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Real time optical and mechano-optical studies during drying and uniaxial stretching of Polyetherimide films from solution

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ABSTRACT

In order to have a fundamental understanding of the temporal evolution of physical characteristics of Polyetherimide (PEI) film and processing parameters, real time measurements are essential. Because drying and stretching processes of solvent-cast polymer film are complex, off line measurements are unable to reveal the temporally varying detailed information, especially for fast "transient events". To solve the problem, two measurement systems, one for drying that tracks real time thickness, weight, surface temperature, in-plane and out-of-plane birefringence of solution casting film, and another for uniaxial stretching that tracks real time true stress, true strain and birefringence of stretched film are used. By using these systems, we are able to systematic investigate the development of optical anisotropy through in and out of plane birefringence monitoring drying of solution cast films and their mechano-optical behavior during stretching, and quantify the influence of solvent N-methyl-2-pyrrolidinone (NMP) on these relationships.

1. Introduction

Polyetherimide (PEI) exhibits excellent thermal, chemical, and mechanical stabilities as well as its good film forming properties [1–4]. These properties allow it to be used in harsh industrial applications including electronics, automotive and aerospace [5–7]. The optical properties of solvent-casting polymer films are of great technological importance in a host of optoelectronic system and devices. They are commonly affected by the intrinsic optical anisotropy of the polymer chain and the orientation induced in the casting processing. Rickert et al. [8] studied that the orientation phenomena of polymer chains was controlled by solution properties, substrate properties and interfacial properties. Cherkasov et al. [9] researched the alignment behavior of polymer chains by free casting, and found the stiffness of the polymer chain had a great influence on the planar orientation. Cohen and Reich [10] investigated the effects of the molecular weight and polydispersity on the ordering of molecular chain in thin films. Similarly, Prest and Luca [11,12] focused on the effects of molecular weight, film thickness, solvent, plasticizer content and temperature on the orientation in polymer films.

Because drying of solvent-cast polymer film involves complex sequence often overlapping events, monitoring solvent evaporation, thickness reduction, and molecular chain orientation are very important to unravel these details. For this purpose, we developed a real-time instrument that can detect these fast changes in physical parameters in the drying behavior of polymer film [13]. These include weight, thickness, surface temperature, in-plane and out-of-plane birefringence during solvent evaporation and thermal or photocuring in a controlled atmosphere (air velocity and temperature).

In the case of mechanical and mechano-optical properties of PEI, Nied et al. [14] studied the deformation behavior of PEI in the uniaxial tension process. They found there was a stable necking over a broad temperature range (22–204 °C). Kanuga [15,16] studied the stress-optical behavior of polyethylene naphthalate (PEN)/PEI blends through using a real-time instrument which tracks the structure development by measuring the birefringence of polymer film. All the work require a relatively high processing temperature due to high glass transition temperature of PEI. Mixing with solvent [17,18] can be a good method to decrease the glass transition temperature of polymer, and thus decrease the processing temperature that is typically set at about $T_g + 20$ °C.

In this paper, we investigate real time drying behavior of solution cast PEI film by tracking birefringence, solid content, surface temperature, thickness, weight under selected air speed and

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temperatures. The effects of varying solid content of solution, drying temperature, initial casting thickness, air speed and different kinds of solvent on the birefringence development are systematically investigated. In addition, this study involves the mechano-optical behavior of PEI film during uniaxial stretching with particular focus on the influence of solvent type and content on these relationships.

2. Experimental

2.1. Materials

Polyetherimide (Ultem 1000P) was kindly donated by Sabic Company and its density is 1.27 g/cm^3. N-methyl-2-pyrrolidinone (NMP) (CAS Number: 872-50-4) and N, N-Dimethylacetamide (DMAc) (CAS Number: 127-19-5) were purchased from Sigma–Aldrich Company. The boiling point and density of NMP are 202 °C and 1.028 g/cm^3, respectively. The boiling point and density of DMAc are 165 °C and 0.937 g/cm^3, respectively.

2.2. Solution casting

The PEI solution (solid contents of solution were 17%, 21%, 25%, and 30%, respectively) was cast on a smooth surface of a glass substrate by using a motorized drawdown coater and a commercial 3″ wide casting doctor blade. The initial length was 7″and the initial width was 3″.

2.3. Rheology

The rheological tests were run on a Bohlin Gemini HR Nano 200 by using a cone and plate 4° incline, 40 mm diameter measuring geometry (CP 4/40) at room temperature. The shear rate was between 0.01 1/s and 1000 1/s.

2.4. Drying apparatus and drying process

The real-time measurement system [13] used in this experiment is shown in Fig. 1. It consists of a wind tunnel shaped frame with three adjustable vertical baffles, an electronic balance, several sensors for tracking changes including in-plane and out-of-plane, thickness and temperature. The air temperature may be adjusted from room temperature to 500 °C and the air speed may be varied from 0 to 4.5 m/s using hot air blower.

Through using spectral birefringence method [19–35], the temporal in-plane and out-of-plane birefringence are calculated by 0° and 45° retardation values. The in-plane birefringence Δn_{12} is calculated by Stein's equation [36]:

$$\Delta n_{12} = \frac{R_0(t)}{d(t)} \tag{1}$$

Also, the out-of-plane birefringence Δn_{23}:

$$\Delta n_{23} = -\frac{1}{d(t)}\left[\frac{R_0(t) - R_\phi(t)\sqrt{1-\frac{\sin^2\phi}{\overline{n}^2}}}{\frac{\sin^2\phi}{\overline{n}^2}}\right] \tag{2}$$

where d(t) is the instantaneous thickness. $R_0(t)$ and $R_\Phi(t)$ are the instantaneous 0° retardations (at 546 nm) and Φ° retardations (in this case, Φ° is 45°), respectively. $\overline{n}$ is the average refractive index of the drying solution, and it is estimated linearly through the concentration change:

$$\overline{n} = n_{polymer}\chi_{polymer} + n_{solvent}\left(1 - \chi_{polymer}\right) \tag{3}$$

where $n_{polymer}$ is the average refractive index of polymer (here the refractive index of PEI is 1.66 at 546 nm), $n_{solvent}$ is the refractive index of solvent (here the refractive indices of NMP is 1.47 at 546 nm), $\chi_{polymer}$ is the solid content in solution.

PEI solution was cast on a glass substrate at room temperature. And when it was placed inside the preheated wind tunnel, the data acquisition began. The air speed and the temperature were kept constant during the drying.

2.5. Stretching behavior

PEI film with 50 μm thickness was peeled off from the substrate after several hours of drying at 60 °C and then was cut into dumbbell shape. The sample was mounted between the clamps of the real-time mechano-optical measurement system [37] and preheated for 10 min before stretching. The deformation behavior was investigated in 100 °C–150 °C temperature range and at 10 mm/min stretching rate.

2.6. DSC and TGA

Differential scanning calorimetry (DSC) data of sample was measured by a differential scanning calorimeter (TA Instruments DSC Q200) under nitrogen atmosphere. All the samples were

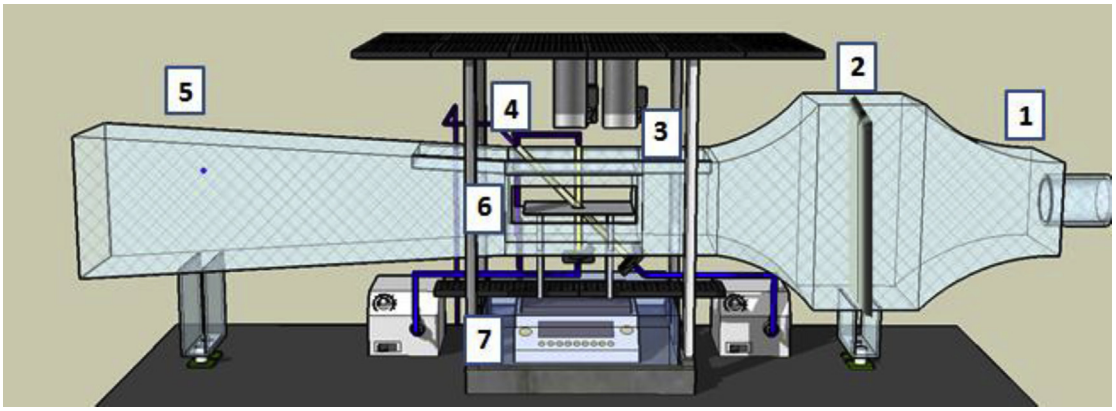

Fig. 1. Real-time solution drying measurement instrument (1. connection of blower to the tunnel, 2. vertical baffles, 3. laser displacement sensors, 4.optical components and sensors, 5. open end of the tunnel, 6. sample platform, 7. electronic balance).