

Effects of polymorphic form and particle size of SiO₂ fillers on the properties of SiO₂-PEEK composites

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Received 25 March 2021; Revised 22 June 2021; Accepted 1 July 2021; Published 6 September 2021

The effects of polymorphic form and particle size of SiO₂ fillers on the dielectric, mechanical and thermal properties of SiO₂-Polyetheretherketone (SiO₂-PEEK) composites were investigated in this paper. Strong low frequency (<10Hz) Debye-like dielectric dispersions could be observed for all samples. The dielectric permittivity at high frequencies of the composite exhibits little morphology or particle size-sensitive characteristics of the SiO₂ fillers. All the composites obtained in this case demonstrate the dielectric permittivities of ~3.5 at high frequencies. The crystalline α -cristobalite filled composite exhibits lower dielectric loss and mechanical strength, but larger thermal expansion coefficient and thermal conductivity, compared with the similar particle sized amorphous SiO₂ filled one. The crystalline α -quartz filled composite demonstrates the lowest mechanical strength and highest dielectric loss. An increase in particle size of the spherical fused silica fillers decreases the dielectric loss, while increases the thermal conductivity of the composite. The flexural strength of the composite reaches the maximum value of 113 MPa when the particle size of spherical SiO₂ filler is ~10 μ m. Particle packing by combining optimal amounts of differently sized spherical fused silica fillers leads to a substantial improvement of mechanical strength (153MPa) coupled with reasonable dielectric and thermal properties due to the synergic effect (dielectric permittivity (ϵ_r) = 3.35, dielectric loss ($\tan\delta$) = 1.63×10^{-3} @ 10 GHz, thermal conductivity (λ) = 0.74 W/m²·k (90 °C), coefficient of thermal expansion (α) = 23.6ppm/°C and relative density (ρ) = 99.72%).

Keywords: SiO₂/PEEK composites; dielectric properties; mechanical properties; thermal conductivity; thermal expansion.

1. Introduction

Printed circuit boards (PCBs) used at the frequencies of micro/millimeter waves are generally required to have low dielectric permittivities and losses, good dielectric and dimensional thermal stabilities, large thermal conductivities, high mechanical strengths and easy machining. Ceramic-polymer composites can combine the advantages of the ceramics and polymers to meet the requirements of the practical applications. Considerable numbers of ceramic-polymer composites have been developed to offer a wide range of possibilities for making cost-effective microwave PCBs with tailored dielectric, mechanical and thermal properties.¹⁻⁶ Among them, polytetrafluoroethylene (PTFE) is the most preferred host matrix that exhibits frequency stable low dielectric permittivity (~2.2), extremely low dielectric loss (~10⁻⁴) and chemical inertness. However, the large coefficient of thermal expansion (CTE), low mechanical strength coupled with processing difficulties of PTFE limits its wide usage. The silica glass woven fabric are widely adopted in most commercially available PTFE-based PCBs in order to overcome the above shortcomings, while the presence of lossy silica glass woven fabric leads to an increase in dielectric inhomogeneity and dielectric loss at micro/millimeter

wave frequencies. Polyetheretherketone (PEEK) has exceptional mechanical strength (flexural strength ~130MPa), relatively excellent thermal chemical stability (T_g of 143 °C, T_m of 343 °C, and decomposing temperature of 580 °C) and low CTE (~56 ppm/°C).⁷⁻⁹ The dielectric permittivity and loss of PEEK reported is ~3.3 (50 Hz) and ~0.003 (1 MHz), respectively.¹⁰ In addition, it has similar thermal conductivity (0.22 W/m·K) as PTFE (0.25 W/m·K).¹¹ Since PEEK shows good mechanical properties, it is currently being studied as a high-performance plastic and as a matrix for fiber-reinforced composites. Less attention has been paid to its dielectric applications in comparison to the many studies on the mechanical properties of PEEK-ceramic composites.¹²⁻¹⁵ A few references on the dielectric properties of ceramic-PEEK composites have been reported by incorporating ceramic fillers, such as BaTiO₃, SrTiO₃, Si₃N₄, TiO₂ and AlN.¹⁶⁻²⁰ However, these composites have several drawbacks such as moisture sensitivity, high CTE, poor dielectric properties and frequency-dependent stabilities at microwave frequencies.

SiO₂ has been widely used as fillers in the ceramic/polymer composites due to its low permittivity, low dielectric loss and good thermal conductivity (2-14 W/m·K).²¹⁻²³ The previous researches on SiO₂-PEEK composites are mainly

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focused on the improvements of their mechanical and thermal properties. Lai *et al.* studied the mechanical properties of nano-SiO₂/PEEK composites.²⁴ The nanoceramic-fillers usually lead to an improvement of mechanical strength at the expense of significant increase in dielectric loss of the composite.¹⁰ Therefore, appropriate particle size should be optimized considering the tradeoff between mechanical strength and dielectric loss. The effects of fillers' structure on microstructure, dielectric and thermal properties of the SiO₂/PTFE composite were investigated in Ref. 25. Most previous works about the effect of particle size of ceramic filler have been focused on the mechanical strength and dielectric properties. The effects of particle size and size distribution of filler on the thermal properties of ceramic-PEEK composites are not explored so far. Crystalline SiO₂ demonstrates three basic polymorphs including cristobalite, tridymite and quartz. Each of these phases also has a high and low form related by a displacive transformation. Because the type of raw material of SiO₂ including polymorphic form and the crystallinity also plays an important role in determining the properties of the product, SiO₂ with different particle size and polymorphs were chosen as fillers and PEEK as polymer matrix in the present work. The objective of this work is to investigate the effects of polymorphic form, particle size and grain gradation of SiO₂ fillers on the dielectric, mechanical and thermal properties of SiO₂-PEEK composites prepared by a hot pressing method for potential application as high frequency and high speed circuit substrates.

2. Experimental Methods

Crystalline silica including α -cristobalite with D50 particle size of $\sim 8 \mu\text{m}$, α -quartz ($\sim 5 \mu\text{m}$) and amorphous silica including synthetic amorphous silica ($\sim 0.2\text{--}6 \mu\text{m}$) and spherical

fused quartz powders ($\sim 3, \sim 7, \sim 10, \sim 20$ and $\sim 30 \mu\text{m}$) were used as ceramic fillers. XRD patterns of the above different kinds of SiO₂ are shown in Fig. 1. 3-Aminopropyltriethoxysilane (KH-550) was used as a coupling agent to modify the surface of the ceramic fillers. SiO₂ particles were mixed with 0–5 wt.% KH-550 to create new active surfaces for binding with PEEK. Initially, an aqueous solution was set by adjusting the pH of the water to three with the addition of acetic acid. A volume equivalent to 1–5 wt.% of KH-550 was added to the acidified water followed by vigorous stirring for about 30 min before it was hydrolyzed and then formed a clear and homogeneous solution. The ceramic fillers were mixed with the KH-550 at the low shear rate for 24 h without additional solvent. After filtering, the resulting mixture was dried at 120 °C for 6 h to obtain the silane-coated fillers. The composites were prepared by powder processing technique in which 0.6 volume fractions of silane-coated SiO₂ fillers and PEEK powders were dispersed in ethyl alcohol using the high magnetic stirring mixer for about 24 h. A dry powder mixture was obtained by removing the solvent at 80 °C under stirring. The SiO₂-PEEK composites were fabricated by hot pressing process under uniaxial pressure of 60–120 MPa at 320–380 °C for 0–6 h. A flowchart of preparation of SiO₂/PEEK composites by powder processing technology is shown in Fig. 2.

A laser scattering particle analyzer (BT-9300H) was used to determine the particle sizes of the SiO₂ powders. Phase assemblages of the obtained composites were characterized by X-ray diffraction (XRD) technique using CuK α radiation (Bruker D8 Advance, America). Microstructures of the composites were investigated by scanning electron microscope (SEM) (Hitachi S4800, Japan). Dielectric properties of the composites were measured with a precision impedance analyzer (Agilent4294A) in the frequency range from 10² Hz to 10⁷ Hz at room temperature. Copper cladded circular disk

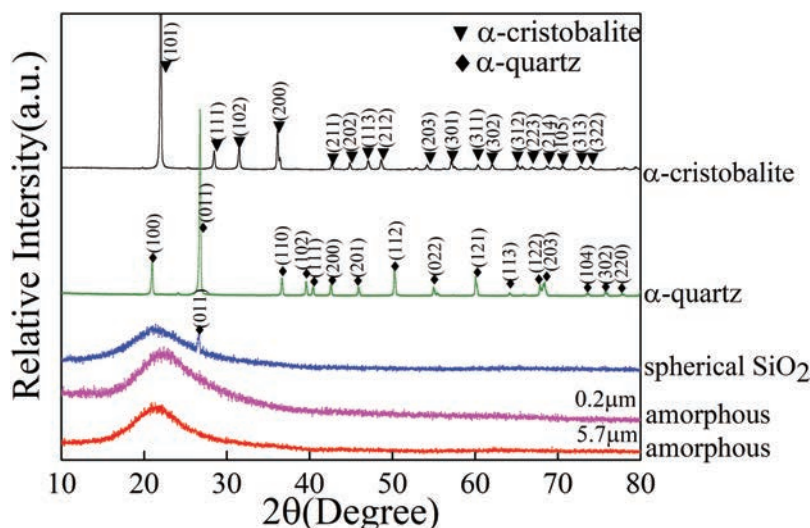


Fig. 1. XRD patterns of polymorphic forms of SiO₂ fillers with comparable particle size ($\sim 5\text{--}8 \mu\text{m}$).



Fig. 2. Flow chart for the preparation of SiO₂-PEEK composites.

with a diameter of ~15 mm and thickness of ~1 mm was used for this measurement. Agilent network analyzer (N5242A, Agilent, Palo Alto, CA) was utilized to characterize the dielectric properties of the composite materials at microwave frequencies. The dielectric permittivity and the loss were measured by split post dielectric resonator (SPDR) method using the pellet with 28 mm in diameter and 0.90 mm high at the frequency of ~10 GHz. Densities of the composites were measured using the Archimedes method. To measure the moisture absorption, the samples were weighed and submerged in distilled water at 100 °C for 12 h. Then the samples were removed and wipe dried. The amount of water absorbed was calculated from the weight again of the samples. Coefficients of thermal expansion (CTE) of the composites were measured using a dilatometer (Netzsch, DIL402 PC, Germany) within the range of 25–140 °C. Thermal conductivity and heat capacity of the prepared composite were measured at

room temperature using laser flash analysis (LFA; LFA-427, NETZSCH). Samples were prepared in disc-shaped forms with a diameter of 12.6 mm and a thickness of 1.5 mm, and then coated with graphite for testing. Flexural properties were measured by a three-point bending test using a universal material testing machine (AG-120KN, Shimadzu) at room temperature with speeds of 2 mm/min.

3. Results and Discussion

Polymorphic forms of SiO₂ fillers with comparable particle size (~5–8 μm) including crystalline phases (α-cristobalite and α-quartz), synthetic amorphous and spherical fused silica powders were adopted in this case in order to investigate the effect of polymorphic form of SiO₂ on the physical properties of SiO₂-PEEK (0.6 Vf) composites. Figure 3(a) shows the frequency-dependent dielectric properties of the

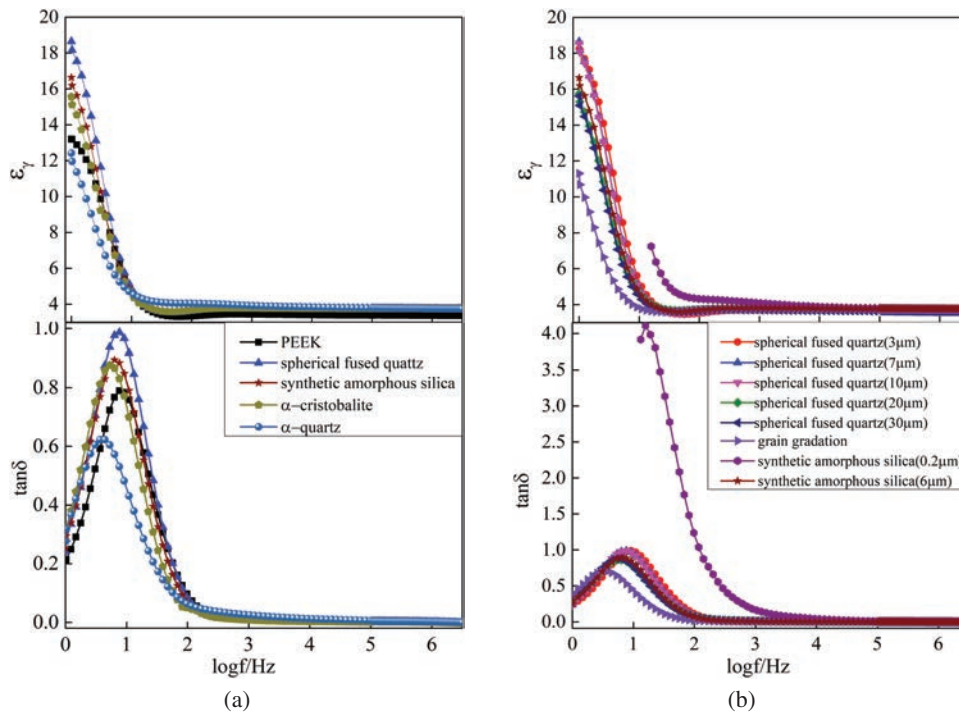


Fig. 3. Frequency-dependent dielectric properties of the composites containing polymorphic forms of SiO₂ fillers in a wide range of frequencies (1 Hz–1 MHz).

Table 1. Properties of SiO₂-PEEK composites with 0.6 Vf polymorphic SiO₂ fillers.

Polymorphic form	Relative density (%)	Porosity (%)	Water absorption (%)	λ^* (W/m*k) (90 °C)	α^* (ppm/°C)	Flexural strength (MPa)	Dielectric properties (1 MHz)		Microwave dielectric properties (~10 GHz)	
							ϵ_r	$\tan\delta$	ϵ_r	$\tan\delta$
Synthetic amorphous silica	99.81	0.19	0.11	0.68	22.0	126	3.76	2.6×10^{-4}	3.47	1.77×10^{-3}
Spherical fused quartz	99.68	0.32	0.18	0.71	23.5	107	3.75	3.1×10^{-4}	3.46	1.75×10^{-3}
α -Cristobalite	99.74	0.26	0.15	1.1	37.5	115	3.76	1.0×10^{-4}	3.49	1.49×10^{-3}
α -quartz	99.47	0.53	0.28	1.11	32.1	65	3.75	2.4×10^{-4}	3.52	2.26×10^{-3}

*: λ : thermal conductivity at 90 °C, and α : coefficient of thermal expansion.

composites containing polymorphic forms of SiO₂ fillers in a wide range of frequencies (1 Hz–1 MHz). For comparison, the frequency-dependent dielectric response of pure PEEK is also included. Strong low frequency (<10 Hz) dielectric dispersions in permittivity with corresponding loss peaks could be observed for all samples, indicating the presence of dipole-like relaxations associated with the polymer chain movement.^{26,27} Note that the loss peaks are slightly asymmetric and the widths at half-height of loss peaks are close to that of the Debye width ($\lambda = 1.14$), implying a Debye-like relaxation dielectric relaxation at low frequencies in this case. The relaxation intensity ($\Delta\epsilon_r \sim 10$) of pure PEEK in this case is much larger than that previously reported ($\Delta\epsilon_r < 1$), indicating the presence of hopping charge carriers which behaves like a jumping dipole and possess Debye-like dielectric response. So, the strong low-frequency dielectric dispersions in this case can be ascribed to the superposition of hopping charge carriers connected with the disorder (defects and/or traps) and dipole-like polarization associated with the polymer chain movement. The variation in relaxation intensity and corresponding loss peak amplitude with different morphology of SiO₂ fillers may be related to the different density of the traps. The properties of SiO₂-PEEK composites with 0.6 Vf polymorphic SiO₂ fillers are summarized in Table 1. It shows that the dielectric permittivities at high frequencies exhibit no morphology-sensitive characteristics. All samples have the dielectric permittivity of ~ 3.75 at the frequency of 1 MHz and ~ 3.5 at ~ 10 GHz, respectively. The slight decrease in permittivity with increasing frequency can be related to the frozen of interfacial polarization with increasing frequency. The composite with crystalline α -cristobalite fillers exhibits lower, while that with α -quartz fillers exhibits larger microwave dielectric loss compared with those with amorphous fillers. The crystalline phase is generally expected to exhibit lower dielectric loss in comparison with its amorphous counterpart. The higher dielectric loss of the crystalline α -quartz filled composite can be rationalized by considering the lower symmetry of space group and possible

piezoelectric polarization of α -quartz presented under the interfacial stress due to the large mismatch of thermal expansion coefficient between the quartz fillers and the PEEK matrix. The presence of piezoelectric polarization in crystalline α -quartz filled composite is also in agreement with the fact that similar dielectric permittivity as others is observed although it has the largest porosity (Table 1). The composites with crystalline fillers, as expected, demonstrate much larger thermal expansion coefficients (CTE) and thermal conductivities (λ) in comparison to those with amorphous fillers. The large CTE values and thermal conductivities in crystalline SiO₂ can be ascribed to the higher densities and cooperative rotational effects of SiO₄ tetrahedron, which are not possible in amorphous structures. Since the increase in crystallinity of quartz glass and/or porosity tends to decrease its bending strength,²⁸ the spherical fused silica containing small amount of crystalline α -quartz (Fig. 1) filled composite exhibits lower bending strength compared with the synthetic amorphous filled counterpart. The crystalline α -quartz filled composite demonstrates the lowest mechanical strength additionally due to the highest porosity/water absorption as illustrated in Table 1 and also evidenced by the BSEM images [Figs. 4(a)-D)].

The effects of particle size of SiO₂ fillers on the density, dielectric properties and mechanical strength of the composite with fixed loading (0.6 Vf) were also studied in this case. Synthetic amorphous silica (~ 0.2 – $6 \mu\text{m}$) and spherical fused quartz fillers with different particle sizes (3, 7, 10, 20 and $30 \mu\text{m}$) were used as ceramic fillers. Back scattering SEM images of the SiO₂-PEEK composites (0.6 Vf) containing different particle sized spherical quartz glass fillers are shown in Fig. 4(b). Spherical particles with ~ 3 – $30 \mu\text{m}$ particle sizes are generally well dispersed throughout the polymer matrix, while inhomogeneous microstructure with agglomeration of SiO₂ particles could be observed for the composite with nanosized amorphous glass fillers [Fig. 4(a)-A)]. Frequency-dependent dielectric properties of the composites containing different size of SiO₂ fillers

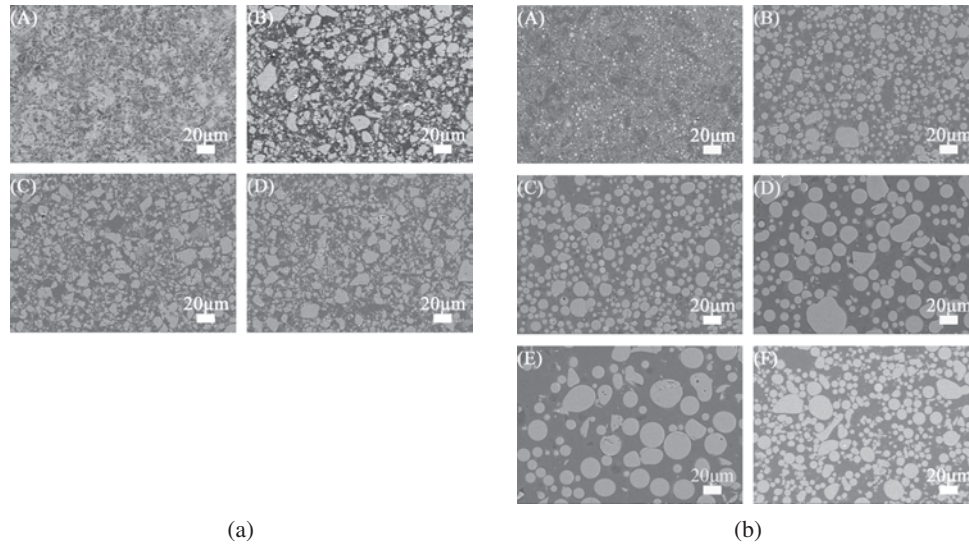


Fig. 4. Back scattering SEM images of PEEK-SiO₂ composites with (a) polymorphic forms of SiO₂ fillers (A: synthetic amorphous silica (~200 nm), B: synthetic amorphous silica (~6 μm), C: α-cristobalite(~8 μm), D: α-quartz (~5 μm) (b) spherical fused quartz fillers with different particle size (A:3 μm, B:7 μm, C:10 μm, D: 20 μm, E:30 μm, F: grain gradation of spherical fused quartz.

in a wide range of frequencies (1 Hz–1 MHz) are shown in Fig. 3(b). The aforementioned strong low frequency (<10 Hz) dielectric dispersions in permittivity with corresponding loss peaks could also be observed for all samples. The increase in particle size of the SiO₂ filler is supposed to decrease the interface areas between the SiO₂ fillers and PEEK matrix, which would lead to the decrease in the interfacial polarizations and thus the dielectric permittivity. On the other hand, the decrease in interface areas is beneficial to the movement of polymer chain, which would result in

the decrease in dipole-like polarization of polymer and hence the decrease in dielectric permittivity. Therefore, the influences of the particle size of SiO₂ filler on the dielectric response at low frequencies are the result of above two competing factors. Note that the nanosized amorphous SiO₂ filled composite demonstrates larger relaxation intensity and loss compared with other samples due to the hydroxyl surfaces of nanosized amorphous SiO₂ fillers.²⁸ Table 2 summarizes the relative densities, porosities, water absorption, and high frequency dielectric properties of the composites

Table 2. Porosity, dielectric, mechanical and thermal properties of SiO₂-PEEK composites (0.6 Vf) containing different particle sized SiO₂ fillers.

SiO ₂	Particle sizes (μm)	Relative density (%)	Porosity (%)	Water absorption (%)	λ*(W/m*k) (90 °C)	α* (ppm/°C)	Flexural strength (MPa)	Dielectric properties (1 MHz)		Microwave dielectric properties (~10 GHz)	
								ε _r	tanδ	ε _r	tanδ
Synthetic amorphous	0.2	99.55	0.45	0.31	0.35	38.5	105	3.77	2.4 × 10 ⁻³	3.48	6.31 × 10 ⁻³
	6	99.81	0.19	0.11	0.68	22.0	126	3.76	2.6 × 10 ⁻⁴	3.47	1.77 × 10 ⁻³
Spherical fused quartz	3	99.67	0.33	0.19	0.70	23.4	86	3.68	2.9 × 10 ⁻⁴	3.36	1.89 × 10 ⁻³
	7	99.68	0.32	0.18	0.71	23.5	106	3.75	3.1 × 10 ⁻⁴	3.46	1.75 × 10 ⁻³
	10	99.57	0.43	0.25	0.73	24.1	113	3.72	2.5 × 10 ⁻⁴	3.49	1.64 × 10 ⁻³
	20	99.65	0.35	0.20	0.72	22.8	98	3.70	2.6 × 10 ⁻⁴	3.39	1.49 × 10 ⁻³
	30	99.37	0.63	0.37	0.90	23.1	78	3.60	2.7 × 10 ⁻⁴	3.47	1.44 × 10 ⁻³
Grain gradation (spherical fused quartz)	1/3V _f (7 μm) + 1/3V _f (10 μm) + 1/3V _f (20 μm)	99.72	0.28	0.16	0.74	23.6	153	3.48	3.1 × 10 ⁻⁴	3.35	1.63 × 10 ⁻³

*: λ: thermal conductivity at 90 °C, and α: coefficient of thermal expansion.

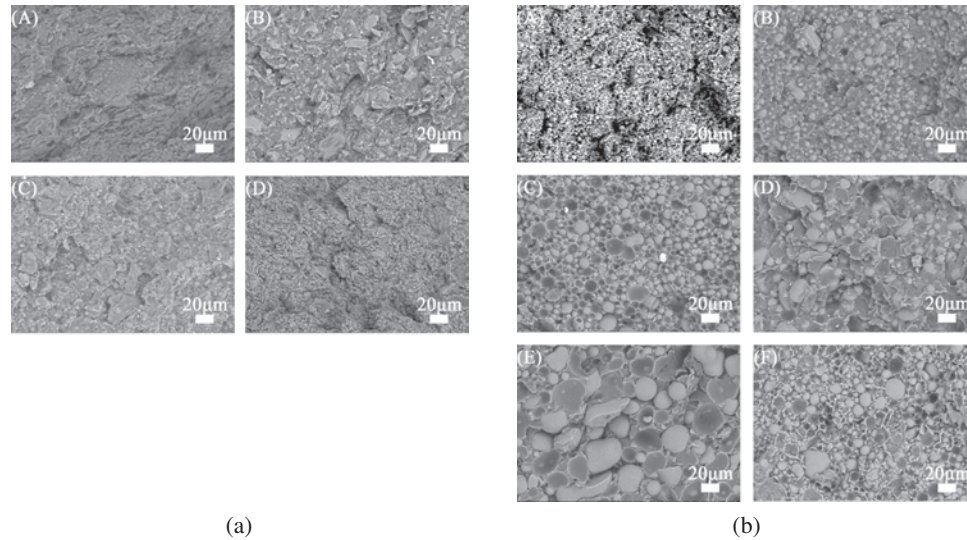


Fig. 5. Fracture surface of PEEK-SiO₂ composites with (a) polymorphic forms of SiO₂ fillers (A: synthetic amorphous silica (~200 nm), B: synthetic amorphous silica (~6 μm), C: α-cristobalite (~8 μm), D: α-quartz (~5 μm) (b) spherical fused quartz fillers with different particle size (A:3 μm, B:7 μm, C:10 μm, D: 20 μm, E:30 μm, F: grain gradation of spherical fused quartz).

(0.6 Vf) containing different particle sized SiO₂ fillers. The particle size of SiO₂ filler demonstrates little influence on the dielectric permittivity of the composite at high frequencies. While increase in particle sizes of the SiO₂ fillers leads to the decrease in interfacial areas between SiO₂ fillers and PEEK matrix, hence, the decrease in microwave dielectric loss and increase in thermal conductivity as a result of the decrease in interfacial polarization and scattering of phonons, respectively. The CTE value of the composite with spherical SiO₂ fillers is about 22–24 ppm/°C, which is compatible with that of the copper clad and change little with the particle size. Although amorphous silica is reported to have extremely low thermal expansion coefficient, notice that the composite with nanosized amorphous SiO₂ exhibits much

larger CTE value (39 ppm/°C) compared with those with other amorphous counterparts. This can be probably related to its inhomogeneous microstructure with agglomeration of SiO₂ particles [Fig. 4(a)-A].

As the particle size of the spherical fused silica filler increases from 3 μm to 10 μm, the flexural strength increases from 86 MPa to 113 MPa for the composite with spherical SiO₂ fillers. Further increase of SiO₂ particle size leads to the significant decrease in flexural strength due to the decrease in homogeneity of microstructure and increase in transgranular fracture as shown in Fig. 5(b). Continuous grading of particles is often required to achieve tight packing and thereby increasing the mechanical strength of the concrete mixture.²⁹ A well-known S-shaped graph (Fuller curve) is still used

Table 3. Comparison of comprehensive properties of the SiO₂-PEEK composite obtained in this work with other similar composites previously reported.

Polymer	Filler	Loading	Water absorption (%)	CTE (ppm/°C)	λ (W/m*K)	Flexure strength (MPa)	f	Dielectric properties		Reference
								ε _r	tanδ	
PTFE	SiO ₂	57 wt.% (9 μm)	0.2	28.81	—	—	10 GHz	2.89	7.0 × 10 ⁻⁴	32
PTFE	SiO ₂	60 wt.% (5 μm)	0.26	38.5	—	—	5 GHz	2.81	6.2 × 10 ⁻³	33
PTFE	SiO ₂	60 wt.% (25 μm)	0.062	38.9	—	—	5 GHz	2.96	1.9 × 10 ⁻³	33
PTFE	SiO ₂	31 wt.% + 31 wt.% (2 μm + 15 μm)	0.05	18.68	—	—	10 GHz	2.99	2.0 × 10 ⁻³	34
PTFE	SiO ₂	31 wt.% + 31 wt.% (5 μm + 15 μm)	0.036	22.0	—	—	10 GHz	2.94	1.3 × 10 ⁻³	34
PEEK	SiO ₂	20 vol% (0.01–0.02 μm)	—	43.5	—	—	1 MHz	3.72	1.6 × 10 ⁻²	35
PEEK	SiO ₂	60 vol% (20 μm)	0.2	22.8	0.72	98	10 GHz	3.39	1.49 × 10 ⁻³	This work

today to optimize the particle size distribution.³⁰ However, this curve is applicable to the materials with a particle size larger than 500 μm and less workable with fine particles.³¹ Furthermore, the gradation that gives the greatest density of the fillers alone may not necessarily give the greatest density when combined with polymer because of the way the polymer fit into smaller pores in this case. We adopted the particle packing gradation by simple mixing of equal volume fractional SiO_2 fillers with three different particle size ($1/3V_f(7\ \mu\text{m})/1/3V_f(10\ \mu\text{m})/1/3V_f(20\ \mu\text{m})$) in this case. Notice that the composite with simple mixture of different sized spherical fused silica fillers demonstrates the lowest porosity and remarkable improvement of mechanical strength (153 MPa) coupled with reasonable dielectric and thermal properties due to the synergic effect by the substantial increase in packing density of the fillers. Table 3 illustrates the comparison of microwave dielectric properties of some SiO_2 /polymer composites. It is seen that the SiO_2 /PEEK composites obtained in this case demonstrate lower dielectric losses at microwave frequencies coupled with reasonable thermal properties and good mechanical strength, compared with those previously reported for the SiO_2 -based composites with similar dielectric permittivity.

4. Conclusions

The effect of polymorphic form and particle size of SiO_2 on the dielectric, mechanical and thermal properties have been investigated in this paper. Strong low frequency ($<10\ \text{Hz}$) Debye-like dielectric dispersions could be observed for all samples, which can be ascribed to the superposition of hopping charge carriers connected with the disorder (defects and/or traps) and dipole-like polarization associated with the polymer chain movement. Both the polymorphic form and particle size of SiO_2 filler demonstrate little effect on the dielectric permittivity at high frequencies for the fixed composition (0.6 Vf), which exhibits low dielectric permittivities ($\epsilon_r \sim 3.5$). The crystalline α -cristobalite filler would reduce, while the α -quartz filler increases the dielectric loss of the composite probably due to the presence of piezoelectric polarization, both of them increase the CTE value and thermal conductivity, compared with the amorphous SiO_2 fillers. The crystalline α -quartz filled composite demonstrates the lowest mechanical strength. An increase in particle size of the spherical fused silica leads to the decrease in dielectric loss and increase in thermal conductivity, which can be attributed to the reduction of interfacial areas. The flexural strength reaches the maximum value of 113 MPa when the particle size of spherical SiO_2 filler is $\sim 10\ \mu\text{m}$. Considerable improvement of mechanical strength (153 MPa) coupled with reasonable dielectric and thermal properties could be obtained through particle packing optimization due to the synergic effect by the substantial increase in packing density of the fillers.

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