



Interfacial effects on the dielectric properties of elastomer/carbon-black/ceramic composites

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Abstract

A systematic series of ethylene-propylene-diene (EPDM) elastomer/carbon-black composites were studied to quantify the effect of additional ceramic fillers, especially of the interfacial contributions, on the dielectric properties of the composites. Substantial interfacial contributions to the composites' dielectric properties were present in all systems. For all composites studied—using ceramic fillers with varied dielectric nature and spanning orders of magnitude in dielectric constants—the interfacial contributions overwhelmed the ceramic filler k -values and dominated the dielectric performance of the composites. Non-trivial interplays between the carbon black and the ceramic fillers were also manifested, casting doubts on the validity of standard models used for the prediction of dielectric permittivities of such composites.

Introduction

Polymeric materials with a high dielectric constant are constantly pursued, necessitated by ever increasing materials demands in electrical and electronic applications, power systems, and energy storage devices [1–3]. Addition of high-permittivity inorganic fillers into polymers is the predominant approach to obtain composites with a large dielectric constant, enabled by the plurality of inorganic (typically ceramic) fillers and the retention of a polymer-like character in the processing/manufacturing and mechanical performance of the composites [4]. Established models that predict composite permittivity values based on the permittivities of the polymer matrix and filler (e.g. Lichtenecker's mixing rule, Maxwell–Wagner equation, Bruggeman model, etc. [5]), are typically applied as design principles for selecting the type and concentration of dielectric fillers in composites with desired properties [5, 6]. However, such

theories/models often result in inaccurate estimations for the composites dielectric properties as interfacial effects begin to dominate (e.g. for multi-filler composites, or for sub-micron sized fillers, or whenever extensive polymer/filler interphases exist, with complex nature and a priori unknown dielectric behavior) [7–9].

In this paper, we present an investigation of elastomer/carbon-black/ceramic composites; we employed a series of ceramic fillers that span orders of magnitude in permittivity values, in order to identify and highlight the interfacial contributions to the composites' dielectric properties.

Experimental

The elastomer matrix comprises ethylene-propylene-diene (EPDM, Vistalon 5420) monomer, paraffin oil (S894, J.T. Baker) plasticizer, and dicumyl peroxide (DCP, 329,541, Sigma-Aldrich) curing agent, measured to have $\epsilon'(20\text{ Hz}–10\text{ kHz}) \cong 2.73$ and $\tan\delta(20\text{ Hz}–10\text{ kHz}) \cong 0.001–0.06$ after curing; addition of 15 wt% carbon black (Spheron 6000, Cabot) for thermomechanical properties reinforcement, change the matrix dielectric properties to $\epsilon' \cong 4.52–4.45$ and $\tan\delta \cong 0.004–0.012$ over the same frequency range.

A series of ceramic fillers—varying in dielectric nature, and permittivity—were used: (a) As-received particulates: SiO_2 (S5631, Sigma-Aldrich); Sakai- BaTiO_3 (BT-04, Sakai Chemical Industries); Ferro- BaTiO_3

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(ZL9000, Ferro Electronic Materials, sieved to separate coarse and fine particulates/agglomerates), and TiO_2 (Rutile 43,047, Alfa Aesar). Additionally, (b) we prepared ionized- BaTiO_3 fillers (by washing the Sakai- BaTiO_3 with distilled water, stirring overnight, and drying at 80 °C, increasing the mobile ions concentration at the BaTiO_3 external surface), and we synthesized a colossal dielectric permittivity (Nb + In) co-doped TiO_2 as per previous work [10] (termed as (Nb,In) TiO_2 , measured to have $\epsilon'(100 \text{ Hz}) \cong 60,000$ after sintering).

Composites were prepared following standard industrial practices for rubber elastomers: by low shear rate folding of all ingredients, in a Haake twin-head kneader, at 80 °C and 50 rpm; all materials were dried under vacuum at 80 °C overnight prior to compounding; composites were cured at 170 °C for 10 min, followed by 24 h at 18 °C. The ceramic filler concentration was varied, under constant monomer:plasticizer and monomer:curing agent ratios (30 phr and 5 phr, respectively), so as to ensure the same polymer matrix composition across all composites.

For the dielectric characterization, rectangular specimens (4 × 1 cm wide, by 3 mm thickness) were coated by colloidal silver electrodes, and the complex permittivity was measured from 20 Hz to 10 kHz frequency, at 1 V, by a charge–voltage converter (GADD, integrated with a Stanford Research SR830 lock-in amplifier [11]).

Results

The dielectric properties of EPDM elastomer composites were studied to distinguish the relative contributions of the fillers and of the filler interfaces to the macroscopic composite permittivity. A series of low-loss ceramic fillers were used, with 0.4 to 2 microns in size, differing in nature (i.e., dielectric/paraelectric SiO_2 and TiO_2 vs. ferroelectric BaTiO_3), and spanning a wide range of dielectric constants (particulate or bulk k ranging from 4 to 60,000). For each filler, a series of EPDM composites was prepared, varying the filler loading from 5 wt% to 25 wt%, while keeping the organic/elastomer matrix the same. The dielectric properties of the composites were measured as a function of frequency, quantified through a “dielectric constant” (denoted also as composite k and measured as the real part of permittivity, $\epsilon'(\omega)$, Fig. 1a) and “dielectric loss” (dissipation factor, $\tan\delta(\omega)$, Fig. 1b).

To a first approach, the composite dielectric constant, k , can be quantified by Lichtenecker’s logarithmic mixing rule applied to the permittivity of the “matrix” and the ceramic fillers:

$$\log k = v_f \log \epsilon_r + (1 - v_f) \log \epsilon_m,$$

with ϵ_r and ϵ_m being the permittivities of the filler and the matrix, respectively, and v_f the filler volume fraction (Fig. 2a). Note the filler concentrations in Figs. 1 and 2 are

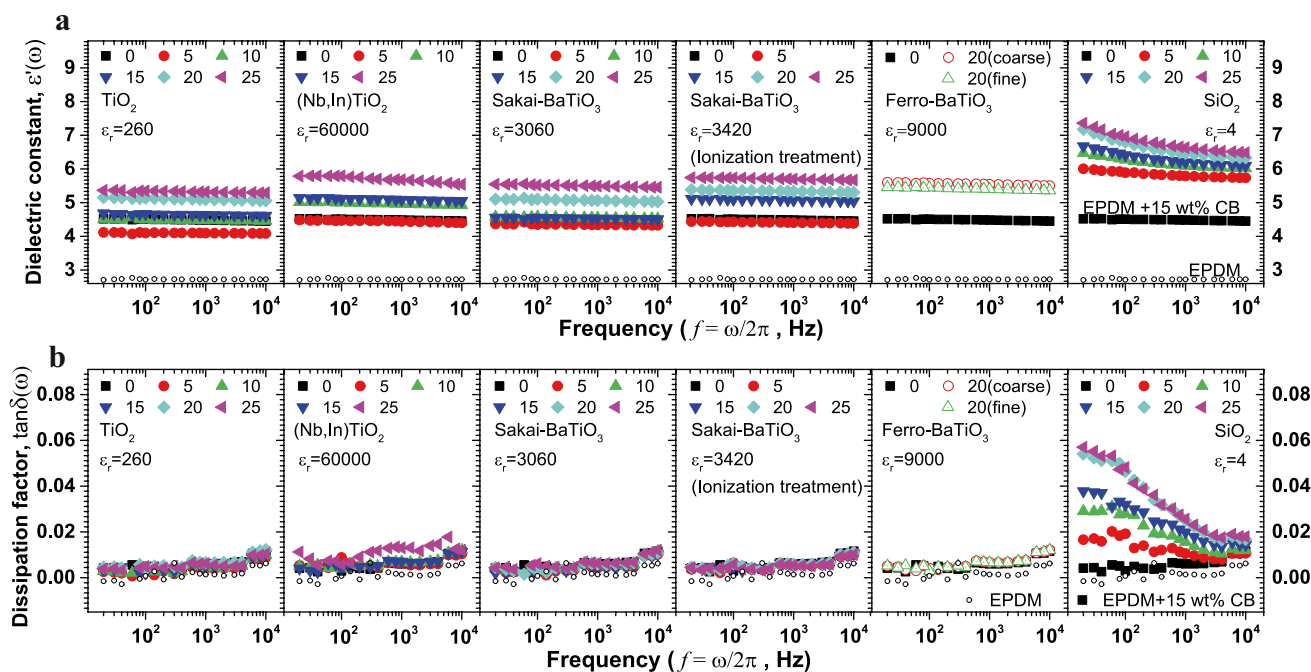


Fig. 1 (a) Dielectric constant (real part of permittivity) and (b) dielectric loss ($\tan\delta$ dissipation factor) as a function frequency for EPDM composites (with 0 to 25 wt% ceramic fillers) at room temperature

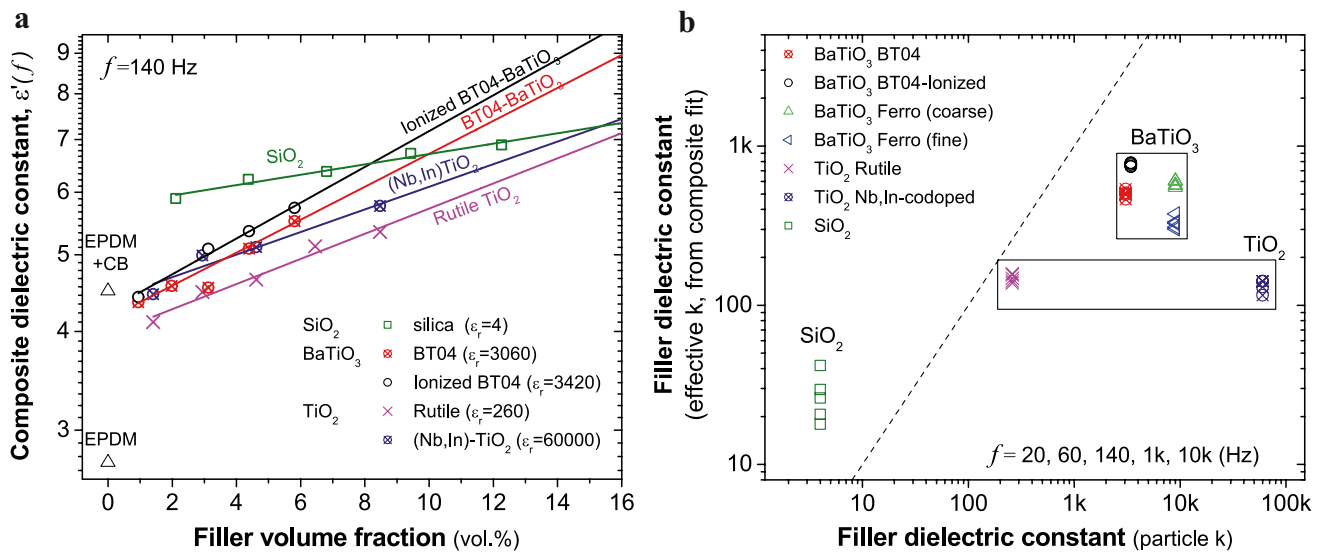


Fig. 2 (a) Measured composite dielectric constants (permittivity at 140 Hz) and fittings of the permittivities vs. filler loading by Lichtenecker's logarithmic mixing rule. (b) The effective filler dielectric constant in the composites including interfacial contributions (as determined by the mixing rule fitting), is compared against the filler

particle dielectric constant (measured or known filler particle permittivity). Measurements at five frequencies, f , provide five values for each filler's effective k (values provided in Table 1). The dashed-line corresponds to an 1:1 relation, i.e., no interfacial contribution

measured by weight fraction and volume fraction, respectively. Keeping the carbon black (CB) content constant at 15wt.% across all systems, allows for simplifying all considerations by treating the combination of all organics (EPDM, plasticizer, and crosslinker) plus the carbon black as the matrix [5].

Subsequent measurement of the macroscopic composite permittivity (k) as a function of ceramic filler loading (v_f), can thus yield an “effective dielectric constant” for each ceramic filler in the composite; i.e., a permittivity value that quantifies the combined *ceramic filler particle plus their interfacial contributions* to the measured composite- k (Table 1, Fig. 2b).

Discussion

The values of $\epsilon_r^{\text{effective}}$ provide a measure of each filler's realistic contribution to the measured composite permittivity, and are found to be markedly different from the values typically expected (e.g. markedly different from the usual filler dielectric constants ϵ_r used in design considerations or for the mixing rule above: either bulk- k values, or typical particle- k values, or measured particle- ϵ' values). This is a clear indication that the interfacial dielectric contributions dominate the overall composite permittivity, rather than the ceramic fillers' ϵ_r .

At the outset, it is immediately obvious that the addition of ceramic fillers increases the permittivity in the composites, compared to the unfilled EPDM elastomer (Fig. 1a);

Table 1 Filler Properties: Particle size; Filler permittivity ϵ_r (particle or bulk, the expected dielectric k value of the fillers in the composites); and measured effective filler permittivity $\epsilon_r^{\text{effective}}$ in composites (filler ϵ_r as quantified from the EPDM composite- k value; combines filler- k plus interfacial contributions)

Filler	Filler particle size (μm)	Filler ϵ_r	Filler $\epsilon_r^{\text{effective}}$ from the composite k				
			20 Hz	60 Hz	140 Hz	1 kHz	10 kHz
SiO_2	1–2	4	42	30	26	21	18
TiO_2	1–2	260	158	138	155	148	142
Sakai- BaTiO_3	0.4	&1 3060	537	506	507	495	462
Ionized- BaTiO_3	0.4	&1 3420	765	780	787	747	740
Ferro- BaTiO_3	(fine) 0.6–0.9	9000	328	375	333	310	302
Ferro- BaTiO_3	(coarse) 0.9–1.7	9000	601	605	570	565	550
$(\text{Nb,In})\text{TiO}_2$	1–2	&2 60000	141	142	142	130	116

&1 measured in suspension

&2 measured after sintering, at 100 Hz

however, this increase is qualitatively and quantitatively different from what is expected from the ceramic particle ϵ_r values.

Typical design models (e.g. mixing rules) predict a larger dielectric constant composite, when fillers with higher-than-matrix ϵ_r are incorporated [5], which however is not the case in this study. As shown in Fig. 2a, the silica composites exhibit the greatest dielectric constant among all the composites, despite SiO₂ being the lowest ϵ_r filler used. Moreover, the composites with the Sakai-BaTiO₃ ($\epsilon_r=3060$) fillers show higher permittivity values than the composites with Nb + In co-doped-TiO₂ ($\epsilon_r=60,000$) fillers. The marked deviation of the measured composite permittivities from the natural expectation that “higher- k fillers should yield higher permittivity composites” [5], strongly suggests that the composite permittivities are dominated by other properties, namely interfacial contributions, which are not considered by most mixing rules [1, 5, 12].

The case of silica is, maybe, the most straight-forward interfacial behavior to explain: A low frequency relaxation process can be clearly identified in the EPDM/CB/SiO₂ composites, manifested both as a step in the permittivity and an associated peak in the loss (Fig. 1). This is a typical behavior of space charges polarization, *i.e.*, Maxwell–Wagner–Sillars (MWS) polarization, arising from the low frequency sub-diffusive transport of the charge carriers (e.g., ions, surfactants, impurities) trapped in filler–polymer interphases or other domain boundaries within the composites, and providing an additional increase in permittivity [13, 14].

For the other fillers, interfacial effects also exist but, rather than a MWS polarization, they seem to influence the composite dielectric performance in a qualitatively different manner: As seen in Fig. 1, there exist no pronounced peaks in $\tan\delta$ as would be expected from a high-strength MWS mechanism; instead the composite permittivity is almost frequency-independent and, in contrast to any common expectation, for multiple low- v_f (ceramic filler loading) composites it lies below the permittivity function of the matrix. This is more clearly seen in Fig. 2a, where at low ceramic filler content (1–2 vol.%) the composite permittivity drops to a value lower than the “matrix” (EPDM + CB) permittivity; this drop in composite dielectric constant cannot be explained by any weighted mixing of matrix and filler permittivities (as it would necessitate a negative filler ϵ_r for the ceramics); and it reflects interfacial contributions antagonistic to the EPDM/CB dielectric response (e.g. local field effects, restricted mobility for filler-sorbed polymer chains, etc., yielding a reduced permittivity for the interphases compared to the matrix [1]). All these interfacial contributions evidently overwhelm the filler k value in determining the composite dielectric properties. One way to quantify these interfacial effects, is to use the Lichtenecker’s approximation of the “effective

permittivity” for each filler (Fig. 2a), which now combines both filler and interfacial contributions (Table 1). In Fig. 2b, when these effective permittivities of the fillers in the composites are compared against the expected values for the filler dielectric constants, an interesting trend is observed: Fillers are clustered in groups of same filler type (enclosed in boxes in Fig. 2b), where the fillers’ dielectric contribution to the composites’ k is measured to relate more to the filler type (e.g. same filler chemistry and, consequently, similar interphase characteristics). This is completely different to the expected behavior, where the fillers’ dielectric contribution to the composites’ k is expected to relate directly to the permittivities (dielectric constant values) of the filler particles. For instance, the effective dielectric constant of the rutile TiO₂ is nearly identical to that of the Nb,In doped TiO₂, even though the two fillers differ in permittivity by two orders of magnitude ($230\times$ difference); also, all four different BaTiO₃ fillers show similar contributions (similar values of effective permittivity) in the composites, despite large variations in the filler/particle dielectric constants (Table 1).

The above comparisons clearly demonstrate that the fillers’ effective permittivity and, therefore, the extent each filler contributes to the macroscopically observed composite dielectric constant, are dominated by the filler interfaces, *i.e.*, the nature of the filler (e.g. chemistry, surface nature and modification, etc.), and less by the filler permittivity. This conclusion can be further quantified by

- the measurable differences recorded in the fillers’ $\epsilon_r^{\text{effective}}$ when considering fillers that only differ in size (e.g., for the Ferro BaTiO₃ fillers, the coarse particles have a higher $\epsilon_r^{\text{effective}}$ than the fine identical-type particles, due to lower volume-fractions of the unfavorable interfaces). Another manifestation supporting this conclusion, albeit in a more qualitative way, can be seen
- when comparing fillers that vary only in surface treatment (e.g., the ionized BaTiO₃ demonstrates the highest effective permittivity among all other BaTiO₃ fillers, because of the extra mobile ions introduced on the filler surfaces, which provide higher space-charge polarization within the interface); but this point’s discussion goes beyond the scope of this paper. Finally, the most counter-intuitive interphasial response is exhibited when considering that.
- the ceramic permittivity contributions are clearly antagonistic to the EPDM/carbon-black dielectric response, as evidenced by the measured reduction in permittivity upon addition of small amounts of ceramics (Fig. 2a); this behavior can be understood in terms of the ceramic particles limiting the carbon black cluster polarization, by interrupting the connectivity (electron tunneling) between CB particles when these ceramic particles are

located between adjacent carbon black particles (Supporting Information) [15].

Conclusions

A systematic series of EPDM composites with low-to-moderate loadings of various ceramic dielectric fillers were prepared and investigated. In correlating the composites' dielectric properties to that of the fillers, a clear manifestation of important interfacial contributions is observed. Namely, the composite permittivity was surprisingly insensitive to the filler permittivities, whereas it was overwhelmed and determined by more obscure interfacial contributions. Namely, high- k fillers, typically considered for high performance dielectric composites, showed substantially lower overall composite dielectric constants than commodity lower- k fillers (due to dielectrically unfavorable interfaces, as in TiO_2 and BaTiO_3 ; or due to extensive MWS space-charge interphasial polarization, as in SiO_2).

This study raises serious repudiations on commonplace conventional composite design practices, in which more importance is placed on selecting or preparing higher- k inorganic filler particles, rather than on controlling the nature of the filler/matrix interphases.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1557/s43580-021-00041-0>.

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Data availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

1. T.B. Jones, *Electromechanics of Particles* (Cambridge University Press, Cambridge, 1995).
2. T. Tanaka, IEEE Trans. Dielectr. Electr. Insul. **12**, 914–928 (2005)
3. M.S. Whittingham, MRS Bull. **33**, 411–419 (2008)
4. Z.M. Dang, J.K. Yuan, J.W. Zha, T. Zhou, S.T. Li, G.H. Hu, Prog. Mater. Sci. **57**, 660–723 (2012)
5. A.H. Sihvola, *Electromagnetic Mixing Formulas and Applications* (IET Books, London UK, 1999).
6. P. Barber, S. Balasubramanian, Y. Anguchamy, S. Gong, A. Wibowo, H. Gao, H.J. Ploehn, H.C. Zur Loye, Materials, **2**, 1697–1733 (2009).
7. R.C. Smith, C. Liang, M. Landry, J.K. Nelson, L.S. Schadler, IEEE Trans. Dielectr. Electr. Insul. **15**, 187–196 (2008)
8. T.J. Lewis, J. Phys. D Appl. Phys. **38**, 202–212 (2005)
9. T. Tanaka, M. Kozako, N. Fuse, Y. Ohki, IEEE Trans. Dielectr. Electr. Insul. **12**, 669–681 (2005)
10. W. Hu, Y. Liu, R.L. Withers, T.J. Frankcombe, L. Norén, A. Snashall, M. Kitchin, P. Smith, B. Gong, H. Chen, J. Schiemer, F. Brink, J. Wong-Leung, Nat. Mater. **12**, 821–826 (2013)
11. T. Okamoto, J. Long, R. Wilkie, J. Stitt, R. Maier, C.A. Randall, Jpn. J. Appl. Phys. **55**, 026601 (2016)
12. M.G. Todd, F.G. Shi, IEEE Trans. Dielectr. Electr. Insul. **12**, 601–611 (2005)
13. G. Polizos, V. Tomer, E. Manias, C.A. Randall, J. Appl. Phys. **108**, 074117 (2010)
14. V. Tomer, G. Polizos, E. Manias, C.A. Randall, J. Appl. Phys. **108**, 074116 (2010)
15. B. Li, E. Manias, *Design of Interphases for High Dielectric Performance in Polymer-Matrix Nanocomposites*, MRS S.CT04.08.03 presentation, 2020 MRS Meeting; publication in preparation.