

MXene/PVDF metacomposites with ultra-high and negative permittivity

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Abstract. The dielectric behavior of MXene/polyvinylidene fluoride (PVDF) metacomposites, which simultaneously exhibit ultra-high dielectric constants and negative permittivity, has been investigated. The material exhibits a substantial enhancement in dielectric constant at low frequencies, with values reaching 10^5 , which is primarily caused by interfacial polarization and the unique architecture of MXene. The composite transitions to negative permittivity with increasing MXene content, a result of conductive network formation and free electron accumulation at high filler levels. The dielectric response is highly morphology-dependent, with accordion-shaped formations producing Drude-type negative permittivity and clay-like formations showing Lorentz-type negative permittivity. These dual characteristics of ultra-high and negative permittivity make MXene/PVDF metacomposites highly promising for applications in advanced electronic devices, energy storage, and electromagnetic wave manipulation.

Keywords: Negative permittivity / ultra-high permittivity / MXene / metacomposites

1 Introduction

Advanced composites with tailored electromagnetic properties have attracted significant attention in recent years, particularly those exhibiting negative permittivity [1,2]. Metamaterials, which exhibit unconventional electromagnetic properties, such as negative permittivity, near-zero refractive index or anomalous anisotropy are widely applied in fields ranging from stealth technology to energy storage [3–5]. Their unique characteristics stem from subwavelength structures, enabling interactions with electromagnetic fields in ways that surpass the limited responses of conventional materials. While natural materials can exhibit certain atypical properties (e.g., near-zero permittivity), the key advantage of metamaterials lies in the on-demand control of these responses across desired frequency ranges. This capability has led to a paradigm shift in materials design, facilitating the development of functional materials with customized properties tailored to specific applications, such as those in the radio-frequency (RF) domain [6]. The pursuit of materials with negative permittivity is primarily driven by the demand for high-performance electromagnetic devices [7]. These materials

exhibit immense potential in applications such as perfect absorbers, super lenses, and sensors, owing to their ability to confine and amplify electromagnetic fields [8,9].

In recent years, MXene materials have drawn widespread research attention due to their excellent mechanical properties, chemical stability, and distinctive electronic performance [10]. These two-dimensional (2D) materials demonstrate significant potential in various composite systems, particularly when combined with polymers such as polyvinylidene fluoride (PVDF), a renowned ferroelectric polymer with high dielectric permittivity and piezoelectric properties. The synergistic interaction between MXene flakes and the PVDF matrix offers a promising platform for developing composites with tunable dielectric properties [11–13].

The ability to control the morphology of MXenes, such as achieving accordion-like or clay-like structures, further expands the possibilities for designing composites tailored to specific electromagnetic response requirements. These morphological variations profoundly influence the interactions between MXene layers and the PVDF matrix, resulting in distinct dielectric behaviours. For instance, accordion-like structures, with their increased interlayer spacing and surface area, may form conductive networks at lower concentrations, while clay-like structures may enhance interfacial polarization effects [14,15].

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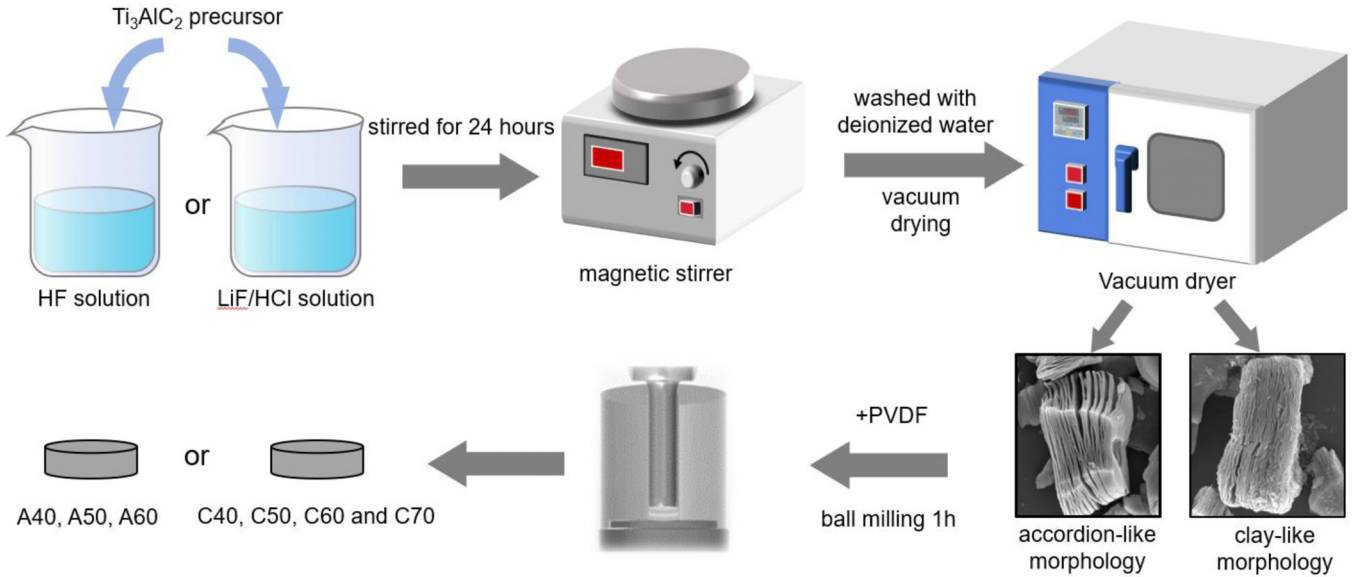


Fig. 1. The synthesis process of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes with different morphologies.

In light of these aspects, the aim of this study is to investigate the dielectric performance of MXene/PVDF composites with varying morphologies and concentrations of $\text{Ti}_3\text{C}_2\text{T}_x$ (where T_x denotes surface terminal groups, typically a mixture of $-\text{O}$, $-\text{F}$, and $-\text{OH}$ functionalities). By employing high-energy ball milling and compression molding techniques, we have fabricated a series of composites and characterized their microstructures and dielectric responses. This research seeks to deepen the understanding of how MXene morphology and concentration influence the dielectric properties of composite materials, providing crucial insights for the design of advanced materials in electronic and energy storage applications.

2 Experimental

As shown in Figure 1, The Ti_3AlC_2 precursor was gradually immersed into HF solution and LiF/HCl solution, respectively. After stirring for 24 hours, the samples underwent multiple washes with deionized water to ensure the removal of residual chemicals, followed by ethanol cleaning to further eliminate impurities. Finally, the samples were vacuum-dried to obtain two types of multilayer $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes with different morphologies (accordion-like and clay-like morphology) [16]. The $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF composites were fabricated using high-energy ball milling and compression molding techniques. The $\text{Ti}_3\text{C}_2\text{T}_x$ with an accordion-like morphology was incorporated at weight fractions of 40%, 50%, and 60% (denoted as A40, A50, and A60), while clay-like $\text{Ti}_3\text{C}_2\text{T}_x$ was used at 40%, 50%, 60%, and 70% (denoted as C40, C50, C60, and C70). The composites with varying $\text{Ti}_3\text{C}_2\text{T}_x$ contents were produced through continuous ball milling of the mixtures at 300 rpm for one hour. Subsequently, the materials were thoroughly blended and compression-molded into cylindrical samples. To ensure precise

dielectric constant measurements, all cylindrical samples were meticulously fabricated with a diameter of 20 mm and a thickness of 1.5 mm. The titanium aluminium carbide (Ti_3AlC_2) power, Polyvinylidene Fluoride (PVDF) powder, Hydrofluoric acid (HF, AR, 40.0%) and Lithium fluoride (LiF, AR, 99.9%) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd.. Hydrochloric acid (HCl, AR, 37%) and ethanol ($\text{C}_2\text{H}_6\text{O}$, AR, 99.7%) were purchased from Shanghai Aladdin Biological Technology Co. Ltd.

The microstructures of the samples were characterized immediately after synthesis (to prevent oxidation) using a scanning electron microscope (SEM, JEOL JSM-IT500HR). The dielectric properties of the composites were evaluated using an LCR meter (Keysight E4980AL, USA) with the parallel plate method, utilizing fixture 16451B. Measurements were conducted over a frequency range of 100 Hz to 1 MHz and taken immediately after the sample were synthesised to prevent the oxidation. To account for residual impedance and stray admittance from the test fixture, both short-circuit and open-circuit compensations were implemented. The two electrodes were carefully aligned in parallel to reduce potential measurement errors. After calibrating and compensating the LCR meter, the samples were placed between the electrodes for dielectric testing. The recorded parameters included capacitance (C), resistance (R), reactance (X), and loss tangent (D).

3 Results

Figure 2 illustrates SEM images of two types of $\text{Ti}_3\text{C}_2\text{T}_x$ powders and MXene/PVDF composites (A60 and C60). The HF-etched $\text{Ti}_3\text{C}_2\text{T}_x$ displays a distinct multi-layered, accordion-like structure (Fig. 2a), characteristic of the exfoliation process induced by hydrofluoric acid. In contrast, the $\text{Ti}_3\text{C}_2\text{T}_x$ etched with a LiF/HCl solution

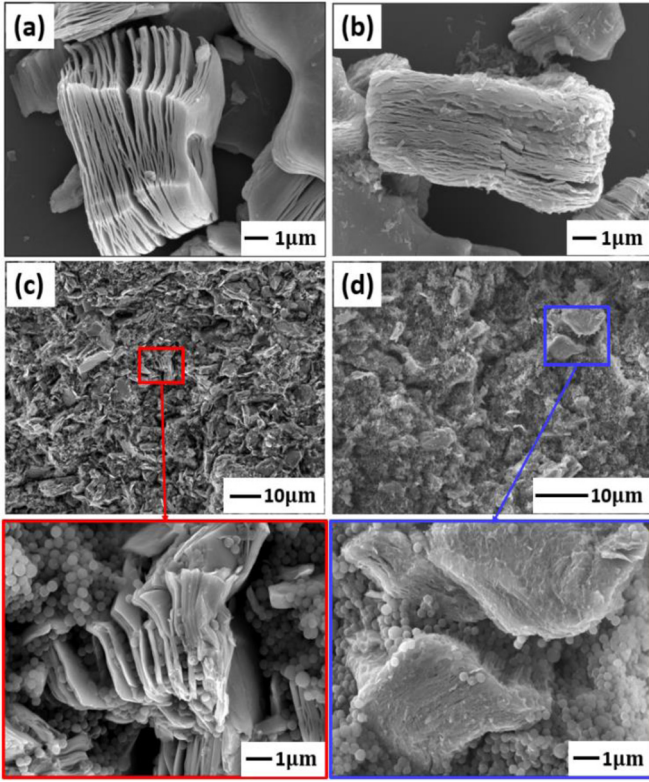


Fig. 2. SEM images of MXene powders ((a) and (b)) and $\text{Ti}_3\text{C}_2\text{T}_x/\text{PVDF}$ composites ((c) A60 and (d) C60).

exhibits a morphology resembling a multi-layered, clay-like structure (Fig. 2b), indicating differences in interlayer spacing and surface texture resulting from the etching method. From the SEM images of the composites (Figs. 2c and 2d), it can be observed that the $\text{Ti}_3\text{C}_2\text{T}_x$ powders are uniformly dispersed within the PVDF matrix. Notably, the inset in Figure 2 reveals that the nanospherical PVDF particles have infiltrated into the interlayer structure of the accordion-like $\text{Ti}_3\text{C}_2\text{T}_x$.

X-ray photoelectron spectroscopy (XPS) was employed to characterize the chemical composition and bonding states of the synthesized two $\text{Ti}_3\text{C}_2\text{T}_x$ materials (Fig. 3). The Ti 2p core-level spectrum (Fig. 3b) displays five distinct doublet peaks, indicating multiple chemical environments of titanium. The characteristic peak at 455.1 eV corresponds to Ti-C bonds, providing direct evidence for successful exfoliation of few-layer $\text{Ti}_3\text{C}_2\text{T}_x$ from the Ti_3AlC_2 precursor through chemical etching. The C 1s XPS spectrum of $\text{Ti}_3\text{C}_2\text{T}_x$ (Fig. 3c) exhibits five distinct peaks at binding energies of 281.8, 282.6, 284.8, 286.3, and 288.7 eV, which are assigned to C-Ti, C-Ti-O, C-C/H, C-F, and C=O/COO species, respectively.

Figure 4 shows the dielectric spectra of the MXene/PVDF composites with different $\text{Ti}_3\text{C}_2\text{T}_x$ concentrations. For samples A40 and A50 (Fig. 4a), the real part of permittivity, ϵ'_r , is positive, decreasing with increasing frequency and increasing with higher $\text{Ti}_3\text{C}_2\text{T}_x$ concentration. Due to the significant contrast in conductivity and

permittivity between $\text{Ti}_3\text{C}_2\text{T}_x$ and the PVDF matrix, interfacial polarization occurs. This effect remains significant at frequencies as high as several hundred kHz, resulting in charge accumulation at the MXene/PVDF boundaries and leading to a dielectric constant for the composite as high as 10^4 to 10^5 . As the $\text{Ti}_3\text{C}_2\text{T}_x$ content is further increased, negative permittivity emerges (Fig. 4b). This phenomenon can be linked to the emergence of conductive networks within the composite due to the high concentration of $\text{Ti}_3\text{C}_2\text{T}_x$ particles [2,17]. The rise in $\text{Ti}_3\text{C}_2\text{T}_x$ content increases free electron density, leading to a negative permittivity that originates from the phase-shifted electron oscillations under alternating electric fields. This behavior is commonly observed in percolative composites, where the dielectric properties transition from insulating to metallic as the filler content reaches or exceeds the percolation threshold [1,18]. As shown in Figures 2a and 2b, when the $\text{Ti}_3\text{C}_2\text{T}_x$ content increased from 50% to 60%, the real part of permittivity transitioned from negative to positive values, indicating that the percolation threshold falls within the 50–60% range. The negative response can be modelled using the Drude model [19],

$$\epsilon'_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + \omega_\tau^2} \quad (1)$$

$$\epsilon''_r(\omega) = \frac{\omega_p^2 \omega_\tau}{\omega^3 + \omega \omega_\tau^2} \quad (2)$$

$$\omega_p = \sqrt{\frac{n_{eff} n^2}{m_{eff} \epsilon_0}} \quad (3)$$

where ω_p ($\omega_p = 2\pi f_p$) is the angular plasma frequency, $\omega = 2\pi f$ is the angular frequency of the applied electromagnetic field, ω_τ is the damping parameter, ϵ_0 is permittivity in vacuum, n_{eff} is the effective concentration of conduction electrons, m_{eff} is the effective weight of electron, and e is the electron charge. The fitted ω_p of A60 is 14.40 GHz and the reliability factor (R^2) is 0.995.

For clay-like MXene/PVDF composites (C40, C50, and C60), a high dielectric constant is also observed in the low-frequency range (Fig. 4d). However, compared to accordion-like MXene/PVDF composites (A40 and A50), its value is lower by an order of magnitude. This disparity is primarily attributed to the distinct microstructure of $\text{Ti}_3\text{C}_2\text{T}_x$. SEM images reveal that accordion-like $\text{Ti}_3\text{C}_2\text{T}_x$ possesses a more pronounced layered structure, resulting in a substantially larger specific surface area. When the $\text{Ti}_3\text{C}_2\text{T}_x$ content reaches 70%, exceeding the percolation threshold, permittivity transitions from negative to positive at 535 kHz, negative permittivity emerges at 535 kHz. (Fig. 4e). The permittivity characteristics is in agreement with the Lorentz model [20,21],

$$\epsilon = 1 + \frac{\omega_p^2 (\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + \omega \omega_\tau^2} \quad (4)$$

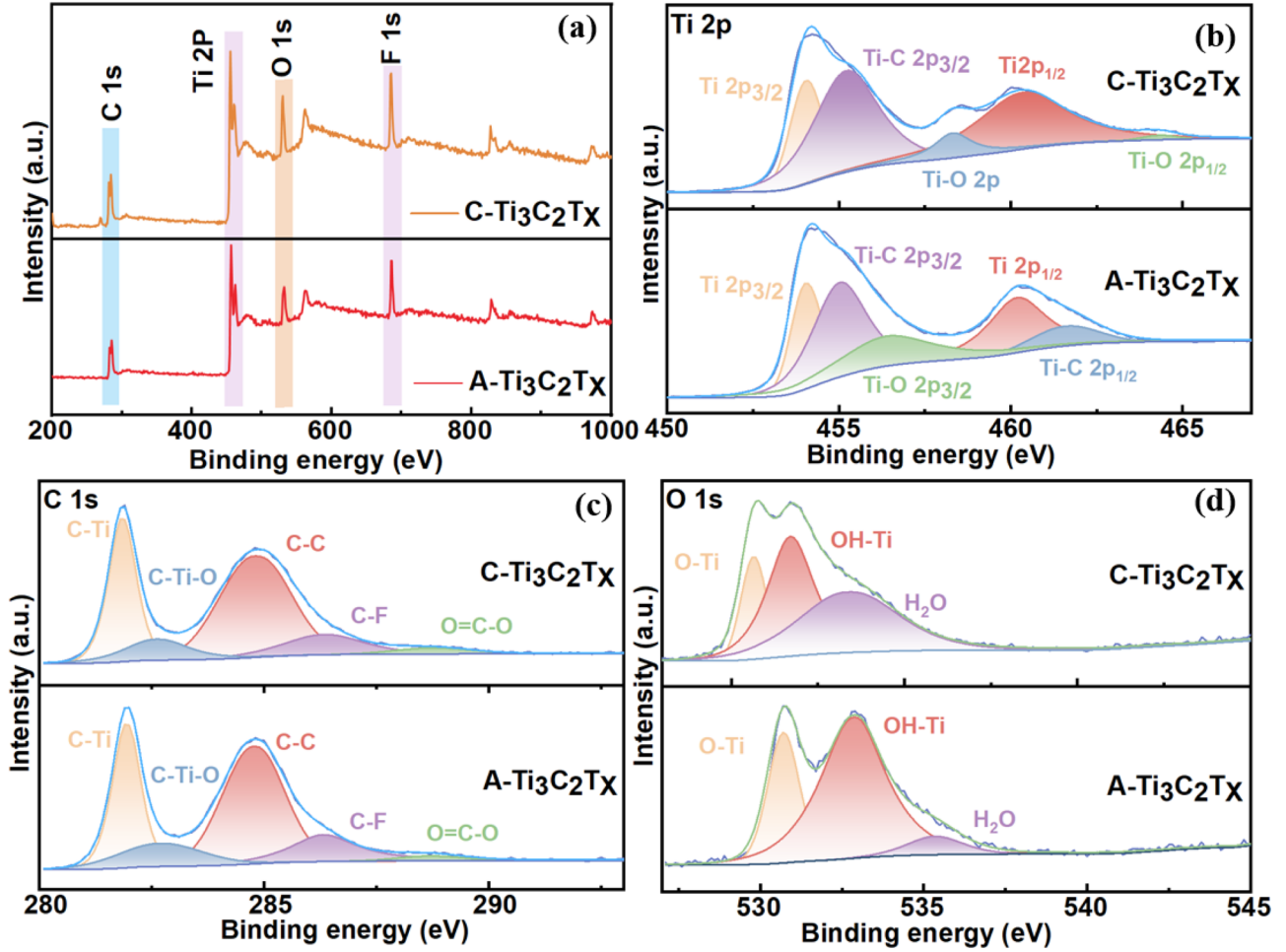


Fig. 3. XPS images of MXene powders ((a) XPS survey, (b) Ti 2p, (c) C 1s and (d) O1s).

where ω_p is the plasma frequency, ω_0 is the characteristic frequency, ω is the angular frequency, and ω_τ is the damping constant. The fitted ω_p is 242.73MHz and the reliability factor (R^2) is 0.981. In clay-like MXene/PVDF composites, this negative permittivity phenomenon is predominantly attributed to interfacial polarization or bound vibrations.

Figure 5 provides the dielectric loss and AC conductivity data for the composites. As depicted in Figures 5a and 5b, the dielectric loss increases with higher $\text{Ti}_3\text{C}_2\text{Tx}$ mass fractions, driven by interfacial polarization. For accordion-like MXene/PVDF composites, when the mass fraction reaches 60%, surpassing the percolation threshold, negative permittivity emerges, and dielectric loss exhibits a frequency-dependent decline, driven by the establishment of conductive pathways [22]. The primary source of dielectric loss is conduction loss, resulting from leakage currents induced by the percolation network. These leakage currents originate from the long-range motion of free electrons. At higher frequencies, the influence of leakage currents diminishes, leading to a corresponding decrease in dielectric loss values.

For clay-like MXene/PVDF composites with positive permittivity, the dielectric loss increases with the rise in MXene content. For epsilon-negative composites, the dielectric loss spectrum exhibits a loss peak at 535 MHz, corresponding to the frequency point where the real permittivity switches to negative. This phenomenon is associated with the LC (inductor-capacitor) resonance within the composites. Below the resonant frequency, the composite exhibits positive permittivity, as the capacitive behavior dominates. However, when the frequency near the LC resonant frequency, inductive behavior of the MXene networks becomes more pronounced. At the resonant frequency, the permittivity transitions from positive to negative, indicating a shift from capacitive to inductive dominance. This transition is accompanied by a peak in dielectric loss, resulting from the maximum energy dissipation at resonance.

The Drude-type negative permittivity composites exhibit significantly lower dielectric loss compared to Lorentz-type, with the difference spanning approximately two orders of magnitude. This distinct behavior highlights the potential of Drude-type materials for applications requiring reduced dielectric loss.

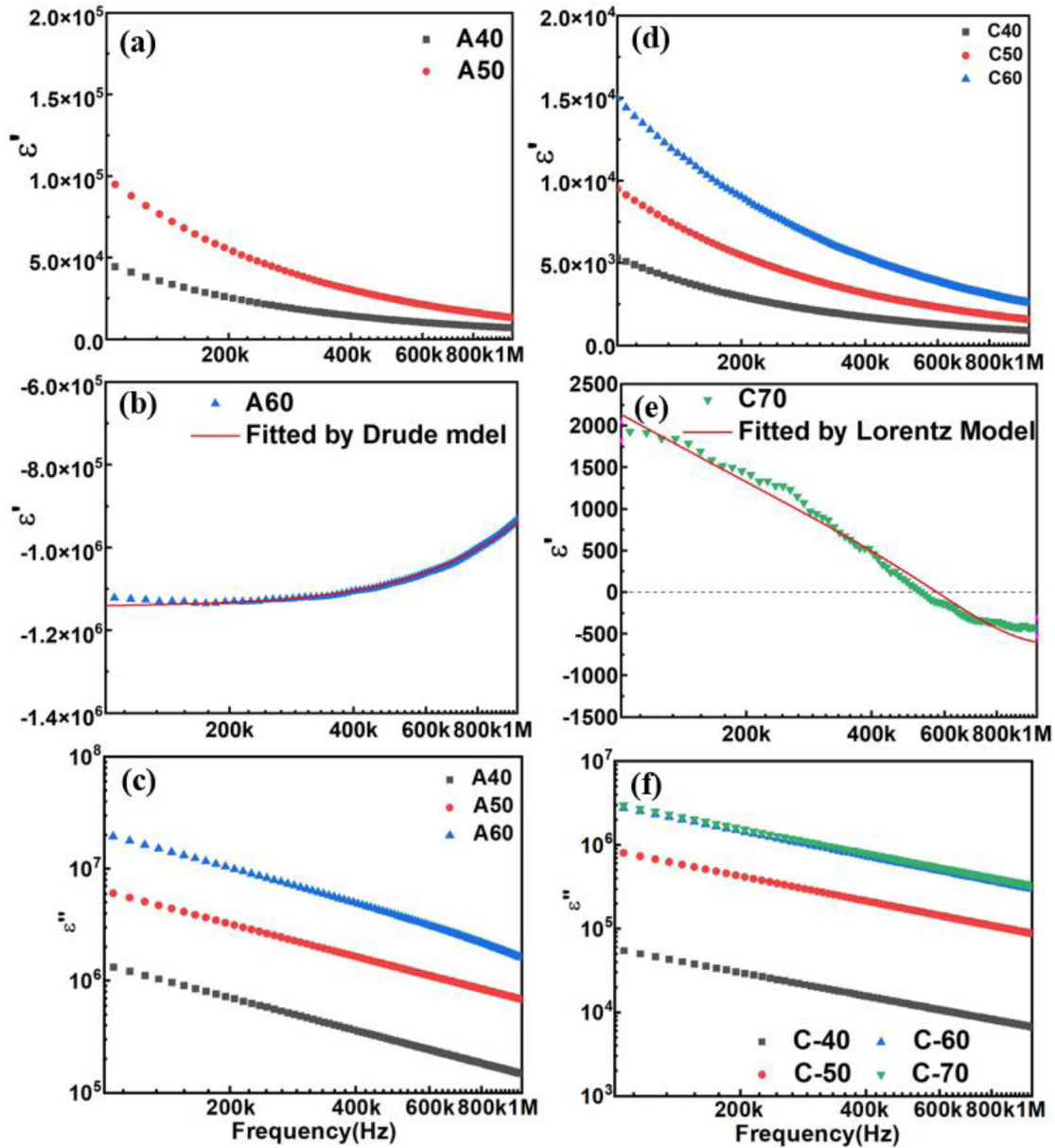


Fig. 4. The permittivity for the MXene/PVDF composites with various $\text{Ti}_3\text{C}_2\text{T}_x$ content ((a)–(c) accordion-like $\text{Ti}_3\text{C}_2\text{T}_x$, (d)–(f) clay-like $\text{Ti}_3\text{C}_2\text{T}_x$).

Figures 5c–5d show the frequency-dependent AC conductivity (σ_{ac}) of the composites. At frequencies below the percolation threshold, the conductivity behavior of the composite materials follows the Jonscher's power-law relationship [23],

$$\sigma_{ac} = \sigma_{dc} + A(2\pi f)^n \quad (5)$$

where σ_{dc} is the direct current conductivity, A is the pre-exponential factor, f is the frequency and n is the fractional exponent, indicating hopping conductivity behavior. Upon reaching the percolation threshold, the conductivity increases significantly, and conductive electrons can travel long distances through the interconnected conductive network, resulting in a transition from hopping conduction

to metallic conductivity. For both accordion-like and clay-like composites, the percolation threshold values differ due to variations in microstructure. The percolation threshold for accordion-like composites is typically lower than for clay-like composites, as the layered morphology facilitates easier formation of conductive pathways. Beyond the percolation threshold, the Jonscher's power-law relationship becomes inapplicable as the material transitions to metallic-like conduction characteristics. In this regime, the DC conductivity becomes the dominant factor, significantly surpassing the frequency-dependent component. The overall conductive behavior of the material conforms to the Drude model, where free electrons dominate charge transport while the contribution of hopping conduction mechanisms becomes negligible.

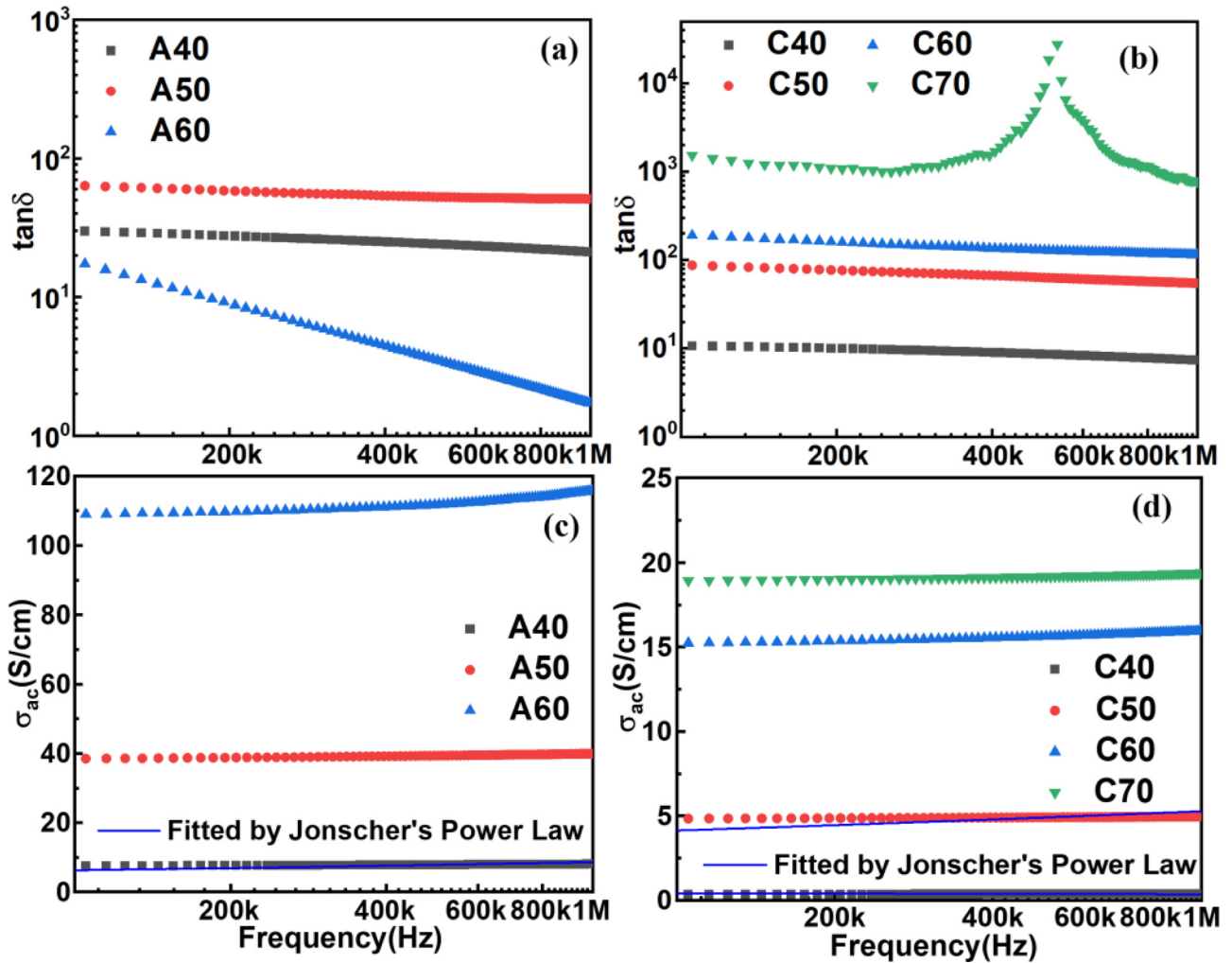


Fig. 5. The dielectric losses ($\tan \delta$) and AC conductivity (σ_{ac}) performances for the MXene/PVDF composites with various $\text{Ti}_3\text{C}_2\text{T}_x$ content ((a), (c) accordion-like $\text{Ti}_3\text{C}_2\text{T}_x$, (b), (d) clay-like $\text{Ti}_3\text{C}_2\text{T}_x$).

4 Conclusions

In this study, MXene/PVDF composites with varying $\text{Ti}_3\text{C}_2\text{T}_x$ contents and morphologies were successfully fabricated and characterized. The dielectric properties of the composites were significantly influenced by both the morphology and concentration of $\text{Ti}_3\text{C}_2\text{T}_x$, showing a significant increase in the low-frequency range, reaching values as high as 10^5 . The accordion-like composites exhibited Drude-type negative permittivity, while the clay-like composites showed Lorentz-type negative permittivity. Below the percolation threshold, the composites demonstrated hopping conductivity, whereas when the $\text{Ti}_3\text{C}_2\text{T}_x$ content exceeded the threshold, a transition from hopping conduction to metallic conductivity occurred. The findings indicate that MXene/PVDF composites, with their tunable dielectric and conductive properties, have promising potential for applications in electronic devices and energy storage systems.

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Conflicts of interest

The authors declare no conflict of interest.

Data availability statement

The data is available upon request.

Author contribution statement

Wei Li: Software, Writing. Fei Lv: Formal analysis. Qing Hou: Conceptualization, Writing, Editing, Supervision, Final preparing.

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