

EFFECT OF CONTROLLABLE MODIFICATION OF SrTiO₃ CERAMIC NANOPARTICLES ON PIEZO-ACTIVE NANOCOMPOSITES PROPERTIES

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Abstract

In this work the P(VDF-co-HFP) was chosen as a matrix due to the better mechanical properties compared to neat PVDF. Strontium titanate (SrTiO₃) was chosen as one of the lead-free ceramics and to observe its impact of modification on nanocomposite properties. SrTiO₃ nanoparticles were successfully coated with (2,2,2-trifluoroethyl methacrylate) short polymer brushes using surface-initiated atom transfer radical polymerization (SI-ATRP) in order to improve the compatibility between the particles and polymer matrix. Polymer grafted from the particles surface was analyzed by gel permeation chromatography (polymer chain length and polydispersity index) and using nuclear magnetic resonance (monomer conversion). Both, neat SrTiO₃ nanoparticles and their modified analogues were characterized and further compounded with poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) to obtain homogenous nanocomposites. Mechanical properties were analyzed using DMA and tensile tests. Characteristic temperatures and crystallinity were evaluated using DSC. The β -phase content was calculated using FTIR. Finally, it was found out that modification of nanoparticles significantly enhanced the piezo-electric activity namely d₃₃ coefficient due to the better homogeneity of the system and improved mechanical properties.

Keywords: PVDF-co-HFP, strontium titanate, SI-ATRP, TFEMA, piezoactivity

1. INTRODUCTION

Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) belongs to the family of Poly(vinylidene fluoride) (PVDF) copolymers. Similarly, as P(VDF), P(VDF-co-HFP) exhibits piezoelectric properties which can be enhanced (by increment of β -phase) by creating a composite by adding various fillers, or polymer blends [1-3]. Furthermore, they can be enhanced by poling [4, 5], stretching [5], or modification of fillers [6]. However, the filler compatible might be incompatible with the polymer matrix. This leads into requirement for further treatment of the matrix, filler or both to achieve better properties [7, 8]. It was found, that it is possible to modify polarizable graphene oxide (GO), with short polymer chains with suitable polymer using surface-initiated atom transfer radical polymerization. Such modification improves compatibility, thus filler dispersion and subsequently mechanical properties, which all together can also cause better vibration sensitivity. It also led to the increment of the piezoelectric coefficient (d₃₃) [9]. P(VDF-co-HFP) and its composites are used in such applications as battery membranes [10], sensor materials [11] solid electrolytes [12] or energy harvesting [13]. This study is focused on the modification of strontium titanate (ST) nanopowder with suitable polymer short polymer brushes and creating a composite by compounding with neat and modified ST nanoparticles. Finally, the mechanical, thermal and piezo properties of those materials were characterized using various methods to determine the influence of ST modification on the overall properties of the fabricated composite systems.

2. EXPERIMENTAL

2.1 Materials

Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP, average Mw ~400,000, average Mn ~130,000, pellets), Strontium titanate (ST, nanopowder, <100 nm particle size, 99% trace metals basis), Double functional ATRP initiator 2-bromo buryril bromide (BBiB, 98%) was covalently bonded to ST particles. Initiator functionalization was performed in the presence of triethylamine (TEA, ≥99%) using dry solvent tetrahydrofuran (THF, 99.99 anhydrous). The polymerization reaction mixture consist 2,2,2 trifluoroethyl methacrylate (TFEMA), ethyl 2-bromopropionate (EBP, 98%), N,N,N',N',N"-pentamethyldiethylenetriamine (PMDETA, ≥99%), copper bromide (CuBr, ≥99%) and anisole (ACS reagent, 99%). Dimethyl formamid (DMF) (ACS reagent, anhydrous, ≥99%) and diethyl ether (ACS reagent, anhydrous, ≥99%) were used as purifying and drying agents. All chemicals were received from (Sigma Aldrich, St. Louis, MO USA) and were used without further purification. Tetrahydrofurane (THF, p.a.), acetone (p.a.), ethanol (absolute anhydrous, p.a.), toluene (p.a.) and hydrochloric acid (HCl, 35%, p.a.) were obtained from (Penta Labs, Prague, Czech Republic). Deionized water (DW) was used during all experimental processes and washing routines.

2.2 Modification of SrTiO₃ particles

First, ST particles were functionalized with ATRP initiator according to the procedure published elsewhere [14]. Then, a measured amount of ST particles were placed to the Schlenk flask and filled with argon. The monomer TFEMA, initiator EBP, PMDETA and anisole were added under argon atmosphere. Reaction mixture was degassed and 4 freeze-pump-thaw cycles were performed. To the frozen mixture the CuBr was added again under argon flow. The molar ratio between the individual components TFEMA:EPB:CuBr:PMDETA was set to 100:1:1:4. The reaction mixture was put into the pre-heated oil bath and carried out for 16 h at 80 °C. Reaction was controlled over 2 h. The final product was filtered using DMF, THF and acetone. Finally, the product was dried in vacuum over at 60 °C overnight.

2.3 Preparation and poling of composites

First, measured amount of pristine P(VDFco-HFP) was poured into the Brabender twin screw mixer preheated to 160 °C with screw speed 50 rpm. Then, measured amount of ST particles were added and speed was increased from 50 rpm to 100 rpm and left to mix for 6 minutes. After mixing, blend was cut into smaller pieces while it was still hot. This process was repeated for all blends including pristine P(VDF-HFP) to achieve same process history. Total there were made 3 blends containing 0% ST, 5% ST and 5%ST-TFEMA. All blends were hot pressed for 3 minutes at 175 °C using steel frame. Then they were quickly cooled down in water cooled cooling press. After cooling, thin polymer/composite sheets were obtained. Using hydraulic press and standardized press knife (ISO 527-2 type 5B), specimens for tensile test and dynamic mechanical analysis (DMA) were made. For Fourier transform infrared spectroscopy (FTIR) and d33 measurements, circles with diameter 30 mm were made using laser cutting machine.

Poling was carried out using rheometer Physica MCR-502 with an electrorheological cell and silicon oil bath preheated at 130 °C. Poling parameters for all specimens were: 12 kV mm⁻¹; 30 min.

2.4 Characterization

¹H nuclear magnetic resonance (NMR) spectra were recorded at 25 °C using an instrument (400 MHz VNMR5 Varian, Tokyo, Japan) with deuterated chloroform (CDCl₃) as a solvent. The molar mass and polydispersity (Đ) of TFEMA polymer chains were investigated using gel permeation chromatography (GPC) on the GPC instrument (PL-GPC220, Agilent, Tokyo, Japan) equipped with GPC columns (Waters 515 pump, two PSS SDV 5 μm columns (diameter of 8 mm, length of 300 mm, 500 Å + 105 Å)) and a Waters 410 differential refractive index detector tempered to 30 °C.

DMA (METTLER TOLEDO DMA 1) with a single cantilever mode was used to determine the storage modulus and glass transition temperature (T_g) of each blend. Tensile test (Testometric M350-5CT) was performed at stretch rate 100mm/min and temperature 25 °C to obtain strain at break, Young's modulus and ultimate tensile strength. Differential scanning calorimetry (DSC) was performed to obtain thermal properties of blend such as melting/crystallization temperature and enthalpy which were used for calculation of crystalline phase by an equation (1). To obtain β -phase content, FTIR (Nicolet iS5, ATR module with Ge crystal) measurement was performed and values were used for equation (2). For d33 measurement, individual equipment was used as can be seen elsewhere [15].

$$X_c = \frac{\Delta H_m}{x \cdot \Delta H_\alpha + y \cdot \Delta H_\beta} \cdot 100 \quad (1)$$

where X_c is the % crystallinity, ΔH_m is the melting enthalpy ($J g^{-1}$), x and y are representing α - and β -phase contents, ΔH_α ($93,07 J g^{-1}$) and ΔH_β ($103,4 J g^{-1}$) are their melting enthalpy values [16].

$$F(\beta) = \frac{A_\beta}{\left(\frac{K_\beta}{K_\alpha}\right) \cdot A_\alpha + A_\beta} \cdot 100 \quad (2)$$

where A_α/A_β are absorbance values at $762 cm^{-1}$ (α -phase) and $840 cm^{-1}$ (β -phase) and K_α/K_β are absorption coefficients $6.1 \cdot 10^4 cm^2 mol^{-1}$ (α -phase)/ $7.7 \cdot 10^4 cm^2 mol^{-1}$ (β -phase). $F(\beta)$ stands for the calculated β -phase proportion [15,16].

3. RESULTS AND DISCUSSION

The SI-ATRP approach was applied to substantially modify the surface of the ST particles. In this respect, the sacrificial initiator EBiB was used to monitor the ongoing reaction from the surface, The ratio between the sacrificial initiator and grafted one was selected according to the published results [17], in order to obtain negligible difference in the polymer chain length, polydispersity index as well as good correlation between theoretical and actual M_n . The M_n measured by GPC was found to be $6200 g mol^{-1}$ with PDI 1.21 and monomer conversion 37 %. All results are in good agreement with initial prediction .

As can be seen in **Figure 1**, adding of ST filler leads to an increment of storage modulus, where modified ST filler is achieving higher values than pure ST. With increasing temperature, the difference between modified and neat ST is decreasing. However, both composites keep higher values of storage modulus. Values of $\tan \delta$ are minimally influenced by the presence of ST filler. T_g of pure P(VDFco-HFP) was 35.1 °C while T_g of composites was a little bit shifted to -36.3 °C.

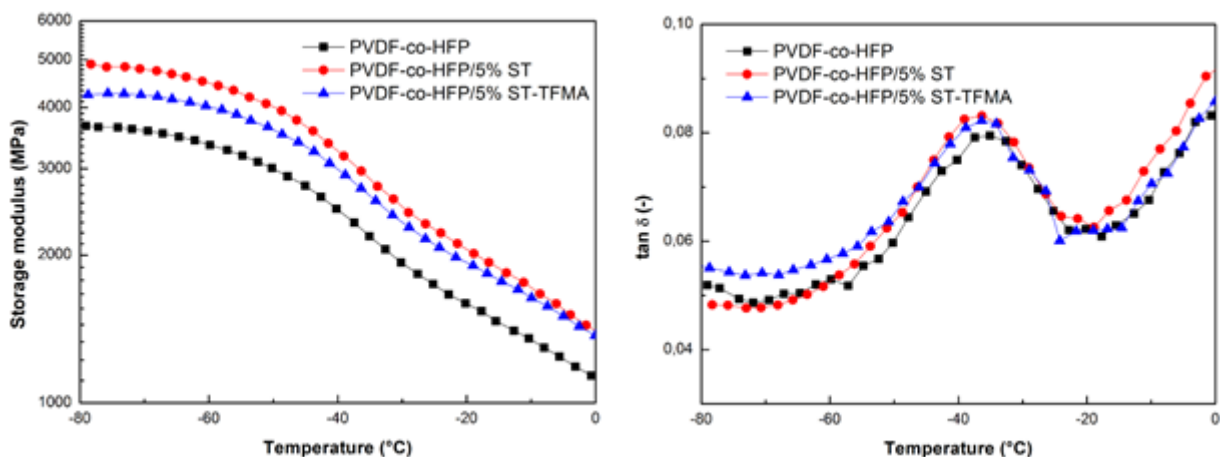


Figure 1 Temperature dependence of storage modulus (left) and $\tan \delta$ (right) for pure polymer and its composites.

Tensile test values that are summarized in **Table 1** show that adding pure ST filler decreases tensile properties compared to pure P(VDFco-HFP) except Young's modulus, where the value has an increasing trend. Adding modified ST filler leads to the preservation of tensile compared to pure ST and an increase of Young's modulus compared to both. This can be a consequence of better compatibility between the filler and the polymer matrix achieved by modification. Compared to the work by Labihi [18] neat polymer in this work achieves only around twenty times lower value of Young's modulus. However, introducing of ceramic particles leads into increment of Young's modulus and both neat and composite materials achieved higher tensile strength. Compared to works by Solarajan[19] and by Lalia [20], higher tensile properties were obtained. This is likely caused by different batch of P(VDFco-HFP) and different fabrication technique used.

Table 1 Strain at break, ultimate tensile strength and Young's modulus, measured at 25 °C for P(VDF-co-HFP) and its blends

Blend	Strain at break (%)	Ultimate tensile strength (MPa)	Young's modulus (MPa)
P(VDF-co-HFP)	990 ± 30	49.0 ± 1.7	217 ± 13
P(VDF-co-HFP)/5% ST	640 ± 20	29.1 ± 0.5	242 ± 12
P(VDF-co-HFP)/5% ST-TFEMA	940 ± 40	50.0 ± 3.0	268 ± 14

DSC measurements summarized in **Table 2** showed no dramatic changes in melting or crystallization temperatures. However, crystallinity calculated by equation (1) has decreasing trend where the biggest decline occurs with modified ST. In this case it seems that ST/ST-TFEMA filler act as a crystallization inhibitor, thus leads to the decrease of enthalpies.

Table 2 Melting temperature (T_m), melting enthalpy (ΔH_m), crystallization temperature (T_c), crystallization enthalpy(ΔH_c) and calculated crystallinity (X_c) by equation (1) for P(VDF-co-HFP) and its blends

Blend	T_m (°C)	ΔH_m (J g ⁻¹)	T_c (°C)	ΔH_c (J g ⁻¹)	X_c (%)
P(VDF-co-HFP)	142.9	-32.7	112.6	37.1	33.1
P(VDF-co-HFP)/5% ST	141.9	-28.8	112.7	32.1	29.3
P(VDF-co-HFP)/5% ST-TFEMA	142.1	-23.9	114.2	29.3	24.2

FTIR and d_{33} measurement are summarized in **Table 3**. All blends keep their β -phase content stable with a little deviation from pure ST. The d_{33} of the composite with modified filler show the highest value. It seems that modified filler helps to achieve better dipole orientation inside the material thus leading into better d_{33} value despite lower crystallinity.

Table 3 Absorbance values at 762 cm⁻¹ (α -phase) and 840 cm⁻¹ (β -phase) and calculated β -phase proportion by equation (2) for P(VDF-co-HFP) and its blends and measured d_{33} coefficient

Blend	A762 (a. u.)	A840 (a. u.)	β -phase (%)	d_{33} (pC/N)
P(VDF-co-HFP)	0,02147	0,01971	53.68	10.6±1.1
P(VDF-co-HFP)/5% ST	0,02217	0,01882	51.73	13.4±1.6
P(VDF-co-HFP)/5% ST-TFEMA	0,02006	0,01847	53.75	16.8±0.4

4. CONCLUSION

In this paper, the ST filler was successfully modified using SI-ATRP with TFEMA polymer brushes. Composites with both fillers, neat ST and coated ST were fabricated, measured and compared together with neat PVDF-co-HFP polymer. The composite with modified filler achieved almost the same or slightly better tensile properties as the pristine polymer. However, the use of modified filler leads to the highest decrease of the crystalline phase, most probably due to the presence of the polymer brushes in the systems. Finally, it was found that modification led to the preservation of the amount of β -phase compared to the neat filler and achieving $d_{33}=16.8\pm 0.4$ pC/N.

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