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Toward improved PVDF-$BaTiO_3$ composite dielectrics: mechanical activation of the filler versus filler content

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Abstract

Barium titanate (BT) perovskite particles were surface modified by means of mechanical treatment and used as inorganic component in polyvinylidene fluoride (PVDF) based composites. The changes in electrical properties of the composite films with increasing in filler content were followed by dielectric spectroscopy, breakdown strength and *D-E* measurements. A comparison of the properties of the composites prepared with untreated and mechanically activated particles revealed that there is a significant difference in their performances at low filler concentrations (<20 wt%). Introduction of the surface modified ceramic particles into PVDF matrix led to an increase of the dielectric constant without affecting significantly the electrical breakdown strength. In contrast, when as received BT particles were used a filler, both dielectric constants and breakdown strengths of the composite films were lower than the corresponding values observed for the pure PVDF. At higher concentrations, however, the influence of pre-treatment of the filler on the effective electrical properties becomes less significant. The obtained results were discussed in terms of the pronounced crystallization of polar β and γ crystal phases of PVDF in the presence of surface modified BT fillers, which is confirmed by Raman spectroscopy.

1. Introduction

Recently, the composites that comprise ferroelectric polymers (typically PVDF and its co-polymers) and high-dielectric constant perovskite particles became a strenuous topic of research [1–3]. These advanced materials play an important role in the development of modern compact electronic components and electrical power systems [4, 5]. They combine excellent properties of the polymers, such as low density and high dielectric strength, with the large dielectric constant of perovskites. Furthermore, matrix polymers can be easily processed into useful forms, which is significant for practical applications. On the other hand, after the introduction of the particles into the polymer matrix, the composite may exhibit additional properties resulting from the synergetic interaction of the components on a microscopic level. For example, in our previous study [6], it was shown that $Na_{0.25}K_{0.25}Bi_{0.5}TiO_3$ (NKBT) particles induce the appearance of a novel dielectric relaxation transition in PVDF-co-HFP matrix. To date, the most studied systems are the composites in which barium titanate (BT) particles are employed as fillers for PVDF and PVDF co-polymer matrices [3]. Since the surface of perovskite particles is hydrophilic and the host ferroelectric polymer matrix is organophilic, attempts were made to

improve their interaction via surface modifications of the filler [1]. Another approach usually employed to enhance matrix-filler interaction is the introduction of nanoparticles [3, 7] and 1-D structures [8, 9], instead of microparticles, as they exhibit much larger specific surfaces. Various types of chemicals were suggested as surface modifiers for $BaTiO_3$-type fillers such as poly(vinyl pyrrolidone) [10, 11], titanate coupling agent [12] phosphonic acid [13–15], dopamine [16], fluoric-polymers [17, 18], galic acid [19] and phthalic acid [20]. Depending on the type of treatment and fabrication method, these surface modifications resulted with composites with modestly or significantly improved dielectric properties (dielectric constant, energy density storage etc).

In our recent studies, we introduced another approach for improving the properties of ferroelectric polymer composites, which is based on the surface modification of the filler by means of mechanical activation [21–23]. First, it was reported that mechanically activated BT fillers affect the crystallization of PVDF leading to an increase in β-crystalline phase content [21]. Then, it was shown that this increase could have beneficial effects on the dielectric properties of the composites [22]. The activated BT particles were found to enhance the dielectric constant of PVDF/PMMA bland (even at very low concentrations $\leqslant$6 wt%), while reducing, at the same time, dielectric losses in the material [22]. Finally, we tested ZnO instead of BT particles to show that the mechanical activation of the filler can be used as a general method for improving the particle-matrix interaction and, consequently, the dielectric properties of PVDF-composites [23]. In the present paper, we make one step forward by testing the effects of mechanically activated fillers at high concentrations (of up to 50 wt%) and trying to find possible limitations of suggested method. We prepared the composites with mechanically activated and untreated BT particles and compared their dielectric spectra, *D-E* characteristics and dielectric strengths. As it will be seen, the activated BT particles strongly affect the dielectric properties of PVDF at lower concentrations ($<$20 wt%), while at higher concentrations, the differences in performances of two types of composites (with modified and unmodified fillers) become less significant.

2. Methods

2.1. Materials

Polyvinylidene fluoride (PVDF, $M_w \sim 570\,000$) powder was purchased from Solvay Solexis, Brussels (Belgium) and dried at 90 °C for 24 h prior to use. Micron-sized $BaTiO_3$ particles (99.9% Aldrich) were mechanically activated for 10 min in a Fritsch Pulverissete 5 planetary ball mill with 10 mm in diameter zirconia balls. The ball/sample mass ratio was 20:1, while tray and vial rotation speeds were 317 and 396 rpm, respectively. In order to achieve homogeneous dispersion of the filler in the polymer matrix, the composites samples with the mechanically activated and untreated $BaTiO_3$ particles were prepared by using two-step procedure. First, the PVDF/$BaTiO_3$ films were prepared by solution mixing. PVDF was dissolved in a dimethyl formamide (DMF) (5 g of polymer per 100 ml of solvent) and mixed with various amounts of $BaTiO_3$ particles dispersed in DMF. Prior to solution mixing, BT dispersions were sonicated in a Branson W-450 D Digital Sonifier for 20 min at 20% amplitude (80 W). The composite films with different BT contents were prepared by casting the mixtures into glass Petri dishes. They were left to dry 24 h at room temperature (~20 °C) and then dried for 1 h at 100 °C. In the second step, the obtained composite films were melt-mixed with 20 g of PVDF powder in a Brabender Plastograph at 205 °C by using a rotor speed of 60 rpm. The pure polymer is melt-mixed for 5 min and, after adding the composite films, the mixing continued for another 5 min. The composite materials with 5, 10, 20, 30 and 50 wt% of inorganic content were further hot pressed at 195 °C into films with thickness of 0.7 mm. The pure polymer films were prepared by using the same procedure. For electrical characterizations, gold electrodes were thermally evaporated on both sides of the films.

2.2. Experimental

The morphologies of the non-treated and mechanically activated $BaTiO_3$ powders were investigated by using a JEOL JSM-6390 scanning electron microscope (SEM). The samples were covered with gold and examined at an acceleration voltage of 15 kV.

Raman spectroscopy measurements of the composite films were carried out at 633 nm laser excitation wavelength (He-Ne incident laser) on a Horiba Jobin Yvon LabRam ARAMIS Raman microscope with a 100 × objective. The data were collected over the Raman shift range from 200 to 3200 cm^{-1}, at room temperature, using an 1800 gr/mm grating and a count time of 5 s with 10 averaging cycles. The reported spectra were obtained after background correction.

Dielectric spectroscopy measurements were performed on a Hameg 8118 instrument in the frequency range between 20 Hz and 60 kHz and a temperature range from 150 to 400 K. The heating rate was 5 $K{\cdot}min^{-1}$, and the acquisition step was 10 K with 1.5 V applied voltage. Conductance (G) and susceptance (B) were measured by using the C_p model of the instrument. *D-E* loops were recorded at 10 Hz using a Sawyer-Tower circuit. The

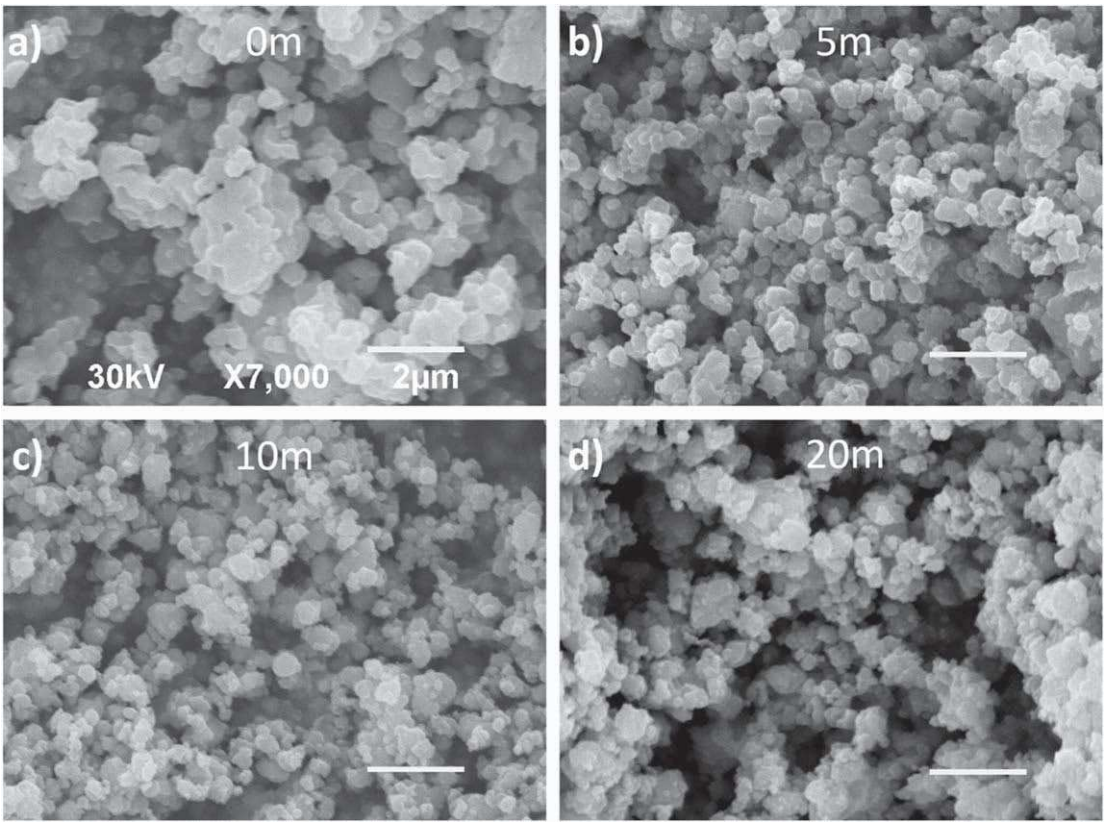

Figure 1. SEM micrographs of: (a) as-received BT powder and BT powders mechanically activated for (b) 5 min, (c) 10 min and (d) 20 min. The scale bars are 2 μm for all images.

electrical breakdown strength characterizations were carried out at room temperature in DC regime by using a Keithley 2401 A-meter and a DC high voltage source. For these measurements, the composite samples were slightly thinner (with thicknesses of ~20 μm). The electrical field was applied in steps of 10 MV m^{-1} per minute.

3. Results and discussion

3.1. Morphology and structure

Scanning electron microscopy (SEM) micrographs of untreated and $BaTiO_3$ powders mechanically activated at different activation times (5, 10 and 20 min) are shown in figure 1. As can be seen, the mechanical activation induces a decrease in the size of the particles, although they have tendency to form larger agglomerated clusters. The size of the particles is estimated from several different positions along the sample taking into account diameter of the individual particles only (when it was possible to distinguish them from the agglomerates). Their diameter was measured manually and the typical procedure was shown in figure S1 (Supporting information). The results showed that the initial average size of the particles of untreated sample of 0.80 ± 0.59 μm decreases with mechanical treatment to 0.64 ± 0.35 μm, 0.24 ± 0.12 μm and 0.32 ± 0.20 μm for 5, 10 and 20 min activation times, respectively. The activation for 10 min produced the particles with the lowest average size and that is why they are further used as the filler for the preparation of the composites. Obviously, the mechanical treatment has its limits and at the longer activation times (20 min) the reverse process may occur due to pronounced agglomeration of the particles with highly activated surfaces.

Due to reduced sizes, the activated particles have higher specific surfaces than their untreated counterparts, but at the same time activation treatment results in an increase in particle surface tensions and much more pronounced grain-size effects. In our previous studies [24, 25], we performed detailed investigation of the effects of the mechanical activation on the structural properties of BT particles and we will briefly comment them here. Structural refinement analysis of XRD spectra showed that the mechanical activation strongly affects the size of BT crystallites. It was found that the mechanical treatments for 10 and 20 min reduced the size of the crystallites from 150 nm (as received Aldrich powder) to 45 nm and 39 nm, respectively. At the same time, the microstrains after the treatments increased from 0.1% to 0.47% and 0.61%, respectively. It should be emphasized that the whole process may also lead to solid state phase transition from ferroelectric-tetragonal to paraelectric-cubic BT

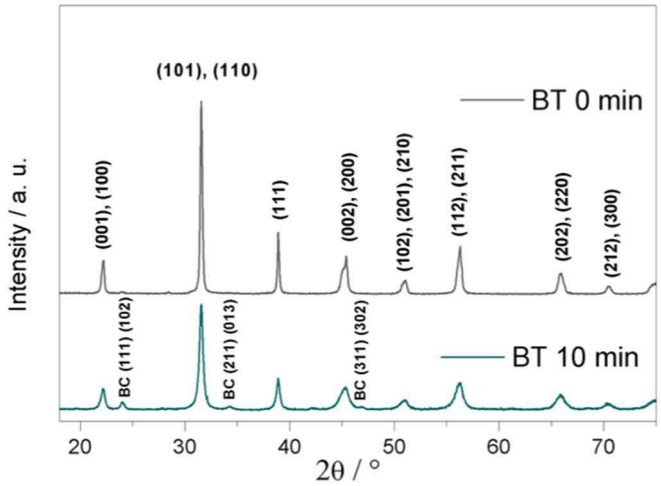

Figure 2. XRD patterns of the unmodified (0 min) and the mechanically activated (10 min) BT particles. The additional peaks (denoted as BC) come from the traces of $BaCO_3$ with witherite (orthorhombic) crystal structure.

crystal phase. Nevertheless, we showed that with a careful adjustment of the activation procedure it is possible to obtain the nano-sized BT particles in which the tetragonal structure is preserved [24]. XRD patterns of the untreated BT particles and the particles mechanically activated for 10 min show that this is the case with the present samples as well (figure 2). Both types of particles clearly show the reflections that correspond to tetragonal BT, although the peaks of the activated samples are broader due reduced average size of the crystallites and more pronounced microstrains.

Some additional peaks are also present in the XRD spectra after the activation (denoted in figure 2 as BC) that originate from the traces of $BaCO_3$ with witherite i.e. orthorhombic crystal structure (JCPDS Card. No. 45-1471, ICSD Card. No 15196). The presence of $BaCO_3$ is a consequence of the pronounced adsorption of the CO_2 on the surface BT particles due to dipole–dipole interaction between ferroelectric BT crystals and polar CO_2 molecule and it is well documented in the literature [26, 27]. The weight contents of $BaCO_3$ in the non-activated and 10 min activated BT powders were estimated to be 0.5% and 2.3%, respectively.

As we mentioned in the introduction, the unmodified and mechanically activated fillers may affect crystallization of PVDF in different ways. Changes in the crystal structure of PVDF matrix after the introduction of the fillers were followed by means of Raman spectroscopy. A detailed analysis of the Raman spectra of the PVDF composite films with non-activated and activated BT particles was presented in the previous work [21]. Here, we will discuss only the spectral lines in the Raman shift range from 700 to 950 cm^{-1}, since they exhibit the most prominent features important for the present study. Figure 2 shows the Raman spectra of the pure PVDF and PVDF-BT composite films with 10 and 30 wt% of inorganic content.

The spectra in figure 3(a) show that both types of fillers reduce the amount of α-crystal phase in the matrix and promote the β-phase crystallization. Namely, in the spectra of composite films the intensity of the Raman peak at ~795 cm^{-1}, attributed to the strongest line of α-crystal phase in pure PVDF, decreases with respect to the Raman peaks that originates mostly from β- and γ-crystal phases (figure 3(a)). It is also important to note that the increase in intensity of peak at ~839 cm^{-1}, relative to the main α-crystal peak at ~795 cm^{-1}, is more pronounced in the films with mechanically activated fillers, suggesting that surface modified particles strongly act as nucleation centers primarily for β-phase crystallization (figure 3(a)). At higher concentrations of the filler (figure 3(b)), this effect becomes less noticeable but it is still present. Since α crystal phase is non-polar, the crystallization of electrically active β- and/or γ-phases can strongly influence the overall electrical properties of the composites. Unfortunately, we could not quantify the exact increase in polar crystal phases since there were no internal standards.

3.2. Electrical properties

Dielectric permittivity (ε') and dielectric loss (ε'') curves of the pure PVDF and PVDF-BT composite films with untreated and mechanically activated fillers are shown in figure 4. The reported curves are recorded in the temperature range from 150 to 400 K at the frequency of 1.8 kHz. The full sets of ε' data obtained at various frequencies (from 20 Hz to 60 kHz) are given in the Supporting information (figures S2 and S3).

It can be seen in figures 4(a) and (c) that ε' of PVDF and PVDF-BT composites increases with an increase in temperature. Such a temperature dependence of dielectric permittivity is typical for ferroelectric polymers at a constant frequency of external field [28] and it is related to the activation of previously frozen dipole segments as

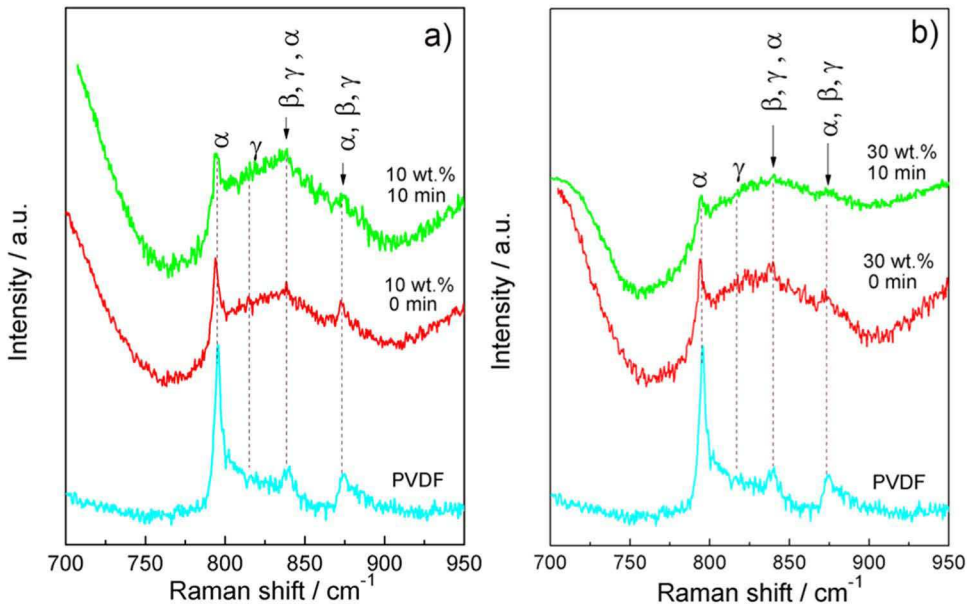

Figure 3. Raman spectra of the pure PVDF and PVDF-BT composites with untreated (0 min) and mechanically activated (10 min) filler particles: (a) 10 wt% and (b) 30 wt% of inorganic content.

more thermal energy is added to the system. In that sense, the most pronounced changes in ε' values are observed during the transition from a glassy to rubbery state in the range from 250 to 300 K. On the other hand, there is a clear difference in the dielectric behavior of the two composite systems at lower concentrations of the filler. The dielectric constant of the composites with 5 and 10 wt% of untreated BT filler is lower than that of the pure PVDF in the whole temperature range (figure 4(a)). At the same time, the corresponding composites with the mechanically activated particles show an increase in dielectric constant with respect to that of the matrix (figure 4(c)). This effect is a direct consequence of the increase in the amount of β- and/or γ-crystal phases after the introduction of activated BT in the matrix, as suggested by Raman spectroscopy results (figure 3). As the inorganic content increases ($>$20 wt%), the former effect becomes less important and the composites with non-treated and activated particles start behaving in a similar manner.

It should be noted that two competing process occur during the crystallization of PVDF in the presence of the mechanically treated particles: the α-phase crystallization which is more thermodynamically favourable and the crystallizations polar-phases that occurred at their highly activated surfaces. At higher contents, however, particles also affect the mobility of the macromolecular chains, which is necessary for their packing into more ordered structure of polar crystals. For this reason, the crystallization of the polar-phases does not depend linearly on the concentration of the activated particles. This can be clearly seen in figure 5, where the dependence of the dielectric permittivity of the PVDF composites at 300 K on the concentration of untreated and mechanically activated BT fillers. The dielectric permittivity increases with increasing in BT content from 20 to 50 wt% regardless of surface modification of the filler. The presented results show that several factors may influence the final dielectric properties of the polymer composite. Besides the strength of the interaction between macromolecules and the high dielectric constant fillers, changes in the crystal polymorphism during the PVDF crystallization in the presence of the particles should also be taken into account.

Concerning dielectric loss curves, both types of composites exhibit a typical low temperature relaxation peak at ~273 K that corresponds to the glass transition of PVDF matrix (figures 4(b) and (d)). In the case of composites with low concentration ($\leqslant$10 wt%) of non-activated BT particles, the glass transition peak, also denoted as β-transition, is slightly shifted towards lower temperature due to a weak particle-chain interaction. In contrast, the position of the glass transition peak is virtually constant after introduction of mechanically activated particles. It is well known that the dielectric constant of the polymer-ceramic composite is the result of the interplay of two main effects that occur at the interfaces: an increase in interfacial polarization and the inhibition of the dipole motions in interfacial regions. According to model suggested by Tanaka [2], the layer formed at the boundary of a polymer and a spherical filler particle consists of bonded layer (~1 nm), bound layer (2–9 nm) and loose layer (several tens of nm). The distribution, orientation and mobility of the dipoles in these interfacial layers will be different from that of the bulk polymer chains further from the particle surfaces. Although the chains in the bonded layer are in direct contact with polymer chains, it is believed that the second and the third layers contribute more to the dielectric properties of the polymer composite. The free volume of

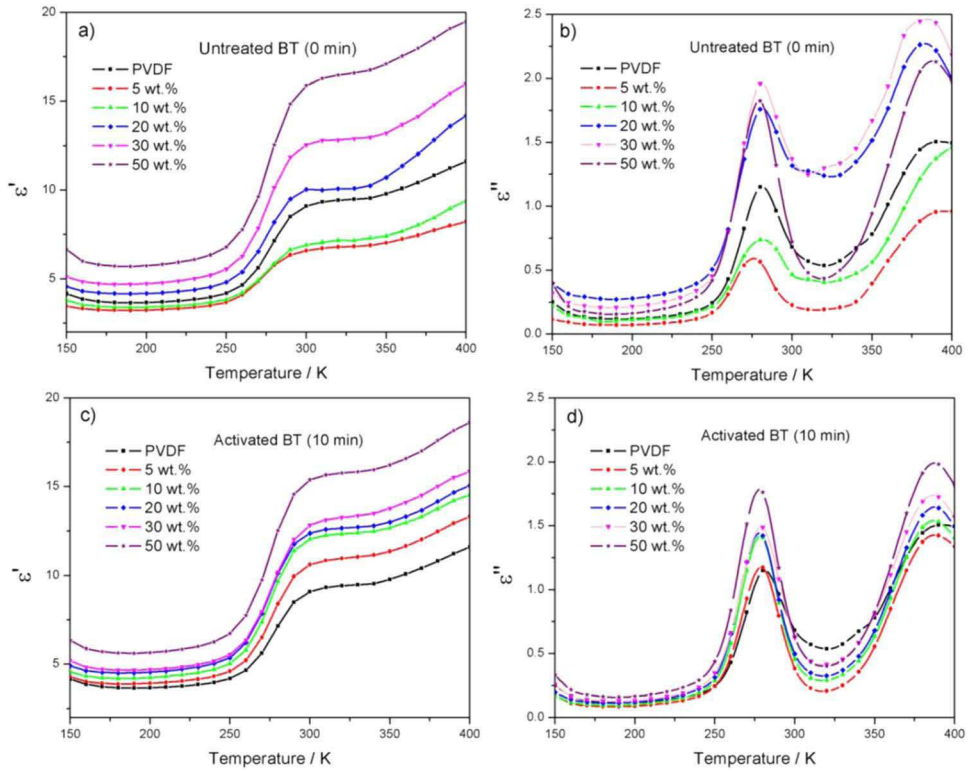

Figure 4. Dielectric constant (ε') and dielectric loss (ε') curves of the pure PVDF and PBDF-BT composites recorded at a frequency of 1.8 kHz and in the temperature range from 150 to 400 K: (a) and (b) the composite films with as-received BT particles (0 min); (c) and (d) the composites films with mechanically activated BT particles (10 min). The inorganic contents in the composites are indicated in the graphs.

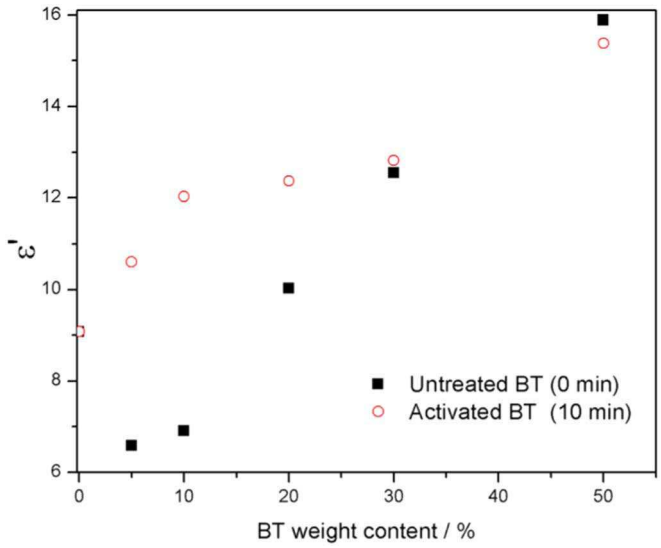

Figure 5. Dielectric permittivity (ε') values of the PVDF-BT composites at 300 K *versus* BT content. (the ε'-value at 0 wt% BT corresponds to the pure PVDF film; squares - untreated BT; circles - BT mechanically activated for 10 min).

the composite is mostly related to the third layer [2]. The results in figure 3(b) suggest that there are changes in that particular layer at low concentration of untreated BT filler (5 wt%). An increase in free volume, observed via decrease in the glass transition temperature, may enable an easier orientation of the dipoles and consequently lower losses. At the same time, due to weaker polymer-particle interaction, the high-dielectric constant fillers do not contribute significantly to the overall dielectric permittivity, which is, in the case of the PVDF-BT composites with 5 and 10 wt% inorganic content, lower than that of the pure PVDF (figure 3(a)). Obviously, an increase in amount of new dipoles, i.e. pronounced crystallization of polar β and/or γ phases in the presence of

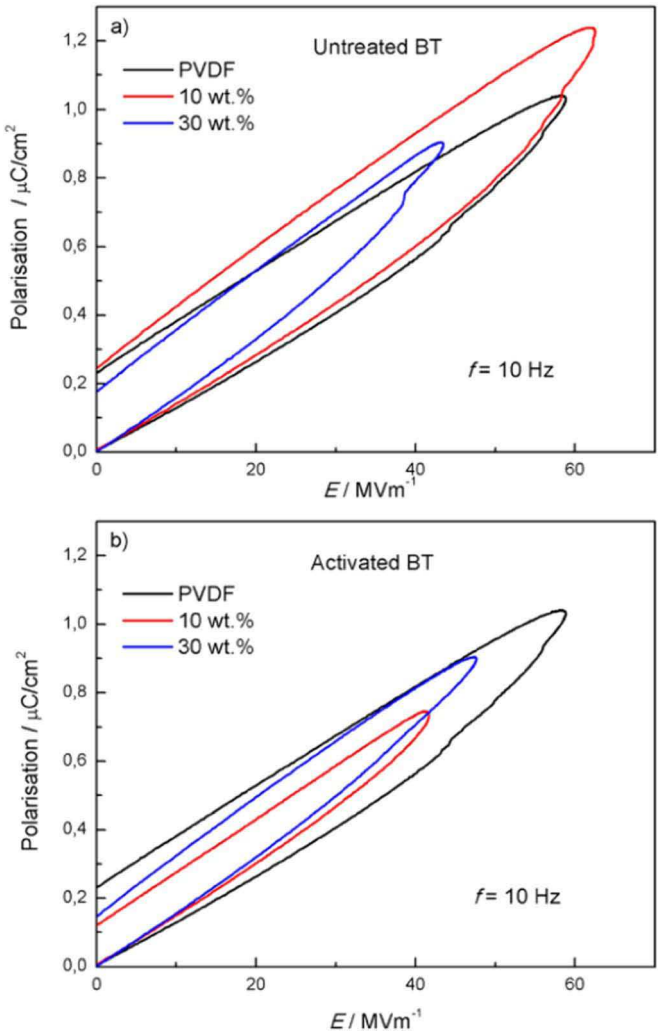

Figure 6. (D)-*E* loops of the pure PVDF and PVDF-BT composites with 10 and 30 wt% of (a) untreated and (b) mechanically activated for 10 min BT fillers.

mechanically activated BT particles, can compensate for the changes in polarizability of the interfacial regions at lower inorganic contents. The dielectric loss spectra of the PVDF and the composites also show high temperature relaxation peak at ~380 K. This so-called α-process is related to the crystalline domains of the polymer. It is attributed to wide-angle oscillations of the main chain dipoles from crystalline regions, which become more flexible as temperature increases [29].

Figure 6 shows *D*-*E* loops of the pure PVDF and PVDF-BT composites measured under unipolar 10 Hz field with 10 kV amplitude. The lower branch of *D*-*E* curves corresponds to the charging cycle and the upper branch is the discharging cycle. The *D*-*E* loops of the composite samples with untreated and mechanically treated fillers are slightly different. The *D*-*E* characteristics of the composites with unmodified filler resemble that of the pure polymer (figure 6(a)). The slope of the loops increases after the introduction of the filler, indicating an increase in the dielectric constant of the material [3, 30]. The same effect is observed in the case of the composites with mechanically activated filler (figure 6(b)) in agreement with dielectric spectroscopy measurements in figure 3. On the other hand, it was difficult to compare the ferroelectric polarization behaviour (remnant polarization) and the areas under loops (proportional to the dielectric loses) since the maximal fields were automatically controlled and they differed for the particular samples.

It should also be noted that that the slope of the composite with 10 wt% of untreated BT filler is slightly higher than that of the pure PVDF, which is not in the line with the results obtained by using dielectric spectroscopy. The observed discrepancy is due to a huge difference in the electric field intensities used in *D*-*E* (up to 60 MVm^{-1}) and dielectric spectroscopy (a few kVm^{-1}) measurements. Due to large dielectric permittivity of BT particles, they contribute more to the overall permittivity of the composites at higher fields. Nevertheless, the

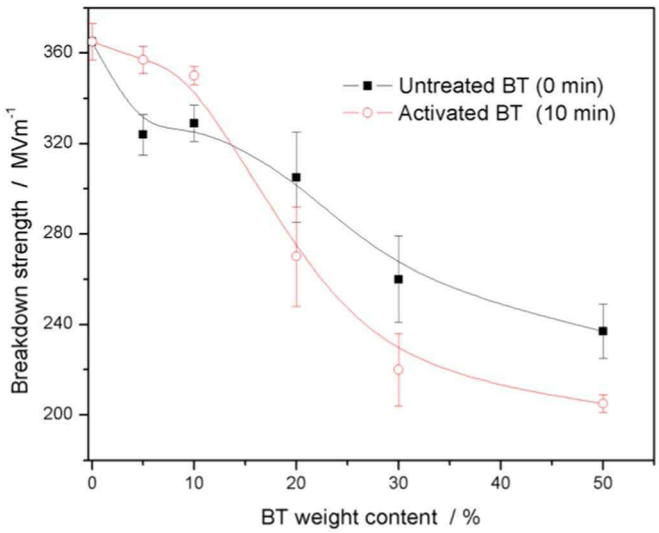

Figure 7. DC-breakdown strengths of the PVDF-BT composites versus BT content (0 wt.% - the pure PVDF; squares - untreated BT; circles - BT mechanically activated for 10 min).

presented results suggest again that the mechanical activation of the filler prior to mixing with the PVDF matrix has a pronounced effect on the final properties of the composites.

DC-breakdown strengths of the pure PVDF and PVDF-BT composites are shown in figure 7. There is a clear difference between the results obtained for composites with untreated and mechanically activated BT fillers.

In order to clarify the different behaviour of the two types of materials, we will start with a discussion of the main factors that may influence the breakdown strengths of polymer-ceramic composites [31]. First, due to a significant difference between the dielectric permittivities of BT particles and PVDF matrix, a highly inhomogeneous electrical field is created within the sample. Also, the degree of agglomeration of the particles strongly influences the overall performance of the composite [3, 31, 32]. Finally, the number of air voids increases after the introduction of the filler, especially at higher concentrations [14]. With respect to the polymer matrix, the breakdown strength of air voids is very low (3 MV m^{-1}) [31], which additionally affects the homogeneity of the electrical field produced. All these factors play their role in reducing of the breakdown strength of the composites and become more important as the concentration of the inorganic particles increases (figure 7). Nevertheless, the mechanical treatment of the BT particles produces the substantial difference in the electrical breakdown strength dependence on the inorganic content in the composites. At low concentrations of the mechanically activated BT filler ($\leqslant$10 wt%), the PVDF-BT composites exhibit similar electrical breakdown strengths as the pure polymer matrix (the changes are within the experimental error). On the other hand, electrical breakdown strengths of the corresponding PVDF-BT composites with unmodified fillers are lower by ~10% (figure 7). As inorganic content increases further ($\geqslant$20 wt%), the breakdown strength values of both types of composites gradually decrease. However, this effect is much more pronounced in the case of the composites with mechanically activated fillers. We believe that the lower values obtained for the composites with activated fillers is due to the reduced size of the particles (after the mechanical treatment) and consequently higher inhomogeneity in the samples at larger inorganic contents. The inhomogeneous distribution of the filler can facilitate the rise of the local electrical field, which enhances the dielectric response, but, at the same time, severely reduces the breakdown strength [3].

4. Conclusion

The surface modification of the BT particles by means of mechanical activation has pronounced effects on the electrical properties of its composites with PVDF, especially at low filler contents ($<$20 wt%). Due to the pronounced crystallization of polar β- and γ-crystal phases of PVDF in the presence of mechanically activated BT fillers, there is an increase in the dielectric constant of the composites with respect to that of the pure polymer, while at the same time, dielectric losses are reduced. As concentrations above 20 wt%, the pre-treatment of the BT particles prior to the mixing with PVDF matrix becomes less important and there are no significant differences in dielectric spectra of the composites with unmodified and modified fillers. The two types of composites differ also in terms of their breakdown strengths. The composites with activated BT fillers

show much better electrical strength at low concentrations (⩽10 wt%), while at higher concentrations, the situation is reversed. Overall, the dielectric properties of the PVDF-BT composites can be improved by the introduction of mechanically activated particles as fillers. However, the suggested approach has its limits, which should be taken into account in possible applications of these materials.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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