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Temporal evolution of structure in uniaxially stretched PET/PEI blends during constrained annealing: A real time birefringence study

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ABSTRACT

Structure evolution that took place during the constrained annealing of uniaxially constrained width oriented Poly (ethylene terephthalate) and Poly (ether imide) blend films was studied using real time spectral birefringence measurement technique and off line differential scanning calorimetry, wide and small angle X-ray scattering and mechanical testing. At lower deformations, heat setting generally lead to complete elimination of birefringence due to relaxation in blends containing as little as 10% PEI. At high deformation levels, annealing leads to initial relaxation nearly to optical isotropy followed by reversal and increase in birefringence associated with development of crystallization. The ultimate birefringence decreases with increasing PEI content as it disrupts crystallization. Latter behavior indicates that despite achieving near optical isotropy during initial relaxation phase, these films still contain oriented nuclei that facilitate the oriented crystallization of the PET phase at longer annealing times as evidenced by the off line WAXS and SAXS experiments.

1. Introduction

In a film casting process, a typical polymer with slow crystallization character (PET, PEN, PEEK) is extruded through a slit die and quenched below its Tg by cooling on a chill roll leading to relatively unoriented amorphous cast films. It is then reheated to processing temperatures between Tg- Tcc where it behaves rubbery and subjected to uni- and/or biaxial stretching and heat-setting via the tenter frame process.

Upon heating, an oriented polymer film may retract strongly at a temperature well below the crystalline melting point [1–5]. This property is utilized in shrink-films, which find wide applications in the packaging field. Unless this application or a similar one is desired, one would prefer a better dimensional stability since the shrinkage can be accompanied with a loss of orientation [6], which may negatively affect mechanical properties and dimensional integrity of the films.

In-plane dimensionally constrained annealing, called heat setting, is typically used after uni- and/or biaxial stretching to increase the crystallinity and relax the oriented amorphous regions to expand the temperature range where these films remain dimensionally stable nearly to the start of crystalline melting range. In reviewing the literature, the thermodynamics and kinetics of oriented crystallization have been studied by many authors [7–11]. These researchers made efforts to correlate the observed changes in melting point and crystallization rate to the orientation function of the molecules and to the applied stress. Smith and Steward [12] and Alfonso et al. [13] have shown that orientation of the amorphous phase promotes a substantial increase in crystallization rate. They have found that PET with a higher amorphous orientation crystallized faster at all temperatures. Althen and Zachmann [14] have studied the kinetics of isothermal crystallization. With increasing orientation, the rate of crystallization also increases and the Avrami exponent n decreases from 3 to 1. Peszkin and Schultz have reported that there are two competing processes during the heat treatment of oriented PET fibers: recoiling of the chains and crystallization [15]. Petermann and Rieck [16] have investigated morphologies of films, crystallized under high elongational flow. During annealing, the morphology changes from single micellar blocks embedded in the amorphous matrix to lamellar crystals.

Even though much has been studied regarding the effects of preferred orientation on crystallization kinetics and consequent morphologies, the details of temporal structure evolution still remain unclear. This is primarily due to the absence of appropriate structural detection techniques that are fast enough to follow the rapid changes that typically occur during this process.

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Serhatkulu et al. [17–19] developed the 'on-line spectral birefringence measurement technique', that allows us to characterize the events in the early stages of structure evolution such as an amorphous domain relaxation and/or rapid crystallization in the pre-oriented films. This technique was utilized in this work.

The purpose of this work is to elucidate the structure evolution during the heat-setting process using real time birefringence technique and correlate the consequent structures by capturing films at strategically chosen intervals and correlate their details to physical properties including mechanical properties. This is a second paper following the earlier study on the structure evolution during the heat-setting process of the pre-oriented PET/PEI films [20].

2. Experimental

PET (Tenite 7352, Eastman Co.) used has intrinsic viscosity of 0.8 dl/g corresponding to molecular weight of Mn = 24,000. PEI (Ultem 1000) with molecular weights of M_n = 12,000 and M_w = 30,000 was purchased from the General Electric Co. Both polymers were dried at 150 °C in a vacuum oven for 24 h and A series of PET/PEI with compositions of PET/PEI 100/0, 95/5, 90/10, 80/20, and 70/30 were prepared using a JSW co-rotating, intermeshing twin screw extruder operated at 130 rpm screw speed. The temperatures along the barrel were kept between 240 and 250 °C with die temperatures set at 256 °C for pure PET and 264 °C for the blends.

2.1. Preparation of films

The blend pellets, dried at 150 °C in a vacuum oven for 24 h, were melt cast using a Prodex single screw extruder (L/D = 24) with a 30 cm wide coat hanger die and a chill-roll take-up device equipped with a water circulating temperature control unit. Temperatures along the barrel were set at 200 °C in zone 1, 270 °C in zone 2, and 285 °C in zone 3 and at the die (zone number increases towards the die). The temperatures on the chill roll ranged from 70 °C for pure PET films to 95 °C for PET/PEI 70/30 in order to obtain good flatness of the films by minimizing thermal shock on the chill roll due to a large temperature difference between the die and chill roll. The screw speed was kept at 30 rpm for all the films. The as-cast 0.5 mm thick films were also transparent.

2.2. Deformation of films

Deformation of the films was carried out on an Iwamoto biaxial stretcher (Model BIX 702) in order to obtain the pre-oriented films. For this purpose, the films were cut into 12 × 12 cm^2 and were inserted into the pneumatic grips placed in the heating chamber of the machine. The films were pre-heated for 5 min for thermal equilibrium and stretched in the uniaxial constant width mode (UCW) at the temperatures where deformation behavior of all the film is identical all the way up the strain-hardening point at the rate of 300%/min. The true stress-stretch ratio curves (or deformation curves) were obtained, assuming incompressibility ($V = V'$; V, V' = volume before and after deformation).

2.3. On-line spectral birefringence measurement technique

Unless otherwise noted On-line spectral birefringence of all the films during the heat-setting process was tracked at 180 °C at which unoriented PET has the highest crystallization rate [21–24]. The instrumented annealing chamber (Fig. 1) with on-line spectral birefringence equipment consists of four parts: white light source, an oven where a film is heat-set, a device that allows ±45° analyzers sitting next to each other to move back and forth, and a detector that delivers the information measured to a personal computer for the calculation of retardation. A pre-oriented film is sandwiched between two circular frames in order to prevent shrinkage and instantly slid into an oven equipped with built in two rails that guide the circular frame to the mid oven position where the white light passes though. This experimental set-up allows the white light, polarized at +45° with respect to *MD*, to pass through a sample in the oven and reaches the alternating ±45° analyzers. The intensity of the light transmitted through a pair of cross and parallel polarizers is used to calculate the retardation (Γ). Thus, birefringence (Δn) is determined by the relation:

$$\Delta n(\lambda) = \frac{\Gamma(\lambda)}{d} \quad (1)$$

Where d and λ are film thickness and wavelength (=543.5 nm in this study), respectively. The details of this technique is described elsewhere [18,19].

2.4. Time resolved study on the films

To study the structure evolution of the films as a function of heat-setting time, several films were prepared with identical stretch ratio and birefringence. With guide rails carrying the film constrained in sandwich frame in and out of the annealing chamber through trap doors rapidly, we were able to freeze these samples at strategically selected time intervals by quenching them in water bath situated below the annealing chamber (Fig. 1). The samples prepared in this way were utilized in the experiments such as DSC, WAXS, SAXS, and mechanical testing, described below.

2.5. Thermal analysis

Thermal analysis of the heat-set PET/PEI blend films were performed using a Dupont 910 DSC under a dry nitrogen environment at the heating rate of 20 °C/min. Degree of crystallinity was determined by the same procedure described previously [20]. For this purpose the area under the cold crystallization was determined and since this crystallization is artificially introduced into the material structure during DSC heating this are is subtracted from the total melting peak area obtained from the DSC diagrams and divided by the heat of fusion of 100% crystalline PET (119.8 J/g) [25]. In blends only PET crystallizes and hence the degree of crystallinity was then normalized by the fraction of PET present in the films.

2.6. Wide angle X-ray scattering (WAXS)

WAXS experiments were carried out using a Rigaku Ultra 18 KW X-ray generator to investigate the crystalline orientation of the heat-set films. It was operated at 50 kV and 250 mA. CuK_α radiation (λ = 1.542 Å) was obtained using a Nickel foil filter.

2.7. Determination of orientation factor

In an oriented symmetric system, only one octant of the entire surface of the orientation sphere is unique. Thus, the mean-square cosine of the angle between a given *hkl* plane normal and the reference axis is expressed as: