

Article

Dielectric and Mechanical Properties of Cyanate Ester-Based Composites Embedded with Different Glass Powders

Caner Başaran ^{1,2,*} and Neslihan Tamsü Selli ¹ 

¹ Department of Materials Science and Engineering, Gebze Technical University, 41400 Kocaeli, Turkey; ntamsu@gtu.edu.tr

² ASELSAN A.Ş., 06200 Ankara, Turkey

* Correspondence: cbasaran@aselsan.com

Abstract

Cyanate ester resins are widely recognized for their excellent thermal stability, low dielectric loss, and high glass transition temperature, making them attractive for advanced electronic and communication applications. However, their inherent brittleness and limited filler compatibility restricts broader use. In this study, cyanate ester composites were developed by incorporating transparent and opaque borosilicate glass powders modified with silane coupling agents—3-Triethoxysilylpropyl isocyanate (TESPI) and 3-Isocyanatopropyl trimethoxysilane (IPTMS)—to enhance interfacial adhesion and crosslink density. The transparent (CTF) and opaque (COF) composite systems were fabricated with varying filler contents (5–20 wt%), and their structural, mechanical, and dielectric performances were systematically characterized through X-ray Diffraction, Fourier Transform Infrared Spectroscopy, Scanning Electron Microscopy, Energy-Dispersive X-ray Spectroscopy (EDX) and dielectric performance analyses. The results revealed that both filler types enhanced the dielectric and mechanical stability of the cyanate ester matrix; however, the COF-15 composite, containing 15 wt% opaque glass, exhibited the highest tensile strength of approximately 125.70 ± 1.50 MPa, and the dielectric constant increased from 2.86 ± 0.1 (neat matrix) to about 5.0 ± 0.1 while maintaining a low loss tangent ($0.007@1$ MHz). These improvements were attributed to the zirconium-enriched opaque glass phase, which promoted strong interfacial bonding, compact microstructure, and effective polarization control.

Keywords: cyanate ester composites; opaque-transparent glass; dielectric properties; tensile strength; electronic applications

1. Introduction

Cyanate ester resins have attracted significant attention in recent years due to their excellent thermal stability, low dielectric loss, high glass transition temperature (T_g), and superior dimensional stability [1–7]. Cyanate esters, derived from bisphenols and cyanic acid, undergo a highly selective thermal or catalyst-induced addition polymerization. Figure 1 presents the general polymerization mechanism of cyanate ester monomers into a highly crosslinked cyanurate network. The monomer structure consists of cyanate ($-O-C\equiv N$) functional groups connected via an organic backbone unit (denoted as A), which is typically an aromatic or aliphatic moiety (e.g., bisphenol A or E derivatives). Upon thermal activation or catalyst introduction, three cyanate groups undergo a highly selective cyclotrimerization reaction, resulting in the formation of a symmetrical, six-membered



Academic Editor: Junwei Zha

Received: 25 January 2026

Revised: 14 February 2026

Accepted: 25 February 2026

Published: 27 February 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

triazine ring. This process occurs without by-product formation and yields a rigid, aromatic-like structure that imparts high thermal stability and a glass transition temperature typically in the range of 250–300 °C. The final cured material exhibits a three-dimensional

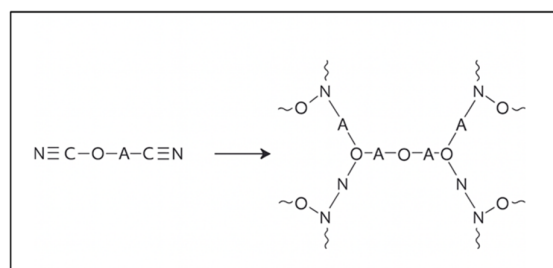


Figure 1. General representation of the cyanate ester monomer, cyclotrimerization, polymerization and cyanurate polymer network structure.

Crosslinked network, where triazine rings are interconnected through the organic backbones, forming a robust cyanurate polymer matrix. This densely reticulated architecture is responsible for the excellent mechanical, dielectric, and thermal properties of cured cyanate ester systems. These properties make them promising candidates for advanced electronic, aerospace, and communication applications, especially where thermal and electrical reliability are critical. However, like many high-performance thermosetting polymers, pristine cyanate ester systems suffer from low tensile strength [8,9] and limited interfacial compatibility with some fillers [10], which can compromise mechanical integrity and long-term dielectric performance in composite structures.

To overcome these limitations, various strategies have been employed to tailor the crosslinking architecture and interface characteristics of cyanate ester composites. For instance, fluorine-containing cyanate esters have been reported to reduce dielectric loss and moisture absorption and dimensional stability [1,11]. Nano and micron-particle reinforcements, such as SiO₂ [12,13], Al₂O₃ [14,15], TiO₂ [16], graphene oxide [17], and graphite [18] have been incorporated to improve thermal conductivity, mechanical strength, and interfacial polarization control. Additionally, hybrid approaches combining inorganic fillers with chemical surface modification have gained increasing attention to enhance filler-matrix compatibility and dispersion uniformity. Surface functionalization using silane coupling agents, such as aminopropyltriethoxysilane (APTES), enables covalent bonding between the cyanate ester matrix and filler surfaces, thereby reducing interfacial defects and improving load transfer efficiency [19,20]. Recent studies have also highlighted the effectiveness of introducing glass or ceramic fillers and fibers with tailored optical transparency or opacity to modulate dielectric permittivity while preserving low loss tangent values [21–23]. Such multi-phase systems not only allow precise tuning of electromagnetic response but also enhance microstructural homogeneity and thermal endurance, making them promising candidates for high-frequency antenna radomes and electronic packaging applications [24,25]. Although previous studies have demonstrated the potential of ceramic, nanoparticle, and glass-based fillers to improve the dielectric and mechanical properties of cyanate ester systems, several important aspects remain insufficiently understood. In particular, a systematic comparison between transparent and opaque borosilicate glass powders within the same cyanate ester matrix has not yet been reported. Moreover, the combined effect of dual silane modification using TESPI and IPTMS on interfacial bonding, crosslink density, dielectric polarization, and mechanical performance has not been comprehensively investigated. Existing studies generally focus on a single filler type, a single surface treatment strategy, or limited property evaluation. Therefore, the fundamental relationships between structure and performance that control the combined dielectric and

mechanical behavior of cyanate ester–glass hybrid systems are still not fully understood, particularly in the context of high-frequency electronic applications.

In the present work, we propose a systematic and comparative investigation of cyanate ester composites reinforced with both transparent and opaque borosilicate glass powders. The aim of this study is to simultaneously optimize dielectric behavior, mechanical performance, and interfacial compatibility through the combined use of dual silane coupling agents (TESPI and IPTMS). By integrating two different glass types within the same matrix and evaluating their structure–property relationships, this work seeks to provide new insights into the design of cyanate ester-based materials for high-frequency electronic applications. The transparent glass phase was selected due to its low dielectric constant (5.0–6.0) and minimal dielectric loss (0.0008@1 MHz), allowing effective control of the dielectric response and reduction of the loss tangent while maintaining the homogeneity of the polymer matrix. On the other hand, the addition of opaque glass powder—typically enriched with ceramic opacifiers and microstructural heterogeneities—serves to enhance interfacial polarization and tailor the composite’s electromagnetic absorption profile when needed. It may also contribute to light scattering, microstructural compactness, or thermal stability depending on the formulation.

To further improve interfacial compatibility, silane coupling agents were employed to enhance the interfacial compatibility between cyanate ester and glass fillers [26]. Two different bifunctional silanes were utilized: 3-Triethoxysilylpropyl isocyanate (TESPI), primarily used as both a crosslinking agent and an interface modifier, and 3-Isocyanatopropyl trimethoxysilane (IPTMS), specifically employed to surface-modify the glass powders. The isocyanate group (–NCO) in both silanes can react with the cyanate ester matrix, promoting crosslinked network formation, whereas the alkoxysilyl groups (–Si(OR)₃) undergo hydrolysis and condensation to form siloxane bonds with glass surfaces. Through these dual mechanisms, TESPI improves crosslink density and interfacial adhesion, while IPTMS-functionalized glass fillers enhance filler–matrix compatibility by covalently bonding to the polymer matrix. This combined strategy leads to hybrid organic–inorganic networks with improved interfacial adhesion [27], increased crosslink density, and reduced dielectric defects. To evaluate these effects, glass powders were incorporated into the cyanate ester matrix at varying loadings (5–20 wt%), with TESPI added at a variation 1–3 wt% in line with literature-reported effective ranges. The study aims to clarify how TESPI and IPTMS contribute to improvements in thermal stability, dielectric loss suppression, and microstructural integrity of cyanate ester composites, providing valuable insights for next-generation electronic substrate materials.

2. Materials and Methods

2.1. Materials

The experimental materials used for preparing the reinforced composite samples in this study included cyanate ester resin and glass powders. A two-part cyanate ester–epoxy resin system (viscosity: 140 cP at 43 °C; cured density: 1.25 g/cm³) supplied by Lepus Chemical (Tekirdağ, Turkey) was employed. TESPI (Merck, Darmstadt, Germany) (Figure 2) and IPTMS (TCI Products, Tokyo Metropolis, Japan) (Figure 3) were used as silane coupling agents. BYK-066 N (Omya Chemicals, Oftringen, Switzerland) was incorporated as a defoaming agent at 0.5 wt%. Ethanol (99% purity; Lepus Chemical, Tekirdağ, Turkey) was used as the solvent in all formulations.

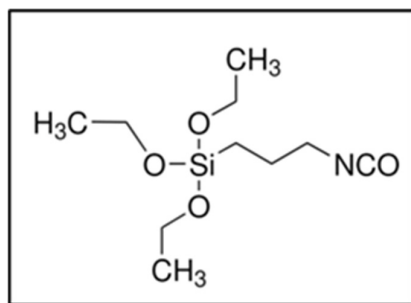


Figure 2. 3-(Triethoxysilyl)propyl isocyanate (TESPI) chemical structure.

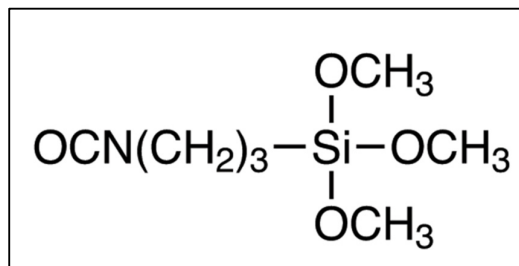


Figure 3. 4-(Isocyanatopropyl)trimethoxysilane (IPTMS) chemical structure.

2.2. Glass Powders Preparation

The raw materials were weighed according to the components and specified quantities in Table 1. All raw materials were obtained with 99.9% purity (Lepus Chemical, Tekirdağ, Turkey).

Table 1. Glass powder compositions (mol.%).

Compound	A Glass Powder	B Glass Powder
Na ₂ O	0.52	1.44
SiO ₂	66.54	64.40
ZrO ₂	-	3.75
K ₂ O	2.45	1.42
CaO	16.92	10.15
MgO	2.32	3.63
Al ₂ O ₃	3.61	2.73
ZnO	6.47	9.50
B ₂ O ₃	1.16	2.88

After weighing, the samples were dry-mixed and subjected to melting at 1600 °C for 2 h (Nannetti Furnace, Italy) by using alumina crucibles. Then, the molten material was quenched in water to form frit. The fritted glass composition was subsequently ground for 40 h (Nanomultimix, 50S Model grinder, Turkey). The glass preparation process is presented in detail in Figure 4.

The reason for selecting the compositions in this manner is that Glass Powder A was intended to be transparent, whereas Glass Powder B was aimed to be opaque. Therefore, XRD analyses were carried out for both Composition A and Composition B. In Composition A, the formation of only the amorphous phase was targeted, while in Composition B, the formation of zircon crystals—responsible for opacity—in addition to the amorphous phase was desired. After XRD examination, powders were added to the cyanate ester matrix.

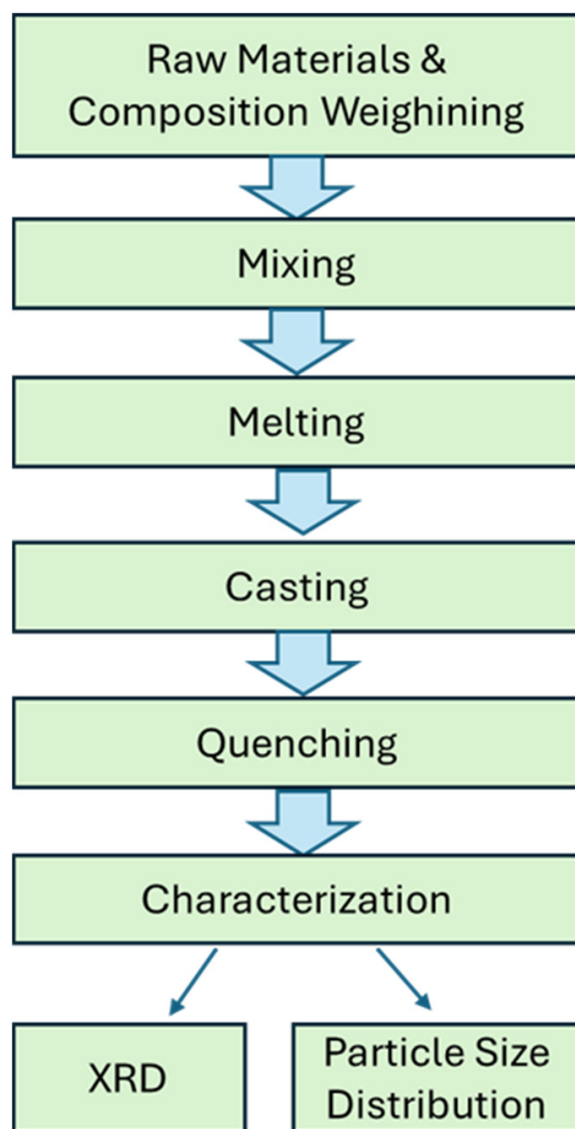


Figure 4. Flow chart for the preparation of the glass composition.

2.3. Specimen Preparation

Cyanate ester resin (cyanate ester resin A/cyanate ester resin B = 2:1, w/w) was used as the polymer matrix. Two silane coupling agents were selected to enhance filler–matrix interactions: 3-Triethoxysilylpropyl isocyanate (TESPI, 1–3 wt%) was introduced into the resin to act simultaneously as a crosslinking agent and an interfacial modifier, while 3-Isocyanatopropyl trimethoxysilane (IPTMS) was employed to surface-modify the glass powders. Prior to incorporation, glass powders (5–20 wt%) were dispersed in ethanol and treated with IPTMS. After solvent removal, the modified fillers were dried and incorporated into the cyanate ester resin together with TESPI. Glass powders were added to the resin matrix in amounts of 5%, 10%, 15%, and 20% by weight. Prior to mixing, the glass powder was dried under vacuum and resin was preheated to 90 °C for 1 h at 800 rpm (IKA RCT Basic Stirrer, IKA Turkey, Istanbul, Turkey). The modified glass powders were then slowly added to the liquefied resin. Subsequently, TESPI was slowly introduced into the solution and mixed for an additional hour. Finally, the second component of the cyanate ester was added. The final addition of the defoaming agent has been made (BYK-066N). All composition details are presented in Table 2.

Table 2. Composition details (wt%).

Component	STD	CTF-5	CTF-10	CTF-15	CTF-20	COF-5	COF-10	COF-15	COF-20
Cyanate ester (Component A)	66.67	57.90	54.80	51.70	48.60	57.90	54.80	51.70	48.60
Cyanate ester (Component B)	33.33	28.90	27.40	25.80	24.30	28.90	27.40	25.80	24.30
TESPI	-	1.70	1.60	1.50	1.40	1.70	1.60	1.50	1.40
Glass powder_A (transparent)	-	5.00	10.00	15.00	20.00	-	-	-	-
Glass powder_B (opaque)	-	-	-	-	-	5.00	10.00	15.00	20.00
BYK-066N	-	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50

2.4. Characterization

The fritted glass compositions were ground prior to characterization, and the particle size distribution of the resulting powders was determined by dynamic light scattering using a zeta potential analyzer (Malvern Zetasizer Nano ZS, Malvern Inc., Malvern, UK). Phase analysis of the glass powders and composite samples was carried out by X-ray diffraction (XRD) using a PANalytical Empyrean (Malvern Inc., Malvern, UK) diffractometer (operating at 40 kV and 40 mA with CuK α radiation ($\lambda = 0.154$ nm), over a 2θ range of 5–70° at a scanning rate of 2°/min. Fourier transform infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR) was performed using a PerkinElmer Spectrum 100 spectrophotometer (PerkinElmer, Waltham, MA, USA) to investigate chemical structure and interfacial interactions; spectra were collected in the range of 550–4000 cm^{−1} with a resolution of 4 cm^{−1} using 32 scans. Tensile properties were evaluated using an MTS 810 universal testing machine (MTS Systems Corporation, Eden Prairie, MN, USA) in accordance with GB 1040-79 (ISO 527-2:1993) [28]. Dumbbell-shaped specimens with a gauge length of 50 mm, a gauge width of 10 mm, and a thickness of approximately 3 mm were tested at a constant crosshead speed of 2 mm/min at room temperature (25 °C). The reported values represent the average of five specimens. Dielectric constant (ϵ_r) and loss tangent ($\tan \delta$) were measured under ambient conditions using a precision LCR meter (Hioki 3532-50, Hioki E.E. Corporation, Nagano, Japan) over a frequency range of 100 kHz to 1 MHz; prior to measurements, the samples were polished and coated with silver paste on both surfaces to form electrodes, followed by heat treatment at 750 °C for 30 min to ensure good electrical contact. Microstructural morphology and elemental composition of the cured samples were examined by scanning electron microscopy (SEM) (Philips, Hillsboro, OR, USA) coupled with energy-dispersive X-ray spectroscopy (EDX) using a Philips XL30 SFEG microscope (Philips, Hillsboro, OR, USA). EDX analyses were performed over selected areas of the fracture surfaces at an accelerating voltage of 15 kV, and the spectra were collected from representative regions to evaluate the elemental distribution of the glass fillers within the cyanate ester matrix.

3. Results

3.1. Particle Size Distribution of Glass Powders

The graph (Figure 5) illustrates the particle size distribution of A and B glass powders. The solid lines represent the volume-based particle size distribution curves, while the dashed lines indicate the cumulative distribution. Both samples exhibit a unimodal distribution, with particle sizes predominantly concentrated in the submicron range. The D (0.1), D (0.5), and D (0.9) values for A glass powder are 201 nm, 244 nm, and 1560 nm, respectively, whereas for B glass powder they are 229 nm, 237 nm, and 1790 nm. The similarity in the peak positions suggest that both powders have comparable median particle

sizes, although slight differences in the distribution tails reflect variations in the presence of finer and coarser particles between the two samples.

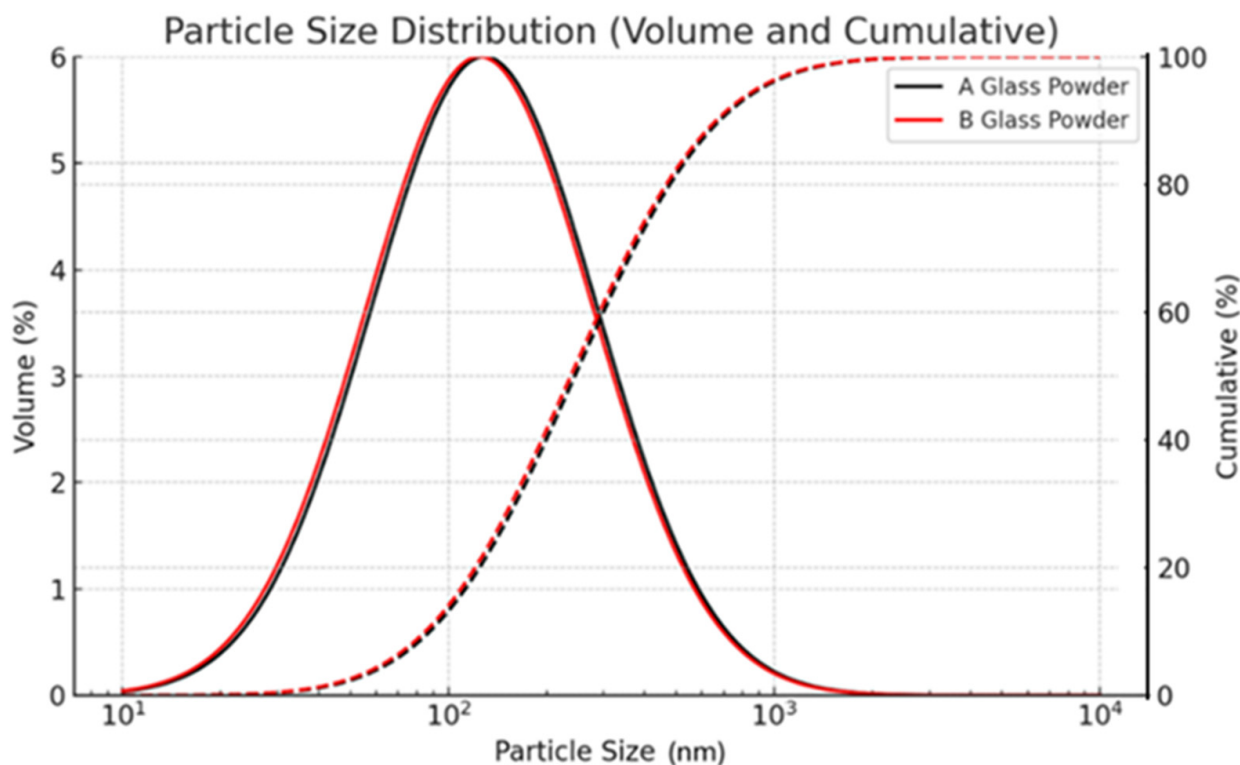


Figure 5. The particle size distributions of A and B glass powders graph.

The size of the glass particles is a key parameter affecting the processing behavior, interfacial adhesion, and overall performance of polymer composites. Particles in the sub-micron range offer a larger specific surface area, which improves filler–matrix interactions and enables more effective stress transfer at the interface. Moreover, smaller particles tend to disperse more uniformly within the resin, decreasing the risk of sedimentation during processing and limiting defect formation. From a dielectric standpoint, finer particles increase the interfacial region available for polarization, which can raise dielectric permittivity while preserving low loss when strong interfacial bonding is present. In contrast, overly large particles or wide particle size distributions may encourage agglomeration and void formation, resulting in stress concentration and higher dielectric loss. For this reason, the median particle size of approximately 200–250 nm is considered appropriate for balancing dispersion quality, interfacial bonding, mechanical strengthening, and dielectric performance in cyanate ester composites.

3.2. XRD Analysis Results of the Specimens

The X-ray diffraction (XRD) pattern of the prepared A-glass powder (Figure 6) displays a broad amorphous hump centered at approximately 24° (2θ), with no distinct sharp diffraction peaks observed throughout the scanned range (10 – 70°). This broad and diffuse peak is characteristic of an amorphous structure [29].

XRD analysis of the B-glass powder (Figure 7) shows both a broad amorphous hump and sharp diffraction peaks, indicating partial crystallization. The crystalline reflections match well with zircon (ZrSiO_4) phases (PDF No: #06-0266) suggesting successful nucleation by ZrO_2 . The presence of zircon contributes to light scattering and opacity, confirming the formation of an opaque glass-ceramic [30].

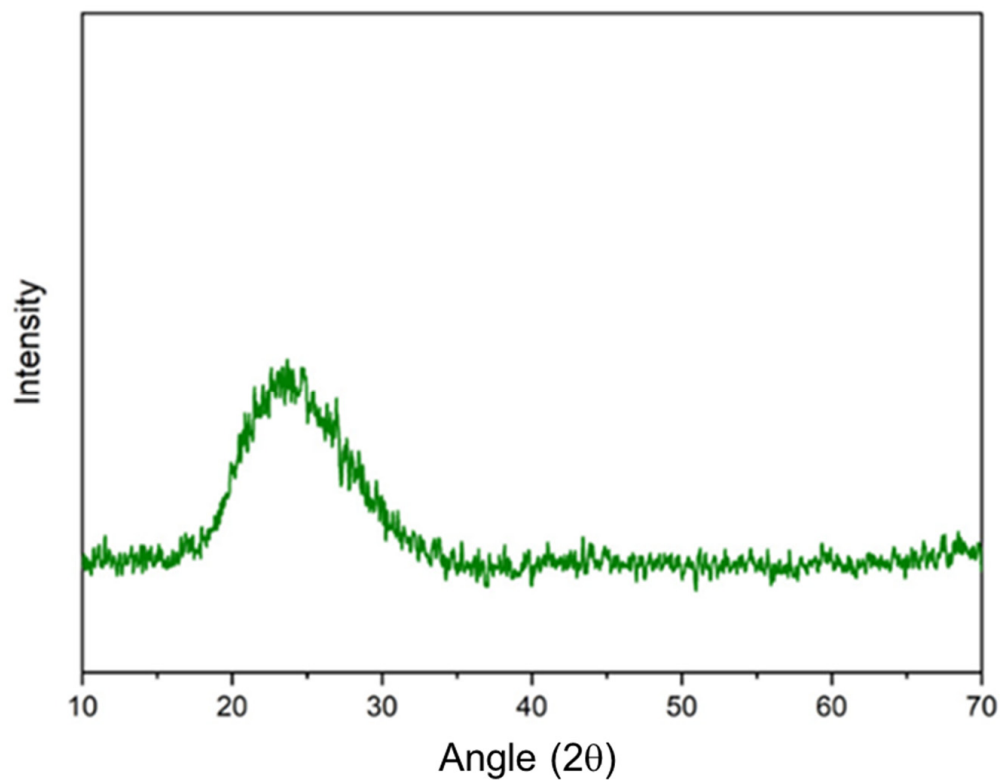


Figure 6. XRD pattern of the A-glass powder.

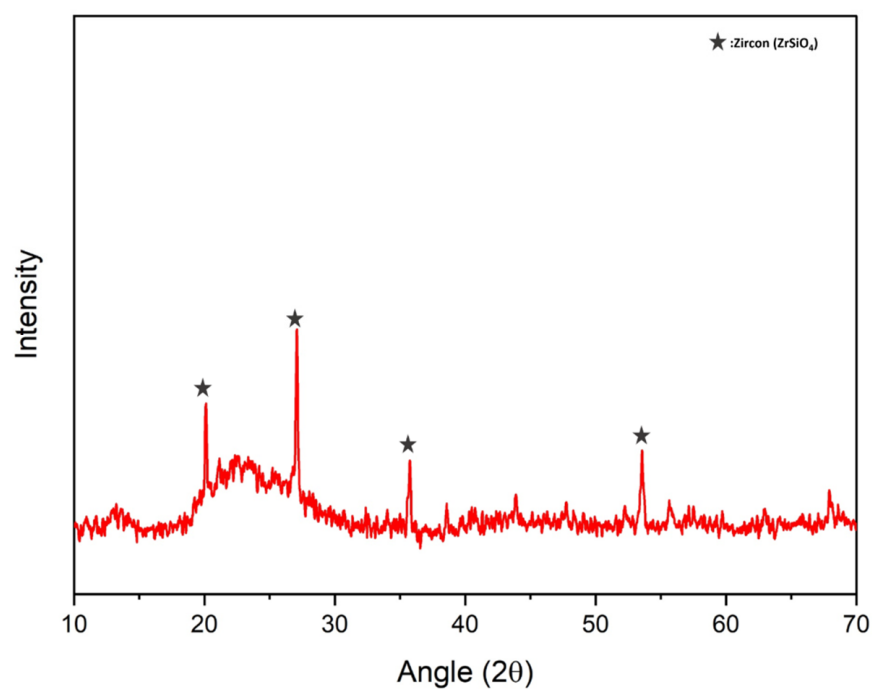


Figure 7. XRD pattern of the B-glass powder.

Figure 8, XRD patterns of neat cyanate ester (STD) and glass-filled composites (CTF 5, CTF10, CTF15, CTF20, COF-5, COF-10, COF-15, and COF-20). All samples exhibit a broad amorphous halo ($\approx 10\text{--}25^\circ$ 2θ) with no crystalline peaks, indicating that both matrix and transparent glass remain amorphous.

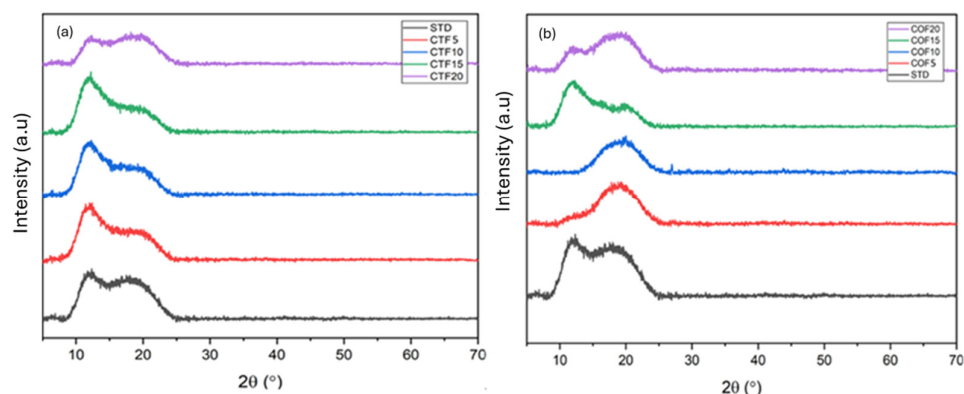


Figure 8. XRD pattern of cyanate ester resin with (a) A and (b) B glass powder additive after curing.

3.3. FTIR Analysis Results

The FTIR spectra of the standard and transparent glass powder-filled cyanate ester composites clearly reveal the progressive increase in crosslinking density with the addition of glass filler (Figure 9). The characteristic absorption band of the -OCN group at around $2270\text{--}2230\text{ cm}^{-1}$, prominent in the neat cyanate ester (STD), gradually decreases in intensity and nearly disappears in the CTF-20 sample, indicating the conversion of cyanate groups into triazine ring structures during polymerization. Concurrently, the appearance and sharpening of the triazine ring vibration bands at approximately $1600\text{--}1550\text{ cm}^{-1}$ (C=N stretching) and $1360\text{--}1350\text{ cm}^{-1}$ (ring breathing) confirm the formation of a more crosslinked network [31–33]. Additionally, the broad O-H/N-H stretching band around $3400\text{--}3200\text{ cm}^{-1}$ becomes weaker and narrower in glass-filled samples, reflecting reduced hydrogen bonding and a more compact molecular arrangement. The Si-O-Si and Si-O-C stretching vibrations observed in the $1100\text{--}900\text{ cm}^{-1}$ region further indicate interfacial bonding between the glass particles and the polymer matrix. Overall, the spectral evolution from STD to CTF-20 demonstrates a systematic increase in crosslinking density and interfacial network formation, confirming that glass incorporation enhances the curing reaction and structural integrity of the cyanate ester matrix.

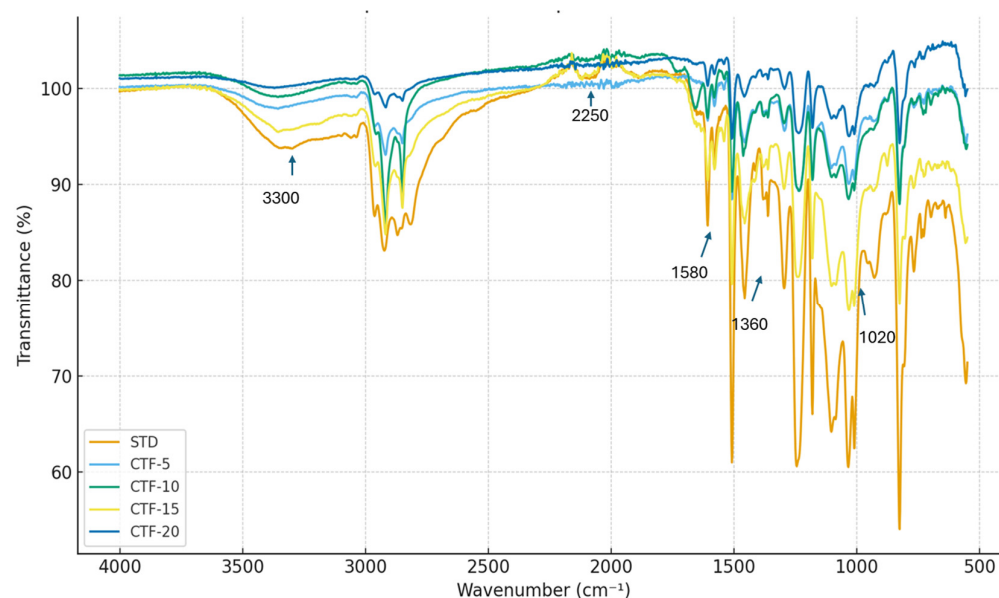


Figure 9. FTIR spectra of standard and A glass powder-filled cyanate ester composites.

The FTIR spectra of the standard cyanate ester (STD) and the B opaque glass powder-filled composites (COF series) show distinct spectral changes that evidence the progressive

increase in crosslinking density and the formation of new interfacial bonds with increasing filler content (Figure 10). The characteristic —OCN stretching band at approximately $2270\text{--}2230\text{ cm}^{-1}$, clearly observed in the neat cyanate ester, becomes gradually weaker and nearly disappears for the COF-20 sample, indicating the extensive conversion of cyanate groups into triazine structures during polymerization [31–33]. Simultaneously, the triazine ring vibration bands around $1600\text{--}1550\text{ cm}^{-1}$ (C=N stretching) and $1360\text{--}1350\text{ cm}^{-1}$ (ring breathing) become sharper and more intense, confirming an increase in crosslinking density. The broad O-H/N-H stretching band at $3400\text{--}3200\text{ cm}^{-1}$ diminishes in the glass-filled samples, suggesting reduced hydrogen bonding and higher network compactness. Furthermore, the bands appearing in the $1100\text{--}900\text{ cm}^{-1}$ region correspond to Si-O-Si and Si-O-C vibrations arising from chemical interactions between the cyanate ester matrix and the B-type opaque glass particles. Overall, the spectral evolution from STD to COF-20 confirms that the incorporation of opaque glass promotes higher crosslinking conversion and interfacial bonding, resulting in a more rigid and densely crosslinked polymer network.

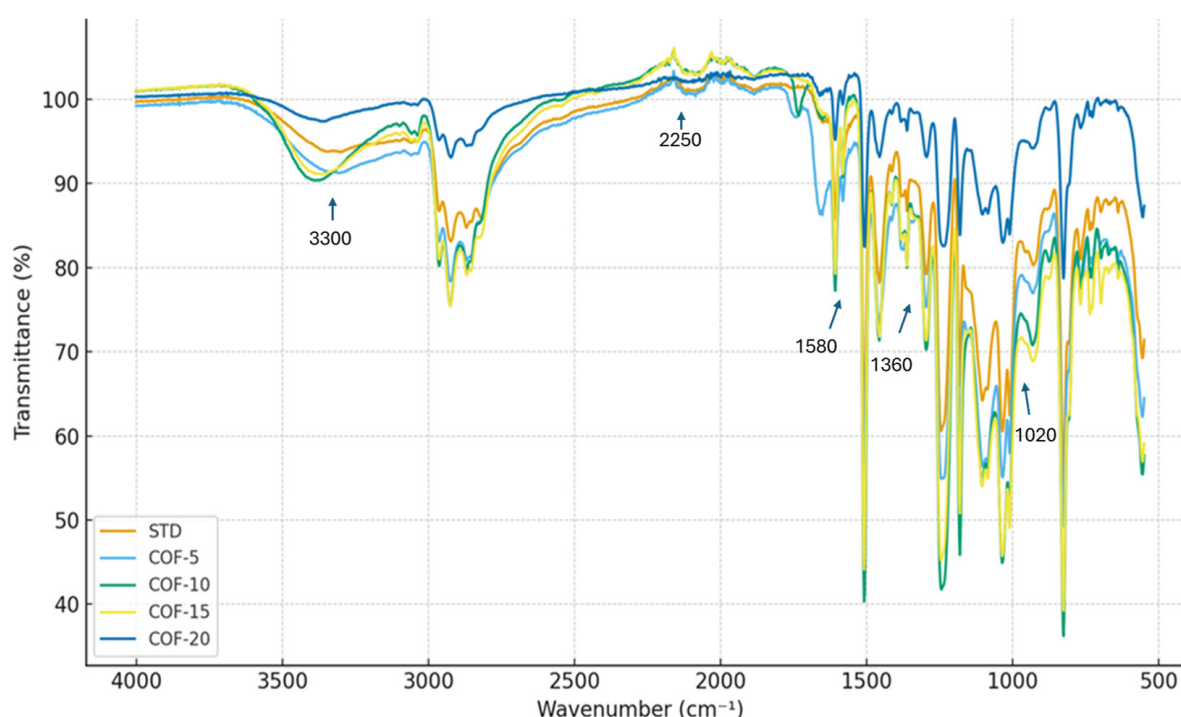


Figure 10. FTIR spectra of standard and B glass powder-filled cyanate ester composites.

3.4. Tensile Strength Results

Tensile stress–strain curves of standard (STD) and A-glass (transparent) powder-filled cyanate ester composites is presented in Figure 11. The tensile stress–strain curves show that the neat cyanate ester (STD) attains the lowest tensile strength while sustaining a relatively large strain at break ($\sim 2.5\text{--}2.6\%$), indicating a more compliant/ductile response compared with the filled systems. In contrast, the composite with 15 wt% glass powder (CTF-15) achieves the highest tensile strength with a moderate strain at break ($\sim 2.0\%$), consistent with efficient load transfer but a more abrupt failure than STD. CTF-10 approaches CTF-15 in peak stress and retains slightly higher strain, suggesting near-optimal interfacial bonding at intermediate loading. At low loading (CTF-5), the strength remains limited despite a comparatively high strain, whereas excessive filler addition in CTF-20 causes premature fracture ($\sim 1.3\text{--}1.4\%$ strain), likely due to particle agglomeration and stress concentration sites. Overall, intermediate glass content (15 wt%) provides the best balance between strength and deformability.

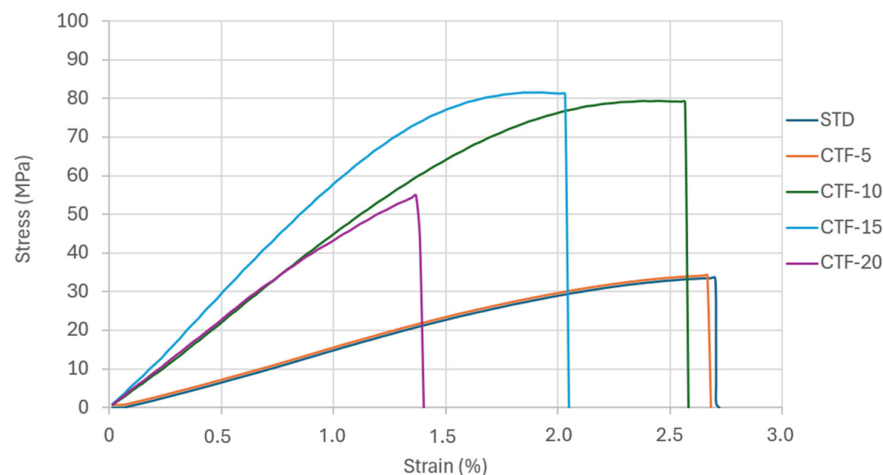


Figure 11. Tensile stress–strain curves of standard (STD) and A-glass powder-filled cyanate ester composites.

Tensile stress–strain curves of standard (STD) and B-glass powder-filled cyanate ester composites is presented in Figure 12. The tensile strength of the B (opaque) glass-filled cyanate ester composites exhibited a clear dependence on filler content. The composite containing 15 wt% opaque glass (COF-15) achieved the highest tensile strength ($125.70 \text{ MPa} \pm 1.50$) with moderate strain, indicating efficient stress transfer between the matrix and the glass particles. The COF-10 sample also showed high strength with slightly greater strain, suggesting good interfacial adhesion at intermediate loading levels. At low filler content (COF-5), the strength enhancement was limited, likely due to insufficient filler–matrix interaction. In contrast, excessive filler addition (COF-20) led to reduced strength and early fracture, attributed to particle agglomeration and increased brittleness. The unfilled STD sample exhibited the lowest tensile strength but the largest strain at break ($\sim 2.5\%$), reflecting its more ductile nature. Overall, an optimal opaque glass loading of about 15 wt% provides the best balance between rigidity and toughness for cyanate ester-based composites.

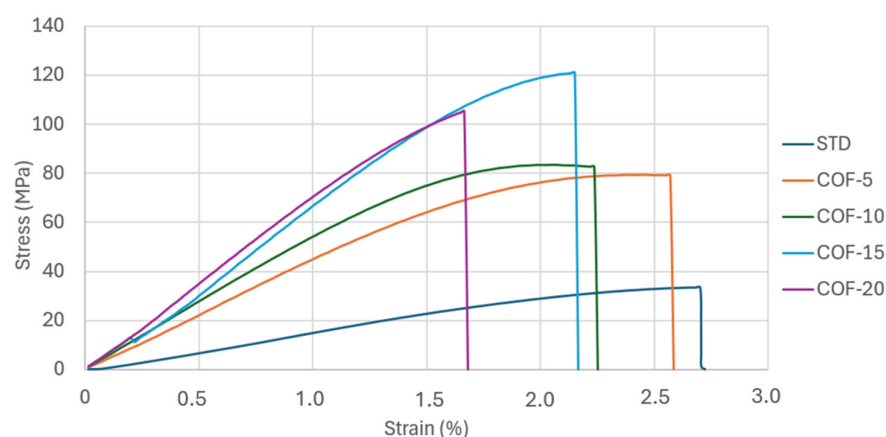


Figure 12. Tensile stress–strain curves of standard (STD) and B-glass powder-filled cyanate ester composites.

The tensile properties of the specimens were reported in Table 3. The tensile strength values were determined from the maximum stress obtained from the stress–strain curves. The results show that the incorporation of glass fillers significantly enhances the tensile stress compared to the neat cyanate ester. For the transparent glass series, the tensile strength increases markedly up to 15 wt% filler loading, reaching a maximum value of 81.0 MPa for CTF-15, followed by a decrease at higher loading due to possible particle

agglomeration and stress concentration effects. In contrast, the opaque glass series exhibits a more pronounced reinforcing effect, with the highest tensile strength of $125.70 \text{ MPa} \pm 1.50$ obtained for COF-15, indicating improved stiffness and interfacial reinforcement associated with the zircon-containing glass composition. However, increasing filler content generally leads to a reduction in elongation at break, suggesting a transition toward a more rigid and brittle network. Overall, the results demonstrate that glass type and filler loading strongly influence the mechanical performance of cyanate ester composites.

Table 3. Tensile properties of cyanate ester composites reinforced with transparent (CTF) and opaque (COF) glass powders.

Tensile Properties	STD	CTF-5	CTF-10	CTF-15	CTF-20	COF-5	COF-10	COF-15	COF-20
Tensile Strength (MPa)	34.00	36.00	79.80	81.00	55.60	79.00	83.00	125.70	105.50
* Std. Dev. (MPa)	± 1.50	± 1.30	± 1.80	± 1.40	± 1.20	± 1.50	± 0.70	± 1.50	± 1.80
Elongation at break (%)	2.50	2.40	2.40	2.00	1.40	2.50	2.20	2.10	1.50
* Std. Dev. (%)	± 0.08	± 0.07	± 0.06	± 0.05	± 0.04	± 0.07	± 0.06	± 0.05	± 0.05

*: Standard Deviation.

3.5. Dielectric and Tangent Loss Evaluation

The effect of incorporating transparent (A-type glass powder) and opaque (B-type glass powder) fillers into the cyanate ester resin on the dielectric constant and loss tangent was also investigated. Variation of dielectric constant (ϵ_r) with frequency for transparent (CTF) and opaque (COF) glass-filled cyanate ester composites is presented in Figure 13. Both transparent (CTF) and opaque (COF) glass-filled cyanate esters exhibit significantly higher dielectric constants than the neat resin (STD), confirming the influence of glass fillers on dielectric polarization. Among the composites, the dielectric constant increases with filler loading, reaching the highest values for the COF-20 and CTF-20 samples (≈ 4.8 – 5.0 @ 1 MHz). The COF series consistently shows slightly higher ϵ_r values than the corresponding CTF series, indicating that the opaque glass particles enhance the interfacial polarization and dipolar alignment more effectively.

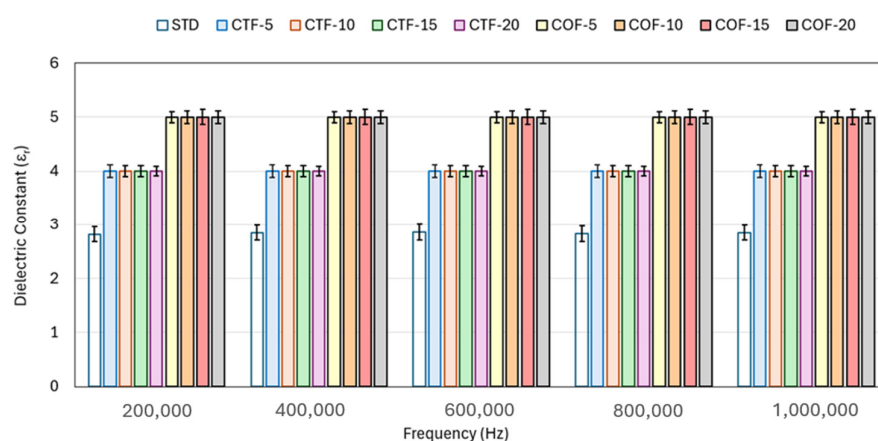


Figure 13. Variation of dielectric constant (ϵ_r) with frequency for transparent (CTF) and opaque (COF) glass-filled cyanate ester composites.

Dielectric loss tangent versus frequency graph of the standard and A glass powder-filled cyanate ester composites is presented in Figure 14. The dielectric loss tangent values of all samples decrease rapidly with increasing frequency, indicating reduced dipolar relaxation and interfacial polarization losses at higher frequencies. At low frequencies

(<200 kHz), a noticeable increase in $\tan \delta$ is observed due to interfacial charge accumulation at the matrix–filler boundaries, which is typical for heterogeneous polymer composites [34,35]. Among the samples, all glass-filled systems (CTF-5 to CTF-20) exhibit slightly lower or comparable loss tangent values compared to the neat cyanate ester (STD), suggesting that the incorporation of transparent glass particles suppresses dielectric losses by restricting molecular mobility and enhancing crosslink density. At higher frequencies (>400 kHz), $\tan \delta$ stabilizes around 0.02–0.03 for all compositions, demonstrating that transparent glass addition maintains low dielectric loss and stable frequency-dependent behavior suitable for high-frequency applications.

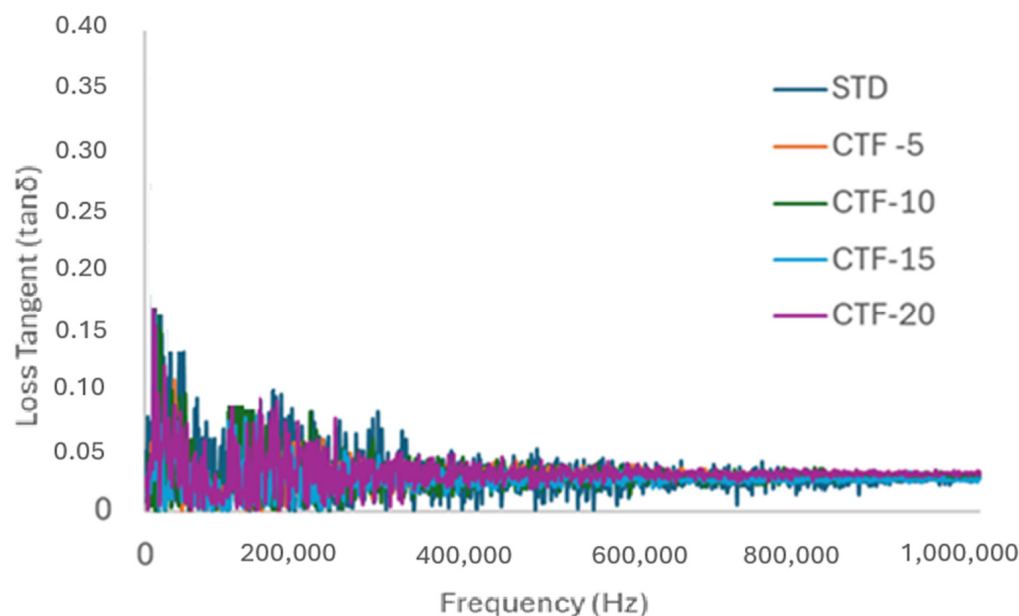


Figure 14. Dielectric loss tangent versus frequency graph of the standard and A glass powder-filled cyanate ester composites.

A comparison of the dielectric loss behavior of the opaque glass-filled cyanate ester composites is presented in Figure 15, illustrating how the addition of glass powder influences polarization losses over a wide frequency range. The loss tangent values for all samples exhibit a sharp decrease with increasing frequency, which can be attributed to the suppression of interfacial polarization at higher frequencies. At low frequencies (<200 kHz), relatively higher $\tan \delta$ values are observed, resulting from charge accumulation at the interfaces between the cyanate ester matrix and opaque glass particles—a behavior typical of heterogeneous dielectric systems governed by Maxwell–Wagner–Sillars polarization [36–39]. The incorporation of opaque glass particles slightly reduces $\tan \delta$ compared to the unfilled resin (STD), indicating improved interfacial compatibility and limited dipole relaxation losses. Beyond 400 kHz, the loss tangent stabilizes below 0.01 for all compositions (specifically, the tangent loss for the COF-15 composite reached a level of 0.007@ 1 MHz), confirming that the composites maintain low dielectric losses and stable polarization behavior across a wide frequency range, which is desirable for high-frequency dielectric and antenna applications.

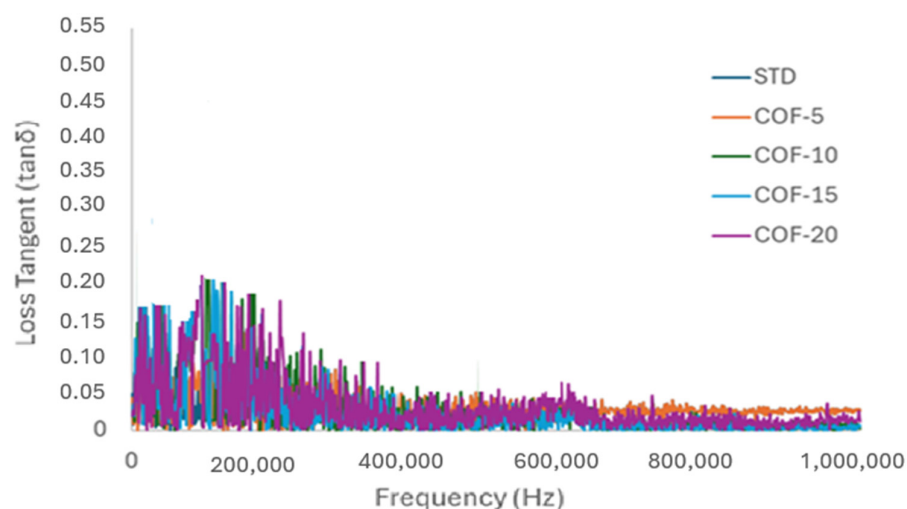


Figure 15. Dielectric loss tangent versus frequency graph of the standard and B glass powder-filled cyanate ester composites.

3.6. SEM/EDX Results

Figure 16 presents the SEM fractographs of the fracture surfaces of the transparent glass-filled cyanate ester composites, providing microstructural evidence that supports the FTIR, tensile, and dielectric results. The neat cyanate ester (STD, Figure 16a) exhibits a smooth and homogeneous surface, typical of a densely crosslinked polymer with limited crack deflection sites. With the addition of glass particles (CTF-5 and CTF-10, Figure 16b,c), the fracture surfaces become progressively rougher, indicating improved interfacial interaction and enhanced energy absorption during deformation. This microstructural change corresponds well with the observed increase in tensile strength and dielectric constant, suggesting efficient stress transfer and interfacial polarization between the glass and the polymer matrix [39,40]. The CTF-15 sample (Figure 16d) displays a uniform particle distribution and well-integrated interfaces, which explains its superior tensile strength and moderate dielectric loss. However, at higher filler loading (CTF-20, Figure 16e), particle agglomeration and interfacial voids are evident, consistent with the slight decrease in mechanical performance and the increase in loss tangent. Overall, the SEM observations confirm that an intermediate filler content (~15 wt%) provides the most homogeneous microstructure and optimal combination of mechanical and dielectric properties. Arrows in the SEM images indicate the pores, while the rectangular markers highlight the particle agglomerations.

Figure 17 presents the SEM fractographs of the fracture surfaces opaque glass-filled cyanate ester composites, illustrating how the addition of opaque glass powder influences the internal morphology and interfacial bonding. The COF-5 and COF-10 samples exhibit relatively uniform filler dispersion and good matrix–filler adhesion, which correlate with their enhanced dielectric constant and moderate $\tan \delta$ values. The COF-15 sample shows the most compact and homogeneous cross-section with well-integrated filler–matrix interfaces, consistent with its superior tensile strength and low dielectric loss, as also supported by FTIR results indicating strong interfacial interactions. However, in the COF-20 sample, localized particle agglomeration and void formation are evident, which likely hinder stress transfer and contribute to the slight reduction in mechanical performance and increase in dielectric loss. These observations confirm that an intermediate filler content (~15 wt%) results in optimal interfacial bonding, efficient stress distribution, and improved dielectric stability. Arrows in the SEM micrographs denote the pores, whereas the rectangular boxes indicate particle agglomerates.

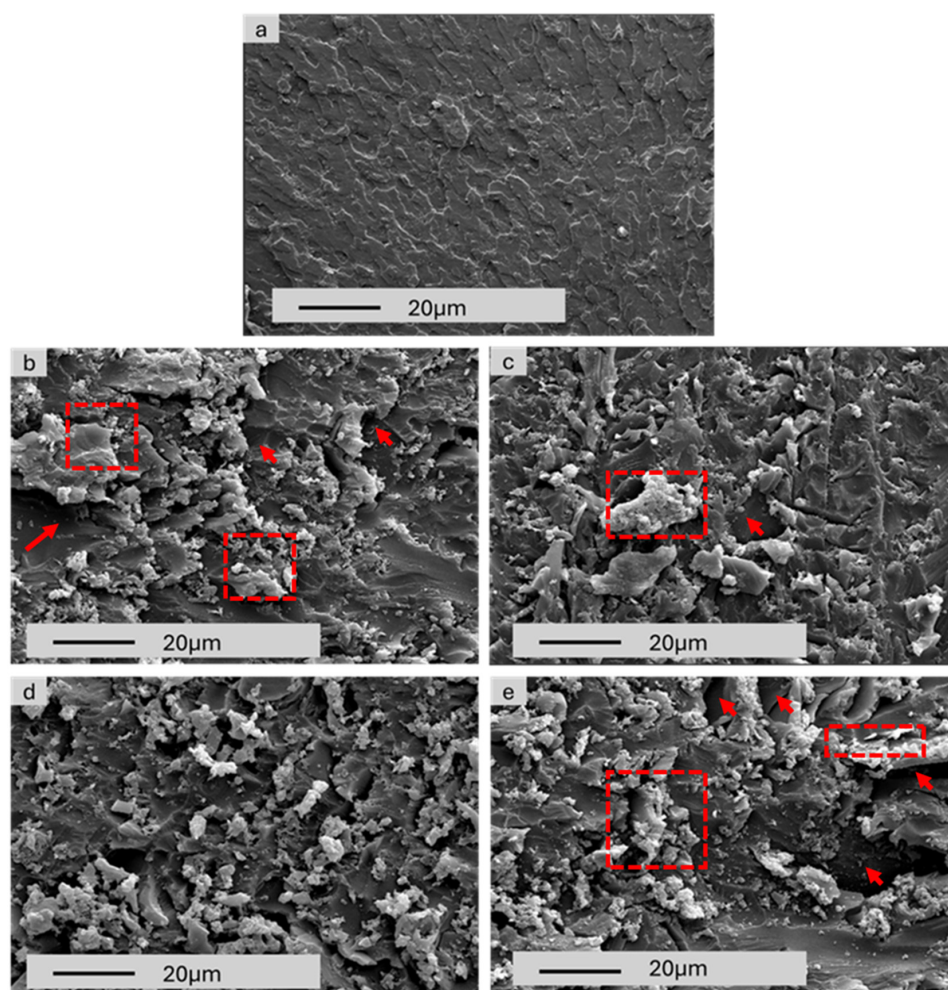


Figure 16. SEM fractographs of the fracture surfaces: (a) neat cyanate ester (STD), (b) CTF-5, (c) CTF-10, (d) CTF-15, and (e) CTF-20.

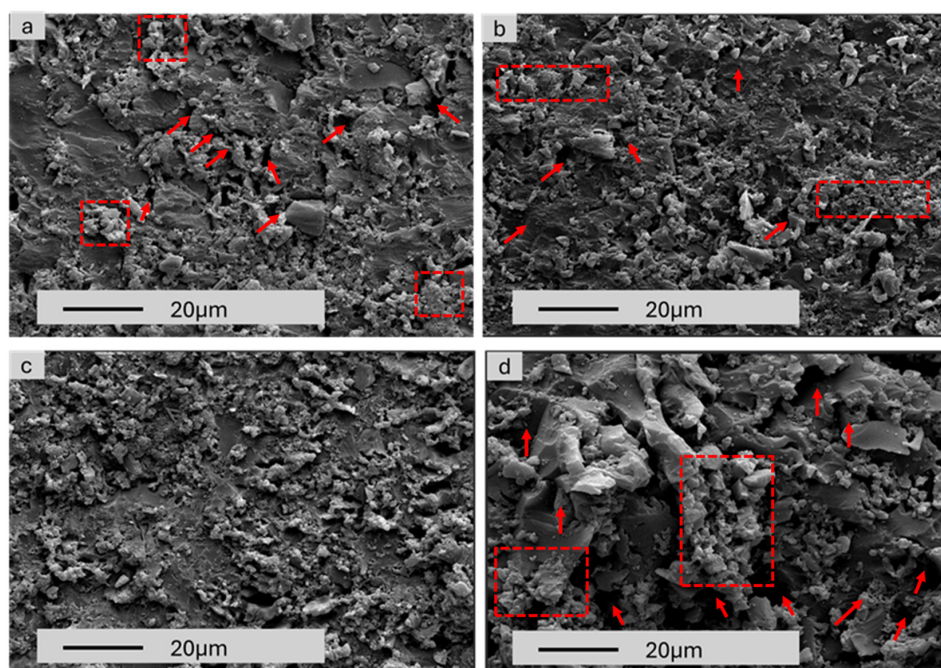


Figure 17. SEM fractographs of the fracture surfaces: (a) COF-5 (b) COF-10 (c) COF-15 (d) COF-20.

The comparison of the cross-sectional SEM microstructures between the transparent (CTF) and opaque (COF) glass-filled cyanate ester composites reveals noticeable differences in filler dispersion, interfacial bonding, and overall matrix morphology. In the opaque glass-filled series (COF), especially in COF-10 and COF-15 (Figure 17b,c), the microstructure appears denser and more homogeneous, with well-distributed glass particles and minimal voids or cracks. This uniform distribution enhances interfacial adhesion, leading to improved stress transfer efficiency, which is consistent with the higher tensile strength, increased dielectric constant, and reduced loss tangent values observed experimentally. In contrast, the transparent glass-filled composites (CTF) display rougher and more irregular cross-sectional surfaces. The micrographs show localized agglomerations and partially debonded regions, particularly in CTF-20 (Figure 16e) indicating weaker interfacial bonding and less efficient load distribution. These microstructural imperfections correspond to the slightly lower mechanical strength and higher dielectric losses measured for the CTF series.

In Figure 18, the microstructures and the corresponding EDX spectra of the CTF-15 and COF-15 samples are presented. The EDX analyses were obtained from the regions marked with red rectangles in the micrographs. For the CTF-15 sample (Figure 18a,b), the EDX spectrum taken from the red-framed area reveals strong peaks of Si, Al, Ca, O, and C, which correspond to the components of the transparent glass filler ($\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO}$ system) and the cyanate ester matrix. The presence of Ca indicates the successful incorporation of the glass phase, while the Si and Al peaks confirm the formation of aluminosilicate-based phases [41]. For the COF-15 sample (Figure 18c,d), the EDX spectrum obtained from the red-marked region shows, in addition to Si, Al, O, and C, a distinct Zr peak, originating from the zirconium-containing opaque glass additive [30].

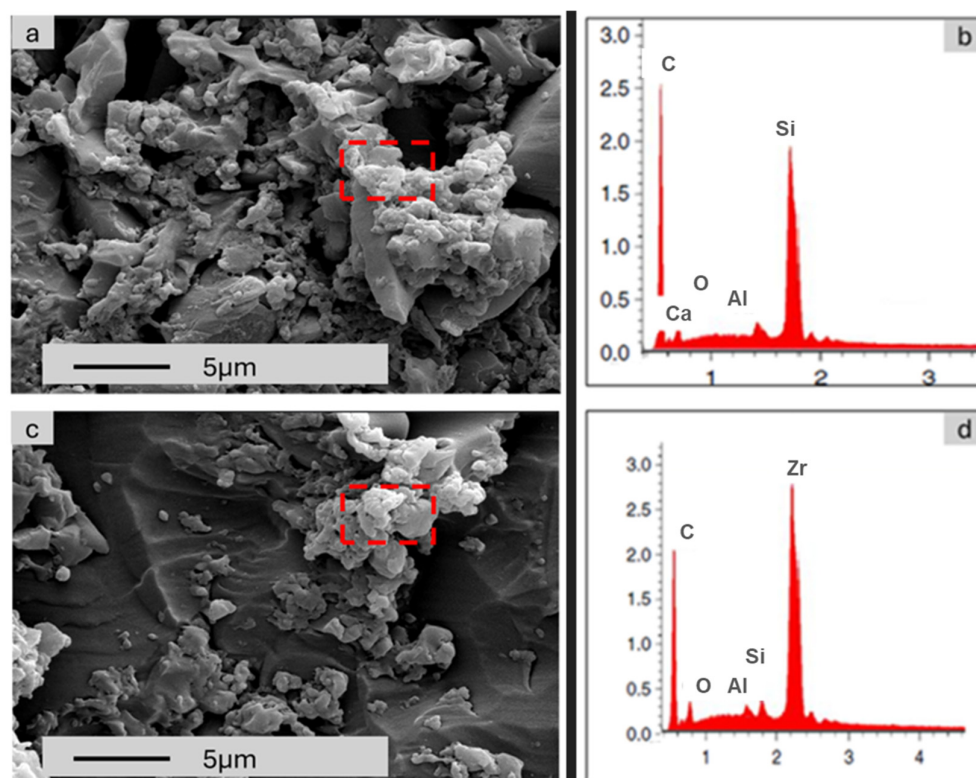


Figure 18. Microstructures of the CTF-15 and COF-15 samples (a,c) and the corresponding EDX analyses obtained from the red-framed areas (b,d).

The prepared cyanate ester/glass composites are expected to exhibit good thermal and structural stability due to the highly crosslinked cyanurate network and the inorganic glass

reinforcement. The FTIR results confirmed the formation of a dense triazine network, while SEM observations showed well-bonded filler–matrix interfaces, both of which are known to enhance long-term dimensional and thermal stability. In addition, the low dielectric loss value obtained at 1 MHz indicates stable dielectric behavior under electrical fields. These findings suggest that the developed composites possess sufficient stability for potential use in high-frequency electronic and insulation applications.

4. Conclusions

In this study, transparent and opaque borosilicate glass powders were incorporated into cyanate ester matrices to investigate their effects on mechanical, dielectric, and interfacial properties. The results demonstrate that both filler type and content strongly govern composite performance. The transparent glass series (CTF) improved dispersion and crosslink density, leading to optimal mechanical behavior at intermediate loadings (10–15 wt%). At higher loading (20 wt%), particle agglomeration and interfacial voids slightly reduced performance. In contrast, the zircon-containing opaque glass series (COF) produced a more pronounced enhancement in both dielectric and mechanical properties, with the best overall balance observed for COF-15. The dielectric constant increased from $\sim 2.86 \pm 0.1$ to $\sim 5.0 \pm 0.1$ while maintaining a low loss tangent ($\sim 0.007 \pm 0.001$ at 1 MHz), which is attributed to enhanced interfacial polarization and the formation of compact, well-bonded microstructures confirmed by FTIR and SEM/EDX analyses. Overall, the optimal filler content depends on glass type, with ~ 15 wt% providing the best balance for both systems, while opaque glass composites exhibited superior dielectric permittivity and mechanical reinforcement. These findings highlight the potential of zircon-containing glass–cyanate ester composites as promising materials for RF and microwave substrate applications, although further GHz-frequency dielectric and long-term thermal studies are required.

Author Contributions: Conceptual: C.B. and N.T.S.; methodology: C.B.; writing—original draft preparation: C.B.; writing—review and editing: N.T.S.; visualization: N.T.S.; supervision, N.T.S.; project administration: C.B.; funding acquisition: C.B. All authors have read and agreed to the published version of the manuscript.

Funding: This study was financially supported by the ASELSAN–TOHUM Project conducted in collaboration with Gebze Technical University (Project No. P6224061).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author.

Acknowledgments: This study was financially supported by the ASELSAN–TOHUM Project conducted in collaboration with Gebze Technical University (Project No. P6224061). The authors gratefully acknowledge ASELSAN for their valuable support.

Conflicts of Interest: The author Caner Basaran is employed by ASELSAN A.Ş. The funding sponsors had no role in the study design, data collection, analysis, or interpretation, in the writing of the manuscript, or in the decision to publish the results. The remaining authors declare no conflicts of interest.

References

1. Mohammed, E.M.; Malini, K.A.; Kurian, P.; Anantharaman, M.R. Modification of dielectric and mechanical properties of rubber ferrite composites containing manganese zinc ferrite. *Mat. Res. Bull.* **2002**, *37*, 753–768. [[CrossRef](#)]

2. Chao, F.; Liang, G.; Kong, W. Dielectric properties of polymer/ceramic composites based on thermosetting polymers. *Polym. Bull.* **2008**, *60*, 129–136. [[CrossRef](#)]
3. Goertzen, W.K.; Kessler, M.R. Thermal and mechanical evaluation of cyanate ester composites with low temperature processability. *Compos. Part A Appl. Sci. Manuf.* **2007**, *38*, 779–784. [[CrossRef](#)]
4. Crawford, A.O.; Howlin, B.J.; Cavalli, G.; Hamerton, I. Examining the thermo-mechanical properties of novel cyanate ester blends through empirical measurement and simulation. *React. Funct. Polym.* **2012**, *72*, 596–605. [[CrossRef](#)]
5. Yan, H.Q.; Chen, S.; Qi, G.R. Synthesis, cure kinetics and thermal properties of the 2,7-dihydroxynaphthalene dicyanate. *Polymer* **2003**, *44*, 7861–7867. [[CrossRef](#)]
6. Tang, Y.; Xu, S.; Xie, Y.; Gu, J.; Song, Z.; Gao, F.; Kong, J. Interfacial RAFT polymerization induced ultra-low dielectric loss ceramic/cyanate ester composites. *Compos. Sci. Technol.* **2016**, *124*, 10–16. [[CrossRef](#)]
7. Wu, G.; Cheng, Y.; Wang, K.; Wang, Y.; Feng, A. Fabrication and characterization of OMMt/BMI/CE composites with low dielectric properties and high thermal stability for electronic packaging. *J. Mater. Sci. Mater. Electron.* **2016**, *27*, 5592–5599. [[CrossRef](#)]
8. Hamerton, I.; Hay, J.N. Recent developments in the chemistry of cyanate esters. *Polym. Int.* **1998**, *47*, 465–473. [[CrossRef](#)]
9. Lei, Y.; Xu, M.; Jiang, M.; Huang, Y.; Liu, X. Curing behaviors of cyanate ester/epoxy copolymers and their dielectric properties. *High Perform. Polym.* **2017**, *29*, 1175–1184. [[CrossRef](#)]
10. Jian, G.; Jiao, Y.; Meng, Q.; Wei, Z.; Zhang, J.; Yan, C.; Moon, K.-S.; Wong, C.-P. Enhanced dielectric constant and energy density in a BaTiO₃/polymer-matrix composite sponge. *Commun. Mater.* **2020**, *1*, 91. [[CrossRef](#)]
11. Gu, J.; Dong, W.; Tang, Y.; Guo, Y.; Tang, L.; Kong, J.; Tadakamalla, S.; Wang, B.; Guo, Z. Ultralow dielectric, fluoride-containing cyanate ester resins with improved mechanical properties and high thermal and dimensional stabilities. *J. Mater. Chem. C Mater.* **2017**, *5*, 6929–6936. [[CrossRef](#)]
12. Goertzen, W.K.; Kessler, M.R. Thermal expansion of fumed silica/cyanate ester nanocomposites. *J. Appl. Polym. Sci.* **2008**, *109*, 647–653. [[CrossRef](#)]
13. Goertzen, W.K.; Sheng, X.; Akinc, M.; Kessler, M.R. Rheology and curing kinetics of fumed silica/cyanate ester nanocomposites. *Polym Eng Sci.* **2008**, *48*, 875–883. [[CrossRef](#)]
14. Ament, K.A.; Kessler, M.R.; Akinc, M. Cyanate ester–alumina nanoparticle suspensions: Effect of alumina concentration on viscosity and cure behavior. *Polym Eng Sci.* **2011**, *51*, 1409–1417. [[CrossRef](#)]
15. Chen, Y.; Li, Z.; Liu, Y.; Teng, C.; Cui, W. Curing Mechanism and Mechanical Properties of Al₂O₃/Cyanate Ester–Epoxy Composites. *J. Electron. Mater.* **2020**, *49*, 1473–1481. [[CrossRef](#)]
16. Tao, J.; Zhou, H.; Qin, Q.; Cui, Y.H. Dielectric property of cyanate ester, nano-TiO₂ particles or TiO₂ whiskers encapsulated by polyaniline. *Key Eng. Mater.* **2017**, *334–335*, 845–884.
17. Fang, R.; Zhu, G.; Ren, P.; Wang, Y.; Cui, X. In situ polymerization of graphene oxide and cyanate ester–epoxy with enhanced mechanical and thermal properties. *Appl. Surf. Sci.* **2014**, *316*, 549–557. [[CrossRef](#)]
18. Lee, B.L.; Holl, M.W. Effects of moisture and thermal cycling on in-plane shear properties of graphite fibre-reinforced cyanate ester resin composites. *Compos. Part A Appl. Sci. Manuf.* **1996**, *27*, 1015–1022. [[CrossRef](#)]
19. Chuang, W.; Geng-sheng, J.; Lei, P.; Bao-lin, Z.; Ke-zhi, L.; Jun-long, W. Influences of surface modification of nano-silica by silane coupling agents on the thermal and frictional properties of cyanate ester resin. *Results Phys.* **2018**, *9*, 886–896. [[CrossRef](#)]
20. Zegaoui, A.; Derradji, M.; Ma, R.; Cai, W.; Medjahed, A.; Liu, W.; Dayo, A.Q.; Wang, J. Silane-modified carbon fibers reinforced cyanate ester/benzoxazine resin composites: Morphological, mechanical and thermal degradation properties. *Vacuum* **2018**, *150*, 12–23. [[CrossRef](#)]
21. Jayalakshmi, C.G.; Anand, A.; Kandasubramanian, B.; Joshi, M. High temperature composite materials for electromagnetic applications through a cost-effective manufacturing process; resin film infusion. *Mater. Today Proc.* **2020**, *33*, 2217–2222. [[CrossRef](#)]
22. Li, J.; Zhang, W.; Gu, Y.; Wang, S.; Li, M.; Wang, Y. Tailoring dielectric and mechanical properties of hollow glass microspheres-modified quartz fiber/hyperbranched polyetherketoneketone laminated composites. *Compos. Part B Eng.* **2025**, *309*, 113107. [[CrossRef](#)]
23. Yang, J.; Pang, Y.; Cai, G.; Zheng, H.; Wang, J.; Li, Y.; Xu, Z. Design, modelling, and validation of electrically tunable multifunctional composites with dynamic control properties from transmission to absorption. *Compos. Part A Appl. Sci. Manuf.* **2025**, *199*, 109261. [[CrossRef](#)]
24. Li, R.; Yang, X.; Li, J.; Shen, Y.; Zhang, L.; Lu, R.; Wang, C.; Zheng, X.; Chen, H.; Zhang, T. Review on polymer composites with high thermal conductivity and low dielectric properties for electronic packaging. *Mater. Today Phys.* **2022**, *22*, 100594. [[CrossRef](#)]
25. Dasgupta, S. Polymer matrix composites for electromagnetic applications in aircraft structures. *J. Inst. Sci. A Multidisciplinary Rev. J.* **2015**, *95*, 275–296.
26. Kumudinie, C. Polymer–Ceramic Nanocomposites: Interfacial Bonding Agents. *Encycl. Mater. Sci. Technol.* **2001**, 7574–7577. [[CrossRef](#)]

27. Pizzi, A.; Mittal, K. *Handbook of Adhesive Technology Revised and Expanded*, 2nd ed.; Marcel Dekker Inc.: New York, NY, USA, 2023; ISBN 0-8247*0986-1.
28. ISO 527-2:1993; Plastics—Determination of Tensile Properties—Part 2: Test Conditions for Moulding and Extrusion Plastics. International Organization for Standardization: Geneva, Switzerland, 1993.
29. Shelby, J.E. *Introduction to Glass Science and Technology*; The Royal Society of Chemistry: Cambridge, UK, 1997.
30. Pekkan, K.; Karasu, B. Production of opaque frits with low ZrO₂ and ZnO contents and their industrial uses for fast single-fired wall tile glazes. *J. Mater. Sci.* **2009**, *44*, 2533–2540. [[CrossRef](#)]
31. Zhou, Y.; Zhang, Z.; Wang, P.; Ma, X. High-performance and low-dielectric cyanate ester resin optimized by regulating the structure of linear polyhydroxy ether modifier. *Compos. Part A Appl. Sci. Manuf.* **2022**, *162*, 107136. [[CrossRef](#)]
32. Devaraju, S.; Rangaraj, V.M.; Mohan, S.; Alagar, M. Low surface free energy cyanate ester–silica hybrid nanomaterials for low k dielectric applications. *RSC Adv.* **2013**, *3*, 12915–12921. [[CrossRef](#)]
33. Alagar, M.; Devaraju, S.; Prabunathan, P.; Mohan, S. Low dielectric and low surface free energy flexible linear aliphatic alkoxy core bridged bisphenol cyanate ester based POSS nanocomposites. *Front. Chem.* **2013**, *1*, 19. [[CrossRef](#)]
34. Lu, W.; Jing, Y.; Wenhua, C.; Jiajia, Z.; Dan, Z. Progress on Polymer Composites With Low Dielectric Constant and Low Dielectric Loss for High-Frequency Signal Transmission. *Front. Mater.* **2021**, *8*, 774843. [[CrossRef](#)]
35. Arous, M.; Hammami, H.; Lagache, M.; Kallel, A. Interfacial polarization in piezoelectric fibre-polymer composites. *J. Non-Cry. Solids* **2017**, *353*, 4428–4431. [[CrossRef](#)]
36. Samet, M.; Levchenko, V.; Boiteux, G.; Seytre, G.; Kallel, A.; Serghei, A. Electrode polarization vs. Maxwell-Wagner-Sillars interfacial polarization in dielectric spectra of materials: Characteristic frequencies and scaling laws. *J. Chem. Phys.* **2015**, *142*, 194703. [[CrossRef](#)]
37. Ariraman, M.; Kumar, R.S.; Alagar, M. Design of cyanate ester/azomethine/ZrO₂ nanocomposites high-k dielectric materials by single step sol–gel approach. *J. Appl. Polym. Sci.* **2014**, *131*, 41097. [[CrossRef](#)]
38. Li, B.; Polizos, G.; Manias, E. Interfacial Effects on the Dielectric Properties of Elastomer Composites and Nanocomposites. In *Dynamics of Composite Materials. Advances in Dielectrics*; Schönhals, A., Szymoniak, P., Eds.; Springer: Cham, Switzerland, 2022. [[CrossRef](#)]
39. Ignaczak, W.; Ladegaard Skov, A.; El Fray, M. Interfacial Polarization in Thermoplastic Basalt Fiber-Reinforced Composites. *Polymers* **2020**, *12*, 1486. [[CrossRef](#)]
40. Zhai, L.; Liu, Z.; Li, C.; Qu, X.; Zhang, Q.; Li, G.; Zhang, X.; Abde-Magid, B. Cyanate ester resin based composites with high toughness and thermal conductivity. *RSC Adv.* **2019**, *9*, 5722–5730. [[CrossRef](#)]
41. Pekkan, K.; Karasu, B. Zircon-free frits suitable for single fast-firing opaque wall tile glazes and their industrial productions. *J. Eur. Ceram. Soc.* **2009**, *29*, 1571–1578. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.