

## Dielectric Properties of Highly Filled Thermoplastics for Printed Circuit Boards

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**ABSTRACT:** In this study, highly filled high-temperature thermoplastics (polyethersulfone [PES], polyphenylsulfide, polyetherimide [PEI], and polyetheretherketone [PEEK]) are used as insulating substrate for printed circuit boards (PCBs). Talc has been added to the thermoplastics to adjust their coefficient of thermal expansion (CTE) to the CTE of the copper circuits, thus reducing the possibility of failure of the PCB owing to thermal stress. The dielectric properties of the substrates were analyzed between 10 MHz and 1 GHz, depending on filler fraction and water absorption. An increase of filler fraction resulted in an increase of dielectric constant  $\epsilon'$ . As expected, the absorption of water molecules led to an increase of both  $\tan \delta$  and  $\epsilon'$ . Moreover, the combination of filler and absorbed water resulted in a strong increase of the dielectric loss factor at low frequencies. Finally, theoretical approaches with fitting parameters could be employed to precisely describe the measured properties between 0.8 and 1 GHz. This study shows that most of the materials investigated here, namely highly filled PPS, PEI, and PEEK, are suitable for high-frequency PCB applications. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 128: 3758–3770, 2013

**KEYWORDS:** dielectric properties; thermoplastics; properties and characterization

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### INTRODUCTION

The electronic industry is actively working on solutions in respect to the increasing consumer demand in telecommunication devices and computers for cost-effective product miniaturization.<sup>1–3</sup> The demand for denser and faster microelectronic circuits requires that printed circuit boards (PCBs) operate at raised frequencies (>1 GHz) with a high signal integrity, which is characterized by a low dielectric loss factor ( $\tan \delta$ ). Moreover, increased logic chip performance in high-speed digital applications, where propagation delay and signal rise times are critical, requires PCBs with low dielectric constants ( $\epsilon'$ ).

Conventional PCBs are mostly based on glass fiber-reinforced epoxy resins (FR4) as insulating substrate materials for the electrical conducting circuits. The reinforcement of the polymer with glass fibers is required to adjust the coefficient of thermal expansion (CTE) of the substrate in the plane to the CTE of the copper circuits (17 ppm/K), which is particularly important during the soldering process of the PCB. During the lead-free soldering process maximum peak temperatures between 230 and 255°C are achieved for approx. 10 s. Without this similarity between the CTEs, thermally induced stresses between the substrate and the copper could cause failure of the PCB.<sup>4</sup>

Materials like FR4 exhibit tailored thermal, mechanical, and electrical properties for a broad range of applications, have low cost, and are widely employed in the PCB industry for more than 40 years. A number of investigations can be found in the literature regarding the further optimization of these material's properties.<sup>5–10</sup> But with growing demands regarding the signal integrity at high frequencies and low signal losses, the limits in terms of dielectric properties of standard epoxy-based substrates (approximately  $\tan \delta > 0.014$  and  $\epsilon' > 4$  at 1 GHz) have been reached, and do not further fulfill the requirements for such new applications.<sup>11</sup> For this reason, the scientific community is working on developing special material compositions, which exhibit low dielectric loss in high frequency ranges. Regarding applications up to 10 GHz, commercially available PCB materials can already be found, such as RO4000 series from Rogers, which exhibit a clearly lower loss angle in comparison to conventional FR4 substrates (<0.004).<sup>12</sup> RO4000 is based on a glass fiber-reinforced hydrocarbon/ceramic laminate. Even lower loss factors (<0.002) at high frequencies can nowadays be obtained by employing fluoropolymer-based substrates in combination with mineral powders or glass fibers. Among fluoropolymers, polytetrafluoroethylene (PTFE) is the most preferred host matrix for substrate applications owing to its low permittivity, low loss factor, and relatively high service temperature.<sup>13–23</sup> But

the wide usage of PTFE-based substrates is restricted owing to high costs and the processing difficulties.<sup>24</sup> Different from other thermoplastics, conventional PTFE typically cannot be processed through injection molding or melt extrusion owing to the high melt viscosity.<sup>25</sup>

On the other hand, commodity thermoplastics, which can be easily manufactured via extrusion or injection molding technology, have also been investigated regarding PCB applications. Polyethylene and polystyrene, for instance, have a very low  $\epsilon'$  and  $\tan \delta$  owing to their nonpolar chemistry.<sup>26–30</sup> Moreover, these polymers show a cost advantage in comparison to other polymer substrates. Nevertheless, these materials can only be used for some special applications owing to their limited thermal stability.

The above-mentioned thermal requirements can be fulfilled by other thermoplastics, such as polyetherimide (PEI), polyethersulfone (PES), polyphenylsulfide (PPS), and polyetheretherketone (PEEK). Moreover, these high-temperature polymers also exhibit low dielectric properties at 1 GHz, comparable to insulating high-frequency substrates for PCBs ( $\tan \delta < 0.005$ ;  $\epsilon' < 3.5$ ), and possess a sufficient high thermal stability for the lead-free soldering process.<sup>31</sup> The CTEs of these polymers are already very low (45–55 ppm/K) in comparison to other thermoplastics, and can be further reduced in the plane by incorporating approximately 25–35 filler vol %. A CTE of approximately 17 ppm/K, which is similar to that of copper, can therefore be reached, as already discussed in a previous study.<sup>32</sup> These compounds can also be continuously manufactured via extrusion technology to thin films, and afterward be used for the manufacturing of electrical multilayer PCBs. In comparison to PTFE-based substrates, these high-temperature thermoplastics therefore represent an economic viable alternative. Moreover, the chemical structure of these high-temperature thermoplastics leads to an intrinsic flame resistance, and consequently halogenated flame retardants are not required. In combination with the possibility of recycling, clear environmental advantages can be observed in comparison to conventional thermosetting PCB substrates. In summary, the mechanical and thermal properties of high-temperature thermoplastics exhibit a good potential for the development of insulating substrates for high-frequency multilayer. However, quite surprisingly, only few investigations regarding the dielectric properties of these materials in the high-frequency range (>10 MHz) can be found in the literature.<sup>32–36</sup>

To deeply analyze the potential of highly filled high-temperature thermoplastics for PCBs in high-frequency applications, the influence of three key factors (namely frequency, the filler fraction [talc, in this study], and the moisture absorption) on the dielectric behavior of PEI, PES, PEEK, and PPS are investigated in this article. A frequency range between 10 MHz and 1 GHz has been used for this investigation. The maximum filler fraction used here is 35 vol %, which is the required amount for a sufficient reduction of the CTE and adjustment to the CTE of copper. Moreover, the influence of the moisture uptake was investigated up to the saturation point, which corresponds to a water absorption value of around 2% in weight.

Finally, a theoretical prediction of the dielectric properties of the filled polymers is relevant for the design of new electronic devices, as a rough estimation of the properties of new material mixtures is required at the initial stages of a manufacturing project. A variety of equations have been suggested in the literature for the calculation of the dielectric constant of composites.<sup>37–43</sup> In this study, the suitability of these equations is addressed and evaluated based on the experimental data.

## MATERIALS AND PROCESSING CONDITIONS

Two amorphous thermoplastics, PES (Ultrason E2010) from BASF, PEI (Ultem 1000) from Sabic, and two semi-crystalline thermoplastics, PPS (Fortron 203) from Ticona, and PEEK (450G) from Victrex have been employed. Talc (Finntalc M15) with a median particle size of 4.4  $\mu\text{m}$  (d50) was supplied by Mondo Minerals. Before compounding, the polymer granulates were dried according to the processing guidelines of the four polymer producers. Talc was compounded in different volume fractions (Table I) into the four thermoplastics with a twin-screw extruder Theysohn TSK-N030/40D (screw diameter  $D$ : 30 mm, length to diameter ratio  $L/D$ : 40). The output was approximately 8 kg/h, the rotational speed 200 rpm, and the temperature zones during extrusion were heated to 370°C for PEI and PES, 320°C for PPS, and 390°C for PEEK. Talc was added to the molten polymer via a side feeder. The screw geometry was chosen to achieve a good distribution and dispersion of the filler in the polymeric matrix, including a mixing zone after the side feeder.

For the dielectric characterization and the measurement of the water absorption, plates with a length of 60 mm, width of 60 mm, and thickness of 3 mm were manufactured using an injection-molding machine Arburg Allrounder 430 C 800-250. The temperatures during injection molding were identical to the processing temperatures during extrusion.

For the theoretical evaluation of the measured values, the dielectric loss factor and the dielectric constants of water and talc have been used as from the literature. Talc has a dielectric constant of 6.5 and a dielectric loss factor of 0.00038 according to the previously published literature,<sup>44</sup> whereas water exhibits a dielectric constant of 80.4 and a loss factor of 0.123.<sup>45</sup>

## CHARACTERIZATION

### Coefficient of Thermal Expansion

The CTE of the different materials was measured according to IPC-TM 650, method 2.4.24C below the glass transition temperature ( $T_g$ ). Rectangular specimens were prepared from the central region of injection-molded plates. The dimensions of the specimens were as follows: thickness = 3 mm, width = 10 mm, and length = 10 mm. Thermal expansion measurements were achieved in flow direction ( $x$ ) and transverse direction ( $y$ ) of the melt flow in injection-molding process. Each specimen was maintained at 60°C for 15 min, followed by a heating ramp of 5°C/min up to 200°C for the amorphous batches ( $T_g$ : 217°C for PEI and 227°C for PES), up to 150°C for the PEEK-based batches ( $T_g$ : 150°C) and up to 100°C for the PPS-based batches ( $T_g$ : 100°C). To avoid nonreversible effects, each specimen was tempered before testing at 150°C for 24 h.

**Table I.** Designation of Characterized Materials, Based on PES, PEI, PPS, and PEEK with Talc as Filler, as Well as Their Coefficient of Thermal Expansion

Talc content (vol %)	Weight % filler	PES	CTE in the plane (x/y) (ppm/K)	PEI	CTE in the plane (x/y) (ppm/K)	PPS	CTE in the plane (x/y) (ppm/K)	PEEK	CTE in the plane (x/y) (ppm/K)
0	-	PES_0	61/58	PEI_0	49/52	PPS_0	53/56	PEEK_0	50/49
15	26	PES_15	35/33	-	-	-	-	-	-
25	41	PES_25	24/24	PEI_25	22/22	PPS_25	25/23	PEEK_25	22/21
35	52	PES_35	20/22	PEI_35	17/17	PPS_35	19/18	PEEK_35	17/18

### Differential Scanning Calorimetry Measurement

In case of the semi-crystalline thermoplastics, differential scanning calorimetry (DSC) measurements have been achieved to determine the crystallization degree of the semi-crystalline specimens. The tests have been conducted according to DIN 53 76 with a heating rate of 10°C/min in a temperature range from 20 to 320°C for PPS and from 20 to 400°C for PEEK. The crystallinity was measured in respect to the first and the second heating cycles.

### DMA Measurement

The glass transition temperature was determined by dynamic mechanical measurements. The storage modulus  $G'$ , the loss modulus  $G''$ , and the loss tangent  $\tan \delta = G''/G'$  were measured using a dynamic-mechanical analyzer (DMTA-RDA III, TA Instruments, USA) from 40 up to 250°C with a heating rate of 3°C/min at a frequency of 1 Hz. The  $T_g$  corresponds to the temperature where  $G'$  achieved its maximum. A torsion mode testing was applied during the DMA scans. Samples of dimensions 50 mm × 10 mm × 3 mm were used.

### Moisture Uptake

This test method according to DIN EN ISO 62 is designed to determine the amount of water absorbed by polymers when immersed in distilled water. The dimensions of the specimens used in this test are as follows: 20 mm × 20 mm and a thickness of 3 mm. Three specimens for every compound were investigated, which were conditioned before the measurement (drying in an oven under vacuum for 72 h at 160°C). In a next step, the weight of the samples has been measured in the dry condition. Afterward, the conditioned specimens were placed in a container of distilled water at 23°C. The moisture absorption was characterized after 12 h, 1 day, 2 days, 3 days, 1 week, 2 weeks, 3 weeks, and 4 weeks (after 4 weeks, the saturated condition was achieved for all compounds). Moreover, the moisture uptake in the standard condition was measured. Therefore, the samples have been stored at 23°C, 50% relative humidity (r.h.) After 72 h, no further increase of the weight of the sample could be observed, so that the standard condition was achieved. Water content was determined using the following equation:

$$M_t (\%) = \frac{W_t - W_0}{W_0} \times 100 \quad (1)$$

where  $M_t$ ,  $W_t$ , and  $W_0$  are the water content at a given time, weight of the sample at the time of the measurement, and initial weight, respectively. The diffusion coefficients have been calculated

according to the following equation (where  $c_s$  is the moisture absorption at saturation,  $d$  the thickness of the sample,  $c(t)$  the measured moisture uptake at the time  $t$  and  $t$  the dwell time):

$$\sqrt{D} = \frac{1}{c_s} \frac{d}{0.52 \pi} \frac{c(t)}{\sqrt{t}} \quad (2)$$

### Dielectric Properties

An Agilent Impedance/Material Analyzer (4291 A) was used to measure the dielectric constant and the dielectric loss factor of the injection-molded samples (lateral dimensions: 20 mm × 20 mm, thickness: 3 mm) over the frequency range 10 MHz–1 GHz according to IPC-TM 650-2.5.5.9. The dielectric properties have been characterized at different conditions regarding the moisture absorption. The dry situation was obtained after drying the samples for 72 h at 160°C. To simulate the standard condition in the case of typical applications, a certain moisture uptake has to be considered. Therefore, the samples were stored for 1 week at 23°C and 50% r.h. in a climate chamber and subsequently characterized (standard condition). Moreover, the influence of increasing water absorption on the dielectric properties was analyzed by measuring the dielectric constant and the dielectric loss factor after immersion in distilled water for 12 h, 1 day, 2 days, 3 days, 1 week, 2 weeks, 3 weeks, and 4 weeks (in the saturated condition).

## RESULTS AND DISCUSSION

### Thermal Properties

As expected, the increase of filler fraction resulted in a clear decrease of the CTEs of the high-temperature thermoplastics as summarized in Table I. With a maximum talc fraction of 35 vol %, the desired CTE value in the plane (around 17 ppm/K, to match the CTE of copper) could be achieved for PES, PEI, PPS, and PEEK, whereby only a small deviation in flow direction and transverse the flow direction of the injection-molded samples could be observed.

The crystallinity ( $X_c$ ) for PEEK and PPS compound was calculated from the heat enthalpy evolved during crystallization based on the cooling scans according to the following equation:

$$X_c (\%) = \frac{\Delta H_c}{\Delta H_m^o \rho} \times 100 \quad (3)$$

where  $\Delta H_c$  is the apparent enthalpy of crystallization of sample,  $\Delta H_m^o$  is the extrapolated value of the enthalpy corresponding to

**Table II.** Crystallinity of the Talc-Filled PEEK and PPS and DSC Measurements

Crystallinity (%)	PEEK_0	PEEK_25	PEEK_35	PPS_0	PPS_25	PPS_35
First heating	22	22	21	42	38	37
Second heating	24	24	24	45	44	41

**Table III.**  $T_g$  of the Talc-Filled PEEK, PPS, PES, and PEI, DMA Measurement, Determined on  $G''$  Curve

Talc content (vol. %)	$T_g$ (°C)			
	PEEK	PPS	PES	PEI
0	159	107	229	220
25	159	111	229	220
35	159	111	230	220

the melting of 100% crystalline PEEK and PPS, which is taken as 130 J/g<sup>46</sup> for PEEK and 80 J/g<sup>47</sup> for PPS, and  $\rho$  is the polymer weight fraction in the compound.

The results of the DSC measurements (Table II) show that the addition of talc leads to a slight decrease of crystallinity of both semi-crystalline polymer composites. Moreover, after the second heating cycle, a higher crystallization degree than after the first heating cycle could be measured, which could be explained by the slower and controlled cooling after the first heating.

Moreover, the DMA measurements (Table III) show that the  $T_g$ s of the PEI-, PEEK-, and PPS-based compounds were not influenced by the addition of talc. Regarding the PPS-based materials, a slight increase of  $T_g$  can be observed with the addition of talc. Moreover, no correlation between the loss factor obtained from DMA and the loss factor, obtained from dielectric measurements, could be observed. It seems that relaxation processes measured during mechanical analysis and observed at low

frequencies (1 Hz) cannot be compared to the dielectric loss at clearly higher frequencies (10 MHz–1 GHz).

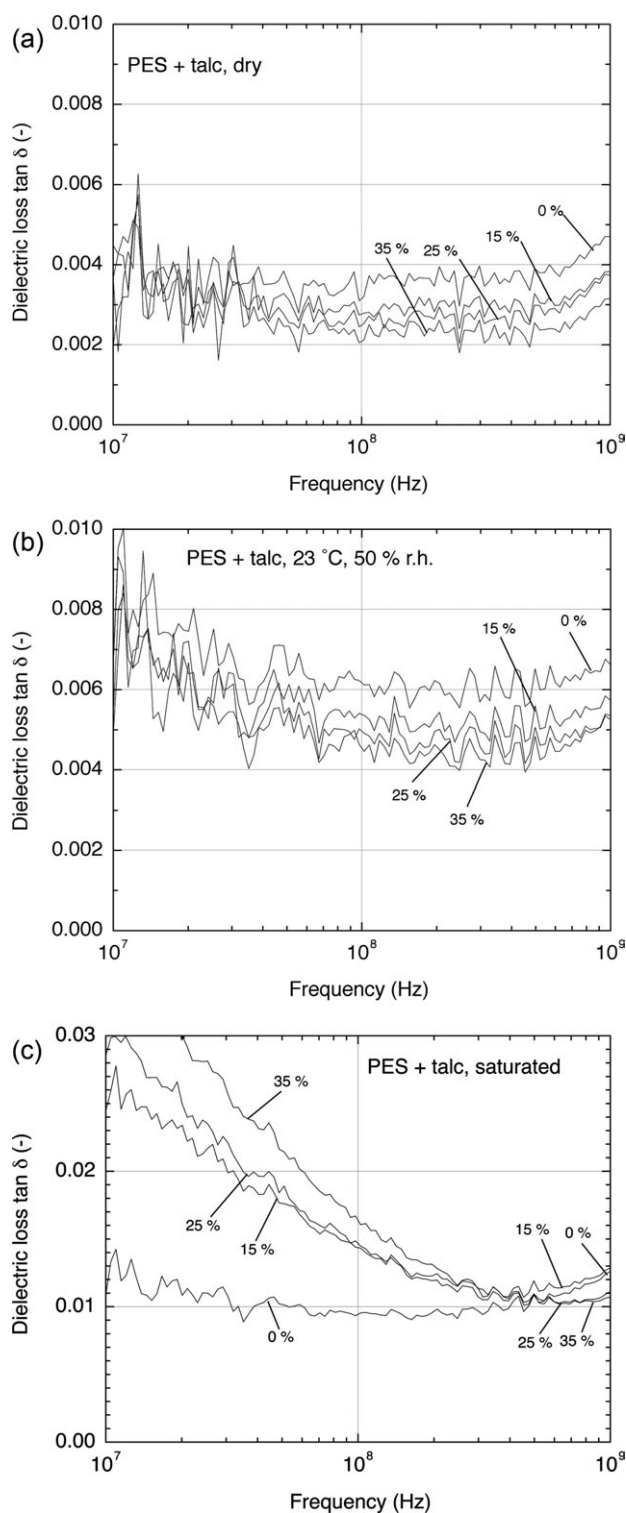
### Moisture Absorption

Absorbed water molecules can be found in the compounds in two different manners. On one hand, the water molecules are bound to the polymeric chains through intermolecular forces. On the other hand, free volume exists, in which water molecules can freely move throughout the material. Free volume stands for the space between the polymeric macromolecules and depends on the chain package density as well as on interphase regions in two-phase systems.<sup>48</sup> As shown in the literature,<sup>49</sup> a significant increase of the free volume and interphases in compounds leads to an increase of moisture uptake. Moreover, the diffusion is activated through thermal-induced vibrations of the water molecules. In this context, the diffusion coefficient describes the velocity of the moisture uptake.

The addition of talc, as summarized in Table IV, leads to a clear reduction of moisture absorption of the compounds. This is owing to the fact that talc exhibits a lower moisture uptake than the polymers investigated here. In the standard condition (23°C, 50% r.h.), neat PES has a moisture absorption of 0.94% and PEI of 0.59%. Water absorption saturation (for the samples immersed in water) was reached for PES at 2.04% and for PEI at 1.22%. With the incorporation of 35 vol % talc, the moisture uptake could be decreased in both conditions between 43 and 62%. The addition of talc to the semi-crystalline thermoplastics leads, despite the low intrinsic moisture uptake of PPS (23°C,

**Table IV.** Moisture Absorption (Standard and the Saturated Condition) and Diffusion Coefficients of PES-, PEI-, PPS-, and PEEK-Based Batches

	23°C 50% r.h. (%)	Reduction of moisture uptake (wt %)	Saturated condition (%)	Reduction of moisture uptake (%)	Diffusion coefficient (10 <sup>-6</sup> mm <sup>2</sup> /s)
PES_0	0.94 ± 0.01	-	2.04 ± 0.00	-	4.30 ± 0.21
PES_15	0.72 ± 0.00	23	1.65 ± 0.02	19	2.56 ± 0.12
PES_25	0.67 ± 0.01	29	1.23 ± 0.01	40	2.85 ± 0.37
PES_35	0.54 ± 0.01	43	0.99 ± 0.01	51	2.98 ± 0.50
PEI_0	0.59 ± 0.00	-	1.22 ± 0.02	-	1.93 ± 0.21
PEI_25	0.39 ± 0.01	34	0.63 ± 0.00	48	1.71 ± 0.09
PEI_35	0.30 ± 0.00	49	0.46 ± 0.00	62	1.65 ± 0.22
PPS_0	0.10 ± 0.02	-	0.16 ± 0.00	-	1.92 ± 0.30
PPS_25	0.05 ± 0.02	50	0.10 ± 0.01	38	2.96 ± 0.63
PPS_35	0.05 ± 0.01	50	0.09 ± 0.00	44	3.56 ± 0.96
PEEK_0	0.27 ± 0.01	-	0.42 ± 0.02	-	2.06 ± 0.14
PEEK_25	0.13 ± 0.00	52	0.24 ± 0.01	43	1.34 ± 0.13
PEEK_35	0.10 ± 0.01	63	0.17 ± 0.01	60	0.71 ± 0.18



**Figure 1.** (a) Influence of the filler fraction on the dielectric loss factor of PES in the dry condition. (b) Influence of the filler fraction on the dielectric loss factor of PES in the standard condition. (c) Influence of the filler fraction on the dielectric loss factor of PES in the saturated condition.

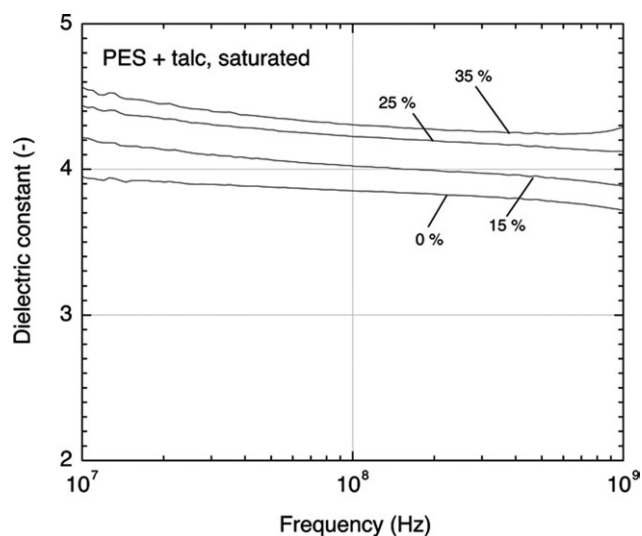
50% r.h.: 0.1%, saturated: 0.16%) and PEEK (23°C, 50% r.h.: 0.27%, saturated: 0.42%), to a further significant reduction (Table IV).

Moreover, the diffusion coefficients of water in the different materials were calculated according to eq. (2). It is known that the presence of plate-like ceramic filler decreases the diffusion coefficient by increasing the average path length required to transport the water molecules around the ceramic particles. Particularly, fillers with high aspect ratios raise the path length and lead to improved barrier properties.<sup>50,51</sup> With regard to the results summarized in Table IV, the increasing addition of talc causes the reduction of the diffusion coefficient in the case of the PEI-, PES-, and PEEK-based samples. Neat PES exhibits in comparison to the other polymers a quite high diffusion coefficient ( $4.3 \times 10^{-6} \text{ mm}^2/\text{s}$ ), which can be reduced to  $2.98 \times 10^{-6} \text{ mm}^2/\text{s}$  through the addition of 35 vol % talc. As expected, this decrease is owing to the extension of the diffusion path of the water molecules in the polymeric compounds. Similar effects could be measured for PEI- and PEEK-based samples. Regarding the diffusion coefficient of the PPS-based samples, an increase of the diffusion coefficient could be observed with an increasing filler fraction. In comparison to PEI, PES, and PEEK, the extreme hydrophobic nature of PPS causes a strong resistance to moisture absorption. The addition of talc creates interphases in which the water molecules can diffuse faster than in the bulk polymeric matrix. Water molecules are marginal bound to the nonpolar macromolecules and can freely move through the compound. Moreover, the relatively lower degrees of crystallinity observed for the materials containing talc do not lead to an increase of the moisture absorption.

Altogether, the moisture uptake is reduced owing to the reduction of the polymeric fraction and the incorporation of a hydrophobic filler. The increase of the overall interphase filler/polymer owing to a higher content of filler does not result here on an increase of water uptake.

### Dielectric Properties

The dielectric properties describe the reaction of a dielectric medium to an applied external electromagnetic field. In the further investigation, the dielectric properties are presented,



**Figure 2.** Influence of the filler fraction on the dielectric constant of PES in the saturated condition.

**Table V.** Dielectric Constant (Dry and Standard Condition) of PES-, PEI-, PPS-, and PEEK-Based Batches

Talc content (vol %)		Dielectric constant (–)							
		10 MHz–1 GHz		10 MHz		100 MHz		1 GHz	
		Dry	50% r.h.	Dry	50% r.h.	Dry	50% r.h.	Dry	50% r.h.
PES	0	3.32 ± 0.03	3.60 ± 0.04	3.35	3.66	3.32	3.60	3.30	3.54
	15	3.49 ± 0.03	3.78 ± 0.03	3.52	3.82	3.49	3.77	3.46	3.74
	25	3.57 ± 0.03	3.91 ± 0.03	3.60	3.97	3.58	3.91	3.53	3.84
	35	3.69 ± 0.02	4.12 ± 0.02	3.71	4.16	3.69	4.11	3.67	4.12
PEI	0	3.02 ± 0.01	3.16 ± 0.02	3.01	3.18	3.02	3.15	3.03	3.18
	25	3.29 ± 0.02	3.49 ± 0.02	3.30	3.50	3.29	3.48	3.32	3.49
	35	3.48 ± 0.01	3.68 ± 0.02	3.48	3.69	3.48	3.68	3.48	3.69
PPS	0	3.11 ± 0.02	3.16 ± 0.01	3.11	3.16	3.11	3.16	3.14	3.17
	25	3.59 ± 0.01	3.62 ± 0.01	3.61	3.63	3.59	3.61	3.61	3.65
	35	3.78 ± 0.02	3.78 ± 0.01	3.80	3.79	3.78	3.78	3.81	3.79
PEEK	0	3.15 ± 0.02	3.25 ± 0.02	3.15	3.26	3.15	3.25	3.11	3.27
	25	3.45 ± 0.03	3.59 ± 0.02	3.46	3.61	3.45	3.59	3.39	3.63
	35	3.66 ± 0.03	3.76 ± 0.02	3.67	3.77	3.67	3.75	3.60	3.77

depending on the frequency, the filler fraction, and the moisture uptake under three conditions: dry, standard condition (23°C, 50% r.h.), and saturated after immersion in water.

### Polyethersulfone

Figures 1(a–c) and 2 and Table V show the influence of filler fraction and moisture absorption on the dielectric properties of PES in the frequency range from 10 MHz to 1 GHz. The curves measured on samples which have been dried, stored at 23°C and 50% r.h. (standard condition) and saturated in distilled water for 4 weeks are presented.

Nearly constant values could be measured for the dielectric constant and the loss factor in the dry and the standard condition over the frequency spectrum investigated here. It is assumed that for these conditions no specific relaxation frequency of the involved dipoles in the macromolecule chains is achieved, and therefore no drastic change in the dielectric properties is observed. In the dry condition, a higher filler fraction reduces the loss factor and increases the dielectric constant owing to the higher dielectric properties of the filler in comparison to those of the polymer. In the standard condition, the influence of the absorbed water can be observed. Generally, the dielectric loss and the dielectric constant of all compounds are shifted to higher values as a result of the higher dielectric properties of the absorbed water ([Figures 1(a–c) and 2(a)] and Table V). The absolute increase of the dielectric loss factor is clearly stronger in comparison to the increase of the dielectric constant.

In the saturated condition, a maximum water uptake for the different compounds is achieved. Regarding the dielectric properties, the high moisture uptake causes a drastic increase of the loss factor and the constant. In this context, the dielectric loss factor of the neat PES is nearly constant over the investigated frequency spectrum. But, it is quite interesting to observe the effect of the addition of filler to PES in the saturated condition [Figure 1(c)]. With increasing filler fraction, the dielectric loss

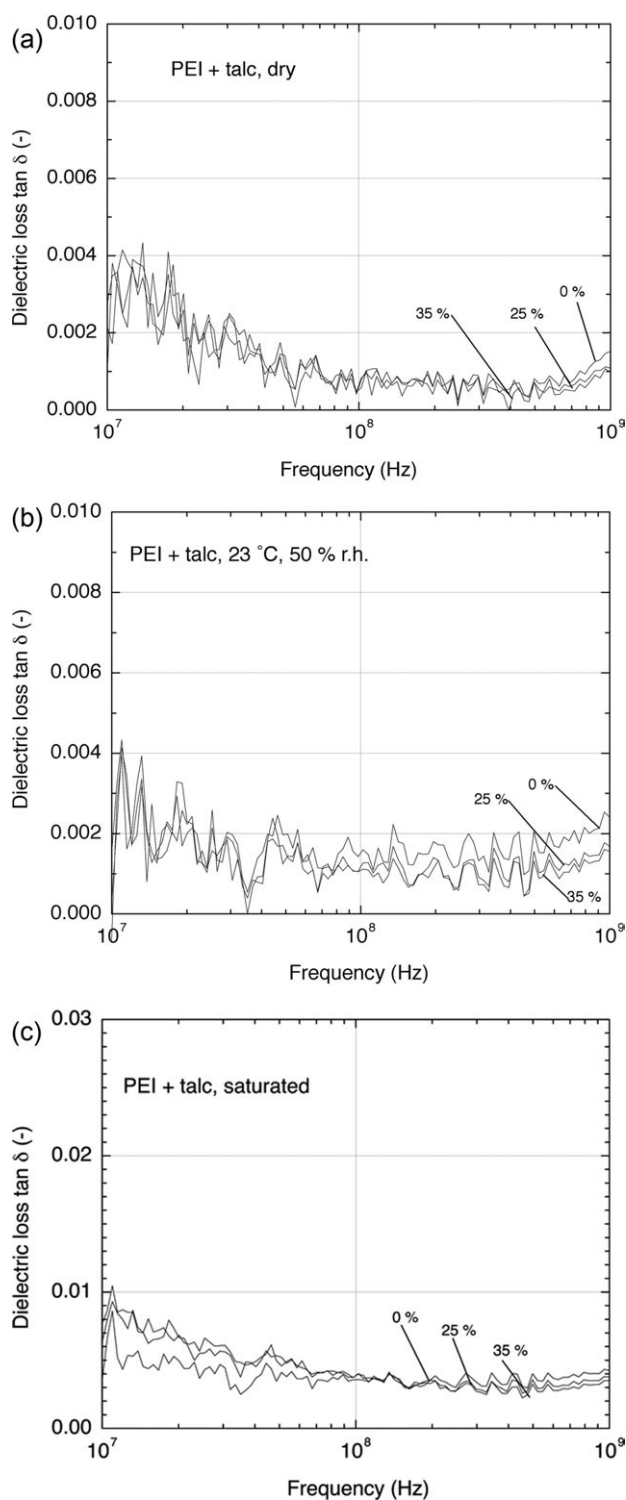
factor is rapidly increased at lower frequencies (<250 MHz). At higher frequencies, the curves of the highly filled PES compounds cross the curves of the compounds with a lower filler fraction, so that the curve with the highest filler fraction exhibits the lowest loss factor between 0.8 and 1 GHz. It is assumed that the combination of the incorporation of filler particles causes the creation of additional interphases in which a high water uptake (saturated condition) leads to an interfacial polarization effect, which is typically observed at low frequency region. This effect is described elsewhere in the literature.<sup>52,53</sup> With increasing filler content, the interphase fraction is increased and the interfacial polarization effect is amplified in combination with the absorbed water molecules though the water absorption is decreased with increased filler fraction. It is suggested that the polar water molecules cause the formation of additional charges at the boundaries to the non-polar filler particles.

Overall, the dielectric properties of the filled PES compounds are slightly above the requirements for high-frequency applications. In the standard condition, these materials have a dielectric loss between 0.005 and 0.007 and a dielectric constant between 3.85 and 4.1.

### Polyetherimide

Figures 3(a–c) and 4 and Table V describe the influence of frequency, filler fraction, and moisture uptake on the dielectric properties of PEI. Similar effects, which have been already described with the PES compounds, are also observed with the PEI-based materials.

Again, an increasing moisture uptake leads to a raise of the dielectric properties. The loss factor increases from the dry condition to the saturated with the factor 3 (from 3.3 to 3.4 for the neat PEI and from 3.5 to 3.8 for the filled polymers) the dielectric constant with a factor of approximately 1.1 (from 0.001 to 0.003 for the neat PEI, from 0.003 to 0.009 for the compounds).



**Figure 3.** (a) Influence of the filler fraction on the dielectric loss factor of PEI in the dry condition. (b) Influence of the filler fraction on the dielectric loss factor of PEI in the standard condition. (c) Influence of the filler fraction on the dielectric loss factor of PEI in the saturated condition.

The dielectric constant is not only in the dry and the standard condition stable over the frequency but also in the saturated, which can be explained in comparison to the PES compounds

with a clearly lower moisture uptake in the saturated condition (Table IV). The addition of filler increases the dielectric constant.

The dielectric loss factor exhibits a nearly constant behavior over the frequency range for the dry and the standard condition as well as for neat PEI after saturation with water. Again, in the saturated condition the addition of filler causes an increase of the loss factor at low frequencies ( $<100$  MHz), which can be explained similarly to the observed behavior of the PES compounds. The raise of the dielectric loss factor at low frequencies in the saturated condition is less marked in comparison to the highly filled PES compounds because of the lower moisture uptake. The intersection of the curves is observed between 100 and 200 MHz. Between 0.8 and 1 GHz, the PEI-based compounds with the higher filler fraction exhibit the lowest loss factor.

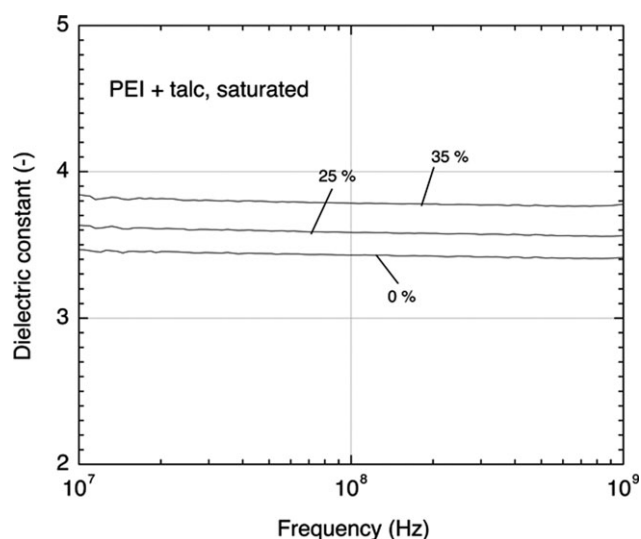
Observing the standard moisture conditions, the batches with 25–35 vol % filler exhibit values suitable for high-frequency applications. The dielectric loss is approximately between 0.001 and 0.002, whereas the dielectric constant exhibits values between 3.5 and 3.7.

#### Polyphenylsulfide

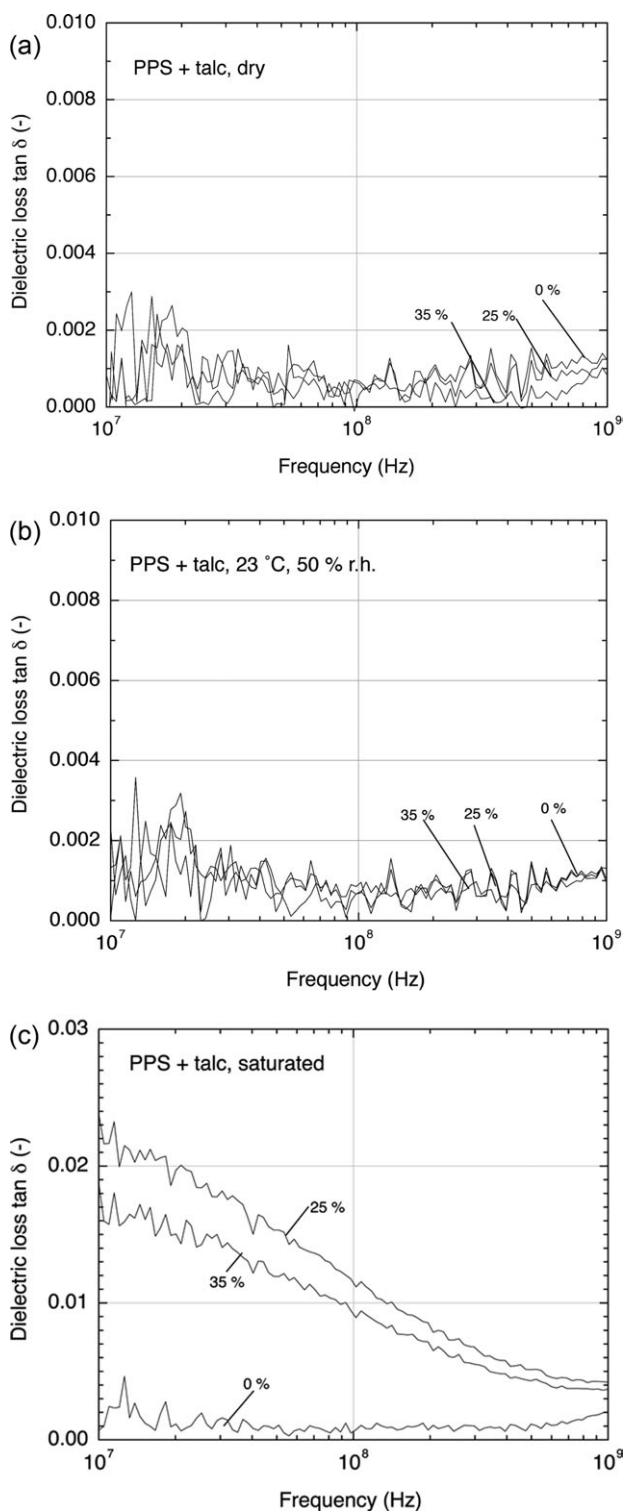
Figures 5(a–c) and 6 and Table V show the influence of filler fraction, frequency, and moisture uptake on the dielectric behavior of PPS.

Owing to the very low moisture uptake, the dielectric constant and the dielectric loss factor are very similar in the dry and the standard stored condition. No shifting of the curves can be observed between these both conditions. With increasing filler fraction, the dielectric constant is raised.

The results observed for this filled polymer in the saturated condition also indicate a particular behavior. Similarly to the amorphous thermoplastics, PEI and PES, a clear increase of the dielectric loss factor at low frequencies is observed, as well as an



**Figure 4.** Influence of the filler fraction on the dielectric constant of PEI in the saturated condition.



**Figure 5.** (a) Influence of the filler fraction on the dielectric loss factor of PPS in the dry condition. (b) Influence of the filler fraction on the dielectric loss factor of PPS in the standard condition. (c) Influence of the filler fraction on the dielectric loss factor of PPS in the saturated condition.

increase of the dielectric constant, although PPS has an extremely low moisture uptake. It seems that not only the amount of the water uptake has an effect on the intensity of the

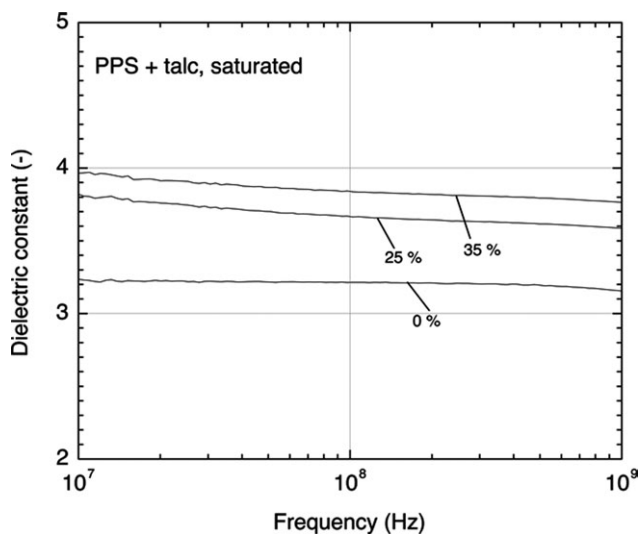
observed interfacial polarization at low frequencies. It is assumed that additional factors as the bonding between the absorbed water molecules and the polymeric chains in interphases must also have an effect on the intensity. One possible explanation is that the nonpolar PPS exhibits a lower bonding force to the water molecules in the interphases. The absorbed water molecules can interact more intensively with the filler particles owing to a lower energy barrier. Again, as already described, the effect of the water molecules is reduced at higher frequencies. The observed effect should not be considered as an ageing effect. The investigated samples have been dried and the same loss factors and dielectric constants as in the dry conditions, described in this article, could again be achieved, showing the reversibility of the process. Moreover, PPS containing 35 vol % exhibits at low frequencies in the saturated condition a lower loss factor in comparison to PPS containing 25 vol %. An explanation is that in the case of PPS the effect of the lower loss factor of the filler also dominates at lower frequencies in the saturated condition. Furthermore, an increase in filler fraction causes a clear increase in the dielectric constant.

In the standard condition, the PPS batches with a necessary filler fraction between 25 and 35 vol % exhibit a dielectric constant between 3.4 and 3.6 and a dielectric loss angle between 0.001 and 0.002.

#### Polyetheretherketone

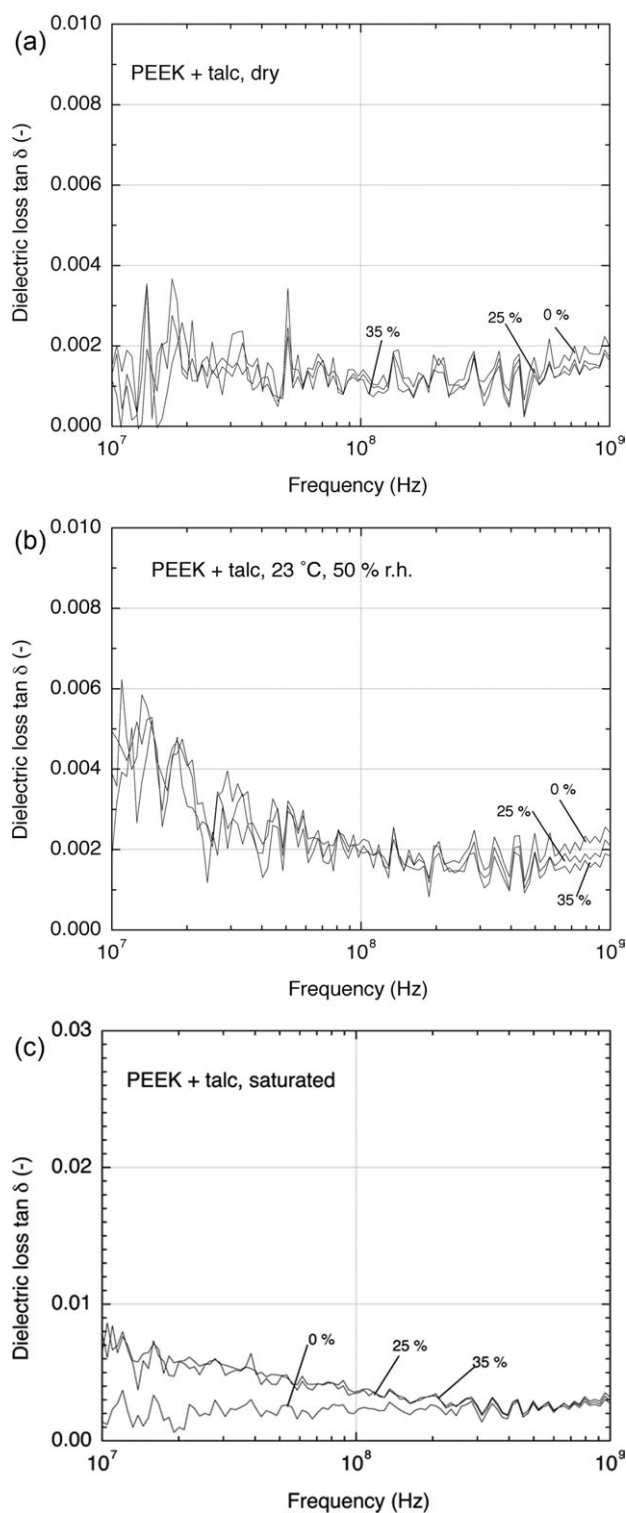
Figures 7(a–c) and 8 and Table V show the influence of filler fraction, moisture uptake, and frequency on the dielectric properties of PEEK.

The moisture uptake has nearly no effect, similarly to PPS, on the dielectric properties of PEEK in the dry and the standard condition, as well as on neat PEEK in the saturated condition. Only the filled fractions in the saturated condition exhibit, similarly to PEI, a slight increase of the dielectric loss factor to low frequencies which can be explained with the same effect as for PEI, PES, or PPS.



**Figure 6.** Influence of the filler fraction on the dielectric constant of PPS in the saturated condition.





**Figure 7.** (a) Influence of the filler fraction on the dielectric loss factor of PEEK in the dry condition. (b) Influence of the filler fraction on the dielectric loss factor of PEEK in the standard condition. (c) Influence of the filler fraction on the dielectric loss factor of PEEK in the saturated condition.

In the standard condition, with the highly filled batches a dielectric constant between 3.5 and 3.7 as well as a dielectric loss factor between 0.002 and 0.003 could be achieved, so

that these materials are also suitable for high-frequency applications.

#### Theoretical Consideration of the Dielectric Properties

A precise prediction of the dielectric properties of the talc-filled polymers is very important for a number of engineering applications where new alternative materials should be used to design electronic parts. It would be a great effort to obtain a first experimental estimation of the dielectric values.

In this study, the following four equations, which have been frequently mentioned in the literature, are discussed, employed, and evaluated for the measured dielectric constants.

In the simplest case, the dielectric constant of the material can be described as a capacitor whose dielectric system consists of two different homogeneous dielectrics connected in parallel or in series. In this case,  $\epsilon_C$  of the composite, consisting of two phases with  $\epsilon_1$  and  $\epsilon_2$  dielectric constants, is expressed by eq. (4)<sup>41</sup>: where  $v_1$  and  $v_2$  are the volume fractions of phases 1 and 2 (mixing rule):

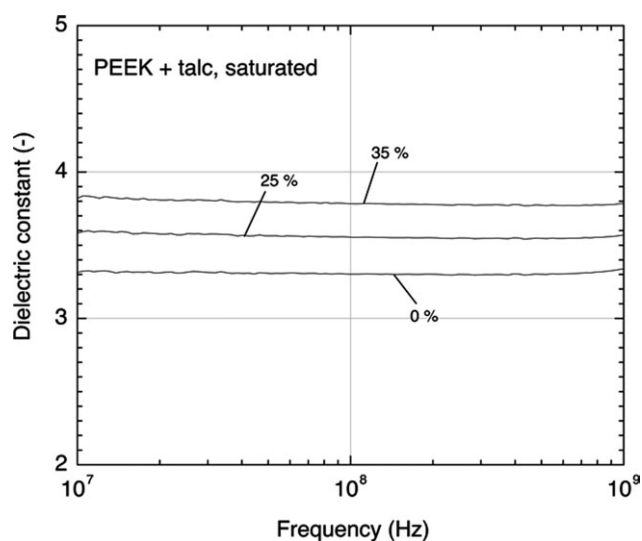
$$\epsilon_C = v_1 \epsilon_1 + v_2 \epsilon_2 \quad (4)$$

Furthermore, the Lichtenecker logarithmic law of mixing has been widely recognized for a composite of two components. However, the equation can be applied in the case where  $\epsilon_1$  differs only slightly from  $\epsilon_2$ .<sup>39,42</sup>

$$\log \epsilon_C = v_1 \log \epsilon_1 + v_2 \log \epsilon_2 \quad (5)$$

The Lichtenecker logarithmic rule considers the composites as a random mixture of spherical inclusions, valid for low filler contents, and deviations from predictions increase with raising filler fractions. This is mainly owing to the imperfect dispersion of filler particles at higher fractions and also owing to porosity or air enclosed in the composite.

Moreover, eqs. (4) and (5) do not consider the matrix–filler interphase interactions. The modified Lichtenecker equation



**Figure 8.** Influence of the filler fraction on the dielectric constant of PEEK in the saturated condition.

includes a fitting factor  $n$ , which represents the interaction between the filler and the matrix.<sup>25</sup>

$$\log \varepsilon_C = \log \varepsilon_1 + v_2 (1 - n) \log \left( \frac{\varepsilon_2}{\varepsilon_1} \right) \quad (6)$$

The relative permittivity of composites also depends on the distribution of the filler, shape, size and, as already mentioned, the interface with the polymers. Rao et al.<sup>43</sup> proposed a model (Effective Medium Theory, EMT) to predict the relative permittivity of the composites. The EMT model is a self-consistent model that assumes a random unit cell consisting of filler surrounded by a concentric matrix layer. The model includes a morphology factor, “ $n$ ,” which is determined empirically. This correction factor compensates derivations caused by the interphase between the polymer and the filler. A small value of  $n$  indicates a near-spherical shape for the filler, whereas a high value of  $n$  shows a largely nonspherical shaped particle.

$$\varepsilon_C = \varepsilon_1 \left( 1 + \frac{v_2 (\varepsilon_2 - \varepsilon_1)}{\varepsilon_1 + n (1 - v_2)(\varepsilon_2 - \varepsilon_1)} \right) \quad (7)$$

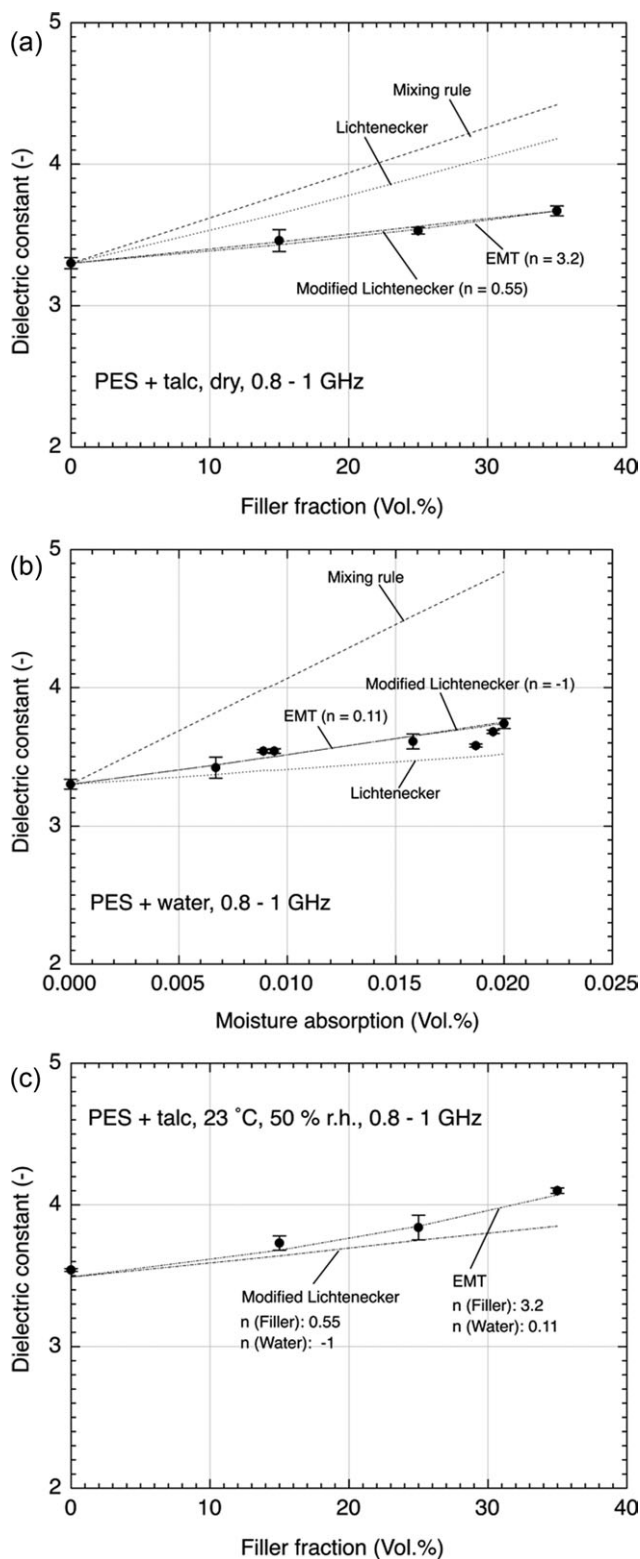
The theoretical models do not completely agree with the experimental observations though. One of the reasons for a possible poor fitting is the difficulty to obtain the correct dielectric constant of the used materials.<sup>25</sup>

To calculate the dielectric properties, the constant and the loss angle of water and talc have been obtained from the literature as mentioned already. As basic value, the dielectric constant and the dielectric loss of the neat polymers in the dry state have been used.

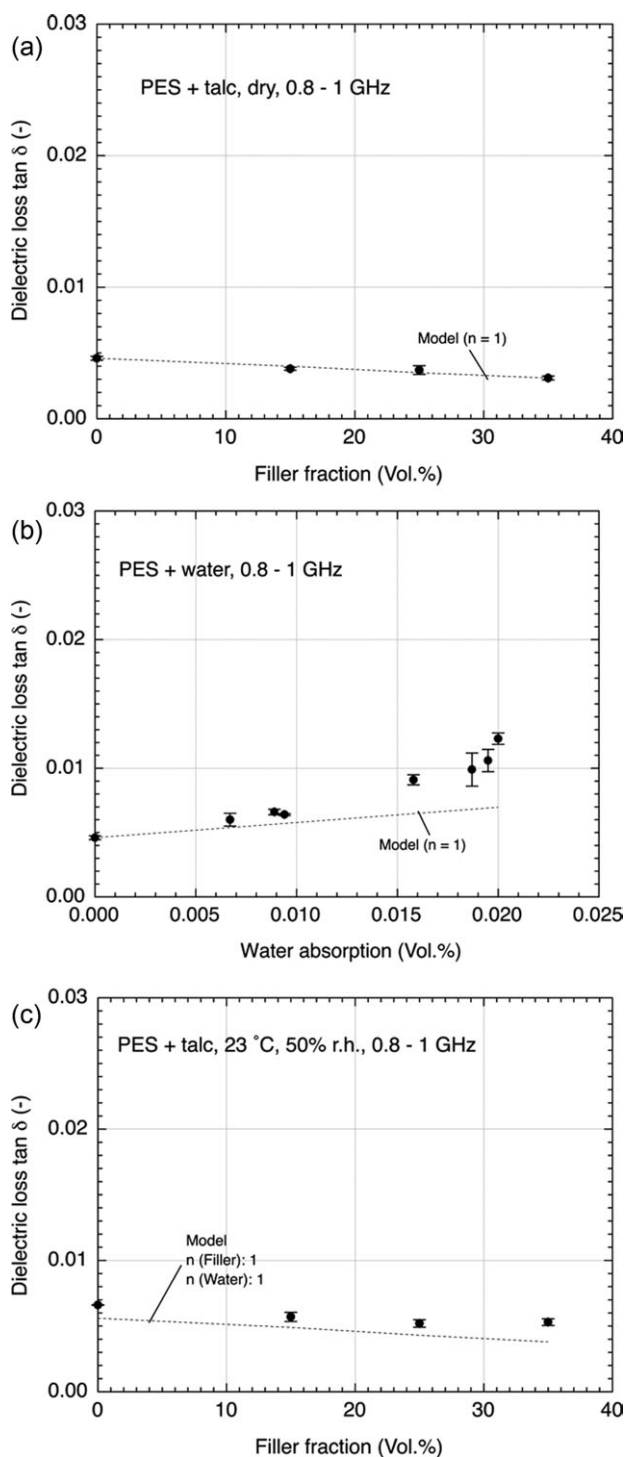
It has to be mentioned that some of the effects observed in this study (such as frequency dependence, strong interactions between filler fraction, moisture uptake, and polymer aging) cannot be precisely described by the models. Therefore, a comparison is taken for the theoretical consideration in the higher frequency range between 800 MHz and 1 GHz where such interactions could not be observed and where the dielectric properties are relatively constant over the frequency range.

To evaluate the possibility to calculate the dielectric constant, as previously described, the four different equations have been employed: the mixing rule, the Lichtenecker equation, the modified Lichtenecker equation, and the EMT model. To calculate the constant via mixing rule or Lichtenecker, the measured and known values have been directly inserted into the equations. In the case of the modified Lichtenecker and the EMT model, a fitting parameter was considered and was iteratively optimized until the calculated values fitted to the measured values.

Figure 9(a,b) compares the calculated and measured values of the dielectric constant for PES, depending on the filler fraction in the case of dried samples and the influence of water on neat PES. In both cases, it can be observed that the mixing rule shows the poorest results in comparison to the measured values, followed from the Lichtenecker equation. The quite large



**Figure 9.** (a) Comparison of measured and calculated dielectric constants depending on the filler fraction in the case of the PES compounds. (b) Comparison of measured and calculated dielectric constants depending on the moisture uptake in the case of the PES compounds. (c) Comparison of measured and calculated dielectric constants depending on the superposed effects of filler fraction and moisture uptake in the case of the PES compounds.



**Figure 10.** (a) Comparison of measured and calculated dielectric loss factors depending on the filler fraction in the case of the PES compounds. (b) Comparison of measured and calculated dielectric loss factors depending on the moisture uptake in the case of the PES compounds. (c) Comparison of measured and calculated dielectric loss factor depending on the superposed effects of filler fraction and moisture uptake in the case of the PES compounds.

differences can be explained as factors such as interphases, size of the filler, and geometry of the filler are not considered in the equations. A quite accurate consistency could be achieved if a

fitting factor was used as for the modified Lichtenecker equation and the EMT model.

Considering the influence of the filler fraction, the fitting factor of the modified Lichtenecker is 0.55 and of the EMT model 3.2 [Figure 9(a)], whereas  $-1$  and  $0.11$  [Figure 9(b)] when the influence of water is correlated. The different values can be explained with the geometry and the alignment of the filler as well as the presence of water molecules in the polymer. In the case of the EMT model, spherical inclusions lead typically to low EMT fitting values, whereas platelet filler to high values, which can be confirmed in this investigation. The same effect is also shown with the modified Lichtenecker equation, as platelet fillers lead to a higher fitting factor in comparison to the spherical inclusions. Figure 9(c) shows that two influence factors can also be described simultaneously with the EMT and the modified Lichtenecker equation. Therefore, the achieved fitting factors from Figure 9(a,b) have been applied on the dielectric constant of the PES compounds in the standard condition. The EMT equation describes the measured values precisely, whereby the calculated values via the modified Lichtenecker equation exhibit a higher deviation [Figure 9(c)].

The number of theoretical models available for predicting the loss angle is relatively low, owing to the difficulties involved in this prediction.<sup>54</sup> The following relation is used in this article to model the measured dielectric loss angle of the composites.<sup>55,56</sup>

$$(\tan \delta_C)^\alpha = \sum v_i (\tan \delta_i)^\alpha \quad (8)$$

The value of the constant  $\alpha$  determines the mixing rule where  $\alpha = -1$  means serial mixing,  $\alpha = 1$  parallel mixing, and  $\alpha = 0$  gives the logarithmic mixing rule.

In Figure 10(a–c), the results from the calculation and the actual measurements of the dielectric loss are compared. The influence of the filler fraction could be described very well with a fitting factor of 1. Regarding the moisture uptake, the theoretical equation has a good consistency with the measured results at low values also with a fitting factor of 1. With increasing moisture uptake, the values increase exponentially, whereby the model describes the increase linearly. In combination of both effects, a slightly shift to lower values could be observed.

In summary, it can be observed that the EMT model and the equation for the description of the loss factor closely described the influence of the filler fraction and the moisture uptake as long as the right fitting factors are chosen and the frequency dependence on the dielectric properties is not considered.

## CONCLUSIONS

This study closely looked at the dielectric properties of highly filled thermoplastics (PES, PPS, PEI, and PEEK) suitable for PCB substrates in high-frequency applications. The dielectric properties are clearly influenced by filler fraction as well as water content. The dielectric constant increased with increasing filler fraction and moisture uptake, whereby the dielectric loss raised with additional moisture absorption. At low frequencies (range, 10 MHz), a clear increase of the dielectric loss is observed for the filled compounds caused by interface

polarization. Neat polymers exhibit a constant loss angle over the investigated frequency range. In the case of a relatively high-moisture uptake, highly filled compounds based on PES exhibited loss angles above the requirements for high-frequency applications. On the other hand, the dielectric properties of highly filled PEI, PPS, and PEEK compounds are suitable for such applications. Regarding the semi-crystalline polymers, the crystallinity was slightly decreased with the addition of talc. This change of the crystallinity seems to have no major effect on the dielectric properties.

For a theoretical consideration, the EMT model and the modified Lichtenecker equation, for the dielectric constant, and the theoretical equation introduced in this study for the calculation of the dielectric loss are appropriate for a prediction of the dielectric properties, as long as the frequency dependency is not considered.

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