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Quasi-static and dynamic piezoelectric d_{33} coefficients of irradiation cross-linked polypropylene ferroelectrets

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Abstract Irradiation cross-linked polypropylene (IXPP) foams show high piezoelectric activity after proper hot-pressing treatment and corona charging. Quasi-static piezoelectric d_{33} coefficients around 400 pC/N were measured by means of the direct piezoelectric effect. Dynamic values of the inverse piezoelectric d_{33} coefficients, determined from the dielectric resonance spectra at 220 kHz, is about 68% of the quasi-static d_{33} values. The difference between the quasi-static and the dynamic values of d_{33} is probably due to the enhancement of Young's modulus of IXPP with increasing frequency. The piezoelectric d_{33} coefficients are slightly dependent on the applied pressure in the range up to 50 kPa. The d_{33}-values decrease by 70% when the samples are exposed to 90 °C for 1 day; and a pre-aging treatment improves the thermal stability of the d_{33} coefficients.

Introduction

Foams based on non-polar polymers receive more and more attention from science researchers and technology engineers because some charged foams show very strong piezoelectric activity, compared to the traditional piezoelectric polymers such as poly(vinylindene fluoride) (PVDF) and its copolymers. Opposite sign charges, generated by tiny dielectric barrier microdischarges in the voids, are deposited on the upper and lower surfaces of the voids, respectively, during electrical charging to form macroscopic dipoles. Such charged polymers show large piezoelectric d_{33} coefficients which are by a factor of 20 or more higher than those of piezoelectric PVDF or its copolymers. Since the charged polymer foams have the characteristics of ferroelectric materials (such as a hysteresis loop) and space-charge electrets (for example, surplus charges), they are now named as ferroelectrets [1–3].

Cellular polypropylene (PP) is the polymer foam extensively investigated and commercially available at present [2, 4–9]. Other void or porous polymers, such as cycloolefine copolymers (COC) [10, 11], polyethylene-terephalate (PET) [12], polyethylene-naphthalate (PEN) [13], and fluorocarbon polymers [14–16] are relatively new members of the ferroelectret family developed in some laboratories. In addition to these studies, some applications of ferroelectrets were also reported [3, 17, 18].

Very recently some original experimental results about irradiation cross-linked PP (IXPP) ferroelectrets were also reported by us [19]. In the present paper, extended research work on this new material, related to the influence of density on piezoelectric activity and the comparison between quasi-static and dynamic values of piezoelectric d_{33} coefficient will be reported and discussed.

Experimental procedures

Electron beam irradiated cross-linked polypropylene foam sheet

Commercial electron beam IXPP foam sheets, with a thickness of 1.5 mm and an area density of 0.067 kg/m^2 (supplied by Shanghai Bozhi Materials Company), were selected for the present study. Figure 1 shows a scanning electron microscopy (SEM) picture of the cross section of such a foam sheet. This picture indicates that the foam is

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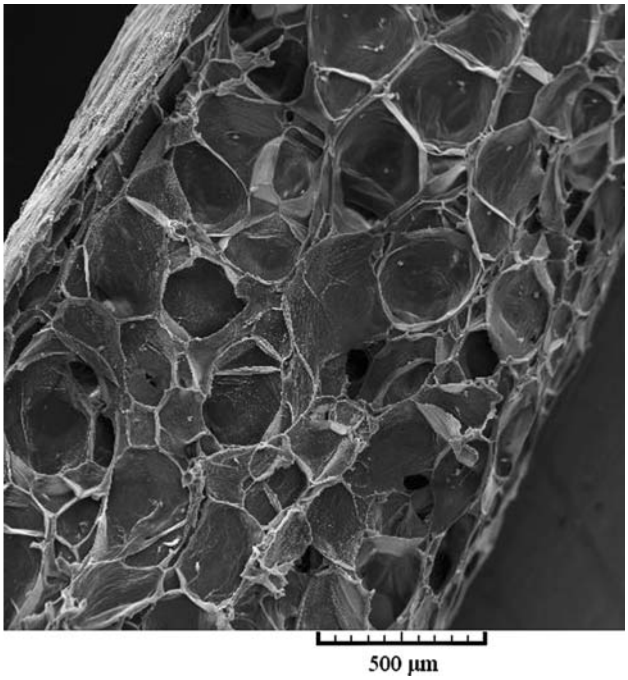

Fig. 1 Scanning electron microscopy image of a commercially available IXPP foam sheet (area density of 0.067 kg/m^2)

built up from a large number of round or hexahedron voids. The voids are closed and their diameters are up to 300 μm, while the thickness of the void-walls is about 2 μm.

Since the piezoelectric activity of voided ferroelectrets is related to Young's modulus and its thermal stability, the dynamic compressive Young's modulus in the thickness direction for IXPP foam sheets was measured by a dynamic mechanical analyzer (DMA) (Netzsch DMA 242). The results are shown in Fig. 2. This figure indicates that the compressive Young's modulus is strongly dependent on the temperature and frequency. At the measurement frequency of 5.0 Hz Young's modulus decreases from 2.5 MPa to

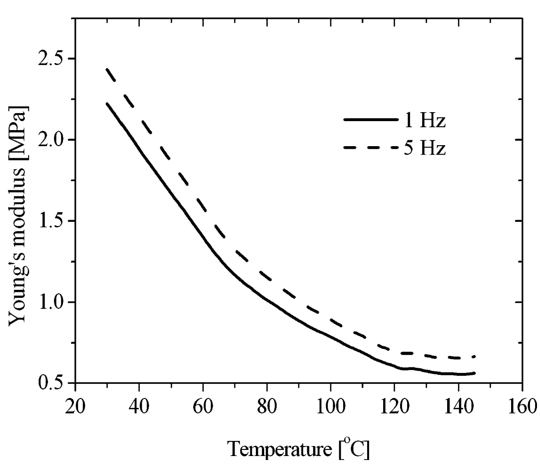

Fig. 2 Thermally dynamic mechanical analyze spectra of IXPP foam sheet with frequency as parameter

0.7 MPa when the temperature increases from 25 °C to 140 °C. At the temperature of 25 °C, the values of 2.2 and 2.5 MPa measured at 1.0 and 5.0 Hz, respectively, show the frequency dependence of Young's modulus for void PP [9].

The gel fraction (ϕ_{gel}) is one of the important parameters characterizing the network polymers. Thus, the gel fraction of the present IXPP foam sheet was determined by using the following procedure [19]. A pre-weighed sample of mass m_0 was exposed to boiling *p*-xylene for 6 h, which extracted the loose chains (sol fraction). Then the remaining undissolved fraction of the sample was dried for 24 h under vacuum. Finally, the dried specimen was weighed (m_1). The gel fraction can then be calculated by

$$\phi_{gel} = \frac{m_1}{m_0} \times 100\% \quad (1)$$

For the presently investigated IXPP foam, the calculated gel fraction is 60.2%. The gel fraction is an important quantity for the piezoelectric properties of the ferroelectret based on IXPP since our primary experimental results show that the thermal stability of charges in IXPP seems dependent on its gel fraction. For the IXPP films positively corona charged at RT, the retained surface potential is around 76% of the initial value after the period of annealing time of 1280 min at 120 °C and no shape change of the samples is observed. The thermally stimulated discharge (TSD) current spectra for the samples aged at elevated temperature prior to the measurement indicate a main current peak at the temperature of around 180 °C. However, no current peak at so high temperature is observed in linear PP electrets earlier. Therefore, the IXPP films with the gel fraction of 60.2% in present study shows improved thermal stability compared to the linear PP films. Studies are under research to further investigate the relation between the charge storage stability and the gel fraction in IXPP electrets.

Hot-pressing process

The commercial foam sheets were clipped between two metal plates, and then hot-pressed by a platen vulcanizing press machine for 10 min at a temperature of 100 °C and a pressure of 15 MPa. Thereafter the samples, together with the clipping plates, were cooled down by using a cold press machine. The thickness of the pressed films was controlled by using a spacer between the metal plates during hot-pressing. The dimension of the voids in the thickness direction of the film is very important for obtaining optimal piezoelectric activity because the breakdown of electric field according to the Paschen curve can be reached only if these voids have proper thickness dimensions [1, 6, 8]. In the present study, the typical thickness value of the hot-pressed IXPP with high piezoelectric d_{33} coefficient is around

120 μm. However, the thicknesses of the hot-pressed IXPP films were controlled in the range of 73–1500 μm in order to investigate the relationship between the piezoelectric d_{33} coefficient and the thickness of the films.

Corona charging and metallization

After the hot-pressing procedure, the samples were charged with a corona method, utilizing a discharge generated between the two-electrode corona setup with a needle voltage of −32 kV. For some experiments in the present study, a grid voltage was used to control the surface potential of the films. The charging time was selected as 60 s. After corona charging, the samples were metallized on both surfaces by aluminum evaporation.

The electric field strength E_g in the voids during corona charging can be estimated from the surface potential V_s and the structure of the sample. Assuming a layered structure of n_p layers of solid IXPP and n_g layers of air gaps [20, 21], E_g can be described by a two-layers system consisting of one solid IXPP layer and one air gap. Taking Gauss law and Kirchhoff's second law, one can obtain the following:

$$E_g = \frac{V_s \varepsilon_{pr}}{\varepsilon_{pr} s_g + \varepsilon_{gr} s_p} \quad (2)$$

where, ε_{pr} and ε_{gr} are the relative permittivities of IXPP and the air gap, respectively, s_p and s_g are the total thickness of IXPP and the air gap, respectively. The total thickness of the solid IXPP and the air gap for a hot-pressed IXPP film can be determined from the thickness and the area density of the film and the bulk density of solid IXPP. For a 120 μm thick hot-pressed IXPP film, the total thickness of the solid IXPP and the air gap are 73 and 47 μm, respectively, taking the area density of 0.067 kg/m^2 and the bulk density of solid IXPP of 910 kg/m^3. Taking $V_s = 4000$ V as the surface potential during corona charging, with $\varepsilon_{pr} = 2.3$ and $\varepsilon_{gr} = 1$ the relative permittivities of IXPP and air, respectively, the field strength in the voids can be calculated as $E_g = (4000 \times 2.3)/(2.3 \times 47 + 73) =$ 50.8 MV/m.

Measurement of quasi-static d_{33} coefficients

A quasi-static method was used in this study for determining the d_{33} coefficients via the direct piezoelectric effect. The following equation describes the relation between the d_{33} coefficient and the induced charges on the electrode under the applied mechanical force to the sample [14, 22]:

$$d_{33} = \frac{Q}{F} = \frac{\sigma}{P} \quad (3)$$

where, Q and F are the induced charge and the applied force, respectively; and σ and P are the corresponding charge density and pressure, respectively. In order to eliminate the uncontrollable effects of applying the force, a static force was firstly applied to the sample for a relatively long time, and then the charge induced over a period of 10 s was recorded after the force was released from the sample.

Determination of dynamic piezoelectricity from dielectric resonance spectra

Dielectric spectroscopy is an extensively used research tool for the investigation of molecular dipole relaxations, determination of acoustic and elastic material parameters, piezoelectric coupling factors, and so on [23–26]. Recently, the measurement of dielectric resonance spectra via the inverse piezoelectric effect became one of the methods to determine the dynamic piezoelectric coefficients and Young's modulus for ferroelectrets [27, 28]. Although the electromechanical coupling factors and mechanical loss for polymers is high in comparison to ferroelectric ceramics, this method is verified reliable in the literatures [27–31]. In the present study, the frequency spectra of the complex capacitance $\tilde{C}(\omega)$ for hot-pressed IXPP samples with a diameter of 25 mm were measured by a precision impedance analyzer (Agilent 4294A). Since the thickness of the hot-pressed IXPP sample, used for these measurements, is around 100 μm, which is much smaller than the diameter of the samples, the resonance or anti-resonance frequency of the thickness extension mode appears at a frequency which is at least an order of magnitude larger than that of the length and width extension modes. In the free boundary condition, the compressive Young's modulus Y in the thickness direction can be determined by [27, 28]

$$Y = 4 f_a^2 h \rho_s \quad (4)$$

where, f_a, h, and ρ_s are the anti-resonance frequency determined from dielectric spectra, the thickness of the sample, and the area density of the sample, respectively. The dynamic piezoelectric d_{33} coefficient, determined by the inverse piezoelectric effect, can be calculated by the following two equations [25, 26]:

$$\tilde{C}(\omega) = \frac{C_0}{1 - k_t \frac{\tan(\omega/4f_a)}{\omega/4f_a}} - iC_{loss} \quad (5)$$

and

$$k_t = d_{33}\sqrt{\frac{Y}{\varepsilon_0 \varepsilon_r}} \quad (6)$$

where, C_0, k_t, f_a, C_{loss}, ε_0, and ε_r are the quasi-static capacitance, the electromechanical coupling factor, the anti-resonance frequency, the capacitor loss, the vacuum dielectric constant, and the relative dielectric constant, respectively. In order to obtain the most accurate parameters from the measured dielectric spectra, a non-linear least squares regression technique was performed on the experimental data [28].

Experimental results and discussion

Microstructure of irradiation cross-linked polypropylene after hot-pressing process

Figure 3 shows the SEM photographs of the cross-sections for two hot-pressed films with different thicknesses. Compared with the microstructure of the IXPP foam sheet shown in Fig. 1, the inner voids of the hot-pressed films are collapsed in the thickness direction and their shapes vary with the thickness of the film. The inner voids get flatter with the reduction of film thickness, while there is no observable change of dimension in lateral direction. In addition, many rumples appear in the hot-pressed film with thinner thickness. Such a rumple structure is different from that of cellular PP ferroelectrets, where the shape of the inner voids is normally "lens-like". Since the thickness reduction of the samples is significant, while almost no change of the dimensions in lateral direction is observed after the hot-pressing procedure, the area density of the samples after hot-pressing keeps a constant of 0.067 kg/m^2, while the volume density of the hot-pressed IXPP films is dependent on their thicknesses. The relative density of such hot-pressed IXPP films can be calculated by the thickness, area density, and the volume density of compact IXPP. When taking the volume density of 910 kg/m^3 for compact IXPP, the calculated relative densities of the hot-pressed films shown in Fig. 3a and b are 0.43 and 0.60, respectively.

Influence of relative density on d_{33} coefficients

Results for the quasi-static d_{33} coefficient of IXPP samples are plotted in Fig. 4 as a function of the relative sample density. This figure indicates that the d_{33} coefficients are enhanced with the increase of the relative density to the range from 0.05 to 0.7, while the value of d_{33} decreases to zero when the relative density is close to 1. A maximum d_{33} coefficient of 400 pC/N is achieved. These results are expected because electric charging of the voids is necessary to obtain piezoelectricity for cellular polymers. For the samples with large thickness, corresponding to the samples with small relative densities, the void can be hardly charged because, according to the Paschen curve, a very large air breakdown voltage is needed. With the increase of relative density, the dimension of the inner voids decreases in the film thickness direction, the air breakdown electric field of the voids can be achieved during corona charging without applying an excessively large voltage. Thus, the charging of the films is enhanced with the reduction of void dimensions. However, if the void dimensions are too small, a higher electric field strength is necessary again to obtain

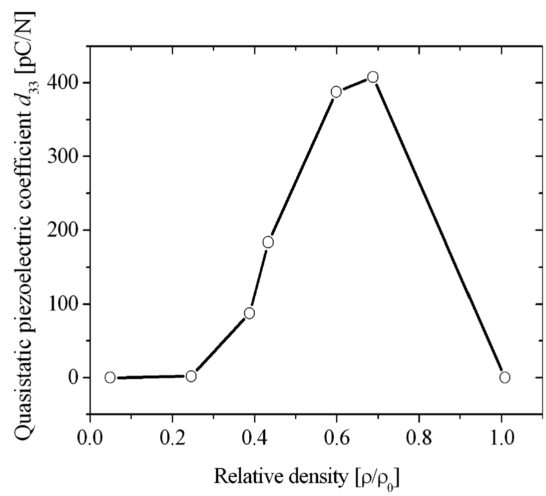

Fig. 4 Quasi-static piezoelectric d_{33} coefficient as a function of the relative volume density for hot-pressed IXPP films (area density of 0.067 kg/m^2). The measured thicknesses of the hot-pressed samples shown in this figure are 1500, 300, 190, 170, 123, 107, and 73 μm, respectively

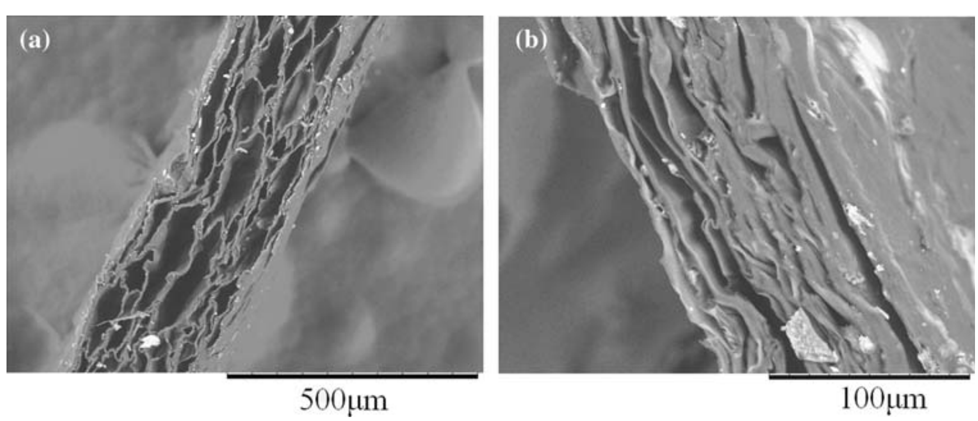

Fig. 3 Scanning electron microscopy images of two hot-pressed IXPP films with different thicknesses (area density of 0.067 kg/m^2)

the air breakdown. Under the present charging conditions, such samples cannot be charged well. For the sample with relative density of 1, there is no void structure and therefore no piezoelectricity at all.

Thermal stability of piezoelectric activity

The isothermal decay of the piezoelectric d_{33} coefficient of IXPP with time at 90 °C was measured to investigate the thermal stability of the samples. Figure 5 shows the decay of the normalized d_{33} coefficients for the samples pre-annealed at 100 °C for various periods of time. For the sample without any treatment, the remaining d_{33} coefficients after 1 day are around 30%, which indicates that the thermal stability of the new IXPP is better than that of PP ferroelectrets, where only 17% of the d_{33} coefficients can be retained under the same conditions [9, 14]. Figure 5 also shows that a pre-annealing treatment of the samples at elevated temperature will even improve the thermal stability of the d_{33} coefficients. After 1 day, the remaining fractions are 35% and 65% of the initial values for the samples annealed at 100 °C for 30 and 60 min prior to the isothermal decay measurements, respectively.

Applied pressure dependence of d_{33} coefficients

The magnitude and the linearity of the piezoelectric coefficients under an applied pressure are of importance in applications of ferroelectret materials. Moreover, information on the structure of the air voids in the films may be obtained by analyzing the dependence of the d_{33} coefficients of ferroelectrets on applied pressure [14]. One of the important aspects of the new IXPP films is the improved pressure dependence of the piezoelectric activity. Results for the quasi-static d_{33} coefficients of IXPP samples, shown in Fig. 6, indicate that the d_{33} coefficients are slightly

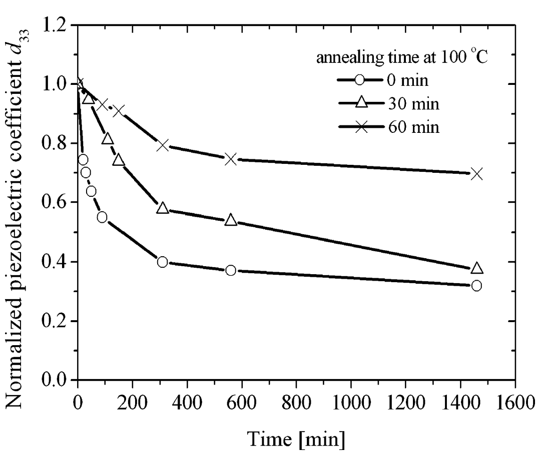

Fig. 5 Decay of quasi-static d_{33} coefficient of hot-pressed IXPP samples at the temperature of 90 °C after pre-aging treatment

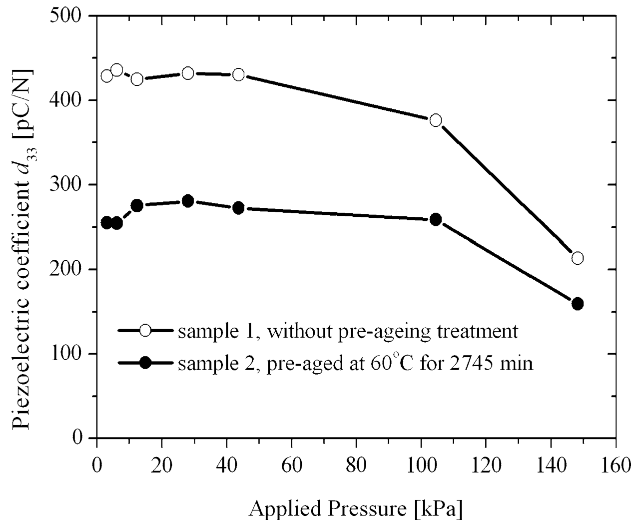

Fig. 6 Pressure dependence of d_{33} coefficient for hot-pressed IXPP samples

pressure dependent over the range from 1.6 to 50 kPa for samples not pre-aged. The change of the d_{33} values is less than 5% in this range. However, there is a significant decrease of the piezoelectric coefficient when the pressure exceeds 50 kPa for this sample. The pre-aged sample, however, shows improved linearity over the larger range from 1.6 to 100 kPa. Also, compared to commercial and modified PP films [8, 32], the presently studied IXPP films have improved linearity of the d_{33} coefficient in this pressure range. Such pressure-independence of the d_{33} coefficients for the IXPP films is probably due to the specific microstructure of the films as shown in Fig. 3, since the shape of the air voids is not "lens-like" as in the commercial PP films. How the microstructure of the void film leads to the applied pressure dependence of d_{33} coefficients is not yet understood well, and has to be investigated further. A potential approach to reveal this relation is to prepare the ferroelectrets with an ordered and artificially controllable void structure. Considering commercial production, the hot-pressing process is a very simple and readily controllable method compared to the gas-diffusion expansion procedure.

Comparison of d_{33} values determined by dielectric resonance spectra and quasi-static method

There are several techniques, such as the acoustic method, the measurement of the dielectric spectrum, and the measurement of sample-surface displacements by interferometry, to investigate dynamic piezoelectricity of ferroelectrets. Measurement of the frequency spectrum of the complex capacitance in a thickness extension (TE) resonance mode was first performed on PP ferroelectret film, developed in Finland, to determine the dynamic d_{33}

coefficient near the resonance frequency [27]. In their research, they found the dynamic d_{33} coefficient for PP ferroelectret film so determined to be much smaller than the d_{33} value measured by the quasi-static method. The dynamic value of d_{33} was around 63% of the quasi-static value. This was explained by the enhancement of Young's modulus of PP material with increasing frequency. In the present study, the measurements of the complex capacitance spectra over frequency were performed in order to compare the dynamic and quasi-static d_{33} values of such hot-pressed IXPP films. Figure 7 shows the frequency spectrum of the complex capacitance (real part) for a hot-pressed IXPP sample in the vicinity of the resonance frequency around 220 kHz. For obtaining accurate results, a least squares fit data analysis was performed on the experimental data as shown in Fig. 7. According to Eqs. 4–6, the calculated d_{33} coefficient, Young's modulus, and the electromechanical coupling factor for such a sample are 216 pC/N, 1.3 MPa, and 0.06, respectively. Considering the d_{33} value of 320 pC/N determined by the quasi-static method at the applied pressure of 2.0 kPa for the same sample, the dynamic d_{33} value is about 68% of the quasi-static value. This is comparable to the results for the PP ferroelectret film reported in [27]. In addition, the electromechanical coupling factor of hot-pressed IXPP film is the same as the value of 0.06 for the PP film studied in the same reference.

Conclusions

In conclusion, commercial IXPP foam can be made piezoelectric by corona charging after hot-pressing treatment.

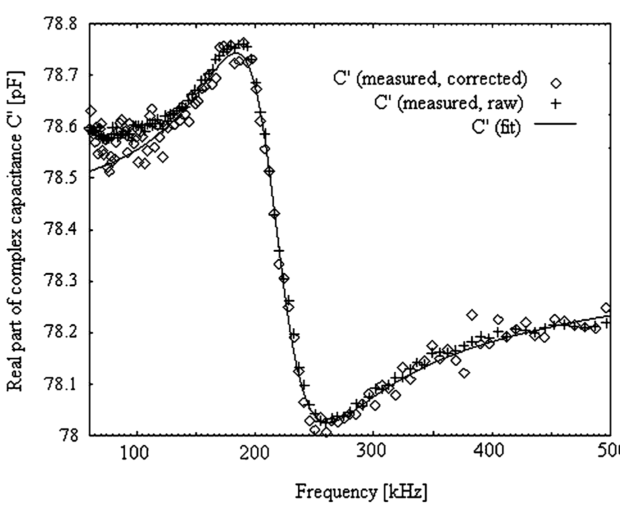

Fig. 7 Experimental and fitted dielectric spectra of a hot-pressed IXPP sample. This sample was corona charged by using a grid voltage of −4500 V. The quasi-static and determined dynamic piezoelectric d_{33} coefficients are 320 and 216 pC/N, respectively

For the samples corona charged at room temperature, d_{33} coefficients up to 400 pC/N are obtained. The piezoelectric d_{33} coefficients are only slightly dependent on the applied pressure in a large range up to 50 kPa. The d_{33}-values decrease to 30% when the samples are exposed to 90 °C for 1 day, which is better than linear PP films, where only 17% of the piezoelectricity can be retained under the same conditions. For the samples annealed at 100 °C for 30 and 60 min prior to the isothermal decay measurements, the remaining d_{33} can be improved to 35% and 65%, respectively, of the initial values. The dynamic d_{33} coefficient for hot-pressed IXPP, determined from the dielectric spectrum at 220 kHz, is around 68% of the value obtained by the quasi-static method, which is comparable to the results from another study on PP film reported in the literature.

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