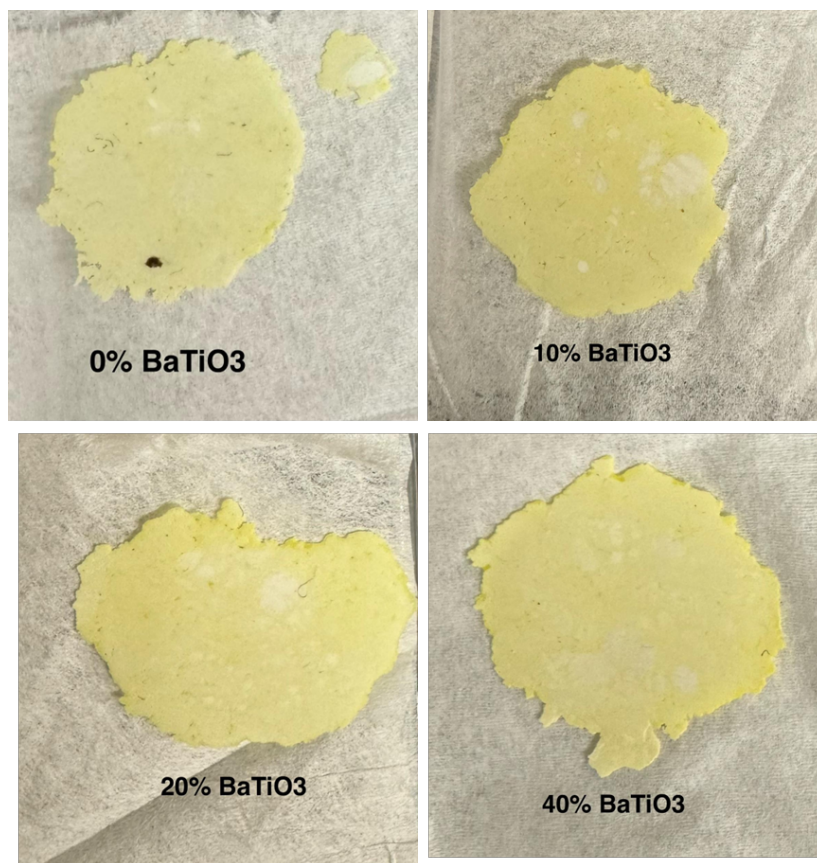


Fig. S9. Images of CNC-i-PAACB12-r-PAA and BaTiO₃/CNC-i-PAACB12-r-PAA nanocomposites.