

Structural impact on piezoelectricity in PVDF and P(VDF-TrFE) thin films

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Abstract PVDF and its mostly used copolymer P(VDF-TrFE) are known to possess piezoelectric properties which strongly vary with processing conditions. As the final target of processing ultimately is the structure of the polymer, establishing a more detailed link between structure and properties would ease both the understanding and the practical usage of films piezoelectric activity. In spite of a number of thorough studies exploiting the nature of piezoelectricity in PVDF, available data does not generally exhibit reliable level of consistency and, in some cases, elements of contradiction are observed. Making no claim to be exhaustive in this vast area, we present a survey and discuss on a number of results both available and obtained by ourselves in an effort to assist to better interpretation and further progress in the field.

1 Introduction

The use of piezoelectric polymer films and layers for sensing and ultrasonic transduction purposes has been known for several decades [1]. Their unique inherent properties of high mechanical flexibility, low dielectric constant, and low elastic stiffness result in high voltage sensitivity, low acoustic impedance, broadband acoustic performance, and availability in large areas that would

be difficult to achieve by conventional materials. Among these polymers, poled and elongated films of piezoelectric polyvinylidene fluoride (PVDF) have attracted major interest mainly due to their relatively large piezoelectric response. Ever since the discovery of the piezoelectric effect in PVDF [2], numerous efforts toward improving the electromechanical coupling have been done. Generally speaking, the obtained results strongly depended on experimental growth and processing conditions, and often lead to incoherent, if not contradictory, conclusions. One common example is the copolymer of PVDF with trifluoroethylene, P(VDF-TrFE), which might acquire a coupling as large as 0.3 but at the expense of increased brittleness [3]. Another example is the still unclear behavior of the shear piezoelectric response of the films that impedes their commercial use in shear wave transducers and surface acoustic wave devices (see for example our earlier studies in refs. [4, 5]). The present study is an effort to shed more light on consequences of the processing options for the final performance of the transducer by shortly reviewing already obtained results and presenting our own results in this area.

We consider it proper to divide the methods to search for increased piezoelectricity in PVDF and P(VDF-TrFE) into three principal groups: (1) direct methods that rely on introduction of piezoelectric nanoparticles in the polymer matrix; (2) indirect methods that aim at improving the piezoelectricity via its connection to other polymer parameters such as degree of crystallinity, nanoparticle content, or polymorphic transition; and (3) geometrical methods that affect the lamellar morphology by the shape of the film and its orientation with respect to the crystallographic axes. Let us consider these in more detail in the discussion to follow.

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2 PVDF piezoelectric nanocomposites

Nanocomposite polymers have attracted serious interest in the last decade, either with conventional thermoplastics like PMMA [6], conventional adhesives like epoxy [7], or technical polymers like piezoelectric ones. This interest is stimulated in fundamental physics by the phenomena that may occur during the interaction between the nanoparticles and the organic matrix [8], but of course also by the new or enhanced functional properties that consequently appear. It has been shown in particular that polymer composites reinforced with a low content of effective fillers can possess significantly improved mechanical, thermal, and electrical properties as compared to the pure polymer matrix. Moreover, these improvements are achieved through conventional processing techniques without detrimental effects on the processability of the matrix. It is intuitive that the addition of strong piezoelectric powders with piezoelectric coefficients stronger than those of the matrix would enhance the piezoelectric properties of the nanocomposite in comparison with the pure polymer. This approach has been applied to PVDF in a number of studies that, sometimes, offer divergent views on the obtained features. An extended experimental analysis can be found in [9] where the piezoelectric longitudinal strain constant d_{33} was enhanced in PVDF/PZT and P(VDF-TrFE)/PZT composites compared to commercial pure matrix values. However, this increase is lower than expected, in contrast to the dielectric constant enhancement. An explanation based on a mechanical shorting effect of the polymer matrix that absorbs almost completely the applied force has been brought forward. This explanation is opposite to another explanation given earlier in [10] which totally ascribes the effect to the action of the ceramic filler. As a whole, the validity of each of these arguments seems not convincing. According to comments in other studies, the piezoelectric activity of the P(VDF-TrFE)/PZT composite strongly depends on the way of poling the samples [11, 12]. The fact that the longitudinal piezoelectric constant has opposite signs in the two phases requires that their permanent polarizations should be of opposite directions. This, of course, needs a two-step polarization. For example, in the hydrophone application described in [11], the ceramics is poled at high temperatures (above the Curie temperature of the copolymer) first and then the polymer matrix is poled at room temperature. The resulting pressure sensitivity of the composite is found about twice that of the copolymer. Neither of these studied elements has, however, been tested in excitation mode as ultrasonic high frequency transducer. As clear from the following discussion, there can be a marked difference between the activity of a piezoelectric element in excitation and reception (including static) mode.

3 Nanocomposites and the effect of crystallinity

It has been generally accepted that the increased degree of crystallinity in a piezoelectric polymer leads to improved piezoelectric properties. This understanding relates to the fact that piezoelectricity comes from the crystallites while the amorphous regions cannot, except for small parts adjacent to crystallites, have a notable contribution. The degree of crystallinity has been known to strongly depend on the polymer processing conditions. Addition of TrFE leads to the formation of the ferroelectric phase due to steric hindrance within the molecular chain and to an improved piezoelectricity largely attributed to the fact that this copolymer can be crystallized to extremely high values [3]. In our present opinion, however, the weight of this factor has been overestimated in not only piezoelectricity. A number of studies have been dedicated to modifying the elastic, dielectric, and electric conductivity properties by introducing various types of fillers in the matrix, similar to what has been discussed in the previous section. The fillers are in most cases crystal particles, and it could be expected that the overall content of the crystal phase will increase. However, no such firm relation can be established for most fillers and discussed properties. For example, introduction of Au nanowires and nanoparticles in P(VDF-TrFE) leads to considerable improvement in electrical conductivity, accompanied, on the other hand, with a net decrease in crystallinity [13]. In this case, it seems like the presence of the nanoparticles has an adverse effect on nucleation in the polymer matrix, thus limiting the formation of polymer crystallites. It has been shown in [13] that the crystal phase can even be completely destroyed above some critical filler concentration. So, it is not clear to what extent the above-mentioned piezoelectricity improvement in the P(VDF-TrFE)/PZT composites is related to transformation of the polymer matrix.

In view of the lack of systematic data on the filler effect on crystallinity in P(VDF-TrFE), we have carried out a study on a number of composites at various filler types and concentrations. Commercial nanoparticles of Al_2O_3 (Aeroxide AluC[®], Degussa, Germany) and ZnO (NanoGard[®]), with mean diameters of 20, 60, and 90 nm and with different coatings denoted C1 (NanoTek[®], hydrophobic non-polar organo-silane coated) and C2 (NanoGard[®], hydrophobic polar organo-silane coated) and homemade nanoparticles of lithium niobate (LN) [14] and iron iodate (IF) [15] have been used. The primary particle size (13 nm for Al_2O_3 , and for ZnO nanoparticles 20, 60, or 90 nm) was determined from transmission electron microscopy images. The copolymer of vinylidene difluoride and trifluoroethylene (P(VDF-TrFE) 70/30 mol %), $M_w = 1,370,000$ from Piezotech S.A.S. (France) was dissolved in methyl ethyl ketone (MEK) (Acros Organics) by stirring at 80 °C

Table 1 Degree of crystallinity of P(VDF-TrFE) nanocomposite films

Weight %	Nanofillers									
	ZnOC1	ZnOC2	ZnO20	ZnO60	ZnO90	IF	LN1	LN2	Al ₂ O ₃	
0	56	56	56	56	56	56	56	56	56	56
1	56	52	54	58	56	60	44	59	55	
2	–	–	–	–	–	–	–	–	–	54
3	53	55	58	57	61	62	52	–	53	
5	56	56	58	57	56	47	48	61	58	
7	–	–	–	–	–	–	–	–	57	
10	58	57	57	61	63	–	57	67	56	

to prepare a 14 wt% solution. The dispersion of nanoparticles in solutions was carried out with a Transducer Digital Sonifier® Model 450 (Branson Ultrasonics Corporation, USA). Its maximum power input and frequency were, respectively, 400 W and 20 kHz. The vessel of suspension was cooled using an ice-water bath [16].

The solutions were casted onto a clean glass plate and dried in air at room temperature to get free-standing films 20 × 20 cm² with thickness around 30 ± 2 μm. Then, the films were annealed at about 140 °C in an oven [17]. For piezoelectric properties, nanocomposite films were polarized by corona discharge using a homemade setup with a voltage of 14 kV for 5 min. The degree of crystallinity has been estimated in each case by differential scanning calorimetry (DSC 204, NETZSCH) method (Table 1; Figs. 1, 2, 3).

The conclusion to be drawn from the above data is that no firm relation of proportionality can be established between filler concentration and degree of crystallinity. Even fillers of the same type seem to produce opposite deviations from the crystallinity of the pure material. However, because of the accuracy of these measurements (±3 %), we can only focus our attention on the largest variations. For the main part of the fillers, no significant

change in the crystallinity can be observed. Anyway, we can notice an increase (11 %) for LN2 at 10 % and a clear decrease for IF at 5 % (see Figs. 2, 3). Although it is difficult to enter in detail the growth kinetics of studied specimens we believe that several phenomena could explain these results. The interaction of nanoparticles with the matrix can lead to decrease in crystallinity by steric effects that prevent the polymer to crystallize, and this is in accordance with matrix disturbance by IF nanoparticles which explained the impossibility to obtain sample with 10 W%. But on the other hand, these nanoparticles can act as nucleation centers and give rise to smaller crystallites with higher density. This could explain why, by adding nanoparticles with piezoelectric coefficient comparable to the matrix one, the properties of the nanocomposite are higher than a simple melt law, starting from each component.

We next concentrate on the results of our study on the piezoelectric response of two of the composites given in Table 1. One is the P(VDF-TrFE)/IF-3 nanocomposite that exhibits one of the highest crystallinities. Fe(IO₃)₃ has been known as a single crystal from space group P63 that can be produced in nanopowder form [18]. Most interest in this material relates to its optical nonlinear properties but what

Fig. 1 Degree of crystallinity of P(VDF-TrFE) nanocomposite films versus weight percentage of nanofillers

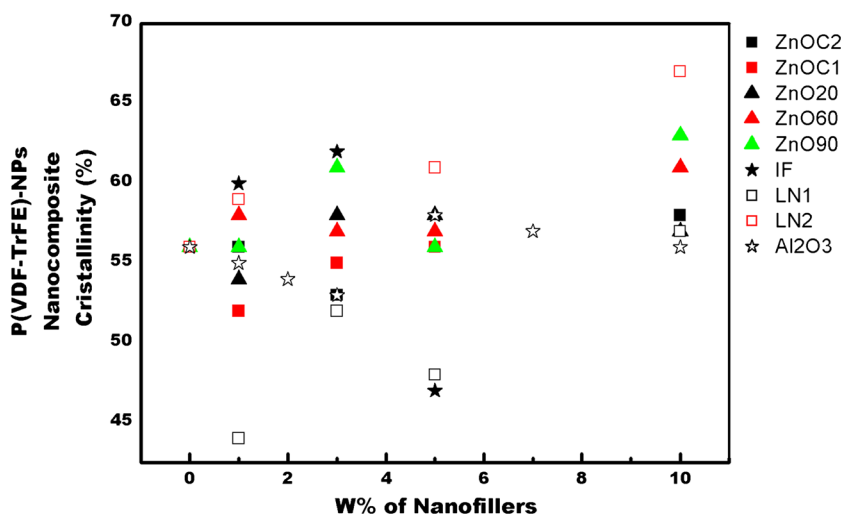


Fig. 2 Degree of crystallinity of P(VDF-TrFE)/LN1, P(VDF-TrFE)/LN2, P(VDF-TrFE)/Al₂O₃ nanocomposite films versus weight percentage of nanofillers

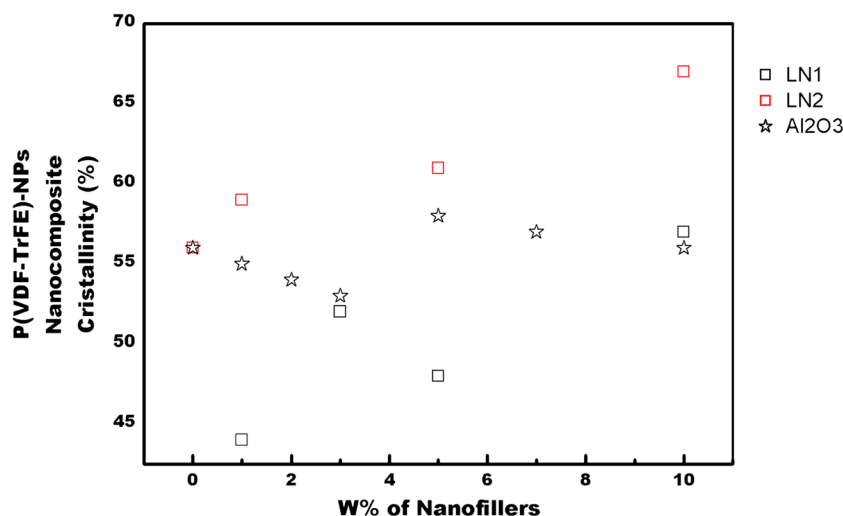
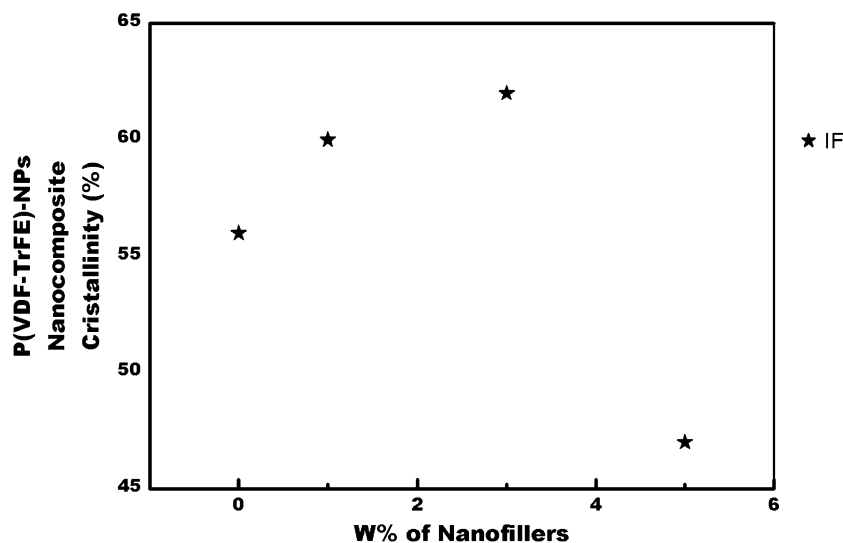


Fig. 3 Degree of crystallinity of P(VDF-TrFE)/IF nanocomposite films versus weight percentage of nanofillers



we wanted to see was its impact on the mechanical and piezoelectrical properties of the nanocomposite film. We have already shown in a previous study that the elastic constant can be increased up to 20 % with 10 wt% of nanofillers [17]. In measurements, we adhered to a modified version of the experimental scheme already applied in our previous study of the shear piezoelectricity in PVDF [4], Fig. 4.

The acoustic power generated in the loading sample is assessed through acoustooptic diffraction. For this purpose, a 12-mW (650 nm) laser beam is shined through the area of a transparent solid sample where the acoustic wave is expected to travel and the intensity of the first Raman–Nath diffraction order is measured. Because the efficiency of the acoustooptic interaction is weak overall, particularly for shear waves, we fed the output of a fast laser diode located at the diffraction order spot to a preamplifier and then a

lock-in amplifier synchronized with a low frequency modulation (generator 2) of the resonant signal activating the transducer. This latter signal comes from a signal generator (generator 1), followed by a 40-dB linear power amplifier (not shown in the figure) in cases where the efficiency of diffraction is not sufficient. In these experiments, the input voltage amplitude was of the order of tens of V while the output of the lock-in amplifier was in the sub-mV range. The laser diode is mounted on a precision table that enables two-dimensional scanning in a plane perpendicular to the light direction to detect the position of diffraction orders. Each studied film has been provided with a pair of electrodes on both surfaces which have further been shaped by etching (split electrode configuration) to apply electric field along two directions—the thickness (normal) and parallel to the surface (lateral). Accordingly, three configuration types have been exploited

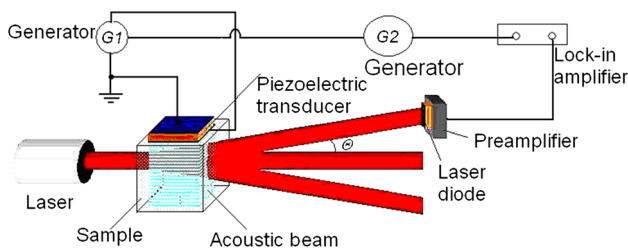


Fig. 4 Experimental setup for acousto-optic studies of piezoelectric polymer foils

as shown in Fig. 5—lateral (a), normal (b), and interdigital (IDT) (c) that combines the lateral field with a small normal component due to the curving of the intensity lines. In configuration (b), the standard thickness extensional resonant mode is excited through the piezoelectric constant d_{33} (X_3 is the polarization axis in thickness direction) which would couple to a longitudinal propagating wave in the sample. In configuration (a), the thickness shear mode of the film is excited through the strain piezoelectric constants d_{15} or d_{24} resulting in a shear propagating wave in the sample. In configuration (c), a combined effect of these two should be expected. The width of the electrode gap is about 1 mm.

The films have been firmly attached by epoxy glue to loading samples in the form of transparent parallelepipeds through which the narrow laser beam has been passed. The

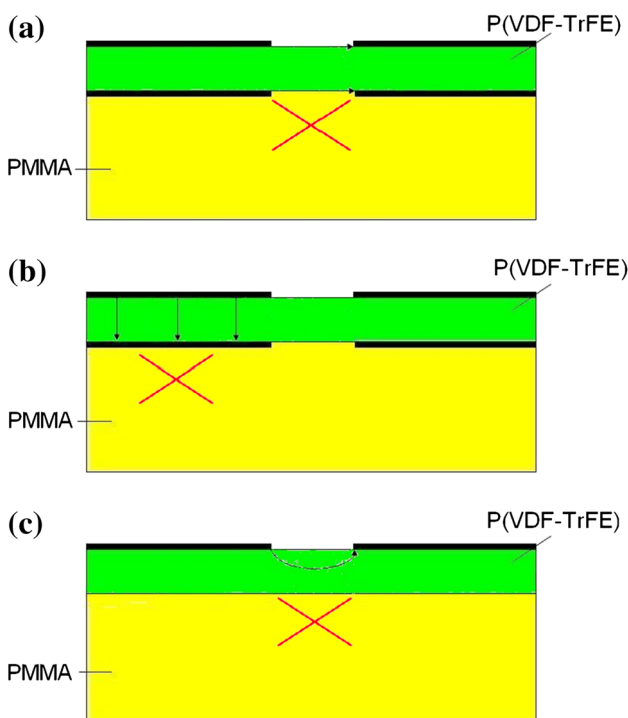


Fig. 5 Lateral (a), normal (b), and mixed (c) electric field configurations

red cross in the figures indicates the crossing point in the zone where acoustic power is expected. The loads used were of PMMA with a view of achieving improved acoustic impedance matching conditions. In each experiment, the frequency has been swept to find maximum reading of the detector at each position in the plane of scan. The piezoelectric strain constant value measured at 100 Hz by using a Berlincourt piezometer (Channel Products Inc., Chesterland, Ohio) is also given. The results obtained in configuration (b) (longitudinal wave excitation) are shown in Table 2.

The inclusion of nanoparticles does not lead to improvement in the action of the films as longitudinal ultrasonic transducers. Both nanocomposites show lower efficiency compared to the pure material. The efficiency of IF-3 is extremely suppressed despite the slight increase in the piezoelectric constant. The resonant frequency of the pure film reveals a $\lambda/2$ resonance, as expected from the acoustic impedance of P(VDF-TrFE) being slightly larger than that of PMMA. The resonances of the composites are in the region of, but not exactly, $\lambda/4$. The larger deviation is again with IF 3 %.

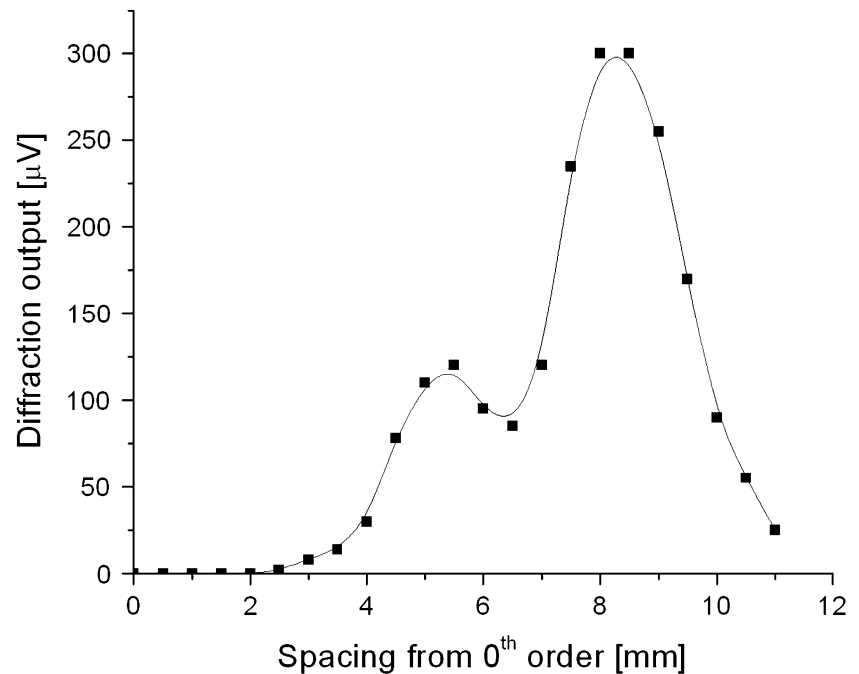
We next proceed with investigating the composites in the mixed configuration (c). The small normal component of the electric field provides a signal from the longitudinal resonance that, being spatially separated, can ease the unambiguous detection of the presence of a shear resonance provided by the lateral electric component. Figure 6 shows the diffraction output of the IF-3 sample at various distances from the zero's order at frequency 9 MHz. Two distinct spots at 5.6 and 8.1 mm are detected indicative of a longitudinal and a shear wave generated simultaneously in the load. The ratio of the two distances roughly corresponds to that of the two velocities in PMMA as diffraction rule predicts. A precise assessment of the velocities is not possible because of the overlap of the frequency bands of the two resonances. The result of the same experiment with the pure sample and that with ZnO was negative in that no shear spot additive to the longitudinal one was detected.

Table 2 Longitudinal diffraction output of P(VDF-TrFE) nanocomposite films

Filler weight %	Film thickness (μm)	Frequency of maximum diffraction intensity (MHz)	Input (V)	Lock-in output (μV)	$ d_{33} $ ($\text{pC} \cdot \text{N}^{-1}$)
None	65	17	10	1,000	20
ZnOC1 3 %	27	17	20	908	20
IF 3 %	30	13	20	76	22

Transducers of equal areas

Fig. 6 Variation of diffraction output with spacing from zeroth order for IF-3 sample. Frequency 9 MHz



The obtained results deny a possible decisive role of the crystallinity degree in the piezoelectric activity of P(VDF-TrFE). Instead, it reveals a serious effect on its mechanical properties. First, this discussion needs a short reference to previous knowledge on the shear piezoelectricity of PVDF. Early theoretical calculations predict three large strain constants: $d_{33} = -2.5 \times 10^{-11}$ C/N, $d_{24} = -0.4 \times 10^{-11}$ C/N, and $d_{15} = -3 \times 10^{-11}$ C/N, associated with longitudinal thickness mode and two shear thickness modes, respectively [19]. Contrary to expectations, however, the role played by the three modes in ultrasonic applications has remained markedly unequal through years. If the longitudinal mode has been largely applied in a multitude of transducers for various aims, no such tradition has been established for the shear mode applications that have been restricted mainly to the field of static stress sensing (see for example ref. [20]). The reason for this inadequacy has been the inefficiency of the shear mode generation in bulk and surface acoustic wave studies [21, 22]. In principle, detectable shear outputs reported at room temperatures have been weak and close to the detection limit. The only study that has been successful in shear mode excitation at acceptable levels [23] exploited a very complicated transducer structure that does not fall within the framework of considerations here and will be discussed later. In our previous studies [4, 5], we made an effort to find the reasons for this poor shear performance of PVDF. The experiments that we have carried out here (see also next paragraph) reveal that the same poor shear behavior is demonstrated by P(VDF-TrFE). So it appears that the arguments stated for PVDF should equally apply to the

copolymer despite the difference in the way of fabrication and some properties. In short, we have attributed the lack of shear activity to a shear softness of the amorphous phase that links the crystallites (lamellas) in the semi-crystalline structure of the polymer. Remember that the shear electromechanical coupling involves the mechanical compliance: $K_{15}^2 = d_{15}^2 / \varepsilon_{11} S_{55}$ where ε_{11} is the dielectric permittivity [5]. A large compliance to mechanical stress is known to lead to a decrease in the electromechanical coupling in spite of the large value of the piezoelectric strain constant demonstrated in static experiments (Table 2). Used in contact with another medium, the transducer cannot develop sufficient mechanical stress to excite efficient acoustic motion in this medium. Figure 7 is a tentative explanation of this “liquid-like” behavior in PVDF where the chain-folded lamellas are positioned

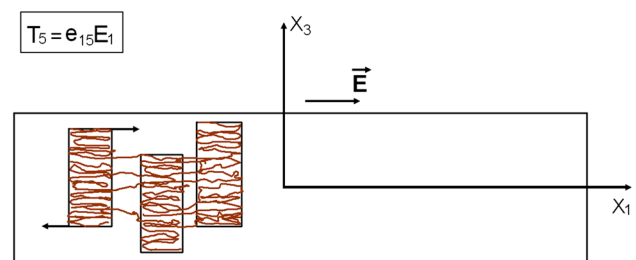


Fig. 7 Chain-folded lamellas under the action of lateral electric field. Chains are oriented parallel to the drawing axis (X_1) so the lamellas should stand perpendicular to it. Because lamellas lateral dimensions are much larger than the thickness, the rotating momentum with respect to X_3 should be significant

normally to the film axis thus allowing a large angular momentum under shearing stress T_{15} excited by the lateral electric field E_1 . We believe that the inclusion of the IF-3 nanoparticles into the copolymer has a matrix stabilizing effect increasing the shear rigidity and thus the electro-mechanical coupling. The lack of such an effect in the case of the ZnO nanoparticles suggests a different matrix organization. Note that, contrary to the previous case, the film demonstrates increased macroscopic brittleness.

Returning to the longitudinal excitation results from Table 2, we need to discuss on two features introduced by the inclusion of nanoparticles: decrease in the diffraction output and switch of the resonance from a $\lambda/2$ to $\lambda/4$ one. The effect on the excitation efficiency appears to be just opposite to that in the shear case, particularly with IF-3. However, we should be careful in formulating the reasons on only microscopic grounds because of the obvious contribution of adhesion. Adhesive layers between the transducer, the load and the backing, if any, have been known to be a very important factor for PVDF transducers, especially at high frequencies [24]. It has even been suggested that they be intentionally eliminated by employing other methods of mechanical coupling such as injecting drops of solvent between the load and the film and applying warm air to make the solvent evaporate [25]. The reason for the adhesion difficulties is that most plastic adhesives have acoustic impedance close to that of PVDF which makes the film resonance very unstable.

It has been more a rule than exception that the resonance could jump from fundamental to $\lambda/4$ or vice versa under small changes in the structure or circuit parameters. To avoid this possibility, the thickness of the adhesive layer should not exceed 1 % that of the polymer which obviously is not the case of this study. The type of resonant transitions observed with the nanocomposites indicates impedance changes of the films toward lower values. However, measurements of the resonant frequencies of the free (unloaded) films that we made by a network analyzer did not reveal such changes—the fundamental resonance keeps at its pure material $\lambda/2$ value. This is in accordance with our previous study [18] where the acoustic velocity was found to vary insignificantly at small filler concentrations. This resonance behavior implies that nanoparticles predominantly affect the surface properties of the films. The changes should be understood as changes in the adhesion strength at the interface between the film and adhesive glue. To support this understanding, the seriously reduced efficiency of longitudinal excitation should be addressed that cannot be attributed to slight impedance changes and resonance transitions. In an effort to modify the surface properties of the films, we soaked them in alcohol and then dried them, which lead to complete loss of activity of the IF-3 films. It should be noted, in addition, that ZnO is a

piezoelectric material with the same piezoelectric matrix as PVDF but its contribution to the film piezoelectricity cannot be significant in this case because of the random orientation of crystallites and no further poling. To conclude this paragraph, nanocomposites based on PVDF and copolymers can in specific cases have improved piezoelectricity but not related to crystallinity. At the same time, surface effects produced by the inclusion of nanoparticles could seriously deteriorate the action of film transducers. Composites also demonstrate modified macroscopic mechanical properties.

4 Pure polymer elasticity and polymorphic transitions

We have carried out the same type of experiments on three different pure films (no nanoparticles added) one of which was a thick PVDF sample made by a mixed rolling-polarization procedure [26]. The results are presented in Table 3.

The studied samples exhibit the expected longitudinal piezoelectric efficiency. However, the thick PVDF sample apparently shows a considerably larger longitudinal electromechanical coupling. If we compare its output (first row of Table 3) to that of the ordinary 65 μm P(VDF-TrFE) sample (second row of Table 3), we notice a factor of 2.6 in its favor. Recall that the intensity of the light diffracted into first order relates to the acoustic power density P according to the formula: $i(l)/i(0) = \sin^2[(\pi l/A_0)\sqrt{MP/2}]$, where l is the length of the transducer along the light propagation direction, A_0 is the vacuum light wavelength, and M is the acoustooptic figure of merit for the load [27a]. This formula is strictly valid for the Bragg case but at low powers is reasonably applicable to that experienced here and, in addition, reduces to simple linear proportionality. On the other hand, the total acoustic power generated by a film piezoelectric transducer is known to be: $P_a = 4K^2 C_0 f_p Z_p / ZV_0^2$, where K is the electromechanical coupling of the transducer, C_0 is the static capacitance

Table 3 Acoustooptic diffraction output of pure PVDF and P(VDF-TrFE) films

Film (μm)	Configuration	Frequency (MHz)	Input (mV^a)	Lock-in output (μV)
540 ^b	3b	2.1	700	42
65	3b	13.8	76	16
65	3c	15	220	42
540 ^b	3a	0–30	0–1,000	0
100	3a	0–30	0–1,000	0

^a Signal before a 40 dB power amplifier

^b PVDF film

involving the transducer area, f_p is the parallel resonant frequency of the electroded film, Z and Z_p are the acoustic impedances of the load and the transducer, respectively, and V_0 is the applied voltage amplitude [27]. The parameters of the two transducers (impedance matching, thickness ratio, and transducer length ratio) have been chosen in a way to ensure approximately equal acoustic powers in case the two couplings were the same. A power difference then means difference in the couplings and should be attributed to an advantage of the thick sample that quantitatively is the square root of 2.6, i.e., 1.6 (60 % increase). This rough estimate could of course be specified by an elaborate analysis of the radiation resistances of the two transducers but the principal validity of the result is of no doubt. To try to find the reason, we studied the degree of crystallinity of the thick sample by a combined DSC–infrared spectroscopy method [28]. The IR characteristic bands at 764 and 839 cm^{-1} provide an extremely high content of the active β -phase—84 %. Then, the DSC data provide the crystallinity degree—50.4 %. It is evident that the gain in electro-mechanical coupling should be attributed entirely to the dominant presence of the β -phase no matter whether the film is predominantly crystalline or amorphous. This view is supported by older data on the investigated type of sample—a comparison between the pressure sensitivities of two hydrophones based on PVDF and P(VDF-TrFE) of equal thickness (0.5 mm) reveals a slight advantage of PVDF [29]. We thus think the widespread understanding for a superior piezoelectric activity of the copolymer should be considered with caution.

The importance of having highest possible content of the β -phase in PVDF concerns not only the piezoelectric activity. An interesting polymorphic change (all β -phase) has been achieved with 2 wt% polyvinylpyrrolidone-coated multiwalled carbon nanotubes in a PVDF matrix, resulting in a 168 % increase in the young modulus [30]. Polymorphic transition from α to β -phase has also been realized in PVDF composites with Au nanoparticles [31].

Finally, we checked the shear piezoelectric activity of the thick PVDF sample along with a 100- μm P(VDF-TrFE) sample for comparison (fifth row in Table 3). Despite the high input voltage levels no output above the noise of the lock-in amplifier has been detected over the frequency range up to 30 MHz. This result is in accordance with our understanding of the shear response of crystallites described previously (Fig. 7).

5 Influence of geometry

Given the practical lack of dynamic shear piezoelectricity in PVDF and P(VDF-TrFE), it appears difficult to realize that such a transducer has still been reported in literature [23].

This transducer type is produced in a complicated manner. It consists of a large number of thin films stacked and bonded together along the thickness direction and then cut normally to it to form a thin plate containing the polarization axis (Fig. 8). Here, we consider the physical side of this solution. Otherwise, it is of course questionable whether it meets satisfactorily well the adopted goals of technological simplicity and reproducibility. The authors explain the efficiency of the transducer by a decreased stray capacitance of the electrode configuration compared to the split electrode one. In our opinion, the explanation is different and should be searched in the framework of the present discussion. The right angle reversed geometry of the film (Fig. 8) reflects different orientation of the lamellas with respect to the shearing stress. Now, the structure appears more rigid in shear and allows weaker mechanical shorting action of the amorphous phase oppositely to the domino-like configuration in Fig. 7. This solution is an indicative example of the way the piezoelectric properties of the studied polymers could be shaped by a proper choice of the film orientation with respect to the crystallographic axes.

6 Conclusion

Piezoelectric activity of PVDF and P(VDF-TrFE) films can be varied by structure modification. Considering the results, a possibility for distinction between the excitation (development of mechanical stress) and reception (reaction to mechanical stress) modes of the films should be envisaged. Introducing nanoparticles in the polymer matrix could affect the piezoelectric activity either directly or indirectly, via the modified mechanical properties of the matrix. Some fillers strengthen the amorphous phase and increase the shear mode coupling. At the same time, adhesion conditions can be seriously affected. When piezoelectric particles are involved, separate poling of the two phases might be required, particularly using piezoelectric ceramics. Contrary to our expectations, the crystallinity, calculated carefully by taken into account the ratio between crystalline phase volume over the matrix one, of the

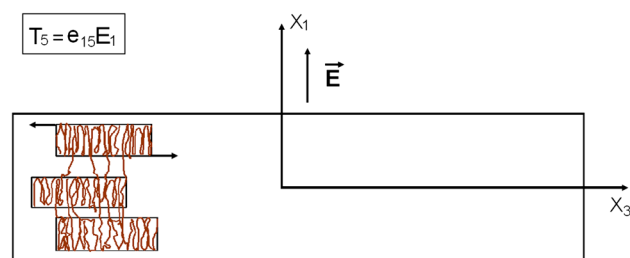


Fig. 8 Chain-folded lamellas under the action of normal electric field with polarization axes in the film plane

polymers appears to have no direct link to piezoelectric activity. Such a link exists to the ferroelectric phase content in PVDF. In some applications, the coupling might be varied by orientation of the film with respect to crystallographic axes.

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References

1. E. Fukada, History and recent progress in piezoelectric polymers. *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **47**(6), 1277–1290 (2000)
2. H. Kawai, The piezoelectricity of poly(vinylidene fluoride). *Jap. J. Appl. Phys.* **8**, 975–976 (1969)
3. L.F. Brown, Ferroelectric polymers: current and future ultrasound applications. 1992 IEEE Ultrasonics Symposium, vol. 1, pp. 539–550
4. V. Strashilov, J. Burov, M. Nikolov, Dynamic shear piezoelectricity of poly(vinylidene fluoride) thin films. *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **44**(6), 1181–1188 (1997)
5. V. Strashilov, Efficiency of poly(vinylidene fluoride) thin films for excitation of surface acoustic waves. *J. Appl. Phys.* **88**(6), 3582–3586 (2000)
6. B. Vigolo, B. Vincent, J. Eschbach, P. Bourson, J.F. Maréché, E. McRae, A. Müller, A. Soldatov, J.M. Hiver, A. Dahoun, D. Rouxel, Multiscale characterization of single-walled carbon nanotube/polymer composites by coupling raman and brillouin spectroscopy. *J. Phys. Chem. C* **113**(41), 17648–17654 (2009)
7. J. Eschbach, D. Rouxel, B. Vincent, Y. Mugnier, C. Galez, R. Le Dantec, P. Bourson, Development and characterization of nanocomposite materials. *Mater. Sci. Eng. C* **27**(5–8), 1260–1264 (2007)
8. R. Bactavatchalou, P. Alnot, J. Bailer, M. Kolle, U. Müller, M. Philipp, W. Possart, D. Rouxel, R. Sanctuary, A. Tschöpe, C. Vergnat, B. Wetzel, J.K. Krüger, The generalized Cauchy relation: a probe for local structure in materials with isotropic symmetry. *J. Phys. Conf. Ser.* **40**(1), 111–117 (2006)
9. J. Stroyan, Processing and characterization of PVDF, PVDF-TrFE and PVDF-TrFE-PzT composites, MS Thesis, Washington State University, 2004
10. T. Furukawa, K. Ishida, E. Fukada, Piezoelectric properties in the composite systems of polymers and PZT ceramics. *J. Appl. Phys.* **50**, 4904–4912 (1979)
11. H.L.W. Chan, S.T. Lau, K.W. Kwok, and C.L. Choy, PZT/P(VDF/TrFE) nanocomposite hydrophones for ultrasonic measurements. 1998 IEEE Ultrasonics Symposium, vol. 1, pp. 611–614
12. K. Ng, H. Lai, H. Chan, C. Choy, Piezoelectric and pyroelectric properties of PZT/P(VDF-TrFE) composites with constituent phases poled in parallel or antiparallel directions. *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **47**(6), 1308–1315 (2000)
13. A. Lonjon, L. Laffont, P. Demont, E. Dantras, C. Lacabanne, Structural and electrical properties of gold nanowires/P(VDF-TrFE) nanocomposites. *J. Phys. D Appl. Phys.* **43**, 345401 (2010). doi:10.1088/0022-3727/43/34/345401
14. M. Aufray, S. Manuel, Y. Fort, J. Eschbach, D. Rouxel, B. Vincent, New synthesis of nanosized niobium oxides and lithium niobate particles and their characterization by xps analysis. *J. Nanosci. Nanotechnol.* **9**(8), 4780–4785 (2009)
15. Y. Mugnier, L. Houf, M. El-Kass, R. Le Dantec, G. Djanta, L. Badie, R. Hadji, B. Vincent, J. Eschbach, D. Rouxel, C. Galez, In situ crystallization and growth dynamics of acentric iron iodate nanocrystals in w/o microemulsions probed by Hyper-Rayleigh scattering measurements. *J. Phys. Chem. C* **115**, 23–30 (2011)
16. V.S. Nguyen, D. Rouxel, R. Hadji, B. Vincent, Y. Fort, Effect of ultrasonication and dispersion stability on the cluster size of alumina nanoscale particles in aqueous solutions. *Ultrason. Sonochem.* **18**(1), 382–388 (2011)
17. R. Hadji, V.S. Nguyen, B. Vincent, D. Rouxel, F. Bauer, Preparation and characterization of P(VDF-TrFE)/Al₂O₃ nanocomposite. *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **59**(1), 163–167 (2012)
18. C. Galez, Y. Mugnier, J. Bouillot, Y. Lambert, R. Le Dantec, Synthesis and characterisation of Fe (IO₃)₃ nanosized powders. *J. Alloys Compd.* **412**, 261–264 (2006)
19. K. Tashiro, M. Kobayashi, H. Tadokoro, E. Fukada, Calculation of elastic and piezoelectric constants of polymer crystals by a point charge model: application to poly(vinylidene fluoride) form I. *Macromolecules* **13**, 691–698 (1980)
20. C. Domenici, D. de Rossi, A. Bacci, S. Benatti, Shear stress detection in an elastic layer by a piezoelectric polymer tactile sensor. *IEEE Trans. Electr. Insul.* **24**(6), 1077–1081 (1989)
21. B. Auld, J. Gagnepain, Shear properties of polarized PVF₂ film studied by the piezoelectric resonance method. *J. Appl. Phys.* **50**(8), 5511–5512 (1979)
22. R.S. Wagers, SAW transduction on silicon substrates with PVF₂ films. 1979 IEEE Ultrasonics Symposium, pp. 645–648. doi:10.1109/ULTSYM.1979.197283
23. K. Omote, H. Ohigashi, Shear piezoelectric properties of vinylidene fluoride trifluoroethylene copolymer, and its application to transverse ultrasonic transducers. *Appl. Phys. Lett.* **66**(17), 2215–2217 (1995)
24. L.F. Brown, The effects of material selection for backing and wear protection/quarter-wave matching of piezoelectric polymer ultrasound transducers. 2000 IEEE Ultrasonics Symposium, vol. 2, pp. 1029–1032
25. A. Ambrosy, K. Holdik, Piezoelectric PVDF films as ultrasonic transducers. *J. Phys. E Sci. Instrum.* **17**, 856–859 (1984)
26. Private communication of F. Bauer, CEO of Piezotech SA (material provided by Solvay)
27. E. Dieulesaint and D. Royer, *Ondes Elastiques dans les Solides: Application au Traitement du Signal*, vol. 9, chap. 9 (Masson, Paris, 1974), chs. 8(a), 7(b)
28. S. Mendes, C. Costa, C. Caparros, V. Sencadas, S. Lanceros-Mendez, Effect of filler size and concentration on the structure and properties of poly(vinylidene fluoride)/BaTiO₃ nanocomposites. *J. Mater. Sci.* (2011). doi:10.1007/s10853-011-5916-7
29. J. Soulier, Hydrophone based on piezoelectric polymer. Proc. Ferroelectric Polymer Shock and Dynamic Sensor Workshop, ISL, Saint-Louis, France, Sept 13–15, 1994, 19.1
30. M. Achaby, F. Arrakhiz, S. Vaudreuil, El M. Essassi, A. Qaiss, M. Bousmina, Nanocomposite films of poly(vinylidene fluoride) filled with polyvinylpyrrolidone-coated multiwalled carbon nanotubes: enhancement of β -polymorph formation and tensile properties. *Polym. Eng. Sci.* **53**(1), 34–43 (2013)
31. W. Wang, S. Zhang, L. Srisombat, T. Lee, R. Advincula, Gold-nanoparticle- and gold-nanoshell-induced polymorphism in poly(vinylidene fluoride). *Macromol. Mater. Eng.* **296**(2), 178–184 (2011)