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Povilas Bertasius, Sebastien Schaefer, Jan Macutkevicius, Juras Banys, Algirdas Selskis, et al.. Dielectric properties of PDMS composites filled with SrTiO₃ nanoparticles. *Polymer Composites*, 2021, 42 (6), pp.2982-2988. 10.1002/pc.26031 . hal-03407737

HAL Id: hal-03407737

<https://hal.univ-lorraine.fr/hal-03407737>

Submitted on 28 Oct 2021

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Dielectric properties of PDMS composites filled with SrTiO₃ nanoparticles

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This paper deals with the dielectric properties of PDMS nanocomposites filled with SrTiO₃ nanoparticles. The investigations were performed over a very broad range of frequencies (20 Hz – 3 THz). Almost no dielectric dispersion was observed in all the composites at room temperature over the entire range of measurement frequencies, and the dielectric losses were also very low under these conditions (less than 1.9). The dielectric dispersion was observed at lower temperatures (below 280 K), due to relaxation at the PDMS/SrTiO₃ interface and in the bulk polymer. The relaxation time for both cases followed the Vogel-Vulcher law, while the freezing temperature was substantially lower for relaxation at the PDMS/SrTiO₃ interface.

SrTiO₃, dielectric permittivity, polydimethylsiloxane

INTRODUCTION

New materials with special linear and non-linear dielectric properties are required in modern industry, people's life and environmental protection. For the progress of flexible electronics, new polymeric composite systems are desired [1]. Polydimethylsiloxane (PDMS) is a widely used elastic transparent polymer [2]. In addition, PDMS has excellent gas impermeability, biocompatibility, UV resistance, heat and oxidation stability, making it an important prospective matrix for polymer composites [3]. However, PDMS has low mechanical properties, low electrical conductivity and low dielectric permittivity values [3]. Nevertheless, these properties can be improved by the appropriate incorporation of nanoparticles [4-6]. PDMS composites are widely used in flexible bioelectronics, as sensors, coatings and batteries, and also for 3D-printing [7-9].

SrTiO₃ is a well-known quantum paraelectric [10-11]. No ferroelectric phase transition occurs in this material down to the lowest temperatures, but the dielectric permittivity decreases sharply on cooling. Moreover, the main dielectric dispersion is observed in the terahertz and infrared frequency ranges, while at lower frequencies the dielectric permittivity is almost independent of the frequency. Therefore, it is applicable in various electronic fields where high dielectric permittivity and low dielectric losses are required over a broad frequency range. In particular, the dielectric tunability of SrTiO₃ by electric field, light and temperature is observed at terahertz frequencies [12]. Therefore, it is possible to make various devices operating in the terahertz frequency range, such as high-speed electronic modulators, photonic crystals and metamaterials [13]. In electronics, SrTiO₃ is also applicable as wide gap semiconductor with a bandgap of 3.2 eV.

SrTiO₃ composites are widely investigated as cooling materials [14], for dielectric capacitors and energy storage applications [15], or for photocatalytic water splitting for hydrogen production [16]. The dielectric properties of SrTiO₃ in various polymer matrices have been mainly investigated at low frequency [17, 18]. It has been established that the dielectric permittivity of composites based on nano SrTiO₃ can be quite high at room temperature (about 60 for polyethylene with 12% SrTiO₃ of volume fraction) and is strongly dependent on the distribution of SrTiO₃ particles in the polymer matrix, being more important for aggregated SrTiO₃ particles [19]. It has also been shown that the dielectric relaxation in polymer composites with SrTiO₃ particles is mainly due to polymer-related relaxation and interfacial relaxation [20]. The dielectric properties of polymeric composites with SrTiO₃ particles can be tuned by the electric field [20]. However, research on composites containing SrTiO₃ nanoparticles in the microwave and terahertz frequency ranges is rather rare [21].

The objective of this paper was to study the dielectric properties of SrTiO₃/PDMS composites in wide frequency (including microwave and terahertz frequency ranges) and temperature ranges (100-300 K, where PDMS is stable [18]).

EXPERIMENTAL

SrTiO₃ with particle sizes of 100 nm was purchased from US Research Nanomaterials, Inc (USA), while the PDMS matrix was purchased from Farnell (France) under the reference Sylgard 184 Silicone Elastomer (Dow Corning®).

Prior to any synthesis, PDMS was degassed under reduced pressure (4 000 Pa, 30 min) at room temperature. For each composite, the corresponding amount of SrTiO₃ was dispersed in isopropanol (IPA) and under inert atmosphere (N₂) to avoid any potential oxidation of silver. The IPA-based suspension containing SrTiO₃ nanoparticles was then sonicated for 3 h in an ultrasonic bath (VWR USC 1200 TH, 600 W), and for 5 min using a sonotrode (VWR DIGITAL, 450 W, with a 13 mm diameter probe) at 20% of its maximum power. The suspension was then poured over the corresponding amount of PDMS and was then sonicated using the same procedure. In order to evaporate the IPA, the IPA/SrTiO₃/PDMS blend thus obtained was placed overnight in a ventilated oven at 60°C. The resultant PDMS/SrTiO₃ paste was sonicated (ultrasonic bath) once more for 1.5 h. The required amount of curing agent specified by the supplier was then added. The resultant mixture was then gently stirred by hand for 10 min. In order to remove air bubbles that may have been trapped during this step, the final mixture was degassed under reduced pressure (4 000 Pa, 2 min). Depending on the viscosity of the final mixes, the composites were cast or manually pressed into moulds before curing. The composites were finally cured for 2-3 h at 90°C in a ventilated oven. Visually, the color of all investigated composites is white, they are not transparent in optical frequency range. Composites with 30 vol.% SrTiO₃ is flexible, while composites with bigger SrTiO₃ concentrations are completely hard.

Scanning electron microscopy (SEM) images were obtained with a JSM 6460 LV electron microscope. Broadband measurements were performed using several techniques. At low frequencies (20 Hz - 1 MHz), the complex dielectric permittivity was obtained from the complex capacitance, which was measured by a HP4824 LCR meter. The measurements accuracy in this frequency range was better than 10%. In the microwave frequency range, from 8 GHz to 50 GHz, the reflectance and

transmission of a thin dielectric rod placed inside a waveguide were studied. A custom-made waveguide spectrometer was used in this frequency range [22]. The typical value for the rod diameter was several hundred micrometres. The best measurements accuracy in this frequency range was in the middle of the band i.e. close to 30 GHz, in this case it is better than 10%. In the terahertz frequency range (from 100 GHz to 3 THz), a terahertz time domain spectrometer (Ekspla Ltd) based on a femtosecond laser was used for the measurements. The spectrometer is based on a femtosecond laser fibre (wavelength 1 μm , pulse duration less than 150 fs) and a GaBiAs photoconductive terahertz emitter and detector. The signal-to-noise ratio was as high as 60 dB at a frequency of 0.5 THz. The complex effective permittivity was calculated according to the Fresnel equation [23]:

$$T(\omega) = \frac{4N \exp\left(\frac{i\omega(N-1)d}{c}\right)}{(N+1)^2} \sum_{k=0}^m \left[\frac{\left(\frac{N-1}{N+1}\right) \exp(i\omega Nd)}{c} \right]^{2k}, \quad (1)$$

where $N=n-ik=(\epsilon^*)^{0.5}$ is the complex refractive index, ϵ^* is the complex dielectric permittivity, d is the sample thickness, c is the light velocity and m labels number of reflections in the sample. These reflections are experimentally resolved and form separate pulses in the measured signal, so that the value of the coefficient m can be easily determined.

The measurement accuracy was better than 1% at frequency 0.5 THz (where a signal to noise ratio is highest). At low frequencies (20 Hz – 1 MHz), the measurements were also performed in the temperature range of 100 to 300 K. Silver paste was used to make electrical contacts with the samples. The real part σ' of the complex electrical conductivity was calculated as $\sigma' = \omega \epsilon_0 \epsilon''$, where ω is the angular frequency, ϵ_0 is the permittivity of vacuum, and ϵ'' is the imaginary part of the complex dielectric permittivity.

RESULTS AND DISCUSSION

SEM images of PDMS-based composite materials filled with SrTiO_3 nanoparticles are presented in Fig. 1. The SrTiO_3 nanoparticles were well dispersed in composites with different filler

concentrations, as all areas studied in the composites with the same filler concentrations were similar.

The temperature dependence of complex dielectric permittivity for PDMS composites filled with 30 vol.% SrTiO_3 nanoparticles is presented in Fig. 2. The main dielectric anomaly was observed at about 175 K. It is related to the glass transition (α relaxation) in pure PDMS [24]. The α relaxation is due to a large-scale collective motion of many backbone segments in the amorphous phase of PDMS. The additional dielectric anomaly was clearly observed as the maximum of dielectric losses in the temperature range 200-250 K (depending on the measurements frequency) and the change in the slope of temperature dependence of the dielectric permittivity. The additional anomaly is related to the glass transition in the polymer-filler interface (α' relaxation) [25, 26]. Both relaxations are related with the orientation polarization [25, 26].

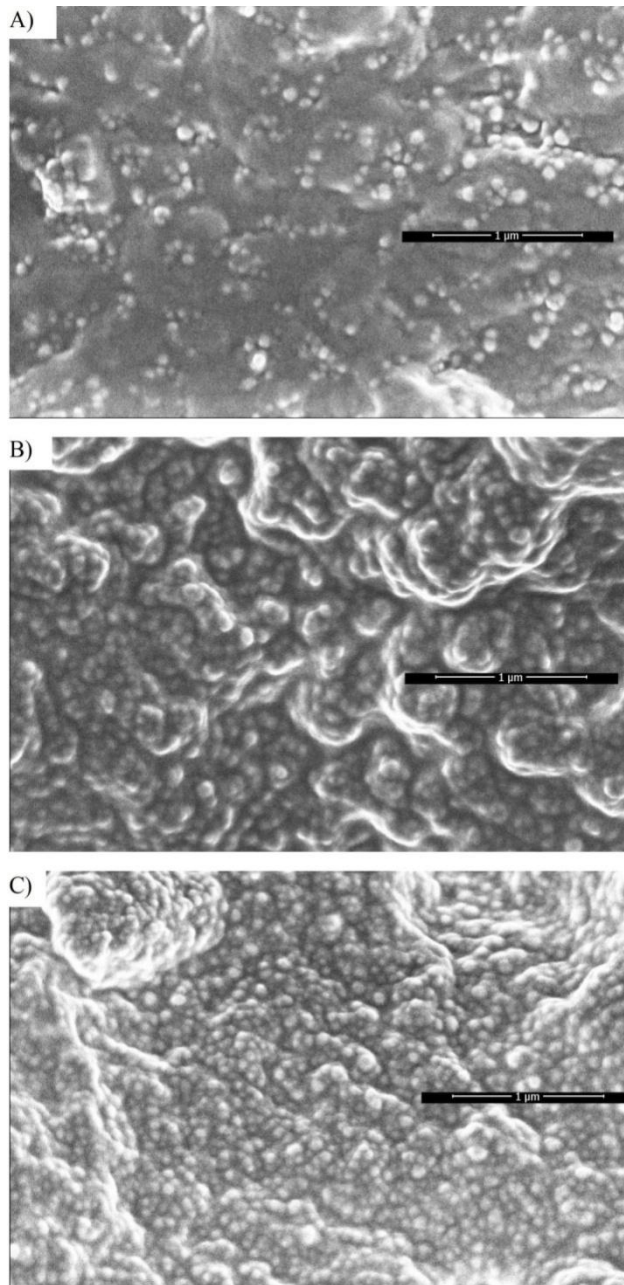


Fig. 1 SEM images of $\text{SrTiO}_3/\text{PDMS}$ composites of different volume fractions of SrTiO_3 nanoparticles: A) 10 vol. %; B) 30 vol. %; C) 40 vol. %.

Dielectric properties of pure PDMS and composites filled with SrTiO_3 nanoparticles at low frequencies (not higher than 1 MHz) are quite similar. The difference is only in the appearance of dielectric dispersion related with α' relaxation (which is related to the glass transition in polymer-

filler interface) in SrTiO₃/PDMS composites, the α' relaxation is completely absent in pure PDMS. The α' relaxation becomes stronger with increasing SrTiO₃ concentration (will be shown below).

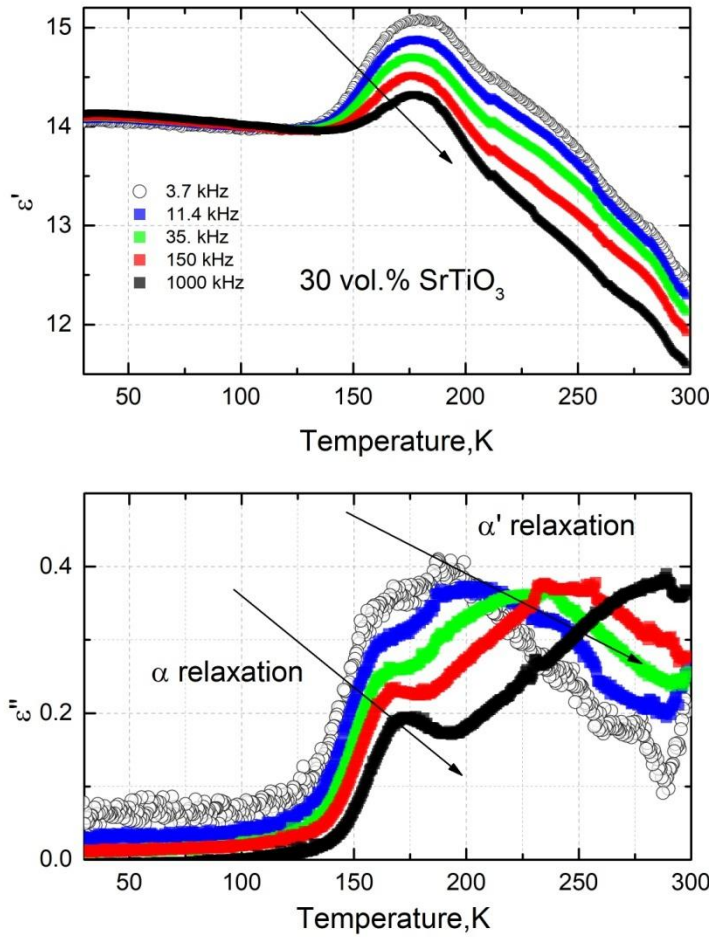


Fig. 2 Temperature dependence of the complex dielectric permittivity of PDMS composites filled with 30 vol.% SrTiO₃ nanoparticles. The arrow indicates the increase in the frequency at which the composites were studied.

The maxima of dielectric permittivity and losses as a function of temperature depend on the frequency. The frequency ν is plotted as a function of the maximum position of the dielectric losses for all investigated composites and pure PMMA in Fig. 3. It can be seen that the α' relaxation appears in SrTiO₃/PDMS composites, while the α relaxation disappears in composites with 50 vol.% inclusions. The dependence was fitted with the Fogel-Vulcher law:

$$\nu = \nu_0 e^{\frac{-E}{T-T_0}}, \quad (2)$$

where k_b is the Boltzmann constant, ν_0 is the attempt frequency and T_0 is the glass transition temperature of the polymer when the cooling rate becomes infinitely slow, E is the activation energy .

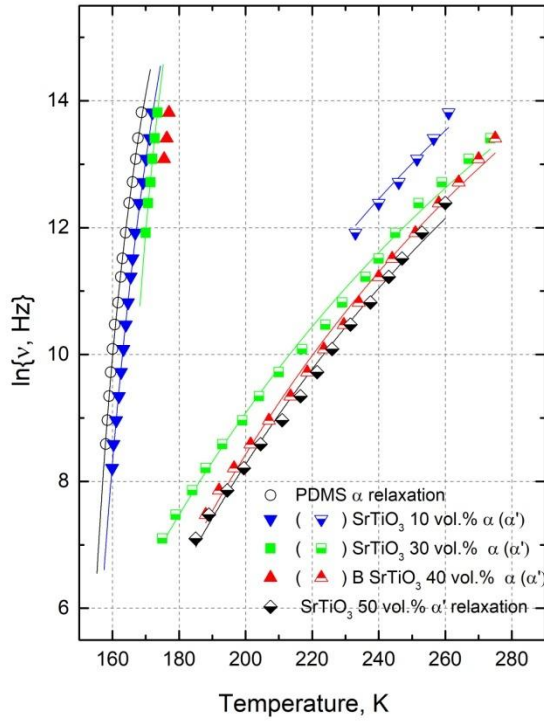


Fig. 3 Measurement frequency versus the temperature of dielectric losses maximum for SrTiO₃/PDMS composites.

The parameters obtained are summarised in Table I. It can be seen that there is no clear dependence of E and T_0 on concentration. However, the activation energy for α' relaxation was substantially higher than the activation energy for α relaxation, while the freezing temperature was lowest for α relaxation.

Table I. Parameters of Vogel-Fulcher fit.

	τ_0 , ps	E , K	T_0 , K
0 vol.% (α relaxation)	0.03	343	135

10 vol.%	α relaxation	4.8	707	126
	α' relaxation	0.53	3637	10
30 vol.%	α relaxation	0.24	331	147
	α' relaxation	0.53	4358	43
40 vol.% (α' relaxation)		0.53	4054	18
50 vol.% (α' relaxation)		0.53	4311	30

Two mechanisms have an impact on the freezing temperature in polymeric composites: the interaction between polymer molecules and nanoparticles increases the freezing temperature, while the appearance of free volume at the polymer/nanoparticle interface decreases the freezing temperature [27]. It can be concluded that both mechanisms are important in the composites under study. Moreover, the free spaces are located closer to the nanoparticles. Both relaxation mechanisms are related with orientation polarization.

The temperature dependence of the complex dielectric permittivity for all composites studied at the frequency of 3.7 kHz is presented in Fig. 4.

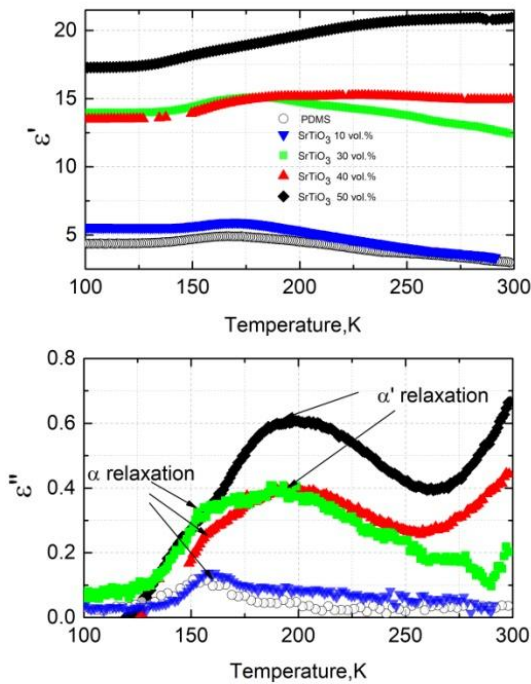


Fig. 4 Temperature dependence of the complex dielectric permittivity at 3.7 kHz for SrTiO₃/PDMS composites.

It can be observed that both dielectric permittivity and dielectric losses strongly increased with the concentration of SrTiO₃. The dielectric permittivity was high (about 20 at room temperature) for the composites with the highest SrTiO₃ concentration, while the losses were low (less than 0.6). The increase of the dielectric permittivity with the SrTiO₃ concentration is related with ionic polarization of SrTiO₃ [18]. Moreover, it is possible from the data presented in Fig. 4 to separate contributions of α and α' relaxations. The α' relaxation becomes stronger with increasing SrTiO₃ concentration, while the α relaxation disappears in composites with 50 vol.%. The small increase in dielectric losses with temperature at higher temperatures (above 270 K) is related to the onset of electrical conductivity of SrTiO₃ nanoparticles [28].

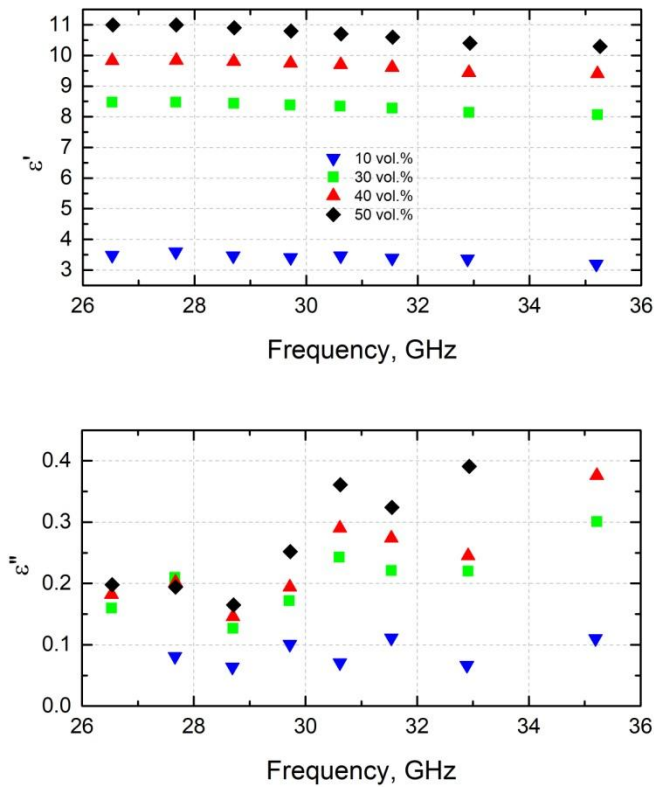


Fig. 5 Frequency dependence of complex dielectric permittivity in the microwave frequency range at room temperature for SrTiO₃/PDMS composites.

The dielectric permittivity of composites with the highest concentration of SrTiO_3 was also high in the microwave frequency range, while the dielectric losses were low (Fig. 5). Moreover, the value of dielectric permittivity at 3.7 kHz (Fig. 4) was almost equal to the value of dielectric permittivity at 39 GHz, indicating that the dielectric dispersion in the frequency range 3.7 kHz – 39 GHz is very low. The small change of dielectric losses presented for composites with highest concentrations of SrTiO_3 could be related with onset of SrTiO_3 phonons, however these changes are very small and SrTiO_3 phonon frequencies are observed usually in terahertz frequency range [12], so it will be further discussed below.

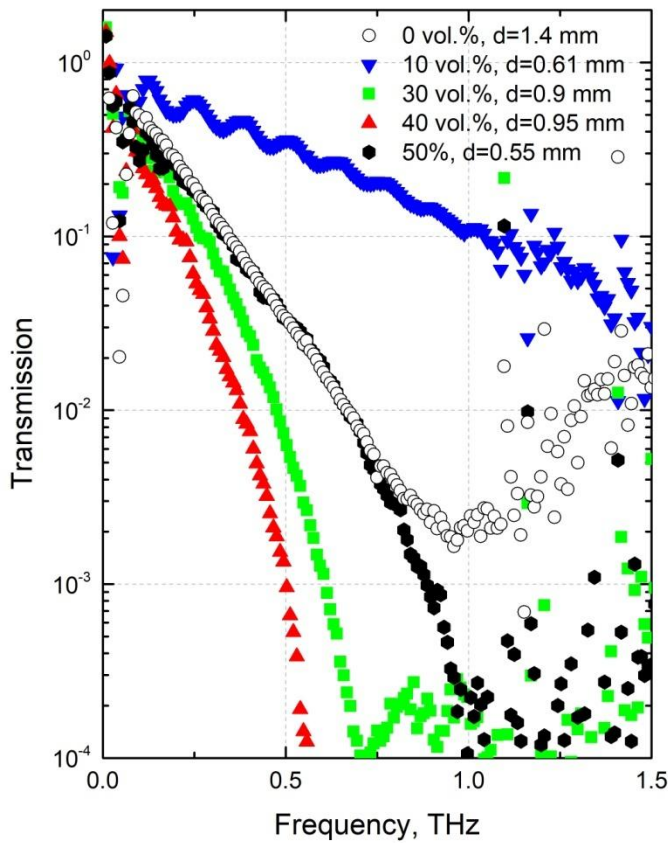


Fig. 6 Transmission spectra of SrTiO_3 /PDMS composites in the terahertz frequency range. The thickness of samples d is indicated in the legend.

The transmission of composites in the terahertz frequency range decreased sharply with frequency up to a certain cut-off frequency, while at higher frequencies it was frequency-independent or even increased with frequency. The latter observation is rather an artefact related to the fact that the samples were opaque at these frequencies. The decrease in transmission with frequency in the terahertz frequency range can be explained by the decrease in complex dielectric permittivity with frequency or by the frequency-independent complex dielectric permittivity. It can be also mentioned, that the thickness of the sample has the strong impact on terahertz transmission (according to Eq. 1) and in possible composites applications, especially for 3D printing where small deviation on the expected thickness could happens [7], the sophisticated geometries can be printed.

The frequency dependence of the complex dielectric permittivity in the terahertz frequency range is presented in Fig. 7. As at lower frequencies, the complex dielectric permittivity increased with the concentration of SrTiO_3 . In composites containing SrTiO_3 nanoparticles, the dielectric dispersion in the terahertz frequency range was very low and related to the onset of SrTiO_3 phonons [12]. The high value of dielectric permittivity of the composites in the terahertz frequency range indicates that it can be changed by external parameters and that the composites are suitable for various flexible electronics components [13].

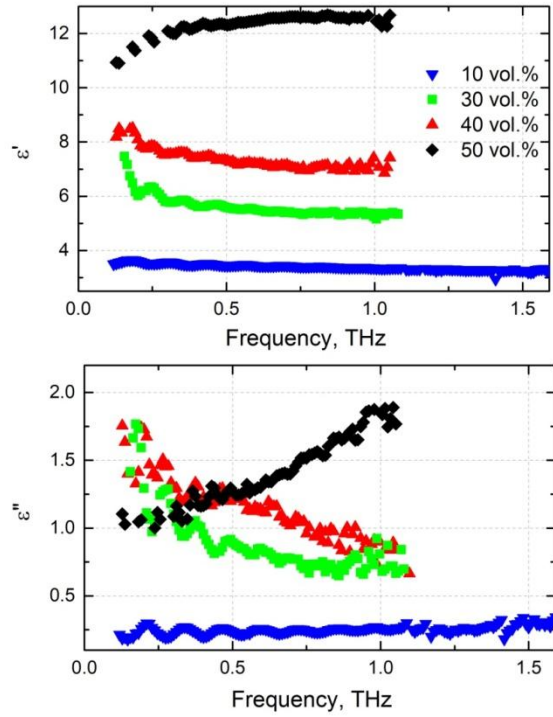


Fig. 7 Dielectric spectra of SrTiO₃/PDMS composites in the terahertz frequency range.

CONCLUSION

Broadband investigations of PDMS composites filled with SrTiO₃ nanoparticles were performed in a wide temperature range, from 100 to 300 K. No dielectric dispersion was detected in the frequency range 20 Hz – 2 THz at room temperature. The dielectric losses under these conditions were very low (less than 1.8), while the dielectric permittivity was rather high (up to 20 for 50 vol.% composites). Therefore, these composites are suitable for various flexible electronic applications. The dielectric relaxation was only observed at lower temperatures (below 280 K) and at lower frequencies (below 1 MHz). It results from a relatively large-scale cooperative motion of many backbone segments in the amorphous phase of PDMS in the bulk polymer and at the PDMS/SrTiO₃ interface. The freezing temperature was substantially lower in the PDMS/SrTiO₃ interface than in the bulk polymer volume, indicating that free spaces are mainly concentrated near the SrTiO₃ nanoparticles.

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