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Research Article

Effects of annealing process on the crystalline morphologies of P(VDF/TrFE) studied by atomic force microscopy

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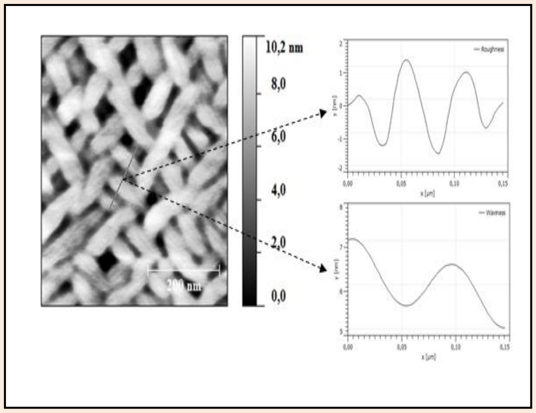
Abstract

Polyvinylidene trifluoroethylene P(VDF/TrFE) (54/46%) ultra-thin film of about 10 nm was elaborated on potassium bromide (KBr) substrates via spin coating technique. The film was heated and cooled at various ranges of temperature including melting point and curie transition. Nanoscale characterization of the copolymer morphology was studied using the atomic force microscope (AFM) in tapping mode. The measurement of the as-deposited film was realized using the AFM line profile software. Results show strong dependence of P(VDF/TrFE) copolymer crystallinity and its lamellar geometry modification with temperature gradient in nanoscale structure.



Keywords: P(VDF/TrFE) ultra-thin film, crystalline lamellae, nanoscale structure, AFM tapping mode

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Introduction

Polyvinylidene fluoride and its copolymer with trifluoroethylene P(VDF/TrFE), have received special attention over their piezo and ferro-electric polymers, many studies have been focused on those ferroelectric polymers due to their widespread applications in transducers, sensors and actuators and a potential use in high-density data storage [1-3]. They have also tremendous applications in infrared imaging and compact capacitors and hold a promising future in the field of non-volatile memory [4,5]. Annealing is a standard procedure used in P(VDF/TrFE) film preparation for improving the changes of crystalline morphology, by the analysis of the grain growth process during annealing using the atomic force microscopy technique (AFM). We notice that the AFM is an excellent tool to study morphology and texture of diverse surfaces. The knowledge of the surface topography and morphology at nanometric resolution made possible to probe dynamic biological process [6], tribological properties [7,8], mechanical manufacturing[9] and mainly thin film surfaces [10,11]. The versatility of this technique allows meticulous observations and evaluations of textural and morphological characteristics of the film, showing better facilities than other microscopic methods. A repetitive or random deviation from the nominal surface forms the pattern of the surface. Surface texture includes roughness, waviness, lay and flaws. Using adequate software, it's possible to evaluate characteristics such as roughness, porosity, average size and particle size distribution, which influence directly the optical, mechanical, surface, magnetic and electrical properties of thin films.

The P(VDF/TrFE) known as one of the most promising ferroelectric copolymers, therefore, we were interested, in this paper, to describe the effect of thermal annealing on the crystalline morphology and topography of P(VDF/TrFE) blend polymer, prepared by spin coating method, at various ranges of temperature, using an atomic force microscope in tapping mode for analyzing and visualizing the surface nano-texture of the copolymer film. The choice of the tapping mode imaging allows examination without damage or surface alteration of a boarder range of soft materials than the traditional AFM contact mode. Tapping of soft surfaces by oscillating AFM tip prevents damage by eliminating the lateral forces that are inherent to contact mode where the tip is simply dragged across the surface of samples.

Experimental

P(VDF/TrFE) ultra-thin film used in this study is prepared as follow : A droplet of methylethyleketone solution P(VDF/TrFE) with 54/46 molar content, was spin coated on a KBr substrates. The ultra-thin film was heated from room temperature 20°C to 140°C and then cooled from 140°C to 20°C. We used a commercially available AFM instrument equipped with a heating stage. Thus, for our copolymer, which is considered as soft material, a silicon probe with low stiffness in the range of 0.3 to 1 N/m are required for tapping mode experiments. The stiffness of the probe is only one of the parameters that influence tip-sample forces in tapping mode. The other parameters are two amplitudes: the amplitude of the free oscillating probe and the set-point amplitude used for the feedback. Higher resonance frequency of about 300 kHz is preferable because it allows for a faster scan rate but it should also be taken into account that polymer surfaces become stiffer at higher frequencies. This property further reduces the possibility of sample damage when using a high resonance frequency cantilever. Our experiments were done in ambient conditions, in order to observe the changes of the crystalline morphologies of P(VDF/TrFE) copolymer. The film surface was imaged instantly for both heating and cooling processes in a tapping mode.

Results and Discussion

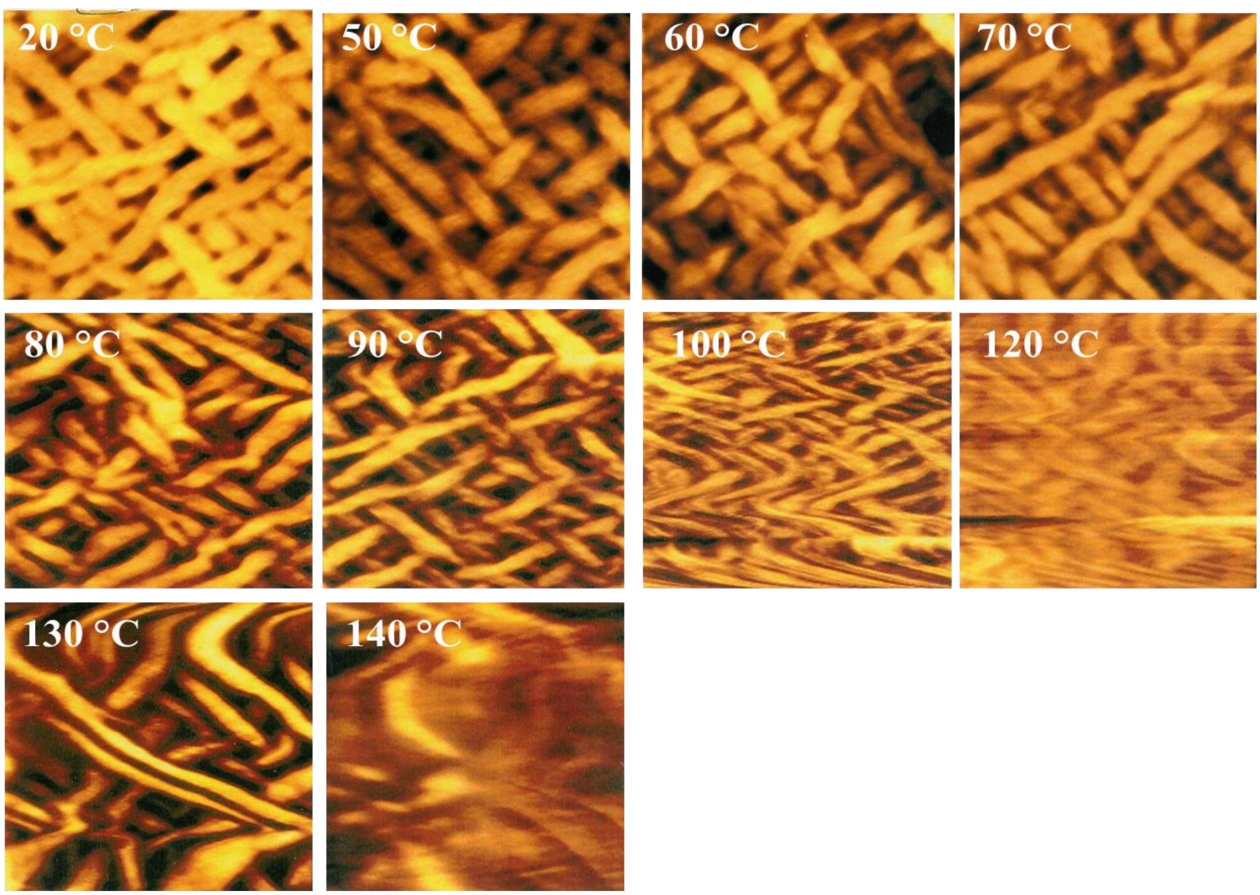

Figure 1 AFM topography images of 10 nm thick P(VDF/TrFE) film in heating process
Scan area: 500nm x 500nm

Atomic force microscopy analysis is ideal for quantitatively measuring the nanometric dimensional surface roughness and for observing the surface nano-texture of the deposited films and films during annealing process. Figures 1 and 2 show the AFM topography images of 10 nm tick P(VDF/TrFE) film in two differents process: heating and cooling process respectively. The horizontal and vertical length scales of each image are about 500 nm. As it can be seen in figure 1, the deposited film at room temperature 20°C consists of ellipsoidal grains with a size in the range of about 300 nm and 75 nm which are randomly oriented in the film surface. Since it is known that this copolymer forms crystalline lamella whose lamellar planes are perpendicular to the substrate (edge-on crystal) by crystallizing at the temperature range between its curie transition and melting point [12,13]. During the annealing process, a careful control of the heating (**Figure 1**) and cooling (**Figure 2**) measurement time is crucial for successful imaging because of the sample drift and morphology changes, for this reason all images were taken instantly. Figure (1) shows topography images of P(VDF/TrFE) heated from 20°C (RT) to 90°C, the lamella became more thinners, we can observe large dark spots due to the partial dewetting of the film during the annealing. With the increase of temperature to 140°C, a melt phase starts to appear, a liquid solid state was observed, structure began to fall apart, chains came out of their ordered arrangement and began to move around freely.

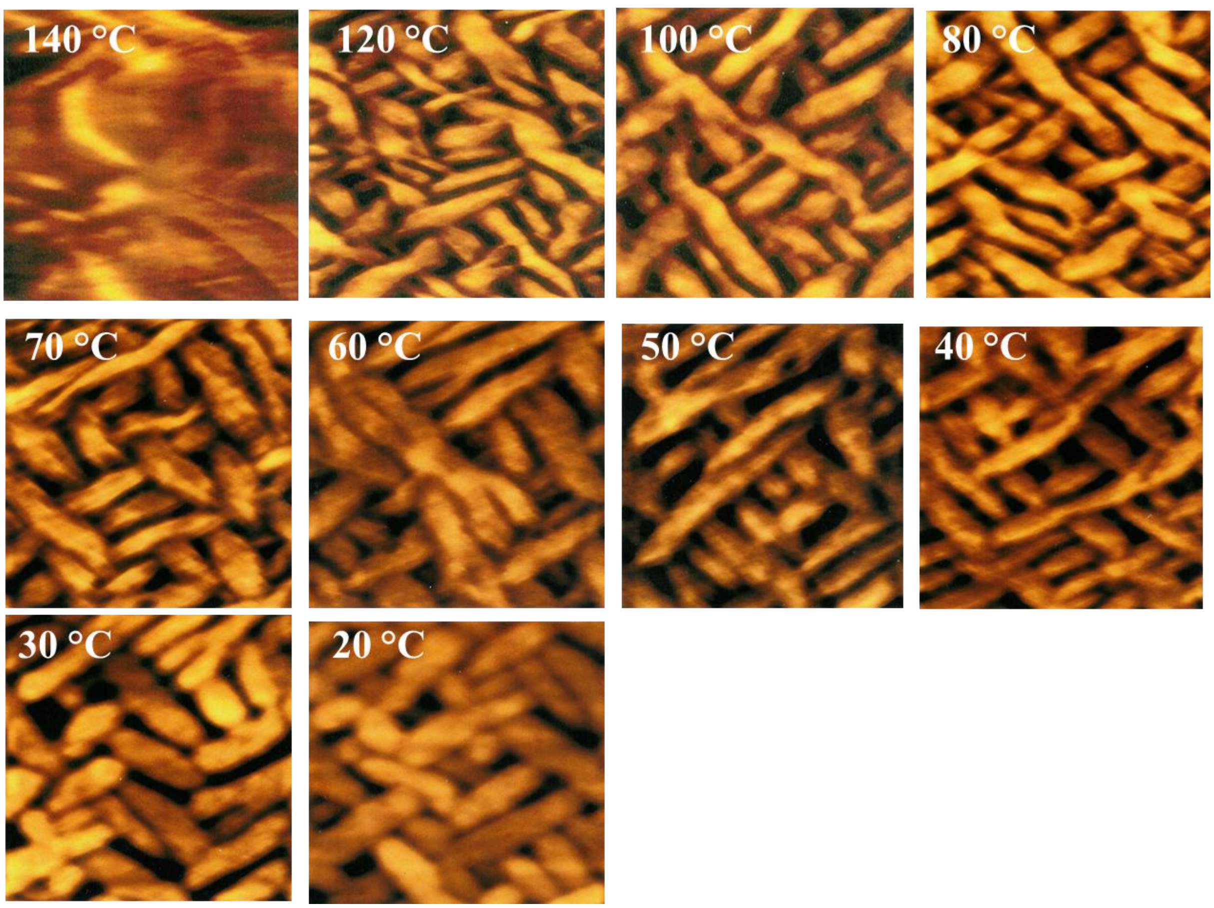

Figure 2 AFM topography images of 10 nm thick P(VDF/TrFE) film in cooling process
Scan area: 500nm x 500nm

During the cooling process from 140°C to 20°C (RT), the copolymer had high shrinkage rates as it cools from its melted state, a tick lamellar structure appears. As we can see in figure (2), P(VDF/TrFE) copolymer develop a partially crystalline structure upon cooling, which is its natural and relaxed state. Crystallization causes to the copolymer the increase of its density as the crystal structure forms, the molecules form more ordered and more tightly and packed structure. As the temperature is reduced below the maximum 140°C to minimum 20°C (RT), the rate of crystallization decreases rapidly because the molecules have reduced freedom of movement to achieve their relaxed state, crystallization continues until a stable crystal structure is obtained.

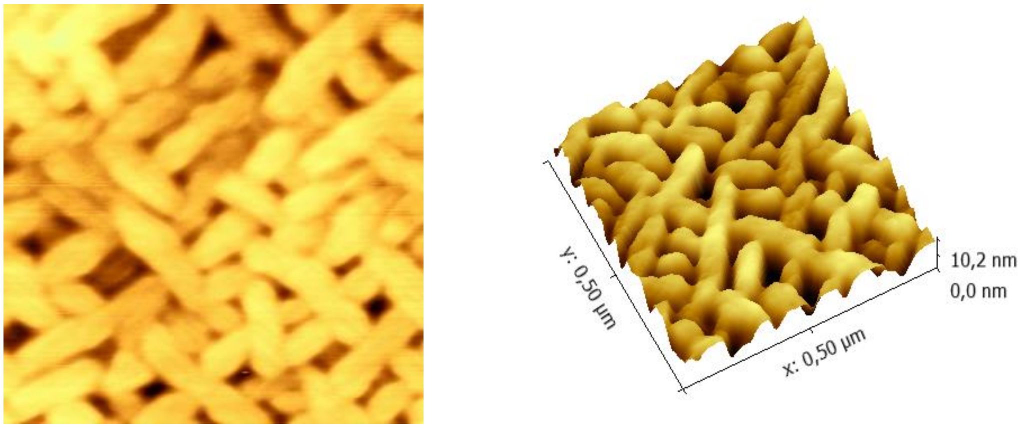

Figure 3 2D (left) and 3D (right) AFM topography imaging of the P(VDF/TrFE) copolymer at room temperature

Figure 3 represents two and three dimensional AFM topography imaging of the P(VDF/TrFE) copolymer at room temperature, both of the two images show the crystalline structure of the copolymer. The dark spots in 2D topography image are clearly observed as valleys where crystalline lamellae are shown as hills. We can suggest that, the 3D image provided by AFM offered interesting information concerning the thickness texture of our thin film, showing the x and y axis of the scan plan area of about 500 nm, and z axis which indicated 10 nm film thickness.

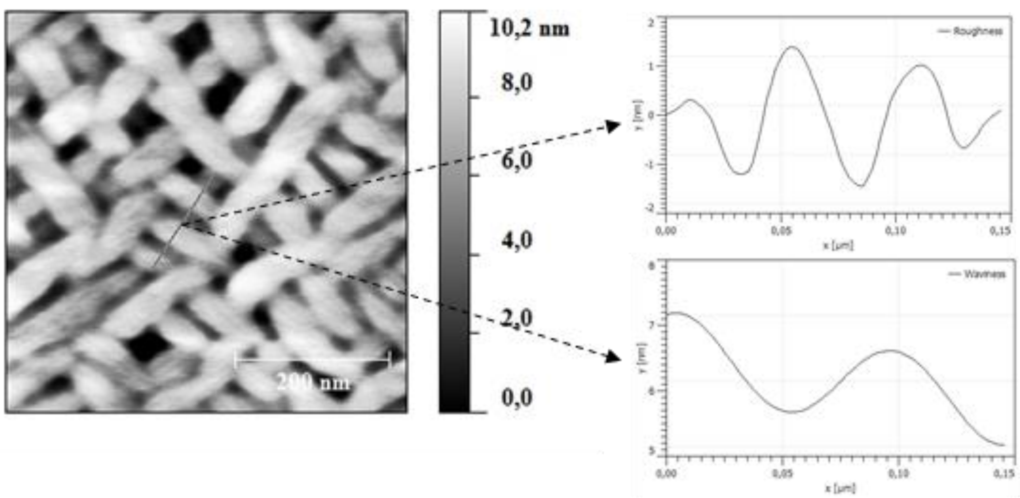

Figure 4 Roughness and waviness curves evaluation of the ultra-thin film P(VDF/TrFE)

Figure 4 illustrated the roughness and waviness curves evaluation from the surface of the thin film P(VDF/TrFE) copolymer. We drew a random black line with distance of 150 nm to determinate the roughness and modulation using an AFM line profile software. Figure 4 allowed us to determine the maximum peak to valley height roughness (Rt), which is the vertical distance between the highest and lowest points in the evaluated length/area and describe the overall roughness of the surface. (Rp) is the maximum peak, (Rv) is the valley height, (Wt) is the waviness height and (Ws) is the waviness spacing. All those characteristics are illustrated in table 1.

Table 1 Roughness and waviness parameters of the ultra-thin film P(VDF/TrFE) deposited copolymer

Rp	Rv	Rt	Wt	Ws
1.4 nm	1.4 nm	2.8 nm	1.5 nm	90 nm

Conclusions

Atomic force microscopy (AFM) in tapping mode was employed to monitor crystalline morphologies of annealing P(VDF/TrFE) ultra-thin film prepared on KBr substrates by spin coating technique. The AFM topography imaging of annealed film from room temperature to 140°C (for heating process) and from 140°C to room temperature (for cooling process), showed that the film surface undergoes a real changes of lamellar structure during the annealing treatment. Structure of annealed film became more oriented and the form of the capsules became more tickers at the end of the cooling process. The roughness and waviness of the surface were also determined by the AFM line profile.

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