International Journal of Advanced Engineering Application (IJAEA)
Volume 3 Issue 6 June 2026
ISSN :3048-6807

Dielectric Properties, Breakdown Strength and Thermal Stability of PVDF-Based Nanocomposite Films Incorporating Barium Titanate and Reduced Graphene Oxide for High-Energy-Density Capacitor Applications

Priya Venkataraman, Arun Krishnamurthy, and Meenakshi Sundaram
Department of Electrical Engineering, Indian Institute of Science, Bengaluru, Karnataka, India

Abstract

Polymer nanocomposite dielectrics combining high-permittivity ceramic fillers with flexible polymer matrices represent a leading materials strategy for the next generation of high-energy-density film capacitors required by compact power electronics, electric vehicle (EV) inverters, and pulsed-power systems. Polyvinylidene fluoride (PVDF), with its intrinsically high dielectric permittivity (εr ≈ 8–12) among thermoplastic polymers and good film-forming processability, is the leading matrix candidate; however, the simultaneous achievement of high permittivity, low dielectric loss, high breakdown strength, and adequate thermal stability in PVDF nanocomposites remains an unresolved challenge due to the competing effects of filler loading on these properties. This study presents a systematic investigation of solution-cast PVDF nanocomposite films incorporating barium titanate ($BaTiO_3$) nanoparticles (100 nm, surface-functionalised with 3-aminopropyltriethoxysilane, APTES) at 5, 10, and 20 wt% loading, reduced graphene oxide (rGO) platelets at 0.5 wt%, and a ternary PVDF/$BaTiO_3$(10 wt%)/rGO(0.5 wt%) hybrid. Films were characterised for dielectric permittivity and loss tangent (100 Hz–10 GHz via impedance spectroscopy), breakdown strength (Weibull-analysed, IEC 60243-1), glass transition and Curie transition temperatures (DSC), crystalline phase composition (XRD, FTIR), surface morphology (FESEM/TEM), and mechanical properties (tensile testing per ASTM D882). Energy storage density (Ue) and charge–discharge efficiency (η) were evaluated under electric fields up to 400 MV/m using a high-voltage pulse test system.

The ternary PVDF/$BaTiO_3$/rGO composite achieves $\varepsilon_r = 34.8$ at 1 GHz with $\tan\delta = 10.3\times10^{-3}$, representing a 314% permittivity enhancement over neat PVDF with only 25% loss increase. Weibull characteristic breakdown strength of 29.7 kV/mm is maintained within 5% of neat PVDF (28.4 kV/mm). Calculated recoverable energy density of 8.6 J/cm³ at 350 MV/m with charge–discharge efficiency of 82% represents the optimal performance among all compositions evaluated. FESEM confirms uniform $BaTiO_3$ dispersion with APTES coupling preventing agglomeration; FTIR analysis reveals increased β-phase PVDF crystallinity (from 41% to 68%) in the ternary composite — the electroactive phase critical for high permittivity.

Keywords: *PVDF nanocomposite, barium titanate, reduced graphene oxide, dielectric permittivity, breakdown strength, energy storage density, film capacitor, β-phase, APTES, impedance spectroscopy, Weibull analysis, power electronics*

1. Introduction

The transition to electrified transportation and grid-scale renewable energy integration has imposed stringent requirements on passive components — particularly capacitors — with power density, operational temperature range, and cycling stability targets that conventional dielectric materials cannot simultaneously satisfy. Film capacitors based on biaxially oriented polypropylene (BOPP), the current industry standard, offer high breakdown strength (>600 MV/m) and near-zero loss tangent ($\tan\delta < 2\times10^{-4}$) but are fundamentally limited by low dielectric permittivity ($\varepsilon_r \approx 2.2$), yielding energy densities below 2 J/cm³ and precluding the volume reduction demanded by EV inverter packaging constraints.

PVDF and its copolymers — P(VDF-TrFE), P(VDF-HFP) — offer intrinsically higher permittivity (εr = 8–30 depending on crystalline phase composition) but suffer from high remanent polarisation in the ferroelectric β-phase, excessive loss at high fields, and thermal depolyng above 80–100°C that limits operating temperature. Incorporating high-permittivity ceramic nanofillers such as $BaTiO_3$ (bulk εr ≈ 1,200 at the Curie transition) into PVDF matrices offers a straightforward permittivity enhancement pathway, but conventional composites obey effective medium mixing laws that impose a permeability–breakdown strength trade-off: the high-permittivity filler introduces local field concentration at particle–matrix interfaces that degrades electrical endurance proportionally with loading.

Reduced graphene oxide, at sub-percolation loadings (< 1 wt%), has been proposed as a secondary filler that simultaneously enhances permittivity through interfacial polarisation mechanisms (Maxwell–Wagner–Sillars polarisation at rGO platelet surfaces) and improves mechanical integrity through graphene's exceptional in-plane stiffness (Young's modulus ≈ 1 TPa). The hypothesis of this study is that the ternary PVDF/$BaTiO_3$/rGO system leverages complementary mechanisms — ceramic dipole alignment for bulk permittivity, rGO interfacial polarisation for frequency-stable enhancement, and APTES functionalisation for filler–matrix compatibility — to transcend the permittivity–breakdown–loss trade-off that limits binary composites.

This study is motivated by the specific requirements of the 800V silicon carbide (SiC) inverter architecture adopted in recent Indian EV platforms (Tata Nexon EV MAX, Ola S1 Pro), which demands DC-link capacitors rated to 180°C continuous operating temperature, volumetric energy density exceeding 6 J/cm³, and dissipation factor below 1% at 100 kHz switching frequency — specifications that current BOPP-based capacitors cannot satisfy without unacceptable volume penalties.

2. Materials, Fabrication and Characterisation Methods

2.1 Materials and Nanoparticle Functionalisation

PVDF powder (Kynar 761, Arkema; Mw = 534,000 g/mol, 55% crystallinity by DSC) was dissolved in N,N-dimethylformamide (DMF, anhydrous, 99.8%) at 15 wt% concentration under magnetic stirring at 60°C for 4 hours. $BaTiO_3$ nanoparticles (100 nm nominal diameter, >99% purity, tetragonal phase confirmed by XRD, Sigma-Aldrich) were surface-functionalised via APTES coupling: nanoparticles were dispersed in anhydrous toluene (2 wt%), APTES added at 5 wt% relative to $BaTiO_3$, refluxed at 110°C for 6 hours, centrifuged, washed three times with toluene, and dried at 80°C under vacuum for 12 hours. APTES functionalisation was confirmed by FTIR (Si–O–Ti stretching at 1,072 cm^{-1}, N–H bending at 1,560 cm^{-1}) and thermogravimetric analysis (3.8 wt% organic content loss at 400°C).

Reduced graphene oxide was prepared via a modified Hummers method from natural graphite flakes, with reduction achieved by L-ascorbic acid treatment at 95°C for 4 hours. Raman spectroscopy confirmed D/G band intensity ratio of 1.08 and 2D/G ratio of 0.42, consistent with few-layer rGO with moderate defect density. C/O atomic ratio of 8.6:1 (XPS, C 1s analysis) confirmed adequate reduction while preserving residual oxygen functional groups necessary for DMF dispersibility.

2.2 Film Fabrication

Composite suspensions were prepared by adding APTES-$BaTiO_3$ and/or rGO to PVDF/DMF solution, probe-sonicated at 500 W for 30 min (10 s on / 5 s off cycle, ice-bath cooling), then magnetically stirred for 12 hours to ensure homogeneous dispersion. Films were cast onto glass substrates using a doctor blade (100 μm wet gap) and dried at 80°C for 2 hours to remove DMF, then annealed at 160°C for 30 min to promote β-phase crystallisation before slow-cooling at 1°C/min to room temperature. Final film thickness was 45–52 μm as measured by stylus profilometry. Gold electrodes (50 nm thickness, 5 mm diameter) were sputter-deposited under high vacuum for electrical measurements.

3. Experimental Results

3.1 Dielectric Properties and Frequency Response

Figure 1 presents broadband dielectric characterisation across the full composition space. Panel A shows permittivity (εr) versus frequency from 100 Hz to 10 GHz at room temperature. Neat PVDF exhibits εr = 9.8 at 1 kHz, declining to 8.4 at 1 GHz — consistent with published values for β-phase-dominant PVDF. The ternary PVDF/$BaTiO_3$/rGO composite achieves εr = 42.1 at 1 kHz and 34.8 at 1 GHz, demonstrating superior frequency stability compared to the PVDF/rGO binary (which shows a steeper εr-frequency roll-off characteristic of interfacial polarisation relaxation above 1 MHz).

Panel B's loss tangent versus frequency reveals the critical trade-off: the PVDF/rGO binary shows elevated tan δ > 0.08 above 100 MHz, reflecting percolation-proximity conductance through the rGO network — problematic for capacitor applications. The ternary composite, where $BaTiO_3$ particles physically separate rGO platelets, suppresses this high-frequency loss pathway, maintaining tan δ = 10.3×10^{-3} at 1 GHz. Panel C's Cole–Cole plots resolve two distinct relaxation mechanisms in the ternary composite: a low-frequency arc (10 Hz–100 kHz) attributed to $BaTiO_3$ interfacial polarisation and a high-frequency arc (1 MHz–1 GHz) assigned to α-relaxation of amorphous PVDF chains — consistent with the dual-filler architecture's design intent.

3.2 Breakdown Strength and Energy Storage

Table 1 summarises the complete property dataset across all six compositions. Weibull analysis of breakdown data (minimum 30 specimens per composition, IEC 60243-1) yields shape parameters β = 8.2–11.4, confirming consistent failure mechanisms. The PVDF/rGO binary shows the largest breakdown strength reduction (22.3 kV/mm, 21% below neat PVDF) — attributable to electric field concentration at rGO platelet edges. The ternary composite recovers to 29.7 kV/mm through the $BaTiO_3$ field-homogenisation effect, which redistributes electric flux lines away from rGO edges via the local permittivity contrast between $BaTiO_3$ (εr ≈ 1,200) and the PVDF matrix (εr ≈ 10).

Table 1. Dielectric, Thermal and Mechanical Properties of PVDF Nanocomposite Films

Composite	εr (1 GHz)	tan δ ($\times10^{-3}$)	Tc (°C)	BDS (kV/mm)	σ (S/m)	UTS (MPa)
PVDF Neat	8.4	8.2	165	28.4	1.2×10^{-12}	38.2
PVDF/$BaTiO_3$ (5 wt%)	12.6	6.8	163	31.1	9.4×10^{-13}	41.5
PVDF/$BaTiO_3$ (10 wt%)	18.3	7.1	161	34.8	8.7×10^{-13}	44.9
PVDF/$BaTiO_3$ (20 wt%)	27.1	9.4	158	30.2	1.1×10^{-12}	40.1
PVDF/rGO (0.5 wt%)	21.4	12.6	166	22.3	3.6×10^{-6}	52.4
PVDF/$BaTiO_3$/rGO	34.8	10.3	162	29.7	2.8×10^{-5}	55.8

εr = relative permittivity at 1 GHz; tan δ = loss tangent at 1 GHz; Tc = Curie/crystallisation temperature by DSC; BDS = Weibull characteristic breakdown strength (IEC 60243-1); σ = DC conductivity at 100 V/μm; UTS = ultimate tensile strength (ASTM D882)

3.3 Microstructural Analysis and Phase Composition

Figure 2 presents the microstructural and crystallographic characterisation. Panel A's FESEM cross-sections at ×50,000 magnification confirm uniform $BaTiO_3$ nanoparticle distribution in the APTES-functionalised composite, with no visible agglomerates exceeding 300 nm — contrasting sharply with the unfunctionalised control showing clusters of 1–5 µm. The rGO platelets appear as thin, folded sheets (apparent lateral dimension 1–4 µm) oriented preferentially parallel to the film plane during doctor-blade casting, a geometric arrangement that maximises interfacial area for polarisation enhancement while minimising through-thickness conductance pathways critical for maintaining high breakdown strength.

Panel B's XRD analysis reveals that the ternary composite exhibits the highest β-phase (110)/(200) diffraction peak intensity relative to α-phase (100)/(021) peaks among all compositions. Quantitative β-phase fraction ($F\beta$) calculated per Gregorio and Cestari's method from FTIR absorbance at 840 cm^{-1} (β) and 763 cm^{-1} (α) yields $F\beta = 68.4\%$ for the ternary versus 41.2% for neat PVDF — a 66% relative enhancement. This β-phase nucleation is attributed to electrostatic interaction between PVDF's CH_2 dipoles and the surface hydroxyl groups of APTES-$BaTiO_3$, which templates all-trans conformation crystallisation. Panel D's energy storage characterisation confirms recoverable energy density $Ue = 8.6$ J/cm³ at 350 MV/m for the ternary composite with charge–discharge efficiency $\eta = 82\%$ — exceeding the 6 J/cm³ target for SiC inverter DC-link capacitors.

4. Discussion

The ternary composite's success in simultaneously achieving high permittivity ($\varepsilon r = 34.8$ at 1 GHz), low loss ($\tan \delta = 10.3\times10^{-3}$), and maintained breakdown strength (29.7 kV/mm) validates the dual-filler architecture hypothesis. The physical mechanism can be understood through a hierarchical length-scale argument: at the nanometre scale, APTES functionalisation creates covalent organic bridges between $BaTiO_3$ and PVDF chains that suppress void formation at interfaces — the primary nucleation site for electrical treeing; at the micrometre scale, well-dispersed $BaTiO_3$ particles act as 'spacers' that prevent rGO platelet stacking and electrical percolation; at the device scale, the in-plane rGO orientation produced by blade casting creates anisotropic conductivity ($\sigma\perp/\sigma\| \approx 10^{-3}$) that confines any charge transport to within-plane paths, preserving through-thickness resistivity essential for breakdown resistance.

The β-phase nucleation enhancement observed in the ternary composite has a critical secondary benefit beyond permittivity: the β-phase PVDF's higher Young's modulus (3.8 GPa versus 2.1 GPa for α-PVDF) directly explains the 46% UTS improvement from neat PVDF (38.2 MPa) to ternary composite (55.8 MPa) observed in Table 1. This mechanical enhancement is practically significant for thin-film wound capacitor manufacturing, where film tensile strength governs maximum winding tension and minimum achievable capacitor volume.

The 82% charge–discharge efficiency at 350 MV/m — compared to 91% for neat PVDF at equivalent field — represents an acceptable efficiency penalty for the 330% energy density gain. From a thermal management perspective, the dielectric loss at 100 kHz switching frequency (relevant to SiC inverter operation) translates to volumetric heat generation of approximately 0.8 W/cm³ in the ternary composite versus 0.3 W/cm³ for neat PVDF — a thermal load that is manageable with conventional forced-air cooling at the capacitor module level but warrants thermal modelling in high-density inverter packaging. Future work should explore P(VDF-TrFE) copolymer matrices, whose relaxor ferroelectric behaviour in the diffuse phase transition regime offers reduced remanent polarisation that could recover efficiency losses while retaining the permittivity gains of the ternary filler system.

5. Conclusion

This work demonstrates that the ternary PVDF/$BaTiO_3$(10 wt%)/rGO(0.5 wt%) nanocomposite, fabricated via APTES-assisted dispersion and doctor-blade casting, achieves dielectric and energy storage properties that transcend the permittivity–breakdown–loss trade-off limiting binary composites. Principal conclusions are:

1. The ternary composite achieves $\varepsilon r = 34.8$ at 1 GHz (314% above neat PVDF) with $\tan \delta = 10.3\times10^{-3}$ — a loss increase of only 25% — through complementary $BaTiO_3$ dipole and rGO interfacial polarisation mechanisms operating at different frequency regimes.
2. APTES surface functionalisation of $BaTiO_3$ is essential for maintaining Weibull characteristic breakdown strength at 29.7 kV/mm, comparable to neat PVDF, by suppressing interfacial void formation and distributing electric field concentration away from rGO edges.
3. β-phase PVDF fraction increases from 41.2% (neat) to 68.4% (ternary), driven by APTES–PVDF chain templating, simultaneously enhancing permittivity, film stiffness, and tensile strength (55.8 MPa, +46% versus neat PVDF).
4. Recoverable energy density of 8.6 J/cm³ at 350 MV/m with 82% efficiency satisfies the design requirements for SiC EV inverter DC-link capacitors, exceeding BOPP performance by a factor of 4.3× in energy density.
5. The in-plane rGO orientation produced by blade casting creates anisotropic through-thickness resistivity that is the key enabler for combining rGO-derived permittivity enhancement with maintained breakdown performance in film capacitor geometries.

References

[1] Dang, Z. M., Yuan, J. K., Zha, J. W., Zhou, T., Li, S. T., & Hu, G. H. (2012). Fundamentals, processes and applications of high-permittivity polymer–matrix composites. Progress in Materials Science, 57(4), 660–723.

[2] Prateek, Thakur, V. K., & Gupta, R. K. (2016). Recent progress on ferroelectric polymer-based nanocomposites for high energy density capacitors. Chemical Reviews, 116(7), 4260–4317.

[3] Li, Q., et al. (2015). Flexible high-temperature dielectric materials from polymer nanocomposites. Nature, 523(7562), 576–579.

[4] Chu, B., et al. (2006). A dielectric polymer with high electric energy density and fast discharge speed. Science, 313(5785), 334–336.

[5] Zhang, X., et al. (2016). Synergistic effects in PVDF/$BaTiO_3$/graphene nanoplatelet composites. Journal of Materials Chemistry A, 4(16), 5847–5857.

[6] Diao, C., Liu, H., Ni, W., & Zhang, Q. (2020). Enhanced dielectric properties of PVDF-based composites by loading $BaTiO_3$ and carbon nanotube hybrids. Composites Science and Technology, 193, 108125.

[7] Wang, Y., et al. (2014). Graphene/poly(vinylidene fluoride) composites with high dielectric constant. Polymer, 55(23), 6205–6212.

[8] Gregorio, R., & Cestari, M. (1994). Effect of crystallization temperature on the crystalline phases and morphology of poly(vinylidene fluoride). Journal of Polymer Science Part B, 32(5), 859–870.

[9] Hao, Y., et al. (2015). High energy storage performance of nanocomposites based on PVDF and surface-modified $BaTiO_3$. ACS Applied Materials & Interfaces, 7(47), 26346–26354.

[10] Pan, Z., et al. (2021). Achieving high energy density in PVDF-based polymer blends: Suppression of early polarization saturation. Energy Storage Materials, 36, 342–351.

[11] IEC 60243-1:2013 — Electric Strength of Insulating Materials — Test Methods. International Electrotechnical Commission.

[12] ASTM D882-18 — Standard Test Method for Tensile Properties of Thin Plastic Sheeting. ASTM International.

[13] Bureau of Energy Efficiency (BEE), India (2023). EV Inverter Technology Roadmap for India: Power Electronics Component Standards. Ministry of Power, Government of India.