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High-Accuracy Prediction of Complex Permittivity in Ternary Composites Using Parameters Provided by Binary Systems

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Abstract

Accurate prediction of the frequency-dependent complex permittivity of ternary composites remains challenging because constituent parameters obtained through inverse modeling are model dependent and are often re-estimated for different composite systems. Here, a binary-informed mixing-law framework was developed for polyaniline (PANI)/carbonyl iron powder (CIP)/polyurethane (PU) composites over 2–18 GHz. Maxwell–Garnett (MG), coherent-potential (CP), and Bruggeman (BR) models were first compared using the same PANI/PU dataset, and MG provided the most consistent overall performance for retrieving the model-dependent effective constituent response of PANI. The retrieved PANI response was examined using a modified Debye–conductivity model and independently assessed through cross-matrix prediction of PANI/paraffin composites without parameter recalibration. The binary-derived effective constituent responses of PANI and CIP were subsequently used as fixed inputs in an MG-based ternary expression. Without fitting the ternary dielectric spectra, the model reproduced the measured complex permittivity of five PANI/CIP/PU formulations at a fixed total filler loading of 30 wt.% and one PANI/PU binary endpoint with good overall agreement. The resulting R^2 values were 0.9891–0.9953 for ϵ' and 0.9375–0.9963 for ϵ'' . The corresponding NRMSE values were 5.62–11.71% for ϵ' and 12.74–18.95% for five of the six ϵ'' datasets, while one narrow-response dataset

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exhibited a higher NRMSE of 35.12%. These results demonstrate that binary-derived effective constituent parameters can support forward permittivity prediction without ternary-specific recalibration, providing a practical basis for reducing experimental screening and guiding composition selection along the investigated composition path.

Keywords

Complex permittivity; Maxwell–Garnett model; Effective constituent parameters; Ternary composites; Parameter transferability

1. Introduction

With the rapid development of next-generation communications, radar detection, aerospace systems, and integrated electronics, the operating spectrum of electromagnetic waves continues to expand [1-3], while service environments are increasingly characterized by multiband coupling and high electromagnetic density. Such complex electromagnetic environments impose more stringent requirements on the regulation of material electromagnetic responses and are driving the development of electromagnetic functional materials from conventional empirical formulation toward model-based prediction and quantitative design [4,5]. Complex permittivity is a key parameter linking material composition and microstructure to macroscopic electromagnetic behavior. Its real and imaginary components characterize polarization energy storage and energy dissipation under an alternating electric field, respectively, and directly govern electromagnetic-wave propagation, reflection, and attenuation [6,7]. Accordingly, theoretical models capable of accurately describing the frequency-dependent dielectric response of composites are essential for elucidating structure–property relationships in multiphase systems, reducing experimental screening costs, and enabling targeted electromagnetic-property design [8-10].

The dielectric properties of composites are commonly investigated through experimental measurements, numerical simulations, and mixing laws [11]. Experimental screening is costly, whereas numerical simulation depends on detailed structural reconstruction [12,13]. By contrast, mixing laws such as the Maxwell–Garnett, Bruggeman, and coherent-potential models can rapidly calculate the effective permittivity from the permittivities and volume fractions of the constituents [14,15].

Chen et al. [16] investigated KTN/PVDF composites using several mixing laws and found that filler morphology significantly affected the effective permittivity. Khouni and Bouzit [17] employed a modified mixing law to describe the broadband dielectric response of an epoxy/SrTiO₃/carbon-black ternary system, obtaining good agreement between the model and experimental data. Brahimi et al. [18] used modified Lichtenecker and Bottreau mixing laws to predict the permittivity of an epoxy/BaTiO₃/oxide ternary system, for which the mean relative error of the Bottreau model was below 0.06%. Nevertheless, most existing studies emphasize fitting to a specific material system, and the cross-system transferability of model parameters and their ability to independently predict ternary composites require further validation [19-20].

The central challenge in predicting ternary systems lies in the reliable determination of effective constituent parameters. Moreover, sequential mixing or refitting to target data can introduce dependence on the mixing order, parameter nonuniqueness, and overfitting [21-23]. For fillers exhibiting frequency dispersion and conduction loss, the effective dielectric parameters are further influenced by morphology, particle contacts, and interfacial states [24,25]. It therefore remains to be established whether model-dependent effective constituent parameters retrieved from binary systems can retain predictive utility when transferred to other matrices and ternary composites without recalibration [26-28].

Accordingly, PANI/CIP/PU composites were selected as the model system in this study. First, the Maxwell–Garnett (MG), coherent-potential (CP), and Bruggeman (BR) mixing laws were applied to the same experimental dataset and evaluated using identical criteria to describe the complex permittivity of binary PANI/PU composites. The most suitable model was selected through a combined comparison of goodness of fit and residual characteristics. The MG model provided the best overall balance between fitting accuracy and residual stability for the real and imaginary parts of permittivity and was therefore used to retrieve the frequency-dependent effective constituent complex permittivity of PANI. The physical consistency of the retrieved parameters was then examined using a modified Debye–conductivity model, and their

cross-matrix transferability was assessed in PANI/paraffin composites without recalibrating the PANI parameters. Subsequently, the effective constituent parameters of PANI, independently retrieved effective constituent complex permittivity of CIP, and PU matrix parameters were fixed as inputs to an MG-type ternary mixing expression, which was used to independently predict the complex permittivity of PANI/CIP/PU composites with different compositions over 2–18 GHz. This study establishes an integrated modeling route encompassing candidate-model comparison, optimal-model selection, binary parameter retrieval and validation, and ternary-property prediction.

2. Experiment

2.1. Materials

Aniline, ammonium persulfate (APS), hydrochloric acid, and butyl acetate were supplied by Aladdin. Carbonyl iron powder (CIP) was supplied by Macklin, and thermosetting polyurethane was purchased from Qingdao Huikun Materials Technology Co., Ltd. Deionized water was prepared in the laboratory. All chemicals were used as received without further purification.

2.2. Synthesis of PANI and PANI/PU Composites

First, 0.05 mol of aniline was dissolved in 80 mL of deionized water, followed by the addition of 50 mL of 1 mol L⁻¹ hydrochloric acid. Separately, 0.05 mol of ammonium persulfate was dissolved in deionized water and slowly introduced into the aniline solution using a peristaltic pump. The reaction was conducted at 0 °C for 6 h. The product was collected by vacuum filtration, washed three times with water and absolute ethanol, and dried in an oven at 60 °C for 12 h. PANI/PU composites were subsequently prepared by physical blending, and their detailed compositions are listed in Table S1. Finally, PANI/paraffin composites containing 10–50 wt% PANI, with an interval of 10 wt%, were prepared by physical blending.

2.3. Preparation of PANI/CIP/PU Composites

PANI/CIP/PU composites were prepared by physical blending. Carbonyl iron powder and PANI were first mixed uniformly, after which a prescribed amount of the powder mixture was dispersed in polyurethane component B. Polyurethane component A and a small amount of butyl acetate as a dispersant were then added, and the mixture

was ultrasonically stirred for 10 min to ensure homogeneous dispersion. PANI/CIP/PU composites with different PANI/CIP ratios at a fixed total filler loading of 30 wt.% were thereby obtained; their detailed compositions are provided in Table S2.

2.4. Characterization

To examine the cross-sectional microstructures of the composites, specimens were cryogenically fractured in liquid nitrogen and observed using a ZEISS Sigma 360 scanning electron microscope (SEM, Germany). X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Scientific K-Alpha spectrometer (USA). Fourier-transform infrared (FTIR) spectra were recorded using a PerkinElmer Spectrum 100 spectrometer (USA), and X-ray diffraction (XRD) analysis was conducted using a Rigaku SmartLab SE diffractometer (Japan). For complex-permittivity measurements, the prepared composite sheets were cut into toroidal coaxial specimens with an inner diameter of 3.04 mm and an outer diameter of 7.00 mm. The complex permittivity was measured over 2–18 GHz by the coaxial transmission-line method using a Ceyear 3656D vector network analyzer. The mixing-law models were fitted using 1stOpt software.

3. Results and discussion

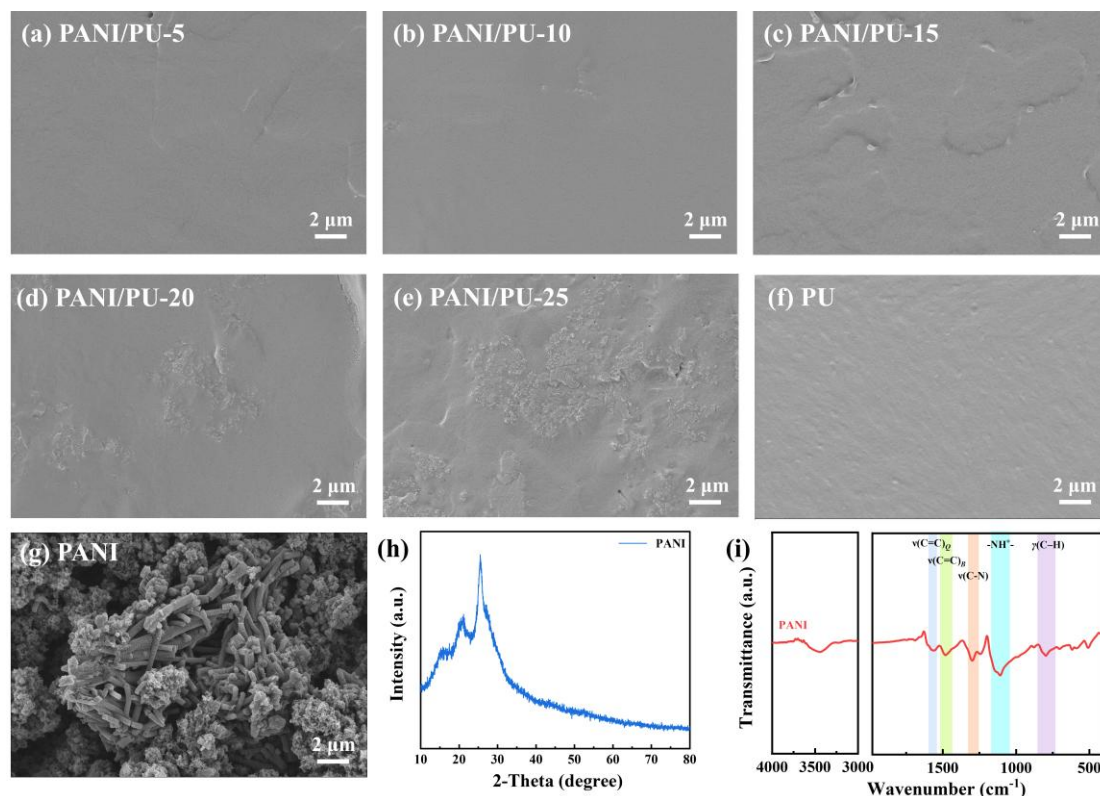


Fig. 1. Cross-sectional SEM images of PANI/PU composites with different PANI loadings: (a) PANI/PU-5, (b) PANI/PU-10, (c) PANI/PU-15, (d) PANI/PU-20, and (e) PANI/PU-25; (f) cross-sectional SEM image of neat PU; (g) SEM image of PANI powder; (h) XRD pattern and (i) FTIR spectrum of PANI.

The composition-dependent microstructural evolution of the PANI/PU composites, together with the structural characteristics of PANI, is presented in Fig. 1. As shown in Fig. 1a and 1b, the fracture surfaces of PANI/PU-5 and PANI/PU-10 are relatively smooth and dense, with no obvious micron-scale PANI-rich regions, indicating that low PANI contents can be effectively embedded within the continuous PU phase and that the dispersion structure remains matrix dominated. When the PANI content increases to 15 wt%, local undulations and irregular regions begin to appear. At loadings of 20 and 25 wt%, both the surface roughness and the extent of local PANI enrichment increase markedly, suggesting reduced interparticle spacing and an enhanced tendency toward PANI–PANI contact and agglomeration. This composition-dependent morphological evolution may increase the number of heterogeneous interfaces, intensify local electric-field distortion [29,30], and raise the probability of forming potential conductive pathways, thereby affecting the dielectric energy-storage and loss behavior of the composites. These observations support treating PU as the continuous phase and PANI as a nonspherical dielectric filler in the subsequent modeling, while suggesting an increasing deviation from the uniform-dispersion assumption at high filler loadings [31,32].

The XRD pattern in Fig. 1h is dominated by broadened diffraction features, with distinct peaks appearing at approximately 15–30°, indicating a semicrystalline structure in which amorphous regions coexist with locally ordered chain segments [33–35]. The FTIR spectrum displays characteristic absorption bands attributable to C=C stretching of the quinoid and benzenoid rings, C–N stretching of aromatic amines, protonated nitrogen-containing groups, and out-of-plane C–H bending of para-substituted aromatic rings, confirming the formation of the conjugated benzenoid-quinoid backbone and protonated structure of PANI [36,37]. The conjugated segments and protonated structure facilitate dipolar polarization, polaron formation, and charge delocalization, suggesting that the microwave dielectric response of PANI may contain contributions

from both relaxation polarization and conduction loss. Overall, PU retains the characteristics of a continuous matrix throughout the investigated composition range, whereas PANI progressively evolves from a dispersed state to local contact and agglomeration as its content increases [38,39].

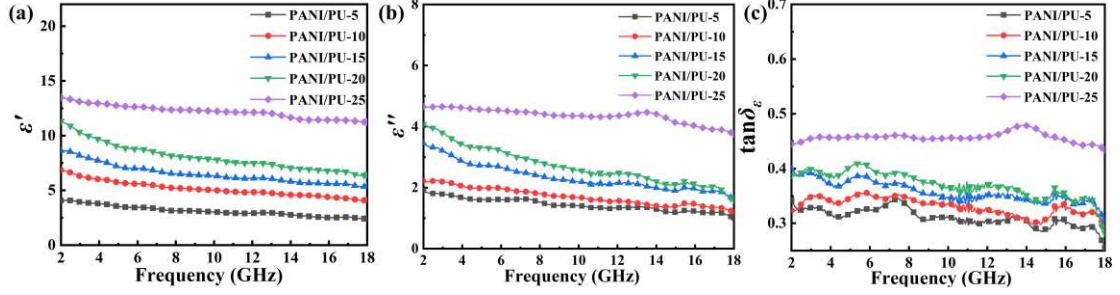


Fig. 2. Frequency-dependent (a) real part (ϵ'), (b) imaginary part (ϵ''), and (c) dielectric loss tangent ($\tan\delta_e$) of PANI/PU composites with different PANI loadings.

The frequency-dependent dielectric response of the PANI/PU composites over 2–18 GHz is presented in Fig. 2a–c. For all samples, both the real part (ϵ') and imaginary part (ϵ'') generally decrease with increasing frequency, indicating evident dielectric dispersion over the investigated frequency range. This frequency dependence is consistent with the dispersive nature of polarization and charge-transport processes in the composite. At a given frequency, both ϵ' and ϵ'' increase overall with increasing PANI content, indicating that the incorporation of conjugated PANI simultaneously enhances polarization energy storage and dielectric loss. This trend is consistent with the composition-dependent morphology shown in Fig. 1: increasing the PANI content reduces the distance between fillers, increases the number of PANI/PU interfaces, and enhances the contributions from local charge transport and interfacial polarization [40–42]. The dielectric loss tangent also varies systematically with frequency and PANI content, consistent with the composition-dependent evolution of the dielectric-loss response [43,44].

To assess the sensitivity of parameter retrieval to the choice of mixing law, the MG, CP, and BR models were evaluated using the same PANI/PU dataset and identical assessment criteria. Model selection was based jointly on the R^2 values for ϵ' and ϵ'' , the frequency-dependent residuals, and the residual distributions, rather than on a single curve or statistical metric.

Given the rod-like or short-fibrous morphology of PANI, the needle-shaped Maxwell–Garnett (MG) model in Eq. (1) was first employed to describe the effective complex permittivity of PANI randomly dispersed in a continuous PU phase and to retrieve the frequency-dependent effective constituent complex permittivity of PANI [45]. Because the model assumes a continuous matrix containing dispersed fillers, its applicability must be assessed in conjunction with the systematic residuals associated with agglomeration and particle contacts at high filler loadings.

$$\varepsilon_{eff}^* = \varepsilon_e^* + V_f(\varepsilon_i^* - \varepsilon_e^*) \frac{\varepsilon_i^* + 5\varepsilon_e^*}{(3 - 2V_f)\varepsilon_i^* + (3 + 2V_f)\varepsilon_e^*} \quad (1)$$

where ε_{eff}^* is the effective complex permittivity, ε_e^* is the complex permittivity of the matrix, ε_i^* is the complex permittivity of the filler, and V_f is the volume fraction of the filler.

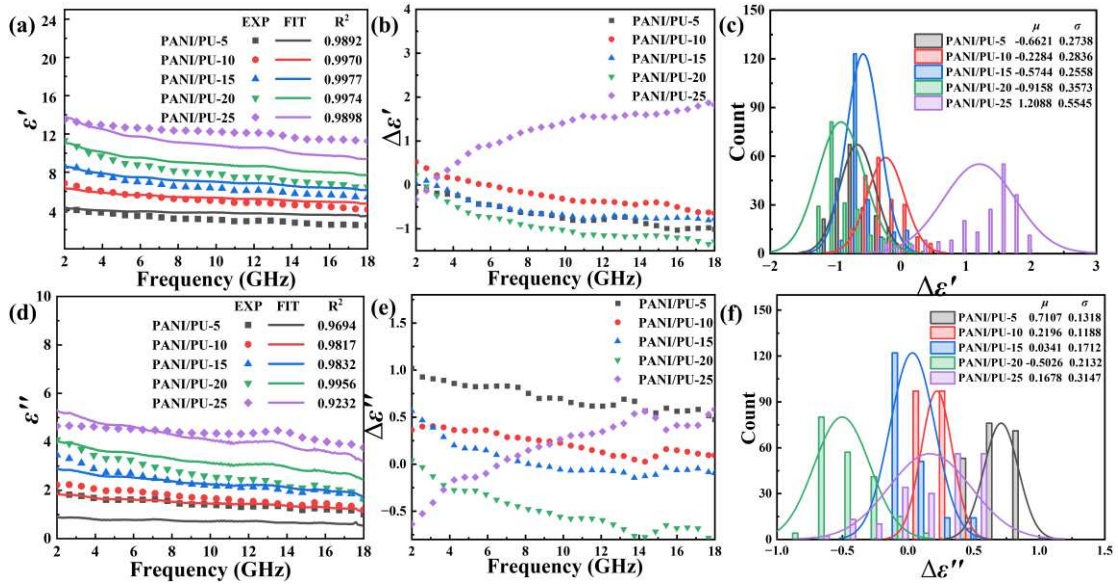


Fig. 3. Comparison between the experimental and MG-fitted complex permittivity of PANI/PU composites with different PANI loadings: (a) real part, (b) frequency-dependent residuals and (c) residual distributions for the real part; (d) imaginary part, (e) frequency-dependent residuals and (f) residual distributions for the imaginary part.

Figure 3 provides a comprehensive evaluation of the Maxwell–Garnett (MG) model for describing the complex permittivity of binary PANI/PU composites. As shown in Fig. 3a and 3d, the calculated curves accurately reproduce both the frequency dispersion and composition dependence of the experimental permittivity over 2–18 GHz. Specifically, the model captures the gradual decrease in ε' and ε'' with increasing frequency, as well as their systematic enhancement with increasing PANI loading. The

R^2 values range from 0.9892 to 0.9977 for ϵ' and from 0.9232 to 0.9956 for ϵ'' , with corresponding mean values of 0.9942 and 0.9706, respectively. These results demonstrate that the MG model describes not only the dielectric energy-storage response but also the principal variation in dielectric loss across the investigated composition range. The frequency-dependent residuals in Fig. 3b and 3e further reveal that the deviations vary smoothly with frequency without pronounced random oscillations, indicating stable model behavior. For ϵ' , the residual means range from -0.9158 to 1.2088 , with standard deviations of 0.2558 – 0.5545 , whereas those for ϵ'' range from -0.5026 to 0.7107 , with standard deviations of 0.1188 – 0.3147 . The corresponding distributions in Fig. 3c and 3f are relatively concentrated, indicating that the discrepancies are predominantly limited systematic offsets rather than broadly dispersed random errors. Nevertheless, the residual sign changes with PANI loading: the negative ϵ' residuals at low and intermediate loadings indicate a slight overestimation by the model, whereas the positive residuals of PANI/PU-25 reflect a moderate underestimation at the highest loading. This behavior may partly reflect the gradual departure of the composite microstructure from the ideal dispersed-filler assumption of the MG model. As indicated by the SEM observations, increasing PANI loading reduces the interparticle distance and promotes local aggregation, particle contact, interfacial polarization, and possible conductive-pathway formation, none of which are fully represented by the idealized effective-medium description. Despite these local deviations, the MG model maintains high fitting accuracy and relatively stable residual distributions across all five compositions. A definitive model selection is made below after comparison with the CP and BR models under identical criteria.

The needle-shaped coherent-potential (CP) model in Eq. (2) was subsequently introduced for comparison. The CP model treats the composite as a homogeneous effective medium and performs orientational averaging of the axial and transverse responses of the needle-shaped fillers [46,47]. Because the unknown effective complex permittivity also enters the local-field calculation, the model must be solved iteratively under a self-consistent condition.

$$\varepsilon_{eff}^* = \varepsilon_e^* + \frac{V_f}{3} (\varepsilon_i^* - \varepsilon_e^*) \left(1 + \frac{6\varepsilon_{eff}^* - 2\varepsilon_e^*}{2\varepsilon_{eff}^* + \varepsilon_i^* - \varepsilon_e^*} \right) \quad (2)$$

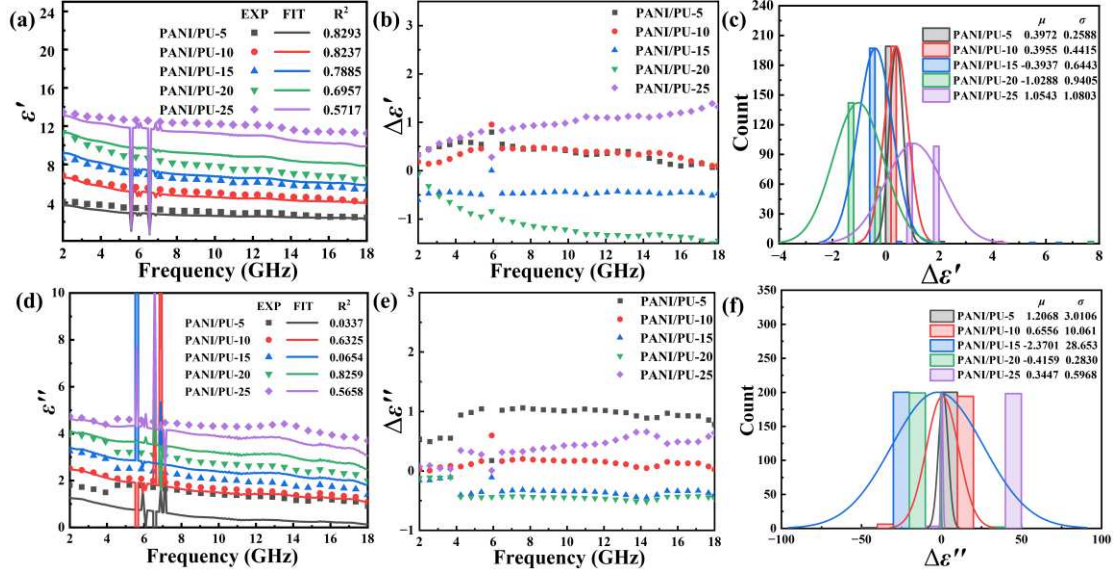


Fig. 4. Comparison between the experimental and CP-fitted complex permittivity of PANI/PU composites with different PANI loadings: (a) real part, (b) frequency-dependent residuals and (c) residual distributions for the real part; (d) imaginary part, (e) frequency-dependent residuals and (f) residual distributions for the imaginary part.

As shown in Fig. 4a and 4d, the CP model qualitatively reflects the overall decrease in complex permittivity with increasing frequency and its increase with increasing PANI content; however, its quantitative agreement is substantially weaker than that of the MG model. The R^2 values for ε' are only 0.5717–0.8293, and both the mean and dispersion of the residuals increase markedly for the high-loading samples. For ε'' , the R^2 values range from 0.0337 to 0.8259, and the residuals of several samples exhibit pronounced frequency dependence and broad distributions. By comparison, the MG model yields R^2 ranges of 0.9892–0.9977 and 0.9232–0.9956 for ε' and ε'' , respectively. Accordingly, the CP model provides a less stable description of the dielectric-loss response than the MG model. The BR model was then evaluated to complete the three-model comparison.

To determine whether a symmetric self-consistent formulation could improve the description, the needle-shaped BR model was evaluated as the third candidate. This model treats the matrix and filler symmetrically within the same effective medium and performs orientational averaging of the axial and transverse dielectric responses of the needle-shaped filler to obtain the effective complex permittivity of the composite [48].

The BR model is likewise an implicit self-consistent model that requires a numerical iterative solution and can describe composites in which different constituents jointly participate in the dielectric response.

$$\varepsilon_{eff}^* = \varepsilon_e^* + \frac{V_f}{3} (\varepsilon_i^* - \varepsilon_e^*) \left(1 + \frac{4\varepsilon_{eff}^*}{\varepsilon_i^* + \varepsilon_{eff}^*} \right) \quad (3)$$

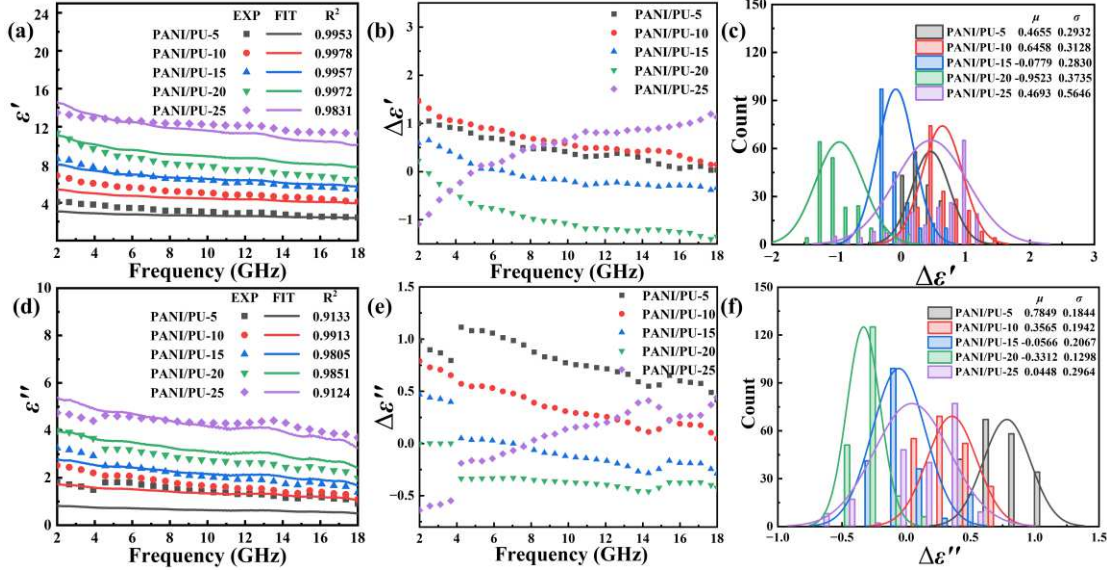


Fig. 5. Comparison between the experimental and BR-fitted complex permittivity of PANI/PU composites with different PANI loadings: (a) real part, (b) frequency-dependent residuals and (c) residual distributions for the real part; (d) imaginary part, (e) frequency-dependent residuals and (f) residual distributions for the imaginary part.

Fig. 5a and 5d show that the BR model describes the overall variations in ε' and ε'' with frequency and PANI content reasonably well, yielding R^2 ranges of 0.9831–0.9978 and 0.9124–0.9913, respectively; its overall performance is therefore substantially better than that of the CP model. However, the residuals in Fig. 5b and 5e remain composition- and frequency-dependent, and several curves deviate systematically from the zero baseline. The R^2 values for ε'' of PANI/PU-5 and PANI/PU-25 are 0.9133 and 0.9124, respectively, indicating that the BR model is less stable than the MG model in describing the loss response under different filling conditions. The mean R^2 values of the BR model are approximately 0.9938 for ε' and 0.9565 for ε'' , which are lower than the corresponding values of 0.9942 and 0.9706 obtained using the MG model. Considering both goodness of fit and residual characteristics, the MG model provided the best overall balance between fitting accuracy and residual stability and was therefore selected for subsequent analyses.

To assess whether the effective constituent complex permittivity of PANI retrieved using the MG model exhibits physically reasonable relaxation and conduction behavior, the modified Debye–conductivity model in Eq. (4) was employed for a physical-consistency analysis. By introducing a relaxation-time distribution exponent and a dc-conductivity term into the single-Debye relaxation model [49], this expression simultaneously describes the dielectric dispersion associated with nonideal dipolar relaxation and the loss contribution arising from charge-carrier transport.

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (j\omega\tau)^{1-\alpha}} - j \frac{\sigma_{dc}}{\omega\varepsilon_0} \quad (4)$$

where ε_s and ε_∞ denote the low and high-frequency limiting permittivities, respectively; τ is the characteristic relaxation time; α characterizes the width of the relaxation-time distribution; σ_{dc} is the dc conductivity; ω and ε_0 are the angular frequency and vacuum permittivity, respectively.

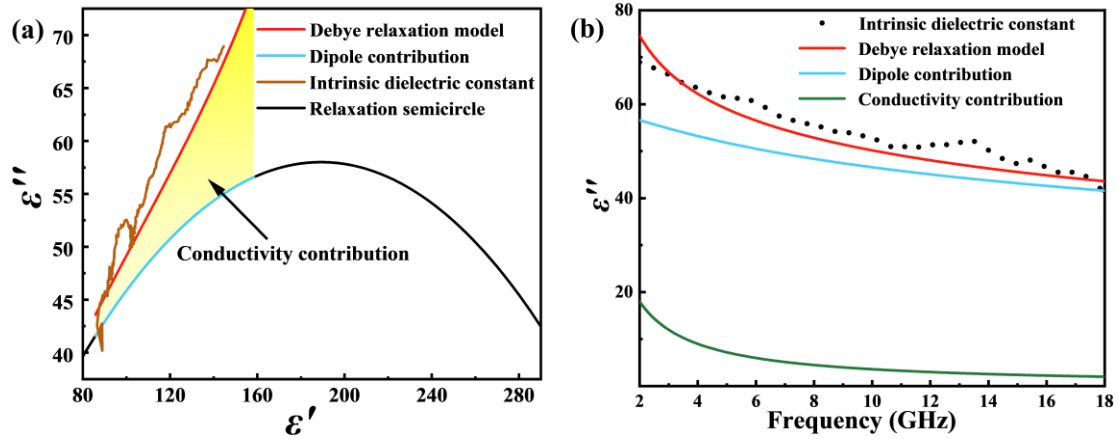


Fig. 6. Dielectric-loss decomposition and physical-consistency assessment of the effective constituent complex permittivity retrieved for PANI: (a) Cole–Cole plot showing the dipolar-relaxation and conduction-loss contributions; (b) frequency dependence of the retrieved imaginary permittivity, modified Debye model, dipolar-relaxation contribution, and conduction contribution.

To examine the physical consistency of the PANI parameters retrieved through MG inversion, the dielectric-loss response was analyzed using the modified Debye–conductivity model in Eq. (4), as shown in Fig. 6. The fitted parameters are listed in Table S6. In the Cole–Cole plane, the retrieved data deviate distinctly from an ideal single-Debye semicircle. The modified model describes this nonideal response through the relaxation-time distribution represented by α and the conduction loss represented by σ_{dc} . In Fig. 6a, within the adopted model decomposition, the difference between

the total loss and the purely dipolar contribution is assigned to a conduction-related contribution, consistent with non-negligible charge-transport effects in the retrieved dielectric response [50]. This interpretation is consistent with the conjugated backbone and protonated nitrogen-containing structures identified by FTIR. Fig. 6b further shows that the modified Debye–conductivity curve follows the overall frequency-dependent decrease in the retrieved ε'' , while the purely dipolar term remains lower throughout the frequency range, indicating that the retrieved response is consistent with contributions from both distributed relaxation and conduction-related loss over 2–18 GHz. Accordingly, this analysis constitutes a test of the physical consistency of the retrieved parameters rather than a repeated numerical validation using a second independent experimental dataset.

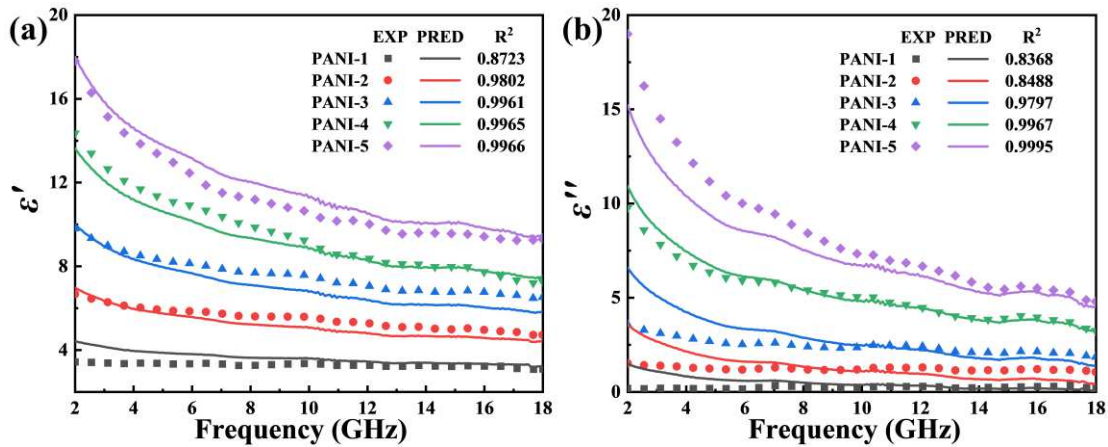


Fig. 7. Experimental and independently predicted (a) real part (ε') and (b) imaginary part (ε'') of the permittivity of PANI/paraffin composites with different PANI loadings.

A more stringent test of parameter transferability was performed by replacing the PU matrix with paraffin while retaining the PANI parameters retrieved from the PANI/PU system, as shown in Fig. 7. Unlike conventional fitting procedures performed separately for each composite system, the frequency-dependent PANI parameters obtained using the MG model were retained without recalibration; only the matrix permittivity and composition-specific volume fractions were updated according to the PANI/paraffin formulations.. Therefore, none of the experimental data for the PANI/paraffin composites were involved in parameter optimization, and the comparison shown in Fig. 7 represents an independent cross-matrix prediction rather than an additional fitting process.

As shown in Fig. 7a and 7b, the predicted curves successfully reproduce the principal frequency- and composition-dependent characteristics of both ε' and ε'' over 2–18 GHz. With increasing frequency, both components gradually decrease, consistent with the frequency-dispersive dielectric response of the PANI-containing composites. At a given frequency, ε' and ε'' increase systematically with increasing PANI loading, consistent with the increasing contribution of the PANI phase to the overall dielectric response. The R^2 values range from 0.8723 to 0.9966 for ε' and from 0.8368 to 0.9995 for ε'' . In particular, for the medium- and high-loading samples PANI-3–PANI-5, the R^2 values reach 0.9961–0.9966 for ε' and 0.9797–0.9995 for ε'' , showing good predictive consistency for both dielectric energy-storage and loss responses at medium and high PANI loadings. The comparatively lower R^2 values obtained for PANI-1 and PANI-2, especially for ε'' , should be interpreted in relation to their narrow dielectric-response ranges. At low PANI loadings, the response is dominated by the low-permittivity and low-loss paraffin matrix; consequently, small experimental fluctuations or minor absolute deviations can produce a relatively large reduction in R^2 . In addition, differences in matrix polarity, filler dispersion, and interfacial states between PU and paraffin may introduce local deviations that are not explicitly represented by the idealized two-phase mixing law. Nevertheless, the model preserves the correct response magnitude, frequency-dispersion trend, and composition dependence across all five formulations. The progressive improvement in prediction accuracy with increasing PANI loading is consistent with the interpretation that the retrieved parameter contains a transferable contribution associated with the dielectric response of PANI itself. These results support the cross-matrix predictive utility of the retrieved PANI parameters within the investigated PU-to-paraffin transfer and justify their use as fixed inputs for the subsequent ternary prediction.

Building on the binary-model comparison, the MG framework was extended to the ternary system using Eq. (5), where ε_{eff}^* and ε_0^* denote the effective complex permittivity of the ternary composite and the complex permittivity of the PU matrix, respectively. The parameters ε_1^* and ε_2^* represent the independently retrieved constituent complex permittivities of PANI and CIP. In Eq. (5), (f_1) denotes the volume fraction

of needle-like PANI and is associated with the corresponding depolarization-factor set, $N_j^{(1)}$ whereas f_2 denotes the volume fraction of platelet-like CIP and is associated with $N_j^{(2)}$, where $j=x,y,z$. The detailed determination of the depolarization factors for the needle-like and platelet-like geometries is provided in the Supplementary Information. Through summation over the three principal directions, the morphology-dependent polarization contributions of PANI and CIP are incorporated simultaneously into the same local-field expression, rather than through the sequential superposition of two binary models, thereby avoiding the explicit mixing-order dependence associated with sequential binary mixing and removing the need to introduce intermediate effective-medium parameters [51]. The PANI input was obtained from the PANI/PU binary system, whereas the CIP input was independently retrieved from the CIP/PU composites, as shown in Fig. S3. PU was treated as the continuous phase, and all constituent permittivities, volume fractions, and depolarization factors were fixed before ternary prediction. Therefore, no parameter was introduced or recalibrated using the experimental dielectric spectra of the ternary composites.

$$\varepsilon_{eff}^* = \varepsilon_0^* + \frac{\varepsilon_0^*}{3} \sum_{j=x,y,z} \frac{f_1 \frac{\varepsilon_1^* - \varepsilon_0^*}{\varepsilon_0^* + N_j^{(1)}(\varepsilon_1^* - \varepsilon_0^*)} + f_2 \frac{\varepsilon_2^* - \varepsilon_0^*}{\varepsilon_0^* + N_j^{(2)}(\varepsilon_2^* - \varepsilon_0^*)}}{1 - N_j^{(1)} f_1 \frac{\varepsilon_1^* - \varepsilon_0^*}{\varepsilon_0^* + N_j^{(1)}(\varepsilon_1^* - \varepsilon_0^*)} - N_j^{(2)} f_2 \frac{\varepsilon_2^* - \varepsilon_0^*}{\varepsilon_0^* + N_j^{(2)}(\varepsilon_2^* - \varepsilon_0^*)}} \quad (5)$$

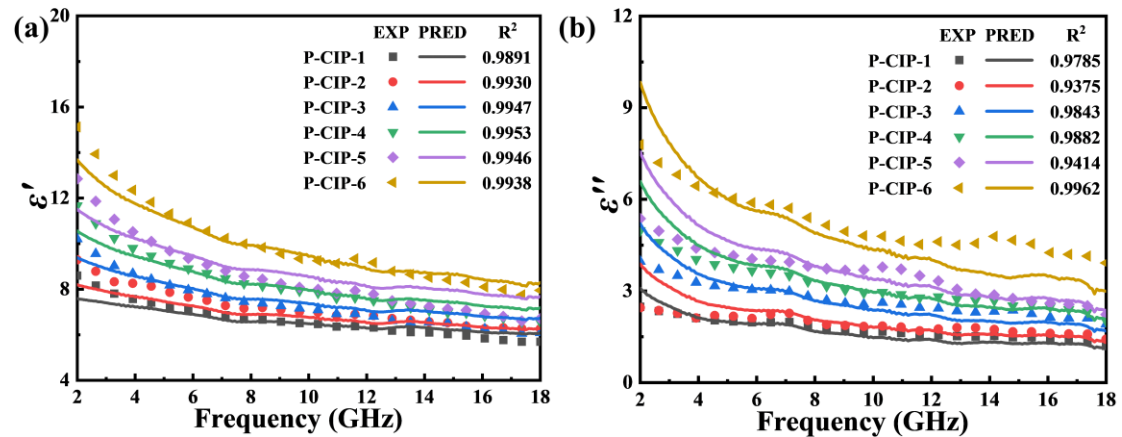


Fig. 8. Experimental and predicted (a) real and (b) imaginary permittivities of the PANI/CIP/PU compositional series, including five ternary formulations and one PANI/PU binary endpoint.

Having established the physical consistency and cross-matrix transferability of the binary-derived constituent parameters, these parameters were subsequently used for ternary-composite prediction. Figure 8 provides the central validation of the proposed

binary-informed ternary prediction framework. Before the ternary calculations were performed, the effective constituent complex permittivity of PANI had been retrieved from the PANI/PU binary system. Its physical consistency was assessed using the modified Debye–conductivity model, while its cross-matrix predictive utility was evaluated through independent prediction of PANI/paraffin composites. The complex permittivity of CIP was independently determined from CIP/PU binary composites, while the PU matrix parameters and constituent volume fractions were obtained separately. These parameters were then introduced as fixed inputs into the ternary MG expression, in which the dielectric contributions of PANI and CIP were incorporated simultaneously within a unified local-field framework. This treatment differs from sequential binary mixing by incorporating the contributions of both fillers simultaneously within a unified local-field expression, thereby avoiding explicit mixing-order dependence. Because no ternary experimental spectra were used to recalibrate the model, Fig. 8 represents an independent prediction rather than a conventional curve-fitting result.

As shown in Fig. 8a and 8b, the model reproduces the overall magnitude, frequency dispersion, and composition dependence of the complex permittivity across all six investigated compositions, including five ternary formulations and one PANI/PU binary endpoint sample, over 2–18 GHz. Both the experimental and predicted results show that ε' and ε'' decrease with increasing frequency and progressively increase from P-CIP-1 to P-CIP-6. The model preserves the correct ordering of the dielectric responses among the different formulations throughout the entire frequency range, demonstrating that it captures not only the frequency dispersion of individual samples but also the continuous evolution of permittivity with composition. In particular, the pronounced decrease in permittivity at low frequencies and the more gradual variation at higher frequencies are consistently reproduced [52]. This agreement is consistent with the transfer of the principal frequency-dependent dielectric response contained in the binary-derived PANI and CIP parameters to the ternary formulation.

For the real permittivity ε' , the R^2 values range from 0.9891 to 0.9953, with an average of approximately 0.9935. The corresponding RMSE and MAE values are

0.295–0.616 and 0.222–0.533, respectively. When normalized by the experimental data range, the NRMSE remains within 5.62–11.71%, demonstrating stable and accurate prediction of the dielectric energy-storage response across different compositions. For the imaginary permittivity ϵ'' , the R^2 values range from 0.9375 to 0.9963, with an average of approximately 0.9710. The RMSE and MAE values remain below unity, ranging from 0.175 to 0.749 and from 0.148 to 0.642, respectively, while the NRMSE ranges from 12.74% to 35.12%. Except for P-CIP-2, the NRMSE values of all samples fall within 12.74–18.95%, indicating reasonable predictive agreement for the dielectric-loss response across most investigated compositions. The comparatively high NRMSE of P-CIP-2 is mainly attributable to its narrow ϵ'' variation range, which increases the sensitivity of range normalization to local fluctuations. Nevertheless, its RMSE and MAE are only 0.364 and 0.223, respectively, indicating that the elevated normalized error does not correspond to a large absolute discrepancy between the predicted and experimental values.

The slightly larger local deviations observed for ϵ'' than for ϵ' are physically reasonable because the imaginary permittivity is more sensitive to filler contacts, charge-carrier transport, interfacial polarization, dispersion heterogeneity, and possible PANI–CIP interfacial coupling. These microstructural effects may produce local spectral fluctuations that are not explicitly represented by the idealized effective-medium expression. Despite these limitations, the model accurately reproduces the overall magnitude, frequency dispersion, and composition dependence of ϵ'' without introducing any ternary-specific correction parameter. This result suggests that, within the investigated composition range, the dominant dielectric response of the ternary composites can be quantitatively described by the independently determined constituent permittivities and their volume fractions. The good agreement indicates that explicit three-phase interfacial correction terms are not required to reproduce the dominant permittivity trends within the investigated composition range, although PANI–CIP interactions and other microstructural effects may still contribute to local spectral deviations [53].

Furthermore, the accurate prediction of the PANI/PU endpoint sample confirms

that the ternary expression exhibits the correct limiting behavior at the compositional boundary, while its successful application to the five PANI/CIP/PU formulations demonstrates predictive continuity from binary to ternary systems. These results suggest that the binary-derived PANI and CIP parameters retain predictive utility beyond the individual binary datasets from which they were obtained and can serve as effective constituent descriptors for forward prediction within the investigated composition range. Accordingly, the proposed strategy provides a route for extending mixing-law analysis from retrospective curve fitting toward prospective composition screening and design. Once the constituent parameters are known, the complex-permittivity spectra of candidate ternary formulations can be calculated by varying the PANI and CIP volume fractions before sample preparation, thereby providing a quantitative basis for reducing formulation-screening experiments and guiding the composition design of multicomponent dielectric composites.

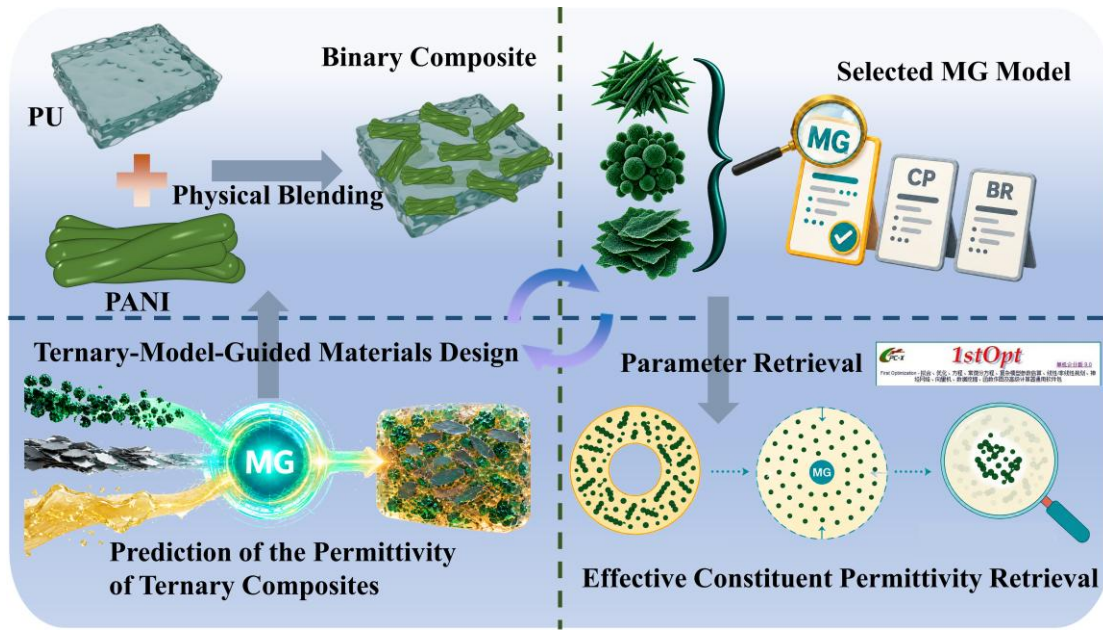


Fig. 9. Schematic illustration of the model-driven workflow from binary-model selection to ternary-composite permittivity prediction.

The complete modeling workflow is schematically summarized in Fig. 9. Binary PANI/PU data were first used to compare the MG, CP, and BR models under identical criteria, after which the MG model was selected for constituent-parameter retrieval. The retrieved PANI response was then subjected to physical-consistency and cross-matrix tests before being combined with the independently determined CIP and PU parameters

in the unified ternary expression. This sequence provides a route from system-specific binary fitting toward transferable parameterization and forward prediction, thereby reducing formulation-screening experiments and providing a quantitative basis for the composition design of multicomponent composites.

4. Conclusion

This study established a binary-parameter-driven mixing-law framework for the forward prediction of the frequency-dependent complex permittivity of polyaniline (PANI)/carbonyl iron powder (CIP)/polyurethane (PU) composites over 2–18 GHz. Comparison of the Maxwell–Garnett (MG), coherent-potential (CP), and Bruggeman (BR) models demonstrated that MG provided the best overall balance between fitting accuracy and residual stability. The PANI response retrieved using the MG model was therefore treated as a model-dependent effective constituent descriptor, whose dielectric-response consistency and cross-matrix transferability were further supported by modified Debye–conductivity analysis and independent prediction of PANI/paraffin composites. By incorporating the independently obtained effective responses of PANI and CIP together with the PU matrix permittivity and constituent volume fractions, the unified MG-based ternary expression successfully predicted five PANI/CIP/PU formulations with a fixed total filler loading of 30 wt.% and one binary endpoint without fitting ternary dielectric spectra. The resulting R^2 values reached 0.9891–0.9953 for ϵ' and 0.9375–0.9963 for ϵ'' , while the NRMSE remained within 5.62–11.71% for ϵ' and below 19% for most ϵ'' datasets. These results show that binary-derived effective constituent responses can support forward permittivity prediction without ternary-specific recalibration and provide a quantitative basis for reducing formulation screening and guiding composition selection within the investigated PANI/CIP/PU system.

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Data Availability

The data that support the findings of this study are available from the corresponding

author upon reasonable request.

Conflict of Interest

The authors declare no conflict of interest.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work, the authors used ChatGPT by OpenAI only for language refinement and readability improvement. The scientific content, data interpretation, conclusions, and references were checked and verified by the authors. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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