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**Abstract.** We present a new group of piezoelectric nanocomposite thin films based on integrating piezoelectric material poly(vinylidene fluoride) and nanoparticles of barium titanate in a matrix of an organic polymer poly(methyl methacrylate). Implementation of piezoelectric properties in designed new nanocomposites allows us not only to increase the sensitivity and functionality of the overall system, where this material is used, but also to expand the application fields in sensing and actuating systems. Results implied that new nanostructures fabricated by nanoimprint lithography exhibit good piezoelectric, surface, and mechanical properties and allow independent control of tribological properties. Formed nanocomposite systems were integrated in designing optical components employed in medicine for sensing applications. © The Authors. Published by SPIE under a Creative Commons Attribution 3.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: [10.1117/1.JMM.12.4.043004](https://doi.org/10.1117/1.JMM.12.4.043004)]

Subject terms: piezoelectric; nanocomposite; nanoparticles; optical component; nanoimprint lithography.

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## 1 Introduction

Due to the large motions that can be generated with low hysteresis and high-available energy densities, piezoelectric structures offer many benefits in microsystems. Thin films with piezoelectric properties are one of an emerging class of materials possessing unique properties including the ability to sense and respond to different stimuli.<sup>1–4</sup> The new piezoelectric ceramic–polymer nanocomposites may be qualified to fill niche areas where polymers, single crystals, and ceramics are incapable of performing its functions in a system as effectively as needed.

Piezoelectric polymer poly(vinylidene) fluoride (PVDF) has unique and unusual properties.<sup>5</sup> It is widely used in engineering applications due to its favorable chemical and mechanical properties, high-piezoelectric coefficient, good flexibility, and biocompatibility.<sup>6–8</sup> Thus, ceramic nanoparticles of barium titanate oxide ( $\text{BaTiO}_3$ ) are of great interest for microsystem applications, where high-electromechanical performance is required.<sup>9–11</sup> Combination of ferroelects, piezoelectric, and thermoelectric properties of  $\text{BaTiO}_3$  make it interesting in electro-ceramic industry, nonlinear optics, miniaturized electronic devices, etc. Piezoelectric materials distinguish themselves with a high bandwidth, high frequency, low-power requirements, fast response, and high-generative forces. They may be used as actuators or as sensors, i.e., property of reversibility.<sup>12</sup> As an actuation mechanism, they may be highly resistive to humidity, temperature, or other environmental effects.

Certain research in the field of sensing applications, like in medicine, face problems such as shortcoming of sensitivity, good surface morphology, and mechanical and optical properties of designed components.<sup>11,12</sup> This article covers the development of novel nanoimprinted thin vibrating components based on novel nanocomposite materials with a unique combination of properties. Research done on PVDF is related to investigations of composites of piezoelectric materials, particularly PVDF and ceramics. Results of these investigations have shown that designed novel piezoelectric ceramic–polymer nanocomposites PVDF– $\text{BaTiO}_3$  and PVDF–PMMA– $\text{BaTiO}_3$  possess exceptional surface morphology and mechanical and piezoelectric properties. Here, organic polymer poly(methyl methacrylate) (PMMA) is used to increase the morphological stabilization and elasticity of formed thin films and periodical microstructures fabricated via nanoimprint. Thus, the implementation of piezoelectric properties in nanocomposites allows us not only to increase the sensitivity and functionality of the overall system, but also to expand the application fields in sensing and actuating.

## 2 Experimental Details

Among the piezoelectric polymers, ferroelectric properties, such as high piezoelectric constant and very good elastic properties, of PVDF make it unique among the other ones. PVDF-based nanocomposites with barium titanate nanoparticles were used to design active diffractive optical

elements exhibiting piezoelectric properties. Barium titanate has makeable properties among inorganic compounds like photorefractive effect, good mechanical and chemical stabilities, electrical properties, and ease of preparation. Thus, substitution of both materials can show potential in specific applications. Moreover, changes in the surroundings do not influence PVDF piezoelectric properties, and it can still maintain its inherent damping capacity and not lose piezoelectric response.

## 2.1 Nanocomposite Synthesis

Blends of piezoelectric ceramic-polymer nanocomposites were prepared from 5% PVDF (average  $M_w = 34,000$ ) and 2-mg nanoparticles of barium titanium oxide  $BaTiO_3$ . PVDF and 5% PMMA (average  $M_w = 15,000$ ) were taken and mixed in suitable and definite compositional ratios, 50/50. Solutions were synthesized with the appropriate amount of sodium dodecyl sulfate ( $M_w = 288.38$ ). Thus, synthesizing PVDF with polymer PMMA is an original way to force PVDF to crystallize into the piezoelectric phase, which is thermodynamically unstable in a pure material. The PMMA here is used because of the direct influence to PVDF-based nanocomposite properties. Moreover, results showed that when synthesizing PVDF with PMMA, it is not necessary to pole the nanocomposite thin films.

## 2.2 Technological Aspects

Thin films of blended solutions were formed by a spin-coating technique (spin speed 1800 rpm, spin time 20 s) on a very thin copper (Cu) plate of thickness 50  $\mu\text{m}$ . With this technique, an even thickness of thin film was obtained, i.e., of 820 nm for PVDF- $BaTiO_3$  and 945 nm for PVDF-PMMA- $BaTiO_3$ .

Further, periodical microstructures were imprinted using nanoimprint lithography. For formation of effective diffractive optical elements, a 4- $\mu\text{m}$  master grating was used (see Table 1).

When forming novel optical components, two substrate types were used—glass substrate and a copper plate. Here, a base of copper plate acts as an electrode, and the other copper electrode was formed on top of thin film at the edge of the element in order to evaluate the piezoelectric properties of the formed films.

Eventually, properties of novel nanocomposites were characterized with an atomic force microscope (AFM) NT-206, microhardness tester PMT-3, a vibrometer stand—Pulse LabShop (OFV-5000 Modular Vibrometer Controller), and a laser diffractometer (Red He-Ne laser of wavelength 632.8 nm incident to grating).

## 3 Results and Discussion

The outstanding properties of piezoelectric materials depend strongly on their structural properties at the global (texture, residual stress, phase distribution, crystalline structure, size and shape of crystallites, and local microdistorsions) and local (stress heterogeneity from grain-to-grain, grain size distribution, and local texture) scales. All those properties are coupled to each other: stress depends on the texture through the elastic anisotropy of the crystal, shape and grain size influence both the level of stress and the heterogeneity of stress from grain-to-grain, which affects the measurement of both

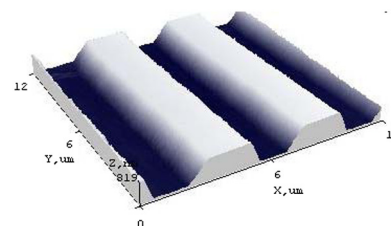
microdistorsions and crystallite size. In this case, the miscibility of piezoelectric polymers PVDF and inorganic compound nanoparticles  $BaTiO_3$  with organic polymer PMMA gave the morphological stabilization and good optical and mechanical properties of formed PVDF-based thin film layers.

Experimental results stated that PMMA in the creation of piezoelectric nanocomposite components acts as a material which improves the thermo-plasticity of the coating. The AFM was used for the determination of formed thin films surface morphology and the evaluation of thin film elasticity. Thus, if the adhesion forces, measured with increasing external loads, remain constant, it can be concluded that the contact is elastic and that no material transfer occurred at these loads. Moreover, adhesion influences the degree of deformation of the roughness structures at the contact and is dominated by the attractive portion of the interacting forces between the surface atoms of the contacts. Thus, for PVDF- $BaTiO_3$  thin film, the required adhesion force was 14,353 nN. Introducing PMMA in PVDF- $BaTiO_3$  reduces the adhesion force to 2413 nN, i.e., meaning a 6 $\times$  improvement of the elasticity of the nanocomposite surface (see Table 1). Surface microhardness of piezoelectric nanocomposites was evaluated by means of microhardness tester PMT-3, using three loads ranging from 0.098 to 0.294 N. The indentation period was 15 s; 10 to 15 indentations were taken for each load. The coefficient of variation was not higher than  $\pm 7\%$ . Calculated microhardness values<sup>13-15</sup> are presented in Table 2.

The adhesion force value was measured from the deflection of a cantilever spring multiplied by the cantilever stiffness—the maximum height from the baseline to minimum value. The importance of adhesion is undisputable in many phenomena even beyond tribology, like coating performance, self-cleaning surfaces, wettability, and micro/nanotechnology. But for the tribology, understanding of adhesion is of fundamental importance, because it is one of the basic mechanisms of friction when used in a certain sensing or actuating system and also influences the deformation of a thin film when

**Table 1** Properties of master grating.

Three-dimensional view		
Grating periodicity	Depth	700 nm
	Periodicity	4 $\mu\text{m}$
Grating dimensions	Length	2 mm
	Width	16 mm
Grating lines	Parallel to the short edge	



**Table 2** Elastic behavior and mechanical properties of piezoelectric ceramic–polymer nanocomposites.

Parameters	PVDF–BaTiO <sub>3</sub>	PVDF–PMMA–BaTiO <sub>3</sub>
Maximum load (nN)	47,895	42,502
Adhesion force (nN)	14,353	2413
The Vickers microhardness $H_V$ (GPa) <sup>13</sup>	0.872	2.75
The absolute microhardness $H_A$ (GPa) <sup>15</sup>	1.54	14.22

forming periodical microstructures by nanoimprint lithography. The importance of mechanical properties evaluation is significant in many phenomena even beyond tribology, like coating performance, wettability, and micro/nanotechnology.

Surface morphology of novel nanocomposite coatings and periodical microstructures were investigated by means of AFM NT–206. Figure 1 shows surface morphologies of PVDF–BaTiO<sub>3</sub> and PVDF–PMMA–BaTiO<sub>3</sub> nanocomposites. Observing PVDF–BaTiO<sub>3</sub> coating surface morphology [Fig. 1(a)], small islands—crystalline structures (with average depth of 491 nm and width of 4273 nm)—were defined, and the surface roughness was 80.7 nm. Thus, introducing PMMA in PVDF–BaTiO<sub>3</sub> influences the surface roughness, i.e., obtaining almost two times smoother surface roughness of 38.2 nm with some small crystalline structures (with average depth of 250 nm and width of 2016 nm) [Fig. 1(b)].

The comparatively big grain diameters in formed coatings may be explained as clumped crystal clusters of BaTiO<sub>3</sub>, i.e., the addition of PMMA to PVDF significantly reduces the grain diameter as well as the maximum height of the peaks. Thus, more research was done by changing the ratios of BaTiO<sub>3</sub> in blends. For example, by increasing the ratio of BaTiO<sub>3</sub>, we may decrease the maximum height of peaks observed on surface of nanocomposite coatings (see Table 3).

Piezoelectric properties of novel nanocomposite thin films on copper substrates were investigated by the indirect piezoelectric effect using a vibrometer stand [Fig. 2(a)]—a Pulse LabShop. Experimental results proved the fact that no poling is needed when PMMA is introduced in PVDF–BaTiO<sub>3</sub> nanocomposite, however, polarization was necessary for PVDF–BaTiO<sub>3</sub>.<sup>16</sup> Applying AC voltage of 260 mV, with a filter of 200 Hz, thin film of

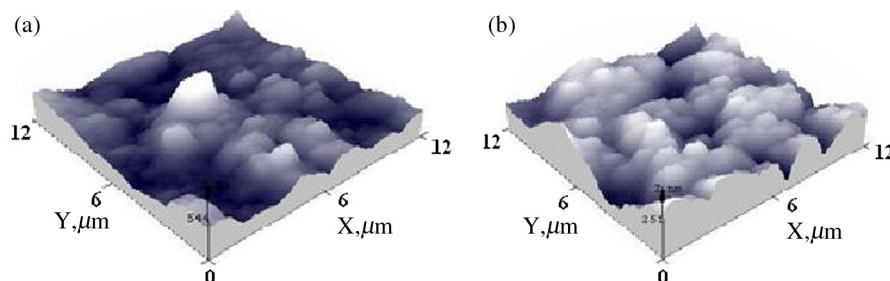
**Table 3** Basic morphological properties of piezoelectric thin films.

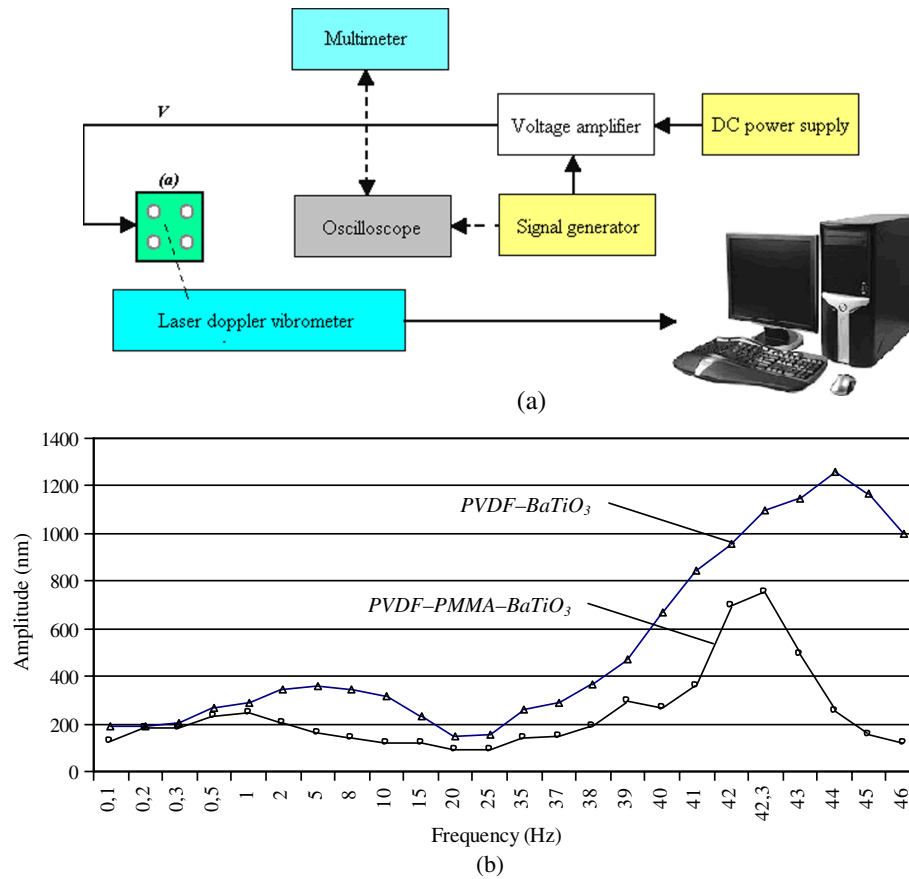
Parameters	PVDF–BaTiO <sub>3</sub>	PVDF–PMMA–BaTiO <sub>3</sub>
$R_a$ (nm)	60.1	31.2
$R_q$ (nm)	80.7	38.2
$R_{sk}$ (nm)	–0.63	–0.3
Maximum height $A$ (nm)	491.6	250.7
Grain diameter (nm)	4273	2016.4

PVDF–PMMA–BaTiO<sub>3</sub> bends in both directions with a peak-to-peak amplitude of 160 to 200 nm. Applying a voltage of 300 mV, with a filter of 200 Hz, piezoelectric nanocomposite thin film bends peak-to-peak by 260 nm. When applying an AC voltage of 130 mV and varying frequency, it can be seen that there is a specific frequency at which the coating produces very strong vibrations. This frequency, the so called resonant frequency, for a PVDF–PMMA–BaTiO<sub>3</sub> piezoelectric film was 42.3 Hz with an amplitude of 751 nm [Fig. 2(b)] and for PVDF–BaTiO<sub>3</sub> was 44 Hz with an amplitude of 1256 nm. When applying too high a voltage (higher than 310 mV), the amplitude decreases and the thin film stops oscillating, i.e., no piezoelectric effect is registered.

It was determined that the effect of piezoelectricity is also dependent on the thickness of coating and the boundary conditions of the sample.

Obtained results imply that here PMMA acts as a material improving adhesion of piezoelectric thin films, but decreases piezoelectric response of the coatings. Good elasticity of the coating is important when imprinting periodical microstructures on formed coatings. Well-defined periodical microstructure is an essential element in the design of optical components for sensing systems in microdevices. Diffraction-based optical components operate at a fixed wavelength and detection angle; they exploit the variation of diffraction efficiency that occurs due to the bonding of a chemical or biological species on a diffraction grating. As AFM measurements showed, periodical microstructure imprinted on PVDF–BaTiO<sub>3</sub> [Fig. 3(a)] coating led to narrow and irregular forms of gratings with an average depth of 0.67  $\mu\text{m}$  and width of 2.8  $\mu\text{m}$ , and with an average depth of 0.74  $\mu\text{m}$  and width of 3.4  $\mu\text{m}$  for PVDF–PMMA–BaTiO<sub>3</sub> [Fig. 3(b)] nanocomposite.

**Fig. 1** Three-dimensional view of surface morphology of (a) PVDF–BaTiO<sub>3</sub> and (b) PVDF–PMMA–BaTiO<sub>3</sub>.



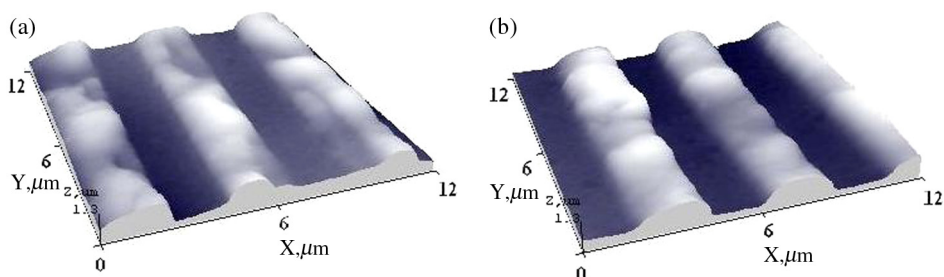
**Fig. 2** (a) The stand for the evaluation of (b) resonant frequency of PVDF-BaTiO<sub>3</sub> and PVDF-PMMA-BaTiO<sub>3</sub> piezoelectric films (voltage 130 mVpp).

Measurements of diffraction efficiency of formed gratings by a laser diffractometer show that around 49% of diffraction efficiency of PVDF-BaTiO<sub>3</sub> was concentrated in its zero order, ~16% to 18% in ±1 order, and ~6% to 10% in ±2 orders of its maximum (Fig. 4). For a periodical microstructure imprinted on PVDF-PMMA-BaTiO<sub>3</sub>, diffracted energy was concentrated similarly in its zero order (~32%) and first order of its maximum (~27%) (Fig. 4).

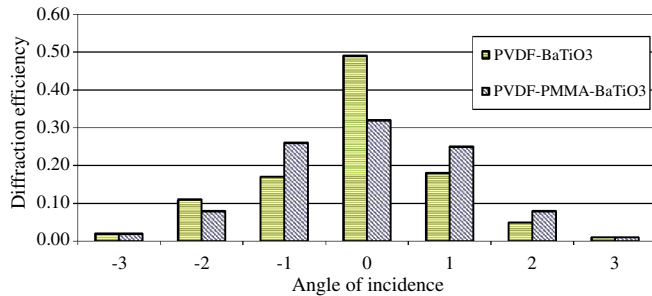
Since the diffraction efficiencies in 0 and ±1 orders of its maximum are of most importance, it may be concluded that periodical microstructures imprinted on PVDF-PMMA and PVDF-PMMA-BaTiO<sub>3</sub> thin films were of different forms and parameters to the master grating which lead to very good diffraction efficiency results, i.e., diffracted energy mainly concentrated in its zero and first orders of its maximum. Around 49% of diffraction efficiency of PVDF-BaTiO<sub>3</sub>

was concentrated in its zero order and ~15% to 17% in ±1 order of its maximum. For a periodical microstructure imprinted on PVDF-PMMA-BaTiO<sub>3</sub>, diffracted energy was concentrated similarly in its zero order (~32%) and first order of its maximum (~25%). Thus, PMMA proves its relevance when forming periodical microstructures in piezoelectric coating, i.e., grating parameters similar to the master grating and much higher diffraction efficiency distribution in its first order of maxima.

Further experimental results showed that novel optical components with piezoelectric properties were both chemically inert and biocompatible. Such designed thin films also possess a unique ability to be configured into an infinite number of shapes and sizes for extreme application versatility. Property of piezoelectricity in nanocomposites was introduced in order to improve the usability of optical



**Fig. 3** Periodical microstructures imprinted on (a) PVDF-BaTiO<sub>3</sub> and (b) PVDF-PMMA-BaTiO<sub>3</sub>.



**Fig. 4** Diffraction efficiencies of periodical microstructures imprinted on piezoelectric nanocomposite thin films.

components as a new technology for sensing or biosensing systems.

For further development, a series of experiments were conducted using attachments of various shape, area, density, and flexibility of designed PVDF-based nanocomposite films, producing different results in the level of power. Novel piezoelectric ceramic-polymer structures may serve as a simple, robust, and easily scaled energy harvesting device, i.e., an effective and unique power generator in a variety of environments: such piezoelectric harvesters mounted on aircraft or vehicles could generate electricity by vibrations to charge batteries or to power on-board electronics. Moreover, novel nanocomposite components with piezoelectric materials may be one-step ahead by creating a method to harvest the renewable sources of energy.

#### 4 Conclusions

Novel nanocomposite thin films exhibit good dielectric and surface and mechanical properties and allow independent control of tribological properties.

Incorporation of polymer PMMA in piezoelectric PVDF-BaTiO<sub>3</sub> nanocomposite influences surface roughness and improves the elasticity, leading to well-defined periodical microstructures fabricated by nanoimprint lithography. Thus, symmetrical gratings influence the sensitivity of optical components, i.e., the results of diffraction efficiencies of PVDF-PMMA-BaTiO<sub>3</sub> in zero and first orders of its maximum were concentrated in its zero and first orders of its maxima with only a small difference of 5%.

The ability for nanocomposites to possess the piezoelectric properties increases the sensitivity and functionality of

the overall sensing or actuating system and expands the application fields. Thus, formed vibrating piezoelectric nanocomposite structures may be integrated in designing optical components for sensing systems in medicine and as actuators for energy harvesting.

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