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Chemical and electrical properties of HMDSO plasma coated polyimide

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ABSTRACT

In this work, surface properties of polyimide (PI) films coated by thin layers deposited from pure hexamethyldisiloxane (HMDSO) vapours in low frequency powered plasma reactor have been investigated. The polymer thin layers were elaborated at different plasma treatment times. The surface characterization of the coated PI film is performed using attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), refractive index, scanning electron microscopy (SEM), water droplet contact angle measurements and surface potential decay. The high carbon content revealed by ATR-FTIR analysis makes the coated surface PI films more hydrophobic. The water contact angle increased from 63° for untreated film to 115° after 10 min of HMDSO plasma coating. The coated PI surfaces were found to stay practically unchanged following storage of the samples in ambient conditions, indicating stable hydrophobic surface treatments. The increase of the refractive index indicates less porous structure. Scanning electron microscopy images showed a homogenous coating without crack. Surface potential evolution after corona charge deposition showed the retention of deposited charges at the surface of coated PI film. Correlation between these different analysis techniques results has been discussed.

1. Introduction

In many polymer applications, hydrophobicity and barrier properties are of great interest in recent years. These applications include packaging films, electrical cables, textiles, non-woven materials, flat panel displays and corrosion protection [1–3]. Aromatic polyimides (PI) have been used today in many applications because of their good physicochemical and electrical properties, including high mechanical strength, low dielectric constant and good thermal stability and chemical resistance [4]. However, applications of PI are often limited by their hydrophilic character [5], which represents a serious problem in many industrial applications. In order to improve the hydrophobicity and other related surface properties, plasma technology for surface modification of polymers has been used. Compared with conventional chemical treatments using solvents and organic reagents, which may cause environmental and health problems, cold plasma treatment is an environmentally friendly process used to create good quality deposit without affecting the good properties of the bulk [3,6]. This process has the advantage of providing a uniform modification of the surface region, yielding more stable hydrophobic properties [2,3,7,8].

Plasma polymerization of HMDSO (ppHMDSO) has been used to improve the water repellency and barrier properties of polymers. Most of the previous studies were focused on the deposition of thin layers from HMDSO on polyethylene terephtalate (PET) substrates in order to reduce the permeation rate of gases and vapours through polymers [2,7]. Other polymeric substrates, such as polyimides, polypropylene (PP) and polycarbonate (PC) have also been investigated [3,9,10]. Until now, physico-chemical properties of deposited thin layers from HMDSO on PI substrate have been the main focus of studies but only few authors have concerned with the surface electrical properties of the deposit in addition to the structural properties [3]. The surface potential decay method was used to measure the surface potential previously charged by corona discharge using a non contacting electrostatic probe. This method was largely used for the characterization of charge ability of electrets [11], which are widely applied in electric-acoustic transducers,

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biomedicine, electrostatic power-generators and other useful properties [11,12]. For example, Rychkov et al. [13] have reported that the chemically modified surface of polytetrafluoroethylene (PTFE) and low density polyethylene (LDPE) films leads to considerable improvement of the electrets properties. The understanding of surface charges transport phenomena in polymer material can be related to the following factors: porosity of the thin layers, their specific surface and their apparent density [14].

In this context, we have used plasma polymerization of pure HMDSO in low frequency plasma reactor for PI surface modifications. The plasma polymer thin layers were elaborated at different plasma treatment times (from 2 to 30 min). The physico-chemical and surface electrical properties of the deposited layers have been studied using attenuated total reflectance Fourier transform infrared ATR-FTIR spectroscopy, refractive index, scanning electron microscopy (SEM), water droplet contact angle measurements and surface potential decay. The obtained results show that plasma polymerization of pure HMDSO greatly enhance the hydrophobicity of the PI film. In addition, the hydrophobicity of the coating was correlated with the surface charge retention stability (surface potential decay).

2. Experimental details

Thin layers were deposited by plasma enhanced chemical vapour deposition technique (PECVD) using pure HMDSO as liquid precursor. The deposition was carried out in a capacitively coupled plasma reactor composed of Pyrex cylinder (360 mm height and 310 mm diameter) powered with low frequency generator (19 kHz). Schematic view of the plasma reactor used for HMDSO thin layers deposition is shown in Fig. 1. The plasma reactor consisted of a pair of parallel symmetrical electrodes (12 cm diameter) separated by a distance of 25 mm, a primary pump vacuum system and a monomer inlet system. Substrates were placed on the grounded lower electrode and the reactor chamber was pumped down to 10^{-2} mbar. A constant partial pressure of HMDSO vapour was adjusted to 0.4 mbar and injected to the reactor without any carrier gas. In order to investigate their effects on the chemical and surface electrical properties of the elaborated layers, treatment times have been varied between 2 and 30 min, while the discharge power has been fixed at 10 W. The plasma polymerized thin layers were deposited simultaneously on PI films and intrinsic silicon wafers for thickness and refractive index measurements. All the experiments were performed at room temperature.

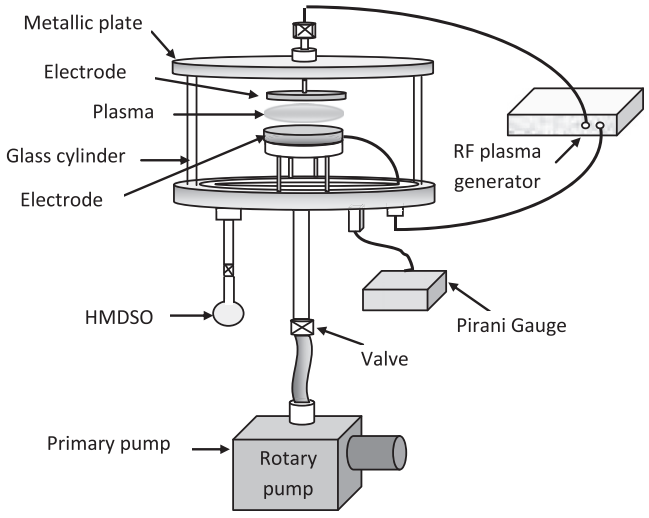

Fig. 1. Schematic view of the plasma reactor.

The treated material is 50 μm PI film (PI; Kapton-HN® of Goodfellow). Before coating procedure, PI substrates were cleaned with demineralised water then dried immediately with dry air to eliminate surface contaminant.

Chemical structure and composition of deposited thin layers were characterized by means of FTIR spectroscopy using a Thermo Nicolet Avatar 360 spectrometer equipped with zinc selenide (ZnSe) crystal prism (incidence angle of 45°), in the horizontal attenuated total reflectance (HATR) mode. All analyses were performed with a resolution of 4 cm^{-1} and 32 scans.

The thickness of the coatings was measured using a Tencor profilometer and a microspot beam spectroscopic ellipsometer (Sopra GES5) with an incident angle of 75.6° (silicon Brewster angle). The layer thickness and the refractive index were deduced from ellipsometric data using the Forouhi Bloomer model [15].

To characterize the evolution of the surface morphological feature of the coated film, scanning electron microscopy (JEOL JMS-6060 LV) has been used.

The hydrophobicity of the thin layers is evaluated by water contact angle. The contact angles with distilled water were measured using a 5 μl water drop. Contact angle measurements before and after HMDSO plasma coating were performed using an optical system permitting the visualisation of the drop image. The drop image was recorded by a numerical camera then transmitted to a computer workstation to calculate the contact angle value. The reported values are the means of three measurements recorded for each sample. The typical standard deviations due to experimental error were estimated as being approximately 5%. All water contact angle measurements were carried out at ambient conditions where temperature and relative humidity are kept approximately constant.

The untreated and coated PI films have been charged by negative corona discharge (Fig. 2). The point to grid configuration has been used to uniform the distribution of the charges and to control the surface potential. The corona tip and the metallic grid were connected to a dc high voltage variable up to 10 kV and 3 kV, respectively. All PI samples have been charged with the same charging conditions (corona tip voltage of 6 kV, grid voltage of 2 kV, tip-sample distance of 10 mm, grid-sample distance of 5 mm and charging time of 30 s). After corona charging, the sample was immediately transferred in a controlled manner under a Monroe vibrating probe (Monroe 1017 AS). The probe is connected to an electrostatic voltmeter (Monroe 244A-2 model), which measures the surface potential in the ±3 kV range. The distance between the probe and the free surface of the sample was kept to 2 mm. The measurements were carried out without contacting the surface

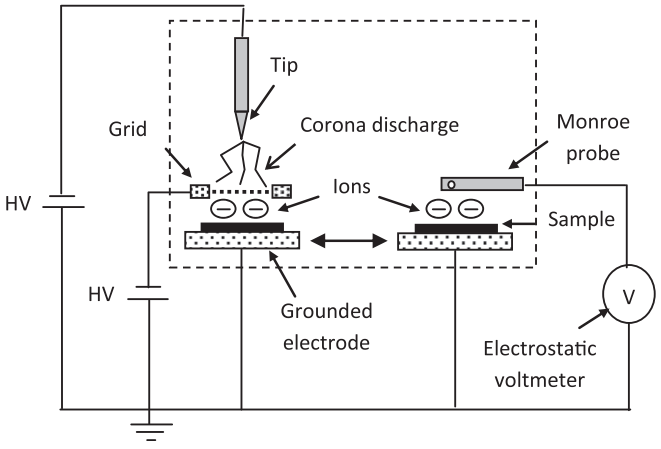

Fig. 2. Experimental set up used for dc corona charging and surface potential measurements.