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# Synergistic Advancements: PANI-Coated Short Nylon Fibers for Enhanced Mechanical and Dielectric Properties in Natural Rubber Conducting Polymer Composites

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**ABSTRACT**

Diving into the dynamic realm of microwave technology, this study explores the potential applications of natural rubber (NR)-based conducting polymer composites (CPCs) with a focus on their dielectric and heating properties for high-frequency applications. Seeking to bolster mechanical strength, short nylon fibers are exclusively integrated into the F series (NR, polyaniline (PANI) and polyaniline coated fibres (PANI-N), while the P series (NR and polyaniline (PANI)) comprises only PANI. Investigating both series reveals intriguing dielectric behaviors: dielectric permittivity increases with frequency, reaching 35 (P series) and 11.6 (F series) at 12.7 GHz, influenced by filler loadings. Loss tangent exhibits distinctive trends, rising with PANI loading and decreasing with PANI-N loading. The heating coefficient displays complex behavior in both series, correlating with frequency and loading variations. Furthermore, conductivity and absorption coefficients increase with frequency, optimizing at 12.7 GHz and specific loadings. This pioneering work underscores the synergistic potential of PANI-N in achieving a delicate balance between superior mechanical and microwave properties in NR-based CPCs.

**Keywords:** Microwave properties, Heating applications, Polyaniline, Chloroprene rubber, Permittivity.

## INTRODUCTION

Characterizing materials are crucial for selecting and implementing substances in industrial, scientific, and medical applications. To evaluate their suitability for applications such as lenses, telecommunications, resonators, microwave-integrated circuits and dielectric wave-guides, it is essential to gather dielectric parameter data across a broad temperature range. Understanding the dielectric properties of materials is important for calculating their response to heating during microwave applications. Microwave heating is widely utilized in both industrial and residential heating applications[1-3]. The design of microwave absorbers and food packages necessitates comprehensive dielectric data for lossy materials, making the measurement of dielectric properties a valuable tool for probing into a compound's molecular mechanisms.

Conducting elastomer composites, specifically designed for microwave applications, hold considerable promise[4]. Previous studies have explored composites of Polyaniline (PANI) with various elastomers, showcasing excellent conducting and shielding properties but displaying subpar mechanical characteristics[5,6]. It is widely recognized that incorporating short fibers into rubber composites can significantly enhance their mechanical properties[7-9].

Recognizing the potential of short fibers to significantly enhance mechanical properties, this research bridges the gap by incorporating short fibers coated or grafted with PANI into rubber composites. Such composites, widely used in industry for their cost-effectiveness and improved strength, damping, stiffness, and modulus, stand as a testament to the versatility and practicality of this approach[7,10,11].

In this context, the integration of PANI-coated short nylon fibers (PANI-N) into natural rubber (NR) emerges as a novel solution to address the shortcomings of poor mechanical properties in PANI/rubber conducting composites. The *in-situ* polymerization technique was employed to coat PANI on short nylon fibers, which were then introduced into NR along with PANI to create natural rubber conducting polymer composites (CPCs).

This innovative approach not only enhances mechanical properties but also imparts sufficient conductivity, presenting a breakthrough in the quest for a harmonious balance between mechanical robustness and microwave effectiveness. The work stands as a pioneering effort to reconcile the dual demands of superior mechanical and dielectric properties in conducting polymer composites, marking a significant advancement in the field. The study evaluates the microwave properties of these composites at room temperature across X and S-band frequencies (8-12 GHz and 2-4 GHz, respectively).

## EXPERIMENTAL

PANI was synthesized via the chemical oxidative polymerization of aniline in hydrochloric acid. Following this, PANI-coated Nylon fibers were created through an etching process with chromic acid[12]. The incorporation of short fibers into rubber composites is recognized for enhancing mechanical properties, and this research integrates PANI-coated short nylon fibers into natural rubber to overcome the limitations of mechanical performance in PANI/rubber composites. The *in-situ* polymerization method was utilized to coat the nylon fibers with PANI, which were then combined with natural rubber to form CPCs.

**Table 1: Formulation for the preparation of CPCs**

| Ingredients | P series | | | | F series | | |
|---|---|---|---|---|---|---|---|
| (phr*) | $NP_0$ | $NP_1$ | $NP_2$ | $NP_3$ | $NF_1$ | $NF_2$ | $NF_3$ |
| NR | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| PANI | 0 | 40 | 90 | 140 | 90 | 90 | 90 |
| PANI-N# | 0 | 0 | 0 | 0 | 40 | 80 | 120 |

*parts per hundred rubber, #PANI coated etched fiber, All the mixes contain Stearic acid-1 phr and DCP-3 phr

CPCs were fabricated using varying proportions of PANI, labeled as the P series, and a fixed PANI (90 phr) combined with different amounts of PANI-N, designated as the F series. The preparation techniques, filler distribution, curing behavior, mechanical properties, thermal stability and electrical conductivity of these composites have been previously documented[12]. Building on this, the present work focuses on evaluating the microwave properties of these composites.

### Microwave measurements

To investigate the dielectric properties of materials, cavity perturbation technique has been widely utilized at microwave frequencies[12,13]. The theoretical framework for microwave characterization using this technique is outlined in other references[14,15]. Microwave measurements of the CPCs was conducted using an Agilent Performance Network Analyzer E8362 B. The measurements were carried out at room temperature across the X- and S-band (8–12 GHz, 2–4 GHz, respectively) frequency ranges.

## RESULTS AND DISCUSSION

### Dielectric permittivity

Figure 1 demonstrates the dependence of dielectric permittivity ($\varepsilon'$) on frequency and loading in composites from both series across the two frequency bands. At lower filler loadings, $\varepsilon'$ exhibits minimal variation with frequency; however, at higher loadings, an increase in permittivity is observed with increasing frequency. In contrast, within the S-band, permittivity remains nearly constant regardless of frequency. Dielectric permittivity is determined by dipolar polarization which in turn is affected by applied field frequency. PANI has persistent electric dipoles when protonated with hydrochloric acid. Furthermore, the composites constitute a heterogeneous mixture. It has PANI, a conducting material dispersed in a non-conducting rubber medium. Hence permittivity is also influenced by interfacial polarization[18].

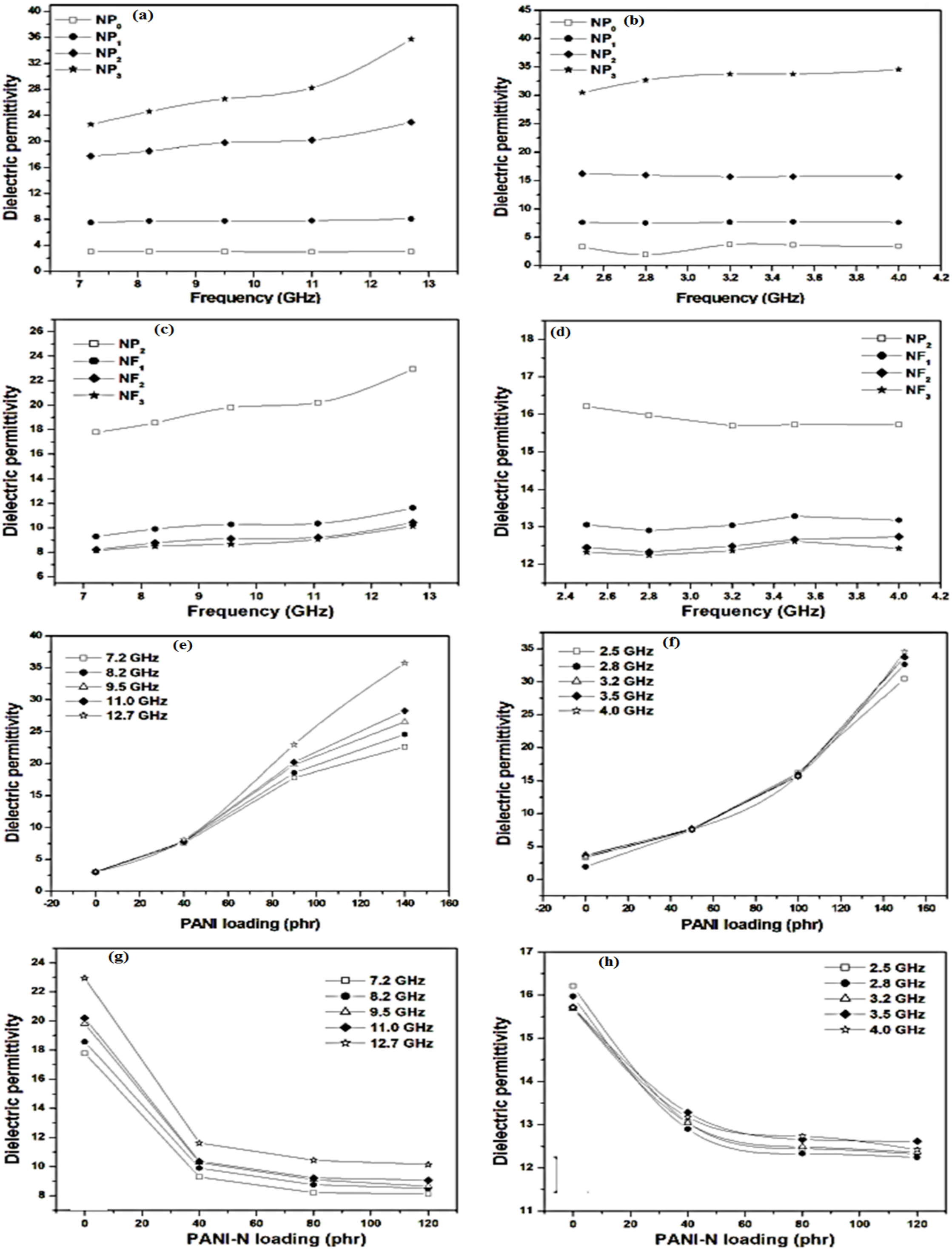



**Fig. 1(a). Dielectric permittivity vs. frequency plots of P series in X band (b). P series in S band (c). F series in X band (d). F series in S band (e). Dielectric permittivity vs. loading plots of P series in X band (f). P series in S band (g). F series in X band (h). F series in S band**

As per Koops, the dielectric permittivity demonstrates an inverse proportionality to the square root of resistivity[16]. In the current study, the DC and AC conductivities of the CPCs were observed to increase with both loading and frequency[17], resulting in a corresponding rise in permittivity, particularly at higher loadings. For instance, a dielectric permittivity of 35 is achieved for the $NP_3$ at 12.7 GHz. John *et al.,* prepared a semi-interpenetrating network formed by PANI and NR from NR latex with different ratios of NR and PANI and measured the permittivity. At ratio 2:1, they reported a value of ~20[17].

Previous studies in the microwave range on chloroprene rubber composites comprising PANI and PANI-N revealed improved dielectric characteristics compared to NR composites[15]. Specifically, composites of CR, at 150 phr PANI loading and 12.7 GHz have a dielectric permittivity of 96, whereas composites of NR have a permittivity of 35[15] at the same frequency and PANI loading of 140 phr. The dielectric permittivity of F series CPCs increases frequency-dependently in the X band, while varying insignificantly in the S band.

$\varepsilon'$ is influenced by the volume fraction of the conducting filler, increasing with higher PANI content due to enhanced conductivity. In both frequency bands, there is a decrease observed with an increase in PANI-N loading. The observed decline in permittivity is due to the low values of conductivity. The DC electrical conductivity of these composites has been studied earlier by us[18]. It exhibits a decrease with increase in the amount of PANI-N though conductivity improves at higher loadings for the F series[18]. At a frequency of 12.7 GHz, the composite NF1 exhibits the highest permittivity of 11.6. The pattern of decreased dielectric permittivity in P series CPCs with rising PANI loading, in contrast to CR-based CPCs, is similarly observed in the F series. Specifically, the dielectric permittivity for the NR-based CPC is only 11.6, while CR-based CPCs with PANI-N (40 phr ) achieve a significantly higher value of 23.6[15].

**Loss tangent**

In Fig. 2, the frequency-dependent and loading- dependent behaviour of the loss tangent for the composites in the X and S bands is illustrated. All CPCs exhibit a similar trend, with the loss tangent increasing as the frequency rises in both bands, observed in both series of CPCs. The movement of free charges in a material causes the dielectric loss at the S band[19,20]. The relaxation process influences the variation in the loss tangent with frequency, which is attributed to the reorientation dynamics of polar groups. At lower frequencies, dipoles align with the applied field, but at higher frequencies, the resistance to dipole movement and internal interactions becomes prominent, resulting in increased dielectric loss.

The NR gum compound ($NP_0$) exhibits remarkably low values for permittivity (3) and loss tangent (0.008). This underscores that the filler, particularly PANI and PANI-N, significantly shapes the material's electrical characteristics and microwave absorption. It is observed that as the PANI loading increases, the loss tangent consistently increases. The trend observed in the F series plot mirrors a similar pattern to the changes in permittivity across both frequency bands

**Heating Coefficient**

When evaluating microwave-absorbing materials, the heating coefficient can be calculated, with the heat produced being proportionate to both the frequency and combined effect of permittivity and the tan. If the material records an elevated heating coefficient value, it is less conducive to dielectric heating applications. It's crucial to recognize that the heat generated within the material is a result of tangent loss, stemming from relaxation loss and the material's conductivity[21].

Figure 3 presents the variation of J with frequency and PANI loading for the composites in both bands. J exhibits a decrease with higher frequencies and increased PANI loading. Improved microwave attenuation is indicated by a lower heating coefficient. A lower heating coefficient signifies improved microwave attenuation. Consequently, as the loading increases, there will be an enhancement in the microwave attenuation of the CPCs.

At the same frequency and PANI-N loading, CR CPC recorded a value of 0.18, suggesting that CR CPCs outperform NR CPCs in high-frequency heating applications. Additionally, the F series CPCs exhibit lower performance compared to the P series composites.

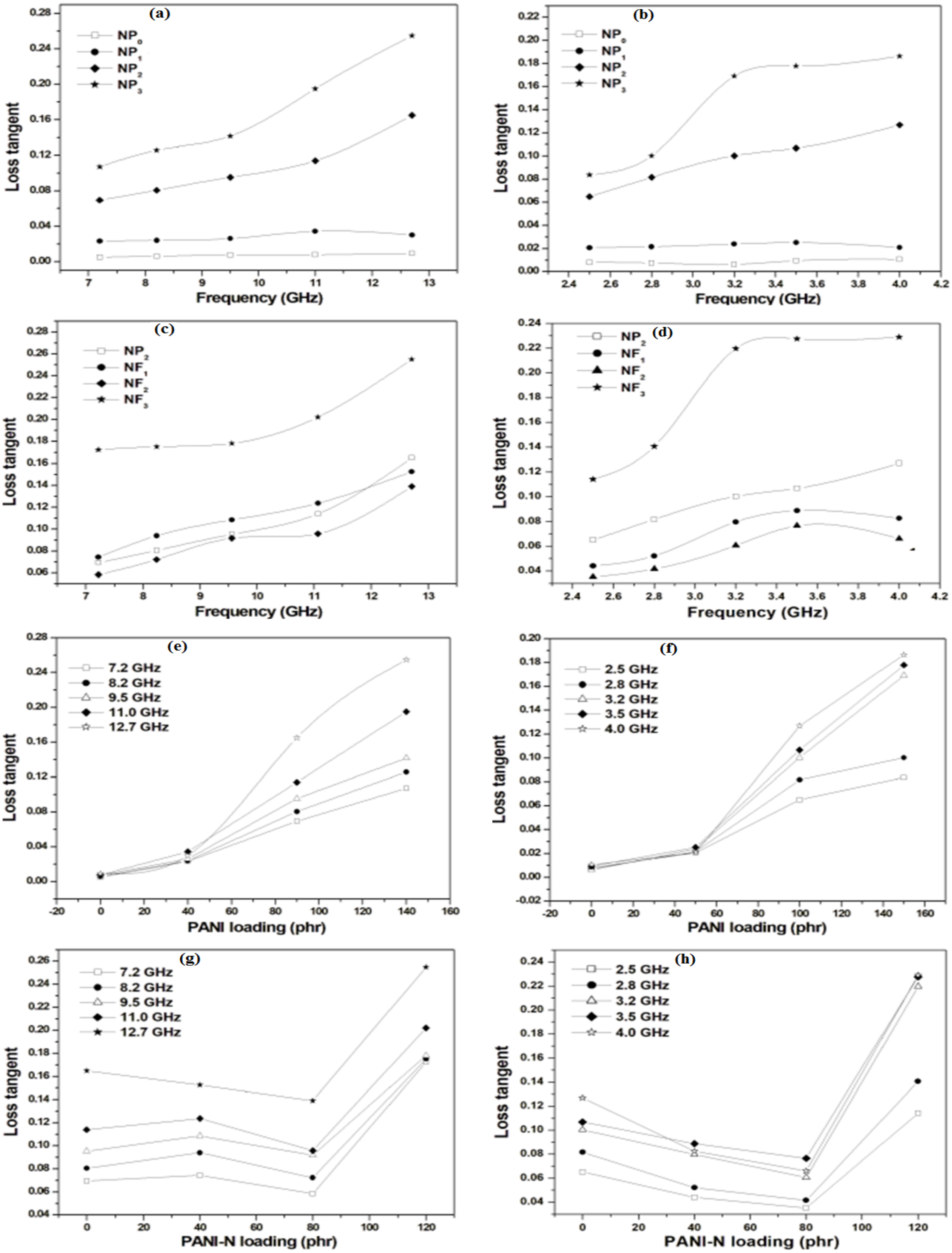



**Fig. 2(a). Loss tangent vs. frequency plots of P series in X band (b). P series in S band (c). F series in X band (d). F series in S band (e). Loss tangent vs. loading plots of P series in X band (f). P series in S band (g) F series in X band (h) F series in S band**

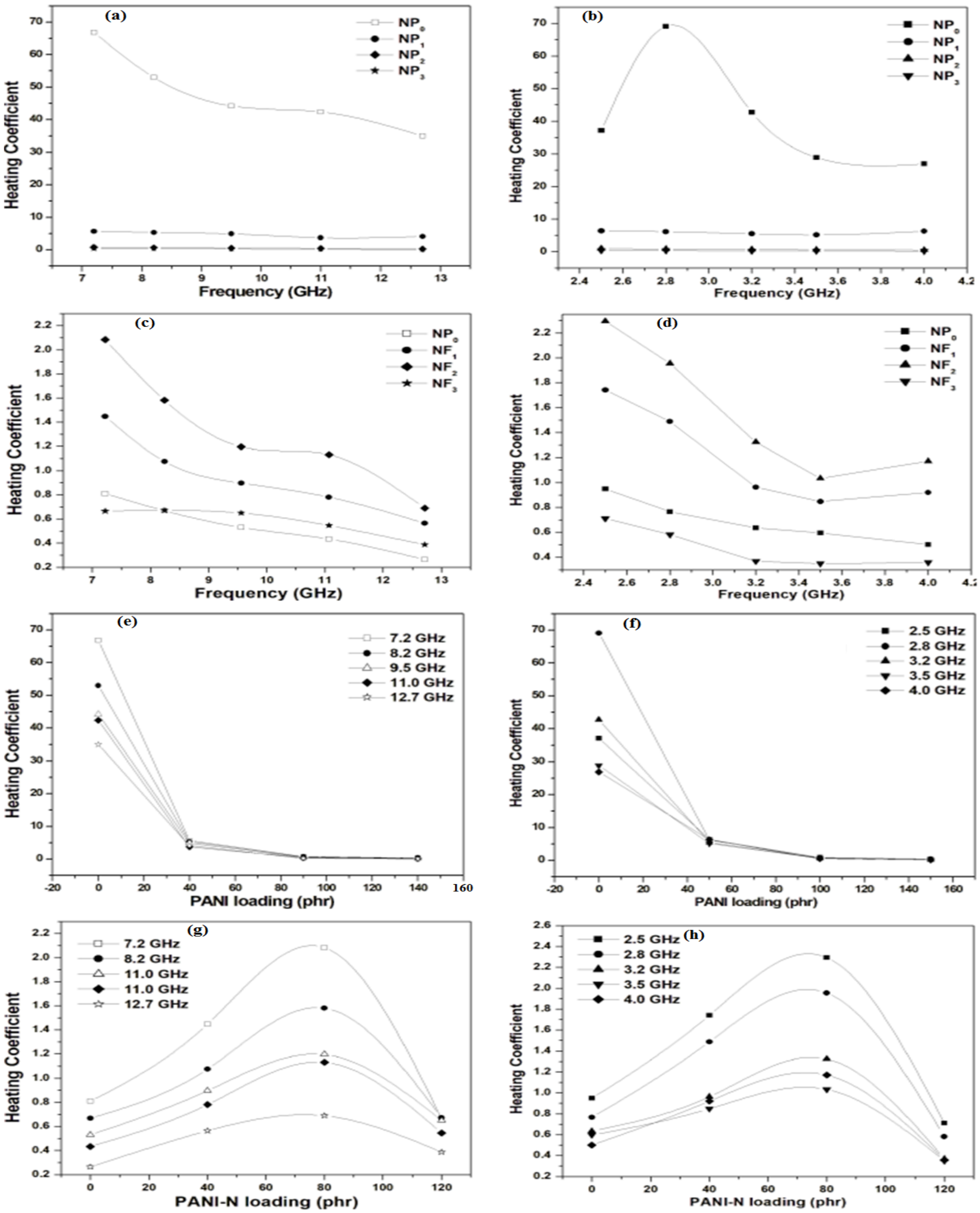



**Fig. 3 (a). Heating Coefficient vs. frequency plots of P series in X band (b). P series in S band (c). F series in X band (d). F series in S band (e). Heating Coefficient vs. loading plots of P series in X band (f). P series in S band (g). F series in X band (h). F series in S band**

## Conductivity

Figure 4 illustrates the frequency-dependent and loading-dependent variation of conductivity for the composites at X band and S band, respectively. Microwave absorption is directly influenced by dielectric loss. Therefore, the trends in the material's conductivity and absorption behavior follow the same pattern as the dielectric loss factor, showing an increase with frequency.

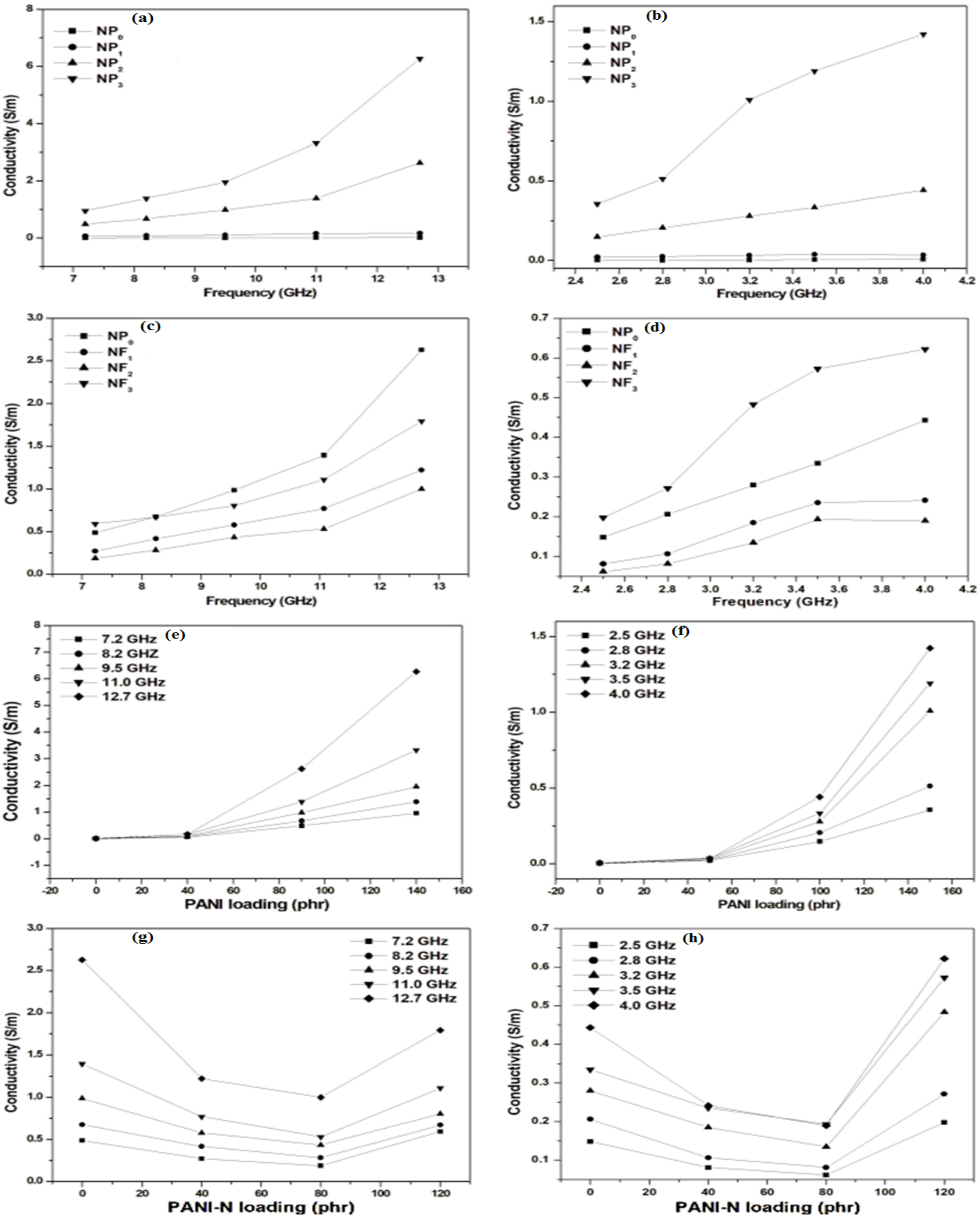



**Fig. 4(a). Conductivity vs. frequency plots of P series in X band (b). P series in S band (c). F series in X band (d) F series in S band (e) Conductivity vs. loading plots of P series in X band (f) P series in S band (g) F series in X band (h) F series in S band**

In the P series, conductivity demonstrates an increase with loading in both frequency bands. Conversely, in the F series, it initially decreases before reaching a higher value at 120 phr loading. Specifically, in the P series, the highest conductivity of 6.27 S/m is recorded at 12.7 GHz for $NP_3$. In the F series, the highest conductivity recorded at the same frequency is 1.79 S/m for $NF_3$.

## Absorption Coefficient

Figure 5 depicts the frequency-dependent and loading-dependent variation of the absorption coefficient for the composites at X band and S band. The absorption coefficient exhibits an upward trend with increasing frequency. Absorption coefficient indicates a material's ability to allow microwaves to pass through with minimal obstruction or absorption[22]. The highest values of the absorption coefficient for the P series are at 12.7 GHz for $NP_3$. Similarly, in the case of F series composites, the optimal value is observed at 12.7 GHz for $NF_3$.

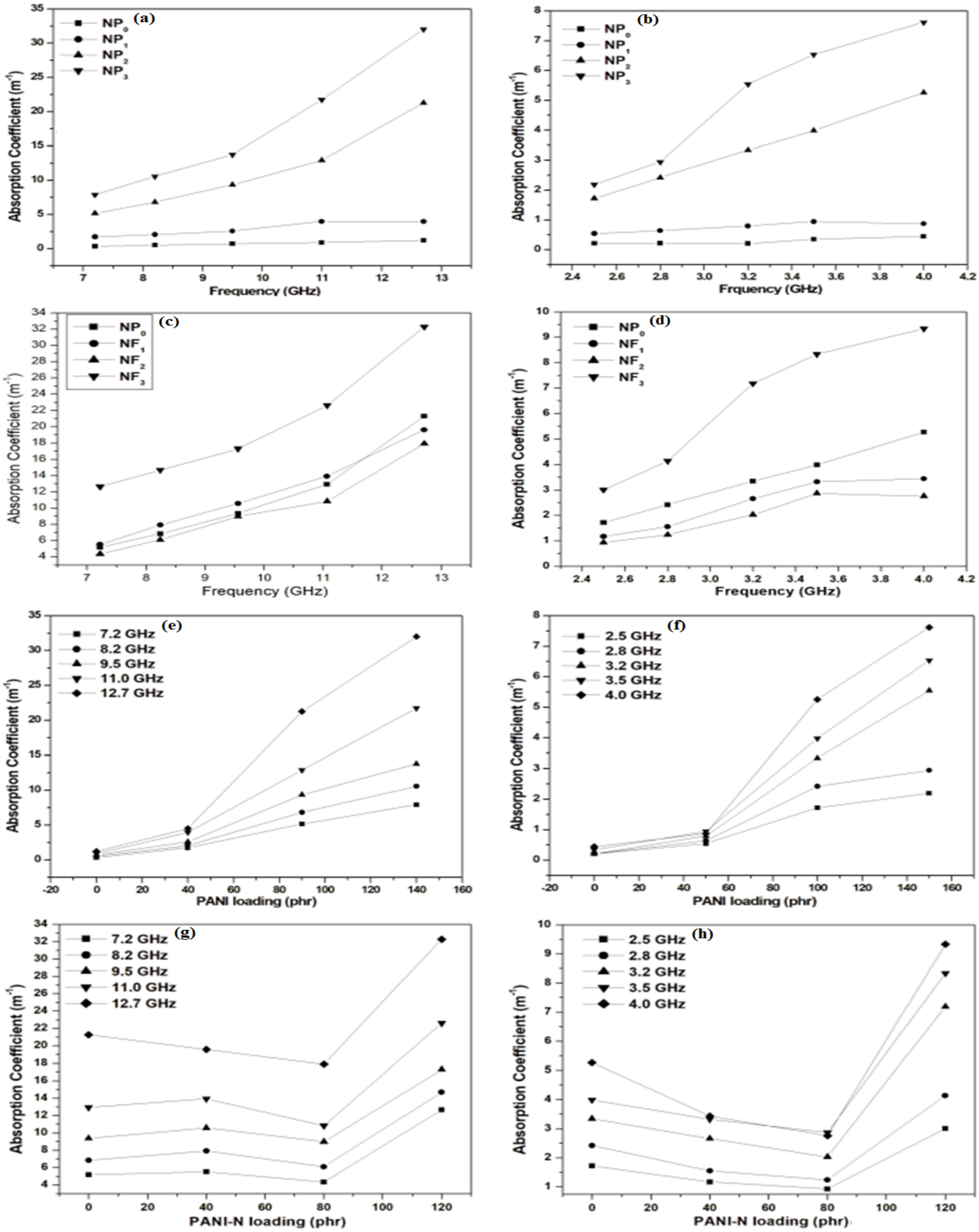



**Fig. 5(a). Absorption Coefficient vs. frequency plots of P series in X band (b) P series in S band (c) F series in X band (d) F series in S band (e) Absorption Coefficient vs. loading plots of P series in X band (f) P series in S band (g) F series in X band (h) F series in S band**

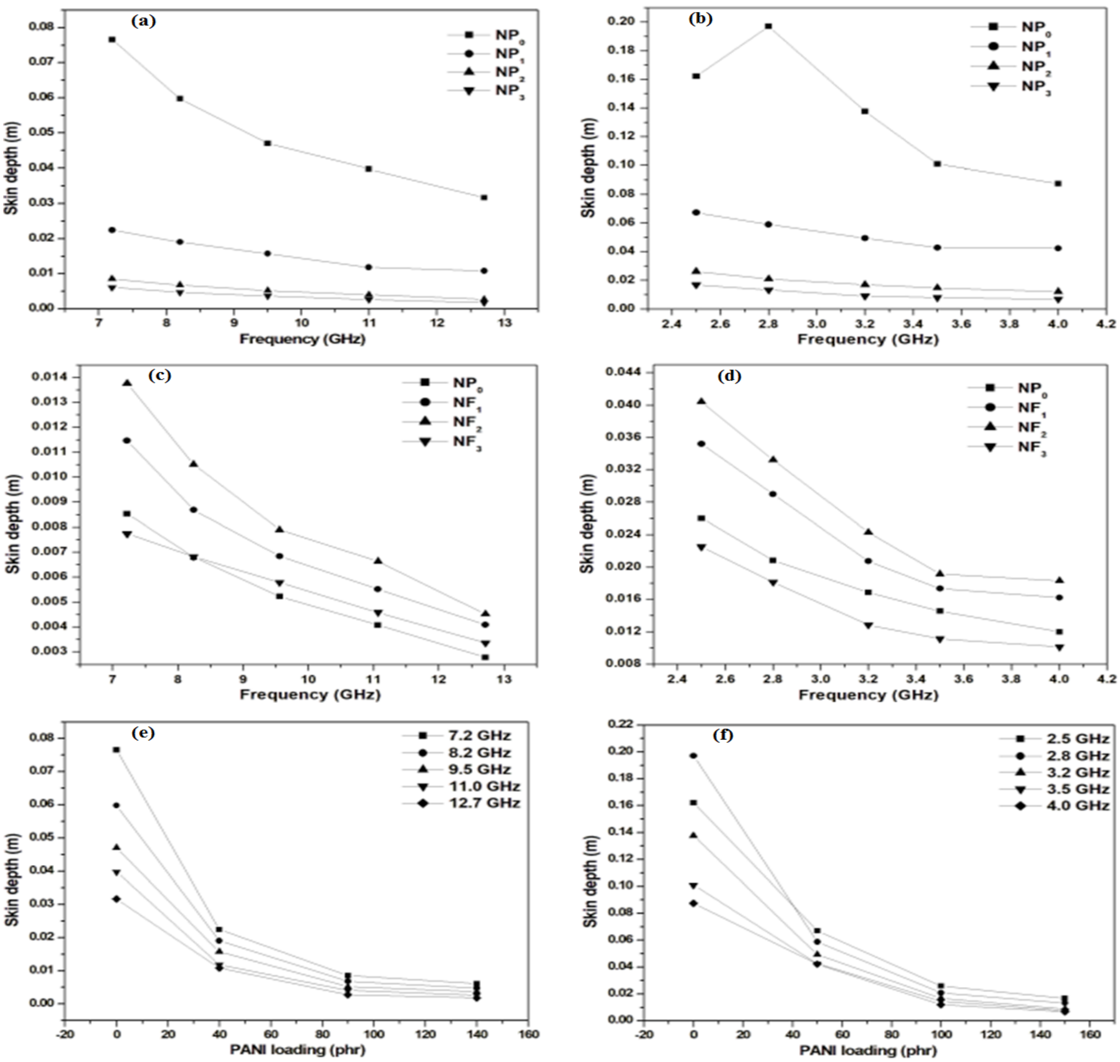
Similar to the conductivity measurements, the absorption coefficient increases with loading for the P series. In contrast, for the F series, it decreases initially and then reaches a maximum at 120 phr loading. The highest values are exhibited by $NP_3$ and $NF_3$ composites, recording 32.07 and 32.27 $m^{-1}$, respectively, at 12.7 GHz.

**Skin depth**

Figure 6 illustrates the skin depth's frequency-dependent and loading-dependent variation of for the composites at X band and S band. The skin depth, or penetration depth, represents how deeply microwaves penetrate into the material[23]. This concept is commonly applied to conductors, where self-inductance restricts signal conduction to the outer layer, known as the skin depth. The skin depth diminishes as the frequency rises. The lowest values of skin depth are recorded at 12.7 GHz for $NP_3$ and $NF_3$, respectively.

With loading, skin depth decreases for P series. For F series, it increases, reaches a maximum and then recorded a lower value for $NF_3$ in both bands.

Table 2 presents the optimum values for the composite properties obtained for the composites. The corresponding values for CR P series CPCs are as follows: conductivity, 13.46 S/m; absorption coefficient, 25.76 $m^{-1}$; and skin depth, 0.0012 m. Regarding the F series, the optimal values is observed at 12.7 GHz for 120 phr loading. Based on these observations, one can deduce that microwave properties are more favorable in conducting composites of CR when contrasted with composites of NR.



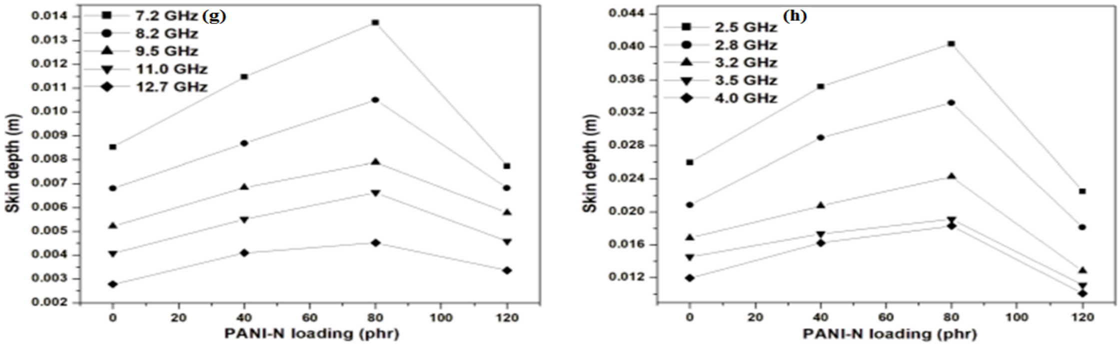



**Fig. 6(a). Skin depth vs. frequency plots of P series in X band (b) P series in S band (c) F series in X band (d) F series in S band (e) Skin depth vs. loading plots of P series in X band (f) P series in S band (g) F series in X band (h) F series in S band**

**Table 2: Composite properties at 12.7 GHz**

| Name of the composite | Conductivity (S/m) | Absorption coefficient ($m^{-1}$) | Skin depth (m) |
|---|---|---|---|
| NP3 | 6.27 | 32.01 | 0.001 |
| NF3 | 1.79 | 32.27 | 0.003 |

## CONCLUSION

In the realm of microwave properties for conducting polymer composites, our extensive research focused on the unique combination of PANI, PANI-N, and CR. Employing the cavity perturbation technique, we delved into the dielectric properties of the prepared CPCs across X and S-band frequencies (8-12 GHz and 2-4 GHz, respectively). Excitingly, the results revealed compelling trends. Generally, the material's permittivity and loss tangent exhibited a commendable upward trajectory with frequency and loading, showcasing their potential for diverse applications. Noteworthy is the superior permittivity of the P series CPCs compared to the F series, with the P series reaching significantly higher values at elevated frequencies and loading levels.

In contrast, the F series, particularly with 40 phr PANI-N at the same frequency, achieved the highest permittivity value of 11.6. However, it's crucial to acknowledge that the F series, leveraging PANI-N and demonstrating superior mechanical properties, faces a nuanced scenario in microwave properties. While excelling in mechanical attributes, the F series exhibits slightly poorer microwave properties.

In the pursuit of practical applications necessitating a harmonious blend of mechanical and microwave properties, the introduction of PANI-N into the composite becomes pivotal. Despite the nuanced microwave performance of the F series, the superior mechanical properties offered by PANI-N underscore its indispensable role in applications where both mechanical resilience and microwave effectiveness are paramount. The P series further demonstrated its prowess in heating properties, showcasing a heating coefficient of 0.11 at 12.7 GHz and 140 phr PANI loading, underlining its efficiency in high-frequency heating applications. While the F series exhibited a nuanced behavior, its versatility, particularly at 120 phr loading, positioned it as a feasible option for similar heating applications. Conductivity and absorption coefficients also displayed promising characteristics, showing a consistent increase with frequency. Notably, the P series at 140 phr loading exhibited maximal conductivity and absorption coefficients with the smallest skin depth at 12.7 GHz, emphasizing its potential for effective microwave absorption.

In conclusion, the meticulously crafted composites of natural rubber with polyaniline, especially PANI-N, and chloroprene rubber have emerged as highly promising materials. The favorable dielectric properties, coupled with remarkable heating and conductivity attributes, position these composites as not only effective but also versatile materials with exciting potential for various applications, where the strategic use of PANI-N becomes justified in the pursuit of an optimal balance between mechanical and microwave performance.

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**Conflict of Interests**

The author has no competing interests to declare that are relevant to the content of this article.

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