

Tailoring the interfacial interactions in ferroelectric fluorinated polymer/ceramic nanocomposites

*Original*

Tailoring the interfacial interactions in ferroelectric fluorinated polymer/ceramic nanocomposites / Dalle Vacche, S.; Oliveira, F.; Leterrier, Y.; Michaud, V.; Damjanovic, D.; Manson, J. -A. E.. - ELETTRONICO. - (2014). ((Intervento presentato al convegno 16th European Conference on Composite Materials, ECCM 2014 tenutosi a Seville, Spain nel 22-26 June 2014 |.

*Availability:*

This version is available at: 11583/2918260 since: 2021-08-21T15:58:09Z

*Publisher:*

European Conference on Composite Materials, ECCM

*Published*

DOI:

*Terms of use:*

openAccess

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

*Publisher copyright*

(Article begins on next page)

## TAILORING THE INTERFACIAL INTERACTIONS IN FERROELECTRIC FLUORINATED POLYMER/CERAMIC NANOCOMPOSITES

S. Dalle Vacche<sup>a</sup>, F. Oliveira<sup>a</sup>, Y. Leterrier<sup>a\*</sup>, V. Michaud<sup>a</sup>, D. Damjanovic<sup>b</sup>, Jan-Anders E. Månson<sup>a</sup>

<sup>a</sup> Laboratoire de Technologie des Composites et Polymères (LTC), Ecole Polytechnique Fédérale de Lausanne (EPFL)

<sup>b</sup> Ceramics Laboratory (LC), Ecole Polytechnique Fédérale de Lausanne (EPFL)

\*yves.leterrier@epfl.ch

**Keywords:** fluoropolymer nanocomposite, coupling agents, functional properties, structure

### Abstract

*In this work composites of PVDF-TrFE containing 60 vol% untreated and surface modified BaTiO<sub>3</sub> were produced by solvent casting with two procedures. Their morphology and structure were characterized by scanning electron microscope, X-ray diffraction and differential scanning calorimetry. The effect of the processing conditions and of the surface modification of BaTiO<sub>3</sub> on the viscoelastic, dielectric and piezoelectric properties was investigated. The surface modification of BaTiO<sub>3</sub> allowed obtaining composite films with low porosity and good filler dispersion, and hence higher storage modulus and lower loss tangent, in a wider processing window. Furthermore it reduced the dielectric losses at low frequency and modified the decay kinetic of the  $d_{33}$  piezoelectric coefficient with respect to composites made with untreated particles.*

### 1. Introduction

For their characteristic properties, polymers based on vinylidene fluoride (VDF), alone or combined with various inorganic fillers, are attractive materials for energy related applications [1-3], and for the development of flexible sensors and actuators [4]. They have one of the highest relative permittivity values among polymers, with low dielectric losses and high breakdown field, and exhibit ferroelectric activity deriving from alignment of the C-F dipoles in the same direction in the crystalline  $\beta$ -phase.

When VDF-based polymers are combined with ferroelectric ceramics with high dielectric constant, as BaTiO<sub>3</sub> or PZT, great opportunities open up for obtaining composites with high energy density or tuned piezoelectric and pyroelectric properties [5-7]. However, to fully exploit these properties high volume fractions of filler (above 50 %) are often needed, and fabrication becomes a challenge, due to the difficulty of homogeneously dispersing the inorganic filler into the fluoropolymer matrix and to the poor matrix-filler adhesion. Particularly for solvent-based processes, porosity may also be an issue [8].

An increasing research effort is underway to overcome this problem by tailoring the matrix-filler interfacial interactions, which have a great influence on the filler's dispersion and on the final structure and properties of the composites [9, 10]. The introduction of different

functional groups on the surface of BaTiO<sub>3</sub> particles allowed increasing the permittivity of VDF-based nanocomposites [11-14], and a similar effect was obtained by generating BaTiO<sub>3</sub> nanoparticles *in situ* in poly(vinylidene fluoride)-*graft*-poly(2-hydroxyethylmethacrylate) (PVDF-*g*-HEMA), in which the –OH group of the HEMA units acted as a bridge with the surface of the nanoparticles [15]. P(VDF-TrFE) based composites containing polydopamine coated BaTiO<sub>3</sub> nanofibers and epoxy based composites containing surface modified PZT showed improved ferroelectric properties [16, 17].

Although several positive results have been obtained so far, systematic investigations on the effect of surface modification of the filler on the process-structure-property relationships for VDF based composites at high filler loadings is still missing. In this work barium titanate (BaTiO<sub>3</sub>) particles were surface modified with alkoxy silanes bearing different functional groups on their organic chain. Composites with a P(VDF-TrFE) matrix containing 60 vol% of untreated and surface modified particles were produced by solvent casting. The effect of the presence of different functional groups on the surface of the BaTiO<sub>3</sub> particles on the morphology and structure of the composite films, investigated by scanning electron microscopy, X-ray diffraction and differential scanning calorimetry, and on the mechanical, dielectric and piezoelectric properties of the composites is discussed.

## 2. Materials and methods

P(VDF-TrFE) (77/23 mol%) in powder form was provided by Solvay Solexis SpA (Italy) and BaTiO<sub>3</sub> (99.95%, electronic grade, 200 nm) by Inframat Advanced Materials LLC (CT, USA). The silane coupling agents were (3-aminopropyl)triethoxysilane (APTES), trifluoropropyltrimethoxy silane (TFTPMS) and propyltrimethoxy silane (all supplied by Sigma-Aldrich, MO, USA).

The BaTiO<sub>3</sub> particles were surface modified by addition of the silanes in ethanol/water (95/5 v/v), then separated by centrifugation and dried at 110 °C for 1 hour to allow for silanol condensation. Washing with ethanol and centrifugation were repeated twice and finally the powders were dried at 80 °C in vacuum overnight.

Solvent cast films containing 60 vol% of the unmodified and modified powders were obtained by dissolving P(VDF-TrFE) in MEK at 60 °C and then adding BaTiO<sub>3</sub> while stirring. The polymer concentration in MEK was 6 wt% in procedure A and 10 wt% in procedure B. Sonication with a Digital Sonifier 450 ultrasound horn (Branson Ultrasonics, CT, USA) and homogenization with an Ultraturrax T25 mechanical disintegrator (IKA – Werke GmbH & Co., Germany), at 5600 rpm in procedure A and 10000 rpm in procedure B, were performed on the mixture before casting on glass. The solvent was evaporated in a vacuum oven at 80 °C, then the films were annealed at 135 °C to increase crystallinity. The films obtained were 80 – 130 μm thick.

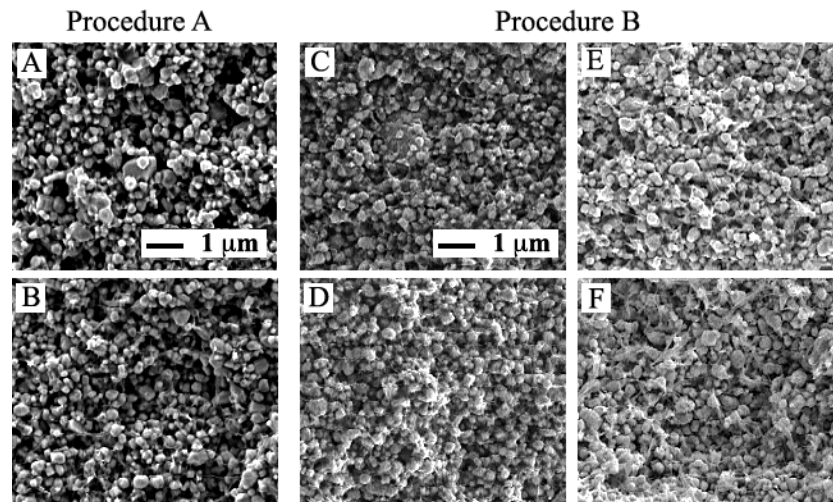
The morphology of the composites was observed in a Philips XL30 FEG (Philips, The Netherlands) scanning electron microscope (SEM). The samples were prepared by cryo-fracture and carbon coated to prevent charging. The porosity of the composites was estimated by measuring their density with an AT261 DeltaRange balance equipped with a density determination kit ME-210250 (Mettler Toledo, Switzerland). X-ray diffraction was performed on the films using CuK $\alpha$  radiation on a D8 DISCOVER diffractometer (Bruker AXS, USA) to assess the crystalline structure of BaTiO<sub>3</sub> in the composites. The crystallinity and thermal transitions of P(VDF-TrFE) in the films were studied by means of differential scanning calorimeter (DSC Q100, TA Instruments, USA), at a heating rate of 10 K min<sup>-1</sup> under N<sub>2</sub> flow. Dynamic mechanical analysis (Q800 DMA, TA Instruments, USA) was performed on the films in tensile configuration with an excitation frequency of 1 Hz and an applied strain of 0.05%, with a heating rate of 3 K min<sup>-1</sup>. After deposition of gold electrodes by sputtering,

capacitance and losses were measured as a function of frequency with an impedance/gain-phase analyzer HP4194A (Hewlett Packard, USA) at room temperature between 100 Hz and 1 MHz and with a voltage of  $1V_{\text{rms}}$ . Relative permittivity was then calculated from capacitance, knowing the area and thickness of each sample. For the study of the piezoelectric properties the solvent cast films made with procedure A were compression molded and coated with sputtered gold electrodes. Then  $5 \times 5 \text{ mm}^2$  specimens were poled in silicon oil, applying an electric field of 100 kV/cm for 30 min at 110 °C and then for further 30 min while cooling to 35 °C. The piezoelectric coefficient  $d_{33}$  was measured with a Berlincourt-type  $d_{33}$ -meter within the first 5 minutes from poling and then regularly checked during the following week to evaluate its stability.

### 3. Results and discussion

#### 3.1 Morphology, structure and thermal properties of the composites

The SEM observation (Figure 1) showed that for composites made with procedure A larger aggregates and more porosity were present when untreated particles were used versus particles treated with APTES. The porosity difference was also confirmed by density measurements, with an estimated porosity of about 25% and 15% for composites made with untreated and APTES treated particles respectively. When procedure B was used, porosity and particle aggregation were reduced with respect to procedure A, particularly in the case of untreated  $\text{BaTiO}_3$ . Porosity was about 16% for untreated and 9-11% for treated particles. The particle aggregation was somewhat lower for surface modified particles.



**Figure 1-** SEM images of freeze fractured cross sections of solvent cast composites of P(VDF-TrFE) with 60 vol% of  $\text{BaTiO}_3$  untreated (A and C) and treated with APTES (B and D), TFPTMS (E) and PTMS (F)

$\text{BaTiO}_3$  is known to have a very high surface energy [18], at least one order of magnitude higher than MEK and P(VDF-TrFE). Therefore during the fabrication process of the P(VDF-TrFE)/ $\text{BaTiO}_3$  composites the pristine  $\text{BaTiO}_3$  particles have a high tendency to agglomeration. The surface modification with organosilanes, lowering the surface energy of the  $\text{BaTiO}_3$  helped reducing the occurrence of large aggregates and promoted a better dispersion of the particles in the composite materials, particularly when the dispersing procedure was less efficient. For composites made with both procedures when APTES treated particles were used the polymer seemed to adhere better and formed a more connected network with the particles than when pristine  $\text{BaTiO}_3$  was used. This enhanced matrix-filler

adhesion may be explained by the formation of hydrogen bonds between the F atoms on the polymer chain and the H atoms of the amino group of the silane [19]. This effect is not visible for TFPTMS and PTMS treated particles that are not able to form hydrogen bonds. For all composites, X-ray diffraction and differential scanning calorimetry showed that the crystal structure of the BaTiO<sub>3</sub> particles and the crystallinity of the polymer were not affected by the particle surface modification.

### 3.2 Viscoelastic properties

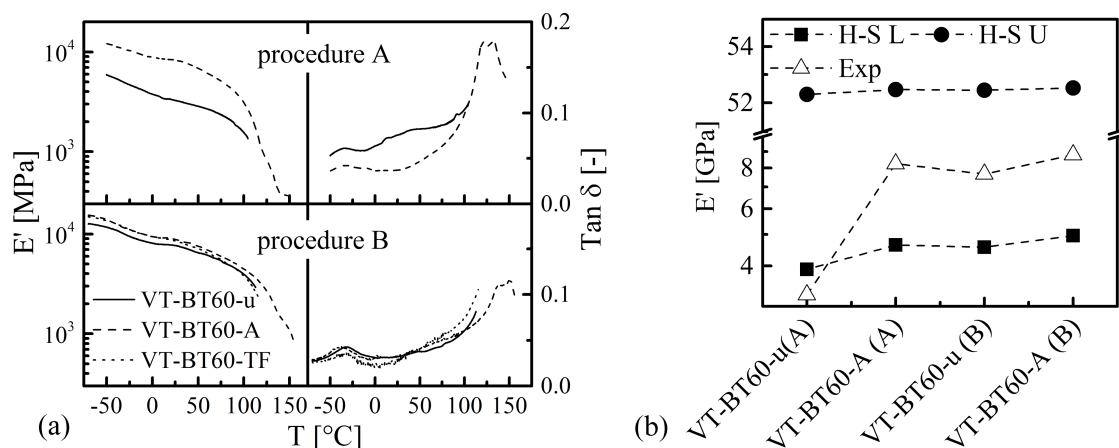
Figure 2a shows the temperature dependence of the storage modulus ( $E'$ ) and of the damping factor ( $\tan\delta$ ) of the composite films. The storage modulus decreased with temperature, and two steep drops of  $E'$  were observed corresponding to the phase transitions of P(VDF-TrFE), i.e. the ferroelectric to the paraelectric phase transition at about 110 °C and the onset of melting above 130 °C. The storage modulus of composites made with procedure A doubled when particles treated with APTES were used. As XRD and DSC results did not highlight difference in crystallinity, the increase may be attributed to decreased porosity and better dispersion of the particles. For composites made with procedure B, the storage modulus of the composites made with particles treated with APTES and TFPTMS was only slightly higher than that of the composite made with untreated particles. Notably, composites made with APTES treated particles with both procedures failed in the dynamic mechanical analysis test at higher temperature than those made with untreated particles, while this was not the case for particles treated with TFPTMS. This better performance at higher temperatures may be related to the hydrogen bonds formation mentioned in the previous section.

The effect of porosity on the storage modulus was estimated by calculating the upper and lower bounds for the modulus at 25 °C with the Hashin-Shtrikman (H-S) model [8, 20], considering the matrix as a closed cell foam in which is concentrated all the porosity of the materials. The modulus of the porous matrix was calculated as:

$$E_f = E_p \left[ 0.32(1 - \phi_v)^2 + (1 - \phi_v) \right] \quad (1)$$

where  $E_f$  and  $E_p$  are the moduli of the foam and of the polymer, respectively, and  $\phi_v$  is the volume fraction of the pores [21]. As shown in Figure 2b, the porosity differences are reflected by the differences in storage modulus. For the composite containing untreated particles made with procedure A an effect due to the presence of large agglomerates, which increase the effective particle size may also be considered, further decreasing the modulus.

The  $\tan\delta$  curves (Figure 2a) of the composites showed the features typically recognized in the  $\tan\delta$  plots of VDF based polymers in the temperature range explored. In the lower temperature range, a well-defined  $\beta$ -relaxation peak, usually attributed to segmental motions in the amorphous phase (glass transition) [22-24], appeared, with similar position and intensity for all composites. Around 50 °C a second peak, broad and not well defined, can be recognized only for the composite made with procedure A with untreated BaTiO<sub>3</sub>, and not for the other composites. This peak could be attributed to the so-called  $\alpha$ -relaxation process. As the nature of this process has not been fully clarified yet [25-27], it is difficult to make hypotheses about the reasons for this difference. Finally, a peak just before the melting of the polymer, corresponding to the Curie transition of P(VDF-TrFE), is visible only for the composites made with APTES treated particles, which resisted up to higher temperatures. For procedure A, the composites made with untreated ceramic particles had higher  $\tan\delta$  values than their homologues made with treated particles, while this was not the case for composites made with procedure B.



**Figure 2.** (a) Storage modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) of composites containing 60 vol% BaTiO<sub>3</sub> unmodified (-u) and modified with APTES (-A) and TFPTMS (-TF), made with procedures A and B. (b)  $E'$  at 25 °C and H-S upper (U) and lower (L) bounds for composites made with untreated and APTES treated particles.

### 3.3 Dielectric properties

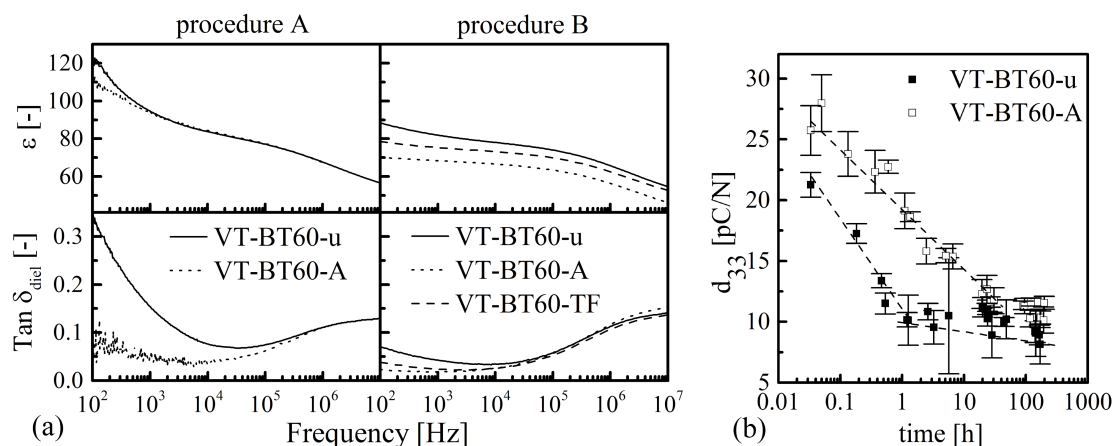
For the composites made with procedure A, despite the higher porosity of the materials made with untreated versus APTES treated BaTiO<sub>3</sub>, no significant difference in permittivity could be detected above 1 kHz. For the composites made with procedure B the relative permittivity was lower when surface modified particles were used. For all composites, with the only exception of those made with procedure A containing untreated BaTiO<sub>3</sub> powder, the  $\tan \delta_{diel}$  was lower than 0.1 up to  $10^6$  Hz. The effect of surface modification on the value of the relative permittivity is believed to be the result of effects acting in opposite directions: while the reduction of porosity increases the relative permittivity of the composites, the presence of the silane layers seems to decrease it. Beier *et al.* found that the dielectric constant of BaTiO<sub>3</sub> particles was lower when they were modified with *n*-hexylphosphonic acid [28]. A similar effect might give a negative contribution to the resulting permittivity of the composites upon surface modification of BaTiO<sub>3</sub>.

At frequencies below 1 kHz, the composites containing untreated BaTiO<sub>3</sub> showed higher permittivity and dielectric loss tangent  $\tan \delta_{diel}$ , and a more marked frequency dependency of their dielectric properties than their homologues made with treated particles. This effect may be attributed to Maxwell-Wagner-Sillars (MWS) polarization at the polymer-ceramic interface as discussed also by Dang *et al.* for PVDF/BaTiO<sub>3</sub> nanocomposites [29]. The presence of the silane layer around the ceramic particles may modify the charge distribution at the interface [30] decreasing the MWS effects.

### 3.4 Piezoelectric response

The piezoelectric coefficient  $d_{33}$  of composites made with procedure A and compression molded to reduce porosity ( $< 10\%$ ) is shown in Figure 3. The initial  $d_{33}$  was about 20% higher for materials made with APTES treated versus untreated BaTiO<sub>3</sub> particles. A clear difference can be observed in the decay kinetics of  $d_{33}$  after poling between the composites made with unmodified BaTiO<sub>3</sub> and those made with modified BaTiO<sub>3</sub>. Composites made with untreated powders showed very rapid  $d_{33}$  decay during the first few hours from poling, and then the piezoelectric coefficient reached a stable or very slowly decreasing value. For the composites made with APTES treated powder the decay in the initial period was slower, however the

decay continued at the same rate for longer time so that after about 100 hours their  $d_{33}$  approached that of the corresponding composites made with untreated powders. The decrease of  $d_{33}$  may be at least partly attributed to the action of depoling fields generated by space charges on the polarization of the ceramic particles, and the surface modification of BaTiO<sub>3</sub> might modify the space charge distribution. On the other hand the decay rate of  $d_{33}$  observed for these composites is much higher than that usually observed for ceramics and for VDF based polymer and other effects, as e.g. electret charging, may not be excluded.



**Figure 3.** (a) Dielectric properties and (b) piezoelectric response of P(VDF-TrFE)/BaTiO<sub>3</sub> composites

## Conclusions

Solvent cast composites of P(VDF-TrFE) containing 60 vol% BaTiO<sub>3</sub> were fabricated with two procedures, differing by the initial polymer concentration in the solvent (procedure A: 6 wt%; procedure B: 10 wt%) and different mixing speeds. Procedure A led to higher porosity and particle aggregation than procedure B when untreated powder was used. In the case of procedure A porosity and particle aggregation were greatly reduced by using APTES treated BaTiO<sub>3</sub>, obtaining a 100% increase of storage modulus. In the case of procedure B only marginal improvements for the morphology and the viscoelastic properties were obtained with BaTiO<sub>3</sub> surface modified with APTES, TFPTMS or PTMS. For composites made with both procedures the introduction of a functional group capable of forming of hydrogen bonds with the polymer chains, as the NH<sub>2</sub> group of APTES, improved the mechanical properties at high temperature. X-ray diffraction and differential scanning calorimetry showed that the particle surface modification did not influence the crystalline structures of the polymer and of the particles. For all composites the marked frequency dependency of relative permittivity below 10<sup>4</sup> Hz was suppressed by surface modification of the ceramics, obtaining a relatively constant value in the 10<sup>2</sup> – 10<sup>5</sup> Hz range, and dielectric losses were lower than when untreated particles were used. Finally the piezoelectric coefficient was somewhat improved by the surface modification of BaTiO<sub>3</sub>, and the evolution of  $d_{33}$  with time after poling was found to be strongly affected by the presence of a silane layer around the particles. The time dependence of the piezoelectric response of piezoelectric fluoropolymer ceramic composites has not been reported up to now and most of the literature works do not specify at which point in time the piezoelectric response has been measured.

These results highlight that surface modification may help widening the processing window, allowing fabrication of films with low porosity and good particle dispersion even with a not fully optimized fabrication procedure. The coupling agents bearing groups that simply reduced the difference in surface energy between the polymer and the filler (the alkyl chain of PTMS and the fluorinated chain of TFPTMS) were less effective than APTES, which could

interact with the polymer forming hydrogen bonds. Although several questions still remain open, a potential for the improvement of the mechanical, dielectric and piezoelectric properties through surface modification of the ceramic particles appears from these results, and work is underway to further elucidate the underlying interaction mechanisms at the polymer-particle interface.

### Acknowledgements

We gratefully acknowledge funding by the Swiss National Science Foundation in the framework of the Marie Heim-Vögtlin and the NanoTera programs. We would like also to thank Solvay Specialty Polymers (Bollate, MI, Italy) for graciously providing the polymer and for fruitful discussion. We are indebted to the other laboratories of EPFL who granted us access to their equipment, namely the Laboratory of Powder Technology (LTP), the Polymer Laboratory (LP) and the Interdisciplinary Center for Microscopy Technology (CIME), and to the semester and summer students who in some way contributed to this work.

### References

- [1] P. Barber, S. Balasubramanian, et al. Polymer composite and nanocomposite dielectric materials for pulse power energy storage. *Materials*, 2(4):1697-1733, 2009
- [2] A. M. Stephan, K. S. Nahm. Review on composite polymer electrolytes for lithium batteries. *Polymer*, 47(16):5952-5964, 2006
- [3] B. P. Tripathi, V. K. Shahi. Organic-inorganic nanocomposite polymer electrolyte membranes for fuel cell applications. *Progress in Polymer Science*, 36(7):945-979, 2011
- [4] F. N. Meyers, K. J. Loh, et al. Active sensing and damage detection using piezoelectric zinc oxide-based nanocomposites. *Nanotechnology*, 24(18), 2013
- [5] B. Ploss, W.-Y. Ng, et al. Poling study of PZT/P(VDF-TrFE) composites. *Composites Science and Technology*, 61(7):957-962, 2001
- [6] B. Ploss, F. G. Shin, et al. Pyroelectric activity of ferroelectric PT/PVDF-TrFE. *IEEE Transactions on Dielectrics and Electrical Insulation*, 7(4):517-522, 2000
- [7] M. Dietze, J. Krause, et al. Thick film polymer-ceramic composites for pyroelectric applications. *Journal of Applied Physics*, 101(5):054113, 2007
- [8] S. Dalle Vacche, F. Oliveira, et al. The effect of processing conditions on the morphology, thermomechanical, dielectric, and piezoelectric properties of P(VDF-TrFE)/BaTiO<sub>3</sub> composites. *Journal of Materials Science*, 47(11):4763-4774, 2012
- [9] A. Kellarakis, S. Hayrapetyan, et al. Clay nanocomposites based on poly(vinylidene fluoride-co-hexafluoropropylene): Structure and properties. *Polymer*, 51(2):469-474, 2010
- [10] R. Song, D. Yang, et al. Effect of surface modification of nanosilica on crystallization, thermal and mechanical properties of poly(vinylidene fluoride). *Journal of Materials Science*, 42(20):8408-8417, 2007
- [11] T. Zhou, J. W. Zha, et al. Improving dielectric properties of BaTiO<sub>3</sub>/ferroelectric polymer composites by employing surface hydroxylated BaTiO<sub>3</sub> nanoparticles. *ACS Applied Materials & Interfaces*, 3(7):2184-2188, 2011
- [12] K. Yu, H. Wang, et al. Enhanced dielectric properties of BaTiO<sub>3</sub>/poly(vinylidene fluoride) nanocomposites for energy storage applications. *Journal of Applied Physics* 113:034105, 2013
- [13] M. F. Lin, V. K. Thakur, et al. Surface functionalization of BaTiO<sub>3</sub> nanoparticles and improved electrical properties of BaTiO<sub>3</sub>/polyvinylidene fluoride composite. *RSC Advances*, 1(4):576-578, 2011



- [14] P. Kim, N. M. Doss, et al. High energy density nanocomposites based on surface-modified BaTiO<sub>3</sub> and a ferroelectric polymer. *ACS Nano*, 3(9):2581-2592, 2009
- [15] M. F. Lin, P. S. Lee. Formation of PVDF-*g*-HEMA/ BaTiO<sub>3</sub> nanocomposites via in situ nanoparticle synthesis for high performance capacitor applications. *Journal of Materials Chemistry A*, 1(46):14455-14459, 2013
- [16] Y. Song, Y. Shen, et al. Enhanced dielectric and ferroelectric properties induced by dopamine-modified BaTiO<sub>3</sub> nanofibers in flexible poly(vinylidene fluoride-trifluoroethylene) nanocomposites. *Journal of Materials Chemistry*, 22(16):8063-8068, 2012
- [17] N. Saber, J. Ma, et al. Effect of surface modification of lead zirconate titanate particles on the properties of piezoelectric composite sensors. *Fourth international conference on smart materials and nanotechnology in engineering*. Proc. of SPIE volume 8793, pages 879309-1-9. SPIE, Bellingham, Washington, 2013.
- [18] R. E. Cohen. *Theory of ferroelectrics: A vision for the next decade and beyond*. *Ferroelectricity*. Wiley-VCH Verlag GmbH, Weinheim, 2007.
- [19] Z. M. Dang, H. Y. Wang, et al. Influence of silane coupling agent on morphology and dielectric property in BaTiO<sub>3</sub>/polyvinylidene fluoride composites. *Applied Physics Letters*, 89(11):112902, 2006
- [20] Z. Hashin, S. Shtrikman. A variational approach to the theory of the elastic behaviour of multiphase materials. *Journal of the Mechanics and Physics of Solids*, 11(2):127-140,
- [21] L. Gibson, M. F. Ashby. *Cellular solids-structure and properties*. Pergamon Press, Oxford, 1988.
- [22] P. Frubing, F. P. Wang, et al. Relation between dielectric and mechanical losses in ferroelectric poly(vinylidene fluoride - hexafluoropropylene) films. *Proceedings of the 2010 IEEE international conference on solid dielectrics*. IEEE, New York, 2010.
- [23] A. Linares, J. L. Acosta. Tensile and dynamic mechanical behaviour of polymer blends based on PVDF. *European Polymer Journal*, 33(4):467-473, 1997
- [24] V. Sencadas, S. Lanceros-Mendez, et al. Characterization of poled and non-poled  $\beta$ -PVDF films using thermal analysis techniques. *Thermochimica Acta*, 424(1-2):201-207, 2004
- [25] V. Sencadas, S. Lanceros-Méndez, et al. Thermal characterization of a vinylidene fluoride-trifluoroethylene (75-25) (%mol) copolymer film. *Journal of Non-Crystalline Solids*, 352(50-51):5376-5381, 2006
- [26] E. J. Parry, D. Tabor. Effect of hydrostatic pressure and temperature on mechanical loss properties of polymers. 2. Halogen polymers. *Polymer*, 14(12):623-627, 1973
- [27] T. Yagi, M. Tatemoto, et al. Transition behavior and dielectric-properties in trifluoroethylene and vinylidene fluoride co-polymers. *Polymer Journal*, 12(4):209-223, 1980
- [28] C. W. Beier, M. A. Cuevas, et al. Effect of surface modification on the dielectric properties of BaTiO<sub>3</sub> nanocrystals. *Langmuir*, 26(7):5067-5071, 2010
- [29] Z. M. Dang, H. P. Xu, et al. Significantly enhanced low-frequency dielectric permittivity in the BaTiO<sub>3</sub>/poly(vinylidene fluoride) nanocomposite. *Applied Physics Letters*, 90(1):012901, 2007
- [30] D. L. Ma, T. A. Hugener, et al. Influence of nanoparticle surface modification on the electrical behaviour of polyethylene nanocomposites. *Nanotechnology*, 16(6):724-731, 2005