CONTROLLABLE MODIFICATION OF THE BaTiO₃ NANOPARTICLES USING SI-ATRP APPROACH AND IMPACT ON THE VIBRATION SENSING CAPABILITIES OF THEIR PVDF-BASED COMPOSITES

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Abstract

In this contribution the ceramic nanoparticles, BaTiO₃ (BT), were successfully and controllably coated with two monomers, poly(butyl acrylate) (PBA) and poly(methyl methacrylate) (PMMA) using SI-ATRP approach. The presence of the polymers on the surface was investigated using FTIR and TGA techniques. The molecular weight and polydispersity index were calculated from the gel permeation chromatography, while monomer conversion was confirmed using nuclear magnetic resonance. Both methods provide clear statement that controlled radical polymerization was successful. The surface of the neat BT, BT-PBA and BT-PMMA nanoparticles was investigated using BET analysis and using contact angle. The nanoparticles were mixed with poly(vinylidene fluoride) (PVDF) using micro compounder. The compatibility of the nanoparticles and PVDF matrix was evaluated investigation of the viscoelastic properties using dynamic mechanical analyzer. The contribution of the enhanced compatibility between the nanofiller and matrix was elucidated by electrical response to vibration testing. Finally, it will be presented how the SI-ATRP modification of BT nanoparticles with PBA and PMMA influence the capability for vibration sensing applications.

Keywords: Poly(vinylidene fluoride), BaTiO₃, nanoparticles, SI-ATRP, poly(butyl acrylate), poly(methyl methacrylate), vibration sensing

1. INTRODUCTION

The poly(vinylidene fluoride) (PVDF) is a material with unique properties showing simple processing, mechanical and thermal stability, tunable electrical and also structural properties [1-4]. Such capabilities can be very effectively utilized in various applications i.e. controllable actuation, sensing or energy harvesting devices [5-7]. Generally, the PVDF performance strongly depends on the electrically-active β-phase [8-10]. However, without any treatment PVDF forms the α-crystalline phase which is useless in a view of mentioned applications. There are various methods to enhance the β-phase content in PVDF material even for already prepared films or non-processed granules. In the case of PVDF films, the useful methods include film stretching [11,12] or poling the films by the application of high external electric field (several kV) [13]. The combination of both methods provides an improved β-phase content in comparison to the individual single method [14]. Another approach for β-phase development is the fabrication of PVDF films via electrospinning [15], or their PVDF co-blending with other polymers such as poly(methyl methacrylate) [16] or the introducing of various fillers forming the PVDF composites. These fillers can be organics (graphite, graphene oxide, reduced graphene) [1,17,18], or inorganic Barium titanate (BaTiO₃) or (BT) [16]. Therefore, this study is aimed on the fabrication of the BT hybrid particles those surface is coated with short polymer brushes. Neat PVDF sheets were compared to the composites containing either neat BT or BT hybrid particles and their dynamical mechanical properties were elucidated. Finally, vibration sensing performance of was analyzed in order to confirm the enhancing effects of BT hybrid filler.

2. EXPERIMENTAL

2.1. Materials

Barium titanate (BT) (99%), 3-aminopropyl triethoxy silane (APTES) (97%), touluene (p.a.), α-bromoisobutyryl bromide (BiBB, 98%) served as an initiator was linked onto BT surface. Initiator bonding was performed in the presence of proton scavenger, triethyleneamine (TEA, ≥99%). Methyl methacrylate (MMA, 99%), *n*-butyl acrylate (BMA, 99%), ethyl α-bromoisobutyrate (EBiB, 98%), *N*,*N*,*N′*,*N′′*,*N′′*-pentamethyldiethylenetriamine (PMDETA, ≥99%), copper bromide (CuBr, ≥99%) and anisole (99%) were used as a monomers, sacrificial initiator, ligand, catalyst and solvent, respectively. Poly(vinylidene fluoride) (PVDF; molecular weight of 275 000 g·mol^{-1}) were purchased from Sigma-Aldrich (USA). All chemicals were of analytical grade and used as received. Demineralized (DEMI) water (conductivity of 25 μS·m^{-1}) was used for purifying procedure after ATRP initiator bonding.

2.2. Synthesis of BaTiO$_3$ hybrid particles

Firstly, the neat BT particles were functionalized using silane coupling agent APTES, when for 2g of BT particles 4 ml of APTES was applied. The particles were put into the 3-neck flask and dispersed in toluene. The APTES was added to the mixture dropwise and after 30 minutes, the mixture was heated to 110 °C and refluxed for 8 hours. The particles collected using centrifuge (8000 rpm) and were washed with toluene and acetone three times. Centrifugation was repeated with every single washing cycle.

Then the functionalized BT particles were placed to Schlenk flask and evacuated and backfilled with argon. Then the freshly distilled dry THF was transferred to the flask under argon atmosphere and cooled down to 0° C. The proton scavenger TEA was added and solution was mixed for 30 minutes. Later, the BiBB initiator was added to the system dropwise (1ml/hr). Reaction was carried out overnight and then refluxed at 70 °C for additional 2 hours.

The BT particles modified with ATRP initiator (0.75 g) were transferred into a Schlenk flask equipped with a gas inlet/outlet and a septum. The flask was evacuated and replaced with argon for several times. BA (17.5 mL, 110mmol) or MMA (11.8 mL, 110 mmol), EBiB (0.162 mL, 1.1 mmol), PMDETA (0.92 mL, 4.4 mmol), and anisole (15 mL) were then added to the flask and the flask was degassed using several freeze-pump-thaw cycles. The CuBr catalyst (0.156 g, 1.1 mmol) was quickly added under argon flow into the frozen system. Anisole was used as a solvent in the amount of 50 vol.%. The polymerization mixture was stirred at 60 °C for two hours and then the polymerization was stopped by exposure to air. The product (hybrid pyarticles) was filtered, washed by DMF (2x200 mL), acetone (2x200 mL) and diethyl ether (2x100 mL). Particles were dried at 30 °C overnight under reduced pressure (100 mbarr)

2.3. Preparation of PVDF/BT-based composites

In order to prepare the composites containing neat BT and hybrid particles, the polymer matrix PVDF and BT particles with 1 wt. % content were mixed using microextrusion machine (Xplore, USA) at 200 °C. Homogenization of the prepared composites carried out 5 minutes. Then the mixed systems were compressed to the sheets with thickness of 100 μm again at 200 °C. The compression takes place for 5 minutes, while cooling procedure was ensured using cooling device providing 15 °C constant cooling for 10 minutes.

2.4. Characterization

Proton nuclear magnetic resonance (1H NMR) spectra were recorded at 25 °C using an instrument (400 MHz VNMRS Varian, Japan) and deuterated chloroform (CDCl3) as a solvent. The molar mass (Mn) and dispersity (Đ) of polymer chains were investigated by gel permeation chromatography (GPC) using a GPC instrument (PL-GPC220, Agilent, Japan) equipped with GPC columns (Waters 515 pump, two PPS 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. The samples for NMR spectroscopy and GPC analysis were prepared by their dilution with CDCl3 and THF, respectively, followed by the purification process, in which they were passed through a neutral alumina column. The contact angle (CA) measurements were evaluated from the static sessile drop method on the pellets carried out on a Surface Energy Evaluation system equipped with a CCD camera (Advex Instruments, Czech Republic). A droplet (5 µL) of distilled water was carefully dripped onto surface and the CA value was recorded. The presented CA results are the average values from 10 independent measurements. The viscoelastic properties of both the nanocomposite and pure polymer matrix were studied by dynamic mechanical analysis (DMA) in tensile mode. All measurements were performed at linear viscoelastic region. The measurement was done at 1 Hz in the temperature range from -150 °C to 150 °C. The dielectric spectroscopy in temperature range from -150 °C to 100 °C and in frequency range from 10-1 to 107 Hz was employed to investigate the polymer chains dynamics. Investigation of the d33 coefficient to prove the vibration sensing capabilities was performed in the similar way as was published elsewhere [19].

3.   RESULTS AND DISSCUSSION

The successfully functionalized BT particles with immobilized ATRP initiator on the surface can be clearly seen in the **Figure 1**. The SI-ATRP polymerization from the surface is showed as well and conditions for the polymerization is clearly visible. The resulting hybrids as the final product of the demonstrated reaction are summarized in the **Table 1**. It can be seen that controlled conditions were confirmed by low value of PDI while monomer conversion calculated from ^{1}HNMR well correlates with results of Mn from GPC measurements.
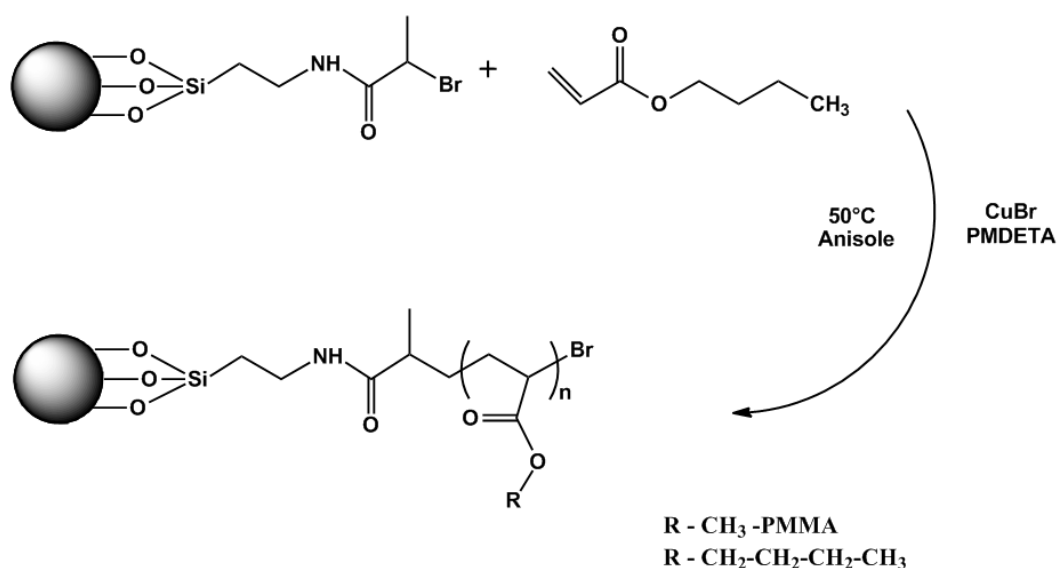
Figure 1 Schematic visualization of the SI-ATRP modification of BT particles with various monomers.

Table 1 Summarized results from GPC and ^{1}HNMR measurements.

| Sample ID	Neat BT	BT-PMMA	BT-PBA
Mn (kDa)	N/A	3.3	4.7
PDI (-)	N/A	1.07	1.22
Conversion (%)	N/A	35	37

The clear confirmation of the BT particles surface modification the specific surface area and contact angle was investigated. The results from this measurements are visible in the **Table 2**. It can be seen that specific surface area of the modified particle significantly decreased from 17 m²/g to 12 m²/g and 11 m²/g, for neat BT, BT-

PMMA and BT-PBA, respectively. On the other hand the water contact angle increased nearly twice indicating the improved surface properties and thus better compatibility of such particles with PVDF can be expected.

Table 2 Summarized values of the surface properties measurements

Sample ID	Neat BT	BT-PMMA	BT-PBA
Specific surface area (m^2/g)	17	12	11
Water contact angle (°	64	91	118

Since the monitoring of the vibrations is dynamic process and mechanical properties play crucial role, the dynamic mechanical characterization was performed (**Figure 1**). In case of the storage modulus, the lower values is representing by neat PVDF matrix while both BT-modified samples showed enhanced capability to store the mechanical energy and effectively release. On the other hand, the investigation of the Tan delta, clearly showed that short polymer chains polymerized from the BT surface acting as the plasticizers and shifted the values of Tg towards lower temperatures. In this respect can be concluded, that SI-ATRP modification provide system with more flexible polymer chains which can positively contribute to the enhanced vibration sensing performance.
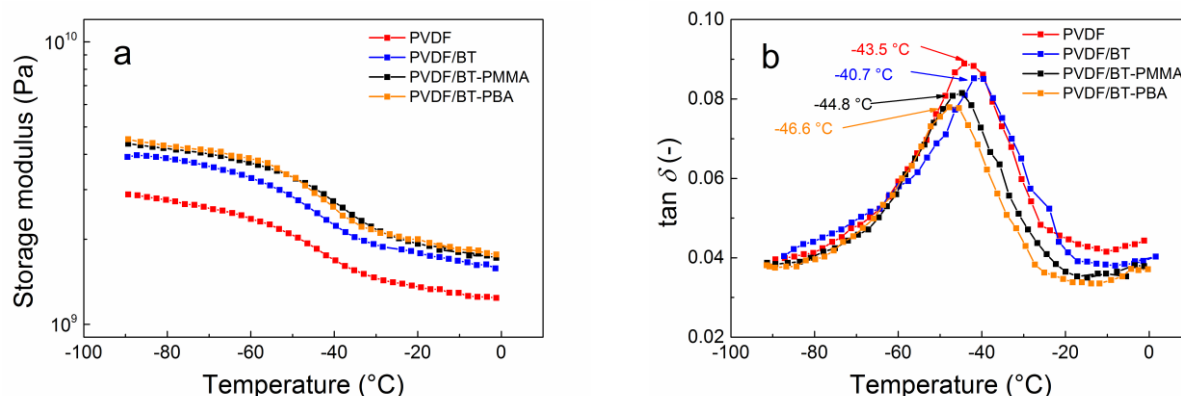
Figure 1 Temperature dependence of the Storage (a) and Tan delta (b) for various composite systems.

Finally, in order to investigate the capabilities of the fabricated PVDF-based composite systems in their potential application, d33 coefficient was measured (**Table 3**). In this case, the presence of the short polymer chains positively influencing the vibration sensing and such samples provide better response on the vibrations than neat PVDF or PVDF/BT composite. Therefore, only small addition of the BT particles positively influencing their vibration sensing capabitilies.

Table 3 The d33 values for the neat PVDF and PVDF/BT-based composites.

Sample ID	Neat PVDF	PVDF/BT	PVDF-BT-PMMA	PVDF/BT-PBA
10 kΩ	12.7±0.7	13.0±1.3	14.2±1.1	15.8±0.7
30 kΩ	12.9±0.9	13.1±1.4	14.5±1.7	16.0±0.4
50 kΩ	13.1±0.5	13.2±1.1	14.8±1.4	16.2±0.5
average	12.9±0.4	13.1±1.3	14.5±1.4	16.0±0.5

4. CONCLUSION

In this paper, the successful modification of the BT particles with PMMA and PBA short polymer chains using ATRP approach is presented. The investigations of the polymerization products clearly proved that

polymerizations were controlled and provided low PDIs. Furthermore, the surface properties of the BT particles were significantly changed after modification and contact angle increased from 64°for neat BT to 91° and 118° for BT-PMMA and BT-PBA, respectively. Moreover, the dynamic mechanical investigations showed that Tg for modified BT particles was shifted towards lower temperatures indicating plasticizing effect of the short polymer brushes. Therefore, also vibration sensing capabilities were proved to be best for hybrid-based PVDF composites in comparison to neat PVDF and PVDF/BT ones.

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