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Short communication

Atomic force microscopy enabled roughness analysis of nanostructured poly (diaminonaphthalene) doped poly (vinyl alcohol) conducting polymer thin films

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ABSTRACT

The Atomic Force Microscopy (AFM) helps in evaluating parameters like amplitude or height parameters, functional or statistical parameters and spatial parameters which describe the surface topography or the roughness. In this paper, we have evaluated the roughness parameters for the native poly (vinyl alcohol) (PVA), monomer diaminonaphthalene (DAN) doped PVA, and poly (diaminonaphthalene) (PDAN) doped PVA films prepared in different solvents. In addition, distribution of heights, skewness and Kurtosis moments which describe surface asymmetry and flatness properties of a film were also determined. At the same time line profiles, 3D and 2D images of the surface structures at different scanning areas i.e. $5 \times 5\,\mu m^2$ and $10 \times 10\,\mu m^2$ were also investigated. From the roughness analysis and the surface skewness and coefficient of Kurtosis parameters, it was concluded that for PVA film the surface contains more peaks than valleys and the PDAN doped PVA film has more valleys than peaks. It was also found that the PDAN doped PVA film with acetonitrile solvent was used for substrate in electronics applications because the film gives less fractal morphology. Thus, the AFM analysis with different parameters suggested that the PDAN doped PVA films are smooth at the sub-nanometer scale.

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1. Introduction

Surface modification of polymers plays a key role in determining their biocompatibility to warrant their biomedical applications such as artificial implants, drug delivery systems, ocular devices etc. (Slepicka et al., 2013). One of the most reliable techniques to examine morphological changes in the surfaces of polymers is Atomic Force Microscopy (AFM) which is a versatile tool to examine architectures of surfaces at nanoscale levels. The method has been exhaustively employed to perform morphological characterization of insulating, semi-conductive or conductive polymer samples (Binnig et al., 1986). In an interesting study, the carbon nanoparticles were grafted onto variety of polymers and their morphology was studied using AFM technique (Svorcik et al., 2014). The AFM was also used to examine morphology of the surfaces of poly (L-lactic acid) which were treated with plasma, etched and further grafted with gold nanoparticles to design biocompatible materials (Slepička et al., 2013). Now a day the discovery of new AFM capabilities have opened new avenues for application of this technique to polymers. High resolution of AFM allows study of surface morphology of polymer films, local materials properties and compositional mapping of the sample surfaces (Cohen et al., 1994). It is worth to mention here that the knowledge of the approaches in both, measurements and data analysis while using AFM technique are essential for the correct interpretation of topographic features of the surfaces. The validity and accuracy of surface properties achieved via AFM are greatly influenced by the scan area, resolution and image data analysis procedures.

There are several parameters which describe the surface morphology in terms of roughness parameters, amplitude or height parameters, functional or statistical parameters and spatial parameters. The average roughness ($R_{ave.}$) and the root mean square roughness (R_{rms}) are the intensively used height parameters which provide the general description of height variations, the deviation in height that represent the standard deviation of surface heights, R_{ave} also as the average/absolute deviation of the surface irregularity from the mean line over one sampling length (Maksumov et al., 2004; Bazaka et al., 2011). The study of different surface structures

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by measuring R_{ave} and R_{rms} values enable this technique to be used in different applications e.g. in biomedical field, electronics and fabrication of electrical devices (Krajcar et al., 2014). A large number of peaks and valleys appeared in the AFM image significantly affects the R_{ave} and R_{rms} values and sometimes it is more convenient to calculate the average peak-to-valley difference (Godinho et al., 2003; Raposo et al., 2007). In order to seek insights into the surface structure of the films like asymmetry and flatness, information related to functional or statistical parameters i.e. Skewness and Kurtosis moments are essential parameters that deserve precise evaluation (Brault et al., 1998; Eklund et al., 1993; Tabor, 2010). It is known that skewness is the third moment of profile amplitude probability density function and is used to measure the profile symmetry about mean line.

The Fisher-Pearson coefficient of skewness is commonly given by the formula (Doane and Seward, 2011):

$$g_1 = \frac{\frac{1}{n}\sum_{i=1}^{n}(x_i-\bar{x})^3}{\left[\frac{1}{n}\sum_{i=1}^{n}(x_i-\bar{x})^2\right]^{3/2}} \quad (1)$$

Similarly, the formula of Kurtosis moment is given by:

$$g_1 = \frac{\frac{1}{n}\sum_{i=1}^{n}(x_i-\bar{x})^4}{\left[\frac{1}{n}\sum_{i=1}^{n}(x_i-\bar{x})^2\right]^{2}} \quad (2)$$

where x_i is i^{th} raw data, $\bar{x}$ is mean data, n and m is no. of lines and columns in a given matrix describing the pair of surface coordinates and image of height parameter. In Eqs. (1) and (2), the denominator terms $\left[\frac{1}{n}\sum_{i=1}^{n}(x_i-\bar{x})^2\right]^{1/2}$ (for 2D image) and $\left[\frac{1}{nm}\sum_{i=1}^{n}\sum_{i=1}^{m}(x_i-\bar{x})^2\right]^{1/2}$ (for 3D image) is known as root mean square (RMS) roughness parameter (R_{rms}).

When the height distribution is symmetrical, the skewness is zero. If the height distribution is asymmetrical, and the surface has more peaks than valleys, the skewness moment is positive and if the surface is more planar and valleys are predominant, the skewness is negative. Similarly, Kurtosis moment is the fourth moment of profile amplitude probability function and corresponds to a measure of surface sharpness. When Kurtosis moment is 3, it indicates a Gaussian amplitude distribution, and the surface is called Mesokurtic, but if Kurtosis is smaller than 3 the surface is flat and called Platykurtic. Another type of statistical distribution where the points along the X-axis are highly dispersed, results in a lower peak (lower kurtosis) than the curvature found in a normal distribution. This low peak, with corresponding thin tails, means the distribution is less clustered around the mean than in a mesokurtic or leptokurtic distribution. Platykurtic is derived from the prefix “platy” which means “broad,” resembling its shape – flat, wide or broad. If the Kurtosis is higher than 3, the surface has more peaks than valleys (Joanes and Gill, 1998). Entropy of the film is another significant spatial parameter derived from the morphological measurements and reflects the degree of order or disorder in the grain structure distribution (Piasecki, 2000). Another spatial parameter, coined as Redundance, provides information about the fractal morphology. The lower the values of the redundance, least disorder of the morphology of the films are obtained.

Morphology of a film is also a significant parameter that affects, for example, the quantum efficiency of the Polymeric Solar Cell (PSC). Roughness parameter often results in many voids which create resistance and, consequently, decreases the charge mobility. Roughness morphology of PDAN doped PVA film via Atomic Force Microscope (AFM) results in highly desirable controlled structure for PSCs. Nano-structured voids generated on the surface of PDAN doped PVA film are filled by the n-type derivatives forming a nanowidth channels between n-type and p-type organic material which is a necessary condition for diffusion lengths of excitons in organic electronic materials.

In the present short communication poly (diamino naphthalene) (PDAN) doped poly (vinyl alcohol) (PVA) films have been analyzed by AFM technique. The authors have also evaluated the roughness parameters of native PVA film and compared with the morphology of monomer DAN doped PVA film and PDAN doped PVA films prepared in different solvents. In addition to the determination of distribution of heights, Skewness and Kurtosis moments were also determined that describe the surface asymmetry and flatness properties of the films. At the same time line profile, 3D and 2D images of the surface structure at different scanning areas i.e. $5 \times 5\ \mu m^2$ and $10 \times 10\ \mu m^2$ were also investigated.

2. Methodology

PVA (99% hydrolyzed, MW 85,000 Da) was purchased from Hi Media Chemicals, Mumbai, India. The monomer DAN was purchased from Merck Chemicals, Mumbai, India. All other reagents were of high purity grade. In a typical experiment, 5 g PVA was dissolved in 100 mL of hot distilled water and to this solution a precalculated amount of glutaraldehyde was added as cross-linking agent. Now, the whole mixture was kept in a Petri dish (Corning glass, 2.5 in. diameter) at oven at 50 °C for 48 h. After 48 h, the whole mass was in the form of semi transparent film. The dry film was equilibrated in distilled water for a week to leach out unreacted chemicals. The swollen gel was than dried at room temperature, cut into rectangular size pieces and stored in air tight plastic bags for further studies. Required quantity of DAN was dissolved in two different solvents, acetonitrile and acrylonitrile, and then the PVA gel prepared as above was allowed to soak in the DAN solution for 24 h in acetonitrile and 72 h in acrylonitrile solvents, respectively because acetonitrile gets easily evaporated than acrylonitrile. The DAN containing swollen gels were dried and dipped into an oxidizing agent, ammonium-per-sulphate. As the polymerization initiator penetrated into the monomer loaded film the polymerization proceeds inside the polymer matrix and the semi transparent gel turns into black. The polymerization reaction was allowed to take place for 24 h and the film was purified by allowing it to equilibrate in distilled water. The thickness of the PDAN doped PVA film with acetonitrile solvent and PDAN doped PVA film with acrylonitrile solvent were measured to be 0.30 and 0.38 mm, respectively.

The AFM analysis for native PVA film, DAN doped PVA film and PDAN doped PVA films with both solvents were carried on the instrument NTEGRA Prima, manufactured by NTMDT, Ireland. All the polymer film samples were analyzed using an AFM in tapping mode and acquired in air, at room temperature (25 °C) using cantilevers with a spring constant of 11 N/m, tip radius of curvature of 10 nm, aspect ratio of 10:1 and resonance frequency of 150 kHz. In all the measurements, at least four samples of each type were used and four areas of each sample were scanned for the data collection. Surface scanning was performed perpendicular to the axis of the cantilever with applied frequency of 1 Hz with the experimental scan area of $5 \times 5\ \mu m^2$ and $10 \times 10\ \mu m^2$. The number of sampling along x-axis for roughness analysis for each sample was 65536.

2.1. Statistical analysis

All measurements were done at least four times and the data summarized in tables have been presented as Mean ± S.D.

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