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Dielectric properties of plasma polymerized poly(ethylene oxide) thin films

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ABSTRACT

Plasma polymerized poly(ethylene oxide) (pPEO) thin films were deposited by plasma assisted physical vapor deposition (PAPVD) with a constant thickness of 500 nm. The crosslinking density of pPEO films was controlled through the discharge power. Differential scanning calorimetry (DSC) and broadband dielectric spectroscopy (BDS) were applied to analyze the structural peculiarities of these coatings. Both DSC and BDS detected an increase of the crosslink density with power, which correlated with the increasing dynamic glass transition temperature (T_g). It was shown that plasma power changes the structure of plasma polymer, and dielectric spectroscopy may be a suitable technique for structural analysis.

1. Introduction

Thermal, electric, and mechanical properties of polymers make them easy to process and beneficial for use in various applications [1–7]. Polyethylene oxide (PEO) is a member of the large polymer family and it has drawn attention owing to its biologic non-fouling properties. Biologic non-fouling is the ability to resist the formation of biofilms. Non-fouling properties were investigated by Choukourov et al. It is known from their studies that there are similarities between plasma polymer samples deposited at low plasma power and precursor polymers [8]. Non-fouling is of high importance in a number of biomedical applications where accumulation of proteins and micro organisms should be limited or completely avoided. It has been recognized that the non-fouling of PEO-attached surfaces is achieved through the presence of repeating ether groups and by the flexibility of their macromolecular chains. Nevertheless, conventional PEO consists of noncross-linked linear macromolecules; therefore, it is prone to dissolution in aqueous media. Cross-linking of PEO chains was suggested in order to enhance the durability of the non-fouling action. Creation of covalent bonds between macromolecular chains results in formation of a branched polymer network, which significantly improves the stability of PEO in a water environment. Branched network products can be homogenous, pin-hole free, insoluble in water, highly electrically resistant, chemically stable, highly crosslinked, good adhesive, and thermally stable [7]. On the other hand, the cross-link density should not be excessively high to keep the flexibility of the macromolecular segments, and non-fouling properties should be retained.

Plasma polymerization of volatile ether-bearing precursors [9–14] or, later, plasma-assisted vacuum evaporation of PEO [15–16] were suggested to deposit thin PEO-like films onto solid supports. Both approaches proved to be versatile in the fabrication of films with controllable properties, including the cross-link density related with the density of C—O—C groups, as reported in the publication by Choukourov et al. The authors reported plasma polymers that were prepared using vacuum thermal depolymerization of PEO as products built from much longer oligomers; therefore, classic theories of polymeric networks could be attempted for their characterization [16]. In many cases, however, the cross-link density was estimated indirectly and only qualitatively as being proportional to the relative concentration of the ether groups that directly correlated with the power delivered to the discharge. Although this assumption seems to be valid for highly cross-linked films, certain indications exist in which dependence deviates from the linear behavior for less cross-linked films and an order of magnitude change in the cross-link density may result only in a slight change in the percentage of the C—O—C groups [16]. It is expected there is much more CH_2 recombination after fragmentation of CH_2 groups, but some C atoms combine with O and the resulting CO groups

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may be exhausted using a vacuum system during deposition, as reported by Choukourov et al. [15]. Swelling experiments combined with a model of constrained swelling of polymeric networks allowed for quantitative calculation of cross-link density in PEO-like plasma polymers and confirmed its non-linear dependence on discharge power [17].

Obviously, analytical methods that are sensitive to structural variations in PEO-like plasma polymers may provide valuable information in addition to those that rely only on chemical composition. Broadband dielectric spectroscopy is a widely used technique for investigating the structure and molecular dynamics of various materials. The first dielectric spectroscopy studies on plasma polymers were performed by Bradley and Hammes [18]. Later, a multitude of works appeared that aimed to establish a relationship between the dielectric properties and structural peculiarities of plasma polymers [19–29]. Surprisingly, plasma polymerized PEO was missing in these records, although chemically-produced PEO networks were the subject of extensive studies. The aim of this work was to fill the gap and to take advantage of BDS to define the effect of discharge power on structural changes in pPEO.

2. Experimental

2.1. Plasma polymerization

Thin film deposition was operated in a vacuum chamber with a base pressure of 10^{-3} Pa produced by rotary and diffusion pumps. A copper crucible was used for vaporization. The crucible was filled with PEO (Sigma-Aldrich, Inc., $M_n = 1500$ g/mol), described as PEO granules by Choukourov et al. [16], mixed with Cu granules for better heat transfer. A radio frequency (RF) magnetron with a graphite target was placed 4 cm below the crucible to ignite a glow discharge. Graphite target was used because the contribution of sputtered carbon to the deposited films was minimal (2.5%). The experiments were performed in argon under 1 Pa pressure and 5 cm^3/min flow rate. The discharge power was supplied by an RF generator (Dressler Ceasar-13, 56 MHz) via a matching unit. The samples were deposited with 2, 5, and 30 W discharge power, as well as without plasma. At deposition without plasma, there is only evaporation. It is thought that fragmentation is low and the structure of the deposited sample is similar to the precursor polymer, as reported by Choukourov et al. [15–16]. Hereafter, these samples are referred to as pPEO2, pPEO5, pPEO30, and PEO0, respectively. A Quartz Crystal Microbalance (QCM) was used to adjust the deposition rate to 10 nm/min. The thickness of the pPEO samples was measured by ellipsometry (Woollam M-2000 DI). When the deposition conditions (Ar pressure and flow rate, the discharge power and deposition rate) were stabilized, the substrates were introduced into the chamber by a load lock.

2.2. Sample fabrication

Glass substrates (76 mm × 24 mm) were cleaned using ultrasound in acetone and ethanol, respectively. Al electrodes were deposited by thermal evaporation technique at 10^{-3} Pa pressure. The bottom electrode was deposited over the glass substrate and the top electrode was deposited after plasma polymerization had been performed through a mask as a strip with an area of 16 mm^2. A short deposition time of 10 s was chosen for the top electrode deposition to protect the underlying pPEO surface from the thermal effect of radiation.

Alternatively, pPEO films were deposited onto 10 cm × 10 cm glass substrates. After deposition, the samples were scratched off the glass for subsequent use in the DSC analysis.

2.3. Dielectric spectroscopy measurements

An Alpha-N Impedance Analyzer (Novocontrol Inc.) was used for dielectric spectroscopy measurements. The measurements were performed in the frequency range from 10^{-1} Hz to 10^7 Hz. The samples were cooled from room temperature 293 K to 173 K (1st cooling), then they were heated up to 353 K (1st heating) and eventually cooled down to 173 K again (2nd cooling). The cooling/heating rate was 10 K/min. The reason of the thermal processes is to investigate the effect of heat on crosslinking in plasma polyethylene oxide structures.

The dielectric constant ε' was derived from the measured capacitance by equation:

$$\varepsilon' = Cd/\varepsilon_0 A \qquad (1)$$

Here, C is the measured capacitance, d is the thickness of the thin film, A is the area of the electrodes, and ε_0 is the permittivity of the vacuum (1).

The electric modulus M′ is derived from the dielectric constant as shown below (2):

$$M' + iM'' = 1/[\varepsilon'\text{-}\varepsilon''] \rightarrow M' + iM'' = [\varepsilon' + \varepsilon'']/\left[(\varepsilon')^2 + (\varepsilon'')^2\right]$$
$$M' = \varepsilon'/\left[(\varepsilon')^2 + (\varepsilon'')^2\right] \qquad M'' = \varepsilon''/\left[(\varepsilon')^2 + (\varepsilon'')^2\right] \qquad (2)$$

2.4. Differential scanning calorimetry analysis

Thermal analysis was performed using differential scanning calorimetry (DSC8500 Perkin Elmer) (DSC). The cooling and heating processes were performed similar to the BDS procedure, except for the lowest temperature being 113 K. The step-like behavior of heat flow depending on temperature was taken to establish the calorimetric glass transition temperature [26,29].

3. Results and discussion

3.1. Dielectric constant

For the PEO precursor, the frequency and temperature dependences of the dielectric constant are shown in Fig. 1a, b. Both the first and the second cooling processes are demonstrated. This behavior refers to all investigated samples.

When the first cooling was compared with the second cooling, the dielectric constant did not show a change depending on frequency and temperature for the PEO precursor. However, for pPEO samples, the dielectric constant exhibited changes for various cooling processes and these changes are presented in Fig. 2a, b. The frequency and temperature dependence of the dielectric constant for pPEO5 in the first and second cooling processes are shown in Fig. 2a, b. It was found that

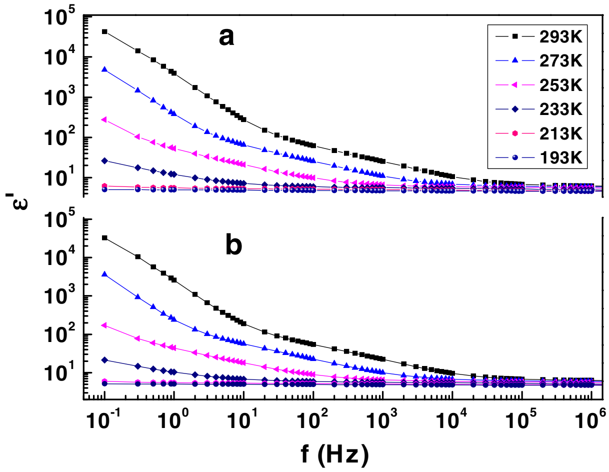

Fig. 1. Frequency and temperature dependence of dielectric constant for PEO precursor in the (a) first cooling, (b) second cooling.