



Structure, morphology and wettability studies on Langmuir-Schaefer multilayer of poly(vinylidene fluoride)/poly(methyl methacrylate) blends

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ABSTRACT

The intermolecular interaction between the polymer chains of different functionality is known to influence the aggregation and molecular chain packing. This way, it is possible to tune the structure, stability and surface quality through the blending of polymers. With this in focus, a systematic studies was carried out to understand structural, morphological and wettability variation in Langmuir-Schaefer multilayer of poly(vinylidene fluoride)/poly(methyl methacrylate) blends. Grazing incidence X-ray diffraction studies on blends showed a Bragg peak around 20.5° indicating the predominant presence of polar β phase up to 40% of poly(methyl methacrylate). Its fraction and dielectric environment are estimated using Fourier transform infrared spectroscopy and fluorescence studies, respectively. Morphological features of the blends studied using field emission scanning electron microscope showed a drastic change with increasing fraction of poly(methyl methacrylate). The surface quality and wettability of blends were assessed using contact angle studies. Contact angle and the volume of the sessile drop linearly decrease with time. A relatively faster evaporation of sessile drop was observed for higher fraction of poly(methyl methacrylate) attributed to its hydrophilicity. The evaporation kinetics was found to be largely dependent on the surface quality and chemical nature of poly(vinylidene fluoride)/poly(methyl methacrylate) multilayer.

1. Introduction

Poly(vinylidene fluoride) PVDF, is a thermoplastic semicrystalline polymer, well known for its various medical and engineering applications [1–3]. It offers interesting properties such as high flexibility, chemical and thermal resistance and biocompatibility. The polymer can be easily processed into various forms such as thin film, fibers and colloidal particles [4]. PVDF is unique due to its ability to crystallize into different crystalline phases. Among these, the polar phases are highly desired. Prominent polar phases of the PVDF are β , γ and δ , which is interesting due to its effective dipole moment dictating piezo, pyro and ferroelectric properties [5]. In addition, the defect sequence plays a role in driving these phases [6–8]. All these phases are of semicrystalline nature and the polymer predominantly crystallizes to α phase, which is of paraelectric nature [9]. The dipolar arrangement of the α phase in the polymer can be altered using a high electric field of the order MV/m [8]. Alternately the polar fraction of the polymer can be enhanced through polymer stretching. These methods create anisotropy in the material and hinder its application as piezo and pyroelectric devices. Therefore alternate methods driving polar phases are preferred. PVDF fibers are increasingly used in active biomedical and tissue engineering applications due to its large piezoelectric response and physicochemical stability [10]. In these cases, the wetting and

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adhesion properties of the polymer are vital. However, the hydrophobic nature of PVDF results in poor wettability and low surface energy. This can be addressed by surface grafting, plasma treatment and nanocomposites [11–13]. Further, they are also used as separator membranes in lithium ion battery applications to control the electrolyte retention, thermal/mechanical stability, lifetime and charging reaction occurring at electrodes [4,14]. Polymer blending is yet another widely accepted methods to tailor low surface tension and wetting behavior. Representative polymers such as poly(methyl methacrylate) (PMMA), poly(vinyl acetate), poly(vinyl alcohol), poly(vinylpyrrolidone) and poly(ethylene glycol) have been mixed with PVDF to balance its mechanical and wettability properties [11]. Blending PVDF with PMMA is known to reduce the roughness to a large extent [15]. The major factor is to ensure the miscibility of the polymers, which are dictated by the mutual interaction of the chain segments and other functional groups [16]. PMMA is miscible in the whole range of composition with PVDF, however incorporation of PMMA >40% by weight results in largely amorphous phase [17].

Most of the blend films deal with the high concentration of polymer in which segmental motion of the polymer chains is hindered due to the constraint in available space. As a result of high concentration of the casting solution, the polymer chains are overlapped and entangled. Such conditions were avoided in our study by choosing a superior Langmuir-Schaefer method of film preparation. There are very few reports on the miscibility and stability of the polymer blend particularly in a 2D confinement such as Langmuir film. Literature available so far mostly deals with polymers which are of amorphous nature. However, very few reports address the behavior of a semicrystalline polymer blend at the air-water interface. In this regard, stability and the miscibility of PVDF with the addition of an amphiphilic poly(N-dodecyl acrylamide) (pDDA) polymer are discussed [18,19]. This stability in the polymer was attributed to the formation of hydrogen bonding of pDDA with PVDF. We put the effort in a similar direction by choosing PMMA as blending polymer with PVDF. PMMA is chosen due to its wide band of compatibility with PVDF. This compatibility originates due to intermolecular interactions between the carbonyl groups of PMMA, and the CF₂ and CH₂ groups of PVDF [20]. We prepare Langmuir-Schaefer multilayer of PVDF/PMMA blends by varying the PMMA weight percentage (wt.%). A semidilute regime of the Langmuir film is chosen for the deposition of multilayer [21]. PVDF/PMMA multilayer is characterized using grazing incidence X-ray diffraction (GIXD), Fourier transforms infrared spectroscopy (FTIR), fluorescence spectroscopy, field emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDS) techniques to study the change in structural and morphological features. The optical parameters of these polymer blends are investigated using ellipsometric measurement. The surface wettability of the blends is investigated through static and dynamic contact angle measurements. Further, the surface quality of the PVDF/PMMA is discussed in terms of contact angle hysteresis and associated surface energy for various wt.% of PMMA is evaluated.

2. Materials and methods

2.1. Materials

Polymer PVDF (powder, MW ~ 550,000) and PMMA (granular, MW ~ 120,000) was purchased from Alfa Aesar and Sigma Aldrich respectively and used as received. The chemical structures of these polymers are shown in Fig. 1. Solvents (dimethyl sulfoxide (DMSO), chloroform and acetone of ACS or HPLC grade of high purity (>99%)) were purchased from Merck. Piranha solution was prepared by mixing H₂SO₄ and H₂O₂ (GR grade) of 70:30 ratio. Silicon (p-type) substrate was purchased from Siltronix. Ultrapure (Millipore) water of resistivity 18.2 MΩ.cm was used as subphase for the Langmuir film. Nile red was supplied from Molecular probe.

2.2. Polymer solubility and deposition of Langmuir-Schaefer multilayer

Polymer and solvent compatibility was estimated using Hansen solubility parameter (HSP). Hansen solubility parameter describes the solvent and the polymer interaction arising from the dispersion, dipolar and hydrogen bondings. The closeness of the respective parameters is desired for better dissolution. Based on HSP, solvent DMSO was chosen as a good solvent for both the polymers. HSP of the polymers and the solvent used in this study is given in Table 1.

For the film transfer, Langmuir trough (KSV instrument, Finland) was cleaned thoroughly using chloroform and ethanol and washed using double distilled water before each run. The cleaned trough was filled with a ultrapure quality of water and the surface was aspirated up to a surface pressure of 0.5 mN/m. A polymeric solution of concentration ~0.5 mg/ml is prepared in DMSO solvents mixing PVDF/PMMA in different weight percentage. In this study, the ratio of PMMA was varied from 0 to 40% and depending upon

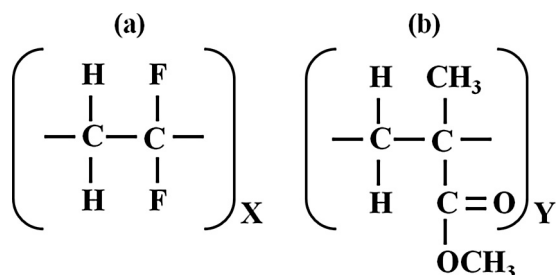


Fig. 1. Chemical structure of the polymers (a) PVDF and (b) PMMA.

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