Stretch-Orientation of LaRC™ RP 50 Polyimide Film

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Abstract

An addition-curable poly(amic acid) film was subjected to various thermal pretreatments and then to uniaxial or biaxial drawing. Hot-stretching to 300% of the initial length produced better than twofold increases in tensile modulus and strength of partially-cured films. Most of the improvement was maintained upon completion of the curing at constant length.

Key Words

Orientation, thermosetting, polyimide, addition polyimide, biaxial, film

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Introduction

It is well known that orientation of fibers and films can lead to improved mechanical, thermal, electrical, optical and barrier properties. Aromatic polyimides [1] tend to be somewhat intractable, however; so conventional melt or solution processing is difficult. In general, the approaches to processing polyimides have been i) to process a precursor polyamic acid in solution and then convert it to the imide form; ii) to synthesize melt- or solution-processable linear polyimides by careful choice of monomers and control of molecular weight; or iii) to employ processable monomers or oligomers that can later be cured and crosslinked via addition chemistry. The first approach has been used to improve properties of films via stretch-orientation of the polyamic acid [2,3]. It works especially well for stiff-chain polyimides. The second approach, stretching of thermoplastic polyimides, has also been demonstrated for fibers and films [4,5]. The third approach could be used to orient and improve the film properties of ultra high temperature thermosetting polyimides such as the Polymerization of Monomer Reactant (PMR) type, but until now, no reports of the method have been published.

The present work concerns stretch orientation of LaRC™ RP-50 polyimide films [6]. The chemistry of RP-50 is similar to LaRC RP46 [7,8], but the synthesis proceeds by way of a polyamic acid oligomer. This oligomeric prepolymer can be cast as a film. After being dried and partially imidized, the film can be stretch-oriented prior to completing the imidization/cure. In the following, the focus is on uniaxial stretching processes. In a few cases, a new laboratory-scale apparatus was used to demonstrate biaxial stretching. Films were characterized by refractive index, dynamic mechanical analysis (DMA), and room-temperature tensile properties.

Experimental

Polyamic acid solutions were prepared in N-methyl pyrrolidone at room temperature by combining 3,3',4,4'-benzophenonetetracarboxylic dianhydride, 3,4'-oxydianiline, and nadic anhydride. The stoichiometry was adjusted to give a formulated molecular weight of 9500. Films were cast on glass plates and kept in a low-humidity cabinet at room temperature until they were dry to the touch (1-2 days). The polyamic acid films were pre-cured ("B-staged") on the glass plates for 2 hours each at 60° and 100° C followed by two hours at either 125°, 150°, 200°, 250°, 275°, or 300°C. Fully-cured ("control") films of RP 50 were heated to a final stage of 325°C for 1 hour. B-staged film thicknesses were 30-90 μm.

Uniaxial stretching was performed in an air-circulating oven using a constant-load apparatus. Samples were 5.08 mm wide with a 50.8 mm gage length. Stretch and temperature were monitored using a long-stroke displacement transducer and type-K thermocouple, respectively. The first type of experiment, thermal deformation analysis (TDA), involved heating a sample under a dead-weight load [9]. In this case, a nominal 7.0 ± 0.6 MPa stress was applied at room temperature; the temperature was then ramped at approximately 5°C/min until the specimen either broke or stopped stretching. Isothermal stretching experiments, on the other hand, involved preheating the oven, inserting the specimen, and then applying the weight. Stretching was halted with a mechanical stop and the specimen was promptly cooled. In all cases, the time spent in the stretching oven was very short relative to the pre-staging time. The central, uniform portion of each stretched specimen was used in further testing; its width and thickness dimensions were redetermined with a micrometer.

For biaxial stretching, the stress in the vertical direction was also 7 MPa. Samples were 50.8 x 50.8 mm squares; the geometry of the apparatus is described in the Appendix.

Film birefringence was measured using a Metricon Model 2010 prism coupling system. By adjusting the polarization of incident light, refractive index parallel and perpendicular to the film surface is determined. DMA was performed in tensile mode with a Rheometrics Scientific DMTA V using a 15 mm gage length and 0.25% strain. Temperature was ramped from 25 to 400°C at 2°C/min. Differential scanning calorimetry (DSC) employed a Perkin-Elmer Pyris I operated at 5°C/min with a nitrogen purge.

Tensile strength and modulus were determined at ambient temperature using a 50.8 mm gage length and a crosshead speed of 5 mm/min. Strain was approximated using crosshead displacement. Between 2 and 12 specimens were tested in each condition; data are reported as mean ± standard error.

Results and discussion

Initial properties DMA results on the precured (unstretched) films are displayed in Figure 1. Room temperature stiffness tended to increase with pre-cure temperature but leveled off around 250°C. It is thought that imidization is largely complete at 250°C. Other authors have shown, using infrared spectroscopy, that conversion to the imide was complete at 225-250°C in at least three chemically-different polyamic acids [10, 11].

As expected, the softening temperatures increased with pre-cure temperature as a result of solvent removal, imidization, and crosslinking [12]. Both refractive index and birefringence increased approximately linearly with pretreatment temperature (Figure 2). Birefringence in these unstretched films is a result of stresses accompanying solvent loss [13].

Thermal deformation analysis (TDA) When heated under constant load, most of the partially-cured samples stretched readily to 200-300% of their initial lengths (Figure 3). This was encouraging because it indicated that substantial orientation might be possible. Stretching generally began at a temperature slightly above that film's previous maximum pre-cure (staging) temperature.

Isothermal stretching On the basis of the TDA results, constant-load isothermal stretching was carried out 10°C above each sample's respective pre-cure temperature. With this choice of temperatures, stretch rates, $d\varepsilon/dt$, turned out to be similar for all films (0.015-$0.04\ s^{-1}$). The maximum stretch attainable without breaking was determined by trial and error. Work with the 300°C cured material was abandoned at this point since deformations were small and non-uniform.

The most ductile material was the one with the 150°C precure condition (Figure 4). This was also the film that gave the largest increase in room-temperature tensile modulus, E, upon stretching. In fact, the modulus in the stretch direction correlated fairly well with the degree of hot-stretching that had been achieved (Figure 5), so modulus seems to reflect in a general way the degree of chain alignment. The best film (150°C precure) produced a better than two-fold improvement in the modulus upon stretch-orienting. Room temperature tensile breaking strength, σ_{ult}, was also improved relative to that of the unstretched film.

Although the relative modulus increase was highest with the 150°C staging, pre-curing at 250°C followed by hot-stretching led to the best strength and stiffness in absolute terms (among the conditions studied). This was because, as was pointed out in discussing Figure 1, the B-staging temperature affected the modulus even in the absence of stretching.

Interestingly, isothermal stretching spontaneously halted or slowed at a certain strain for all except two cure conditions (125°C and 300°C). This self-limiting behavior suggests, but does not prove, that crystallization might have been occurring [9]. Another bit of evidence for stretch-crystallization was the cloudiness in some stretched samples. DSC traces revealed a small melting endotherm (Table 1).

Samples that had been pre-cured at 150°C were also drawn simultaneously in two directions using the apparatus described in the Appendix. Biaxial orientation was confirmed by optical measurements, which showed that refractive indices increased in two orthogonal directions in the plane of the film, Table 2. Furthermore, DMA showed that the modulus was approximately the same in both directions.

Curing Complete reaction of the polymer's nadic end groups requires curing at 325°C. A three-step process is therefore envisioned: B-staging at an intermediate temperature, stretching, and then further heating to 325°C. An important question, therefore, is whether stretch-alignment can be maintained during the final cure.

For this part of the study, two B-stage temperatures were chosen: 150°C and 250°C. Samples in the 150°C group were drawn uniaxially as before (isothermally, 160°C) and then cured in a stepwise manner (200°, 250°, 300°, 325° C for 1 hour each) while holding their length constant. Similarly, samples in the 250°C group were uniaxially drawn (isothermally, 260°C) and cured (300°, 325°C for 1 hour each) at a constant length. Attempts to complete the cure at a constant load (7.0 MPa) rather than at a constant length led to specimen failure as additional stretching occurred at higher temperatures. After curing to 325°C, melting endotherms were seen in the DSC at 353 and 356°C, with enthalpies of 27 and 10 J/g, respectively. This implies a loss of crystallinity relative to the stretched-but-not-completely-cured films in Table 1.

Resulting tensile properties are summarized in Table 3. The 150°C specimens increased in strengths and moduli upon curing, whereas further heating of the 250°C specimens during the cure step reduced their moduli, presumably due to a relaxation of polymer chain orientation. Note, however, that either process is a substantial improvement over the unstretched case, even though no special efforts were made to optimize either the drawing or the curing process.

Conclusions

Partially imidized, B-staged films of RP50 were successfully stretch-oriented both uniaxially and biaxially. Films pre-cured at 150°C to 250°C could be hot-stretched to give up to twofold improvements in strength and stiffness. A portion of this improvement was carried over to the fully-cured addition polyimide. The results of this study clearly demonstrate that highly intractable, ultra high temperature thermosetting polyimides can be stretch oriented to improve their properties.

Appendix

The laboratory-scale biaxial stretching device was designed to operate at high temperatures using relatively small quantities of material. Clamps on the four corners of the specimen (Figure 6) are attached to turnbuckles that are free to rotate about their ends. Force is therefore transmitted only along their primary axes (Figure 7).

A dead-weight stretching force is applied to the horizontal bars pictured in Figure 6, each of which is connected to two of the turnbuckles. The sample is thus subject to a constant force in the vertical direction; the force in the horizontal direction varies as the sample stretches and the relative angle of the turnbuckles changes (Figure 8). The lengths of the turnbuckles can be adjusted to fine-tune the starting angle and bias the stretching forces to give various stretch ratios. Because the deformation is not homogeneous, specimens for further tests are cut from the center of the sample.

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Table 1. DSC results

Pre-cure temperature, °C	Degree of uniaxial stretch	Glass transition temperature, °C	Melting endotherm peak temperature, °C	Enthalpy of melting, J/g
150	2.46	174	321	37
250	1.78	239	336	15
325	0 (control)	283	349	19

Table 2 Refractive Index in the Machine Direction (MD), Transverse Direction (TD), and perpendicular to the film plane (Through).

	MD	TD	Through
Unstretched	1.6605 ± 0.0007	1.6605 ± 0.0007	1.6581 ± 0.0006
Uniaxial	1.6838 ± 0.0045	1.6345 ± 0.0094	1.6384 ± 0.0073
Biaxial	1.6834 ± 0.0012	1.6741 ± 0.0005	1.6372 ± 0.0011

Table 3 Mechanical Properties

$T_{pre\text{-}cure}$, °C	125	150	200	250	275	300	325
ε_{final}	1.05 ± 0.14	2.46 ± 0.15	1.53 ± 0.15	1.78 ± 0.05	1.22 ± 0.13	0.32 ± 0.03	0 (control)
$d\varepsilon/dt$, s^{-1}	0.019 ± 0.001	0.043 ± 0.004	0.014 ± 0.001	0.024 ± 0.002	0.015 ± 0.002	--	--
E (Unstretched), GPa	2.86 ± 0.53	3.31 ± 0.05	3.73 ± 0.12	3.88 ± 0.05	3.95 ± 0.01	3.97 ± 0.03	3.11 ± 0.19
E(Stretched), GPa	4.37 ± 0.21	7.33 ± 0.48	5.76 ± 0.30	8.45 ± 0.52	6.76 ± 0.32	--	--
E (Stretched and cured), GPa	--	7.87 ± 0.12	--	5.64 ± 0.07	--	--	--
σ_{ult} (Unstretched), MPa	89 ± 11	98 ± 3	115 ± 4	136 ± 4	138 ± 14	149 ± 6	133 ± 6
$\int_{ult}$ (Stretched), MPa	112 ± 3	152 ± 19	197 ± 9	323 ± 26	294 ± 27	--	--
$\int_{ult}$ (Stretched and cured), MPa	--	282 ± 14	--	294 ± 11	--	--	--

Figure 1 Dynamic tensile moduli of unstretched, precured RP50 films. Curves are labeled with respective pre-cure temperatures.

Figure 2 Refractive index parallel (□) and perpendicular (△) to the plane of unstretched films.

Figure 3. Thermal deformation analysis of samples with six precure conditions. Label on curve is maximum precure temperature for that sample.

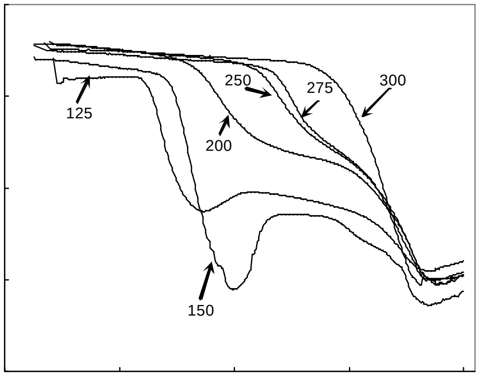
Figure 4. Degree of hot-stretching achieved with partially-cured films (average of 3-6 specimens each). Each film was stretched isothermally at its respective precure temperature + 10°C.

Figure 5. E(stretched)/E(unstretched) at room temperature vs. degree of hot-stretching. Each point represents a different cure (and stretch) temperature.

Figure 6. Biaxial stretching device.

Figure 7. Decomposition of forces.

Figure 8. Ratio of horizontal and vertical forces versus angle of turnbuckle relative to horizontal.



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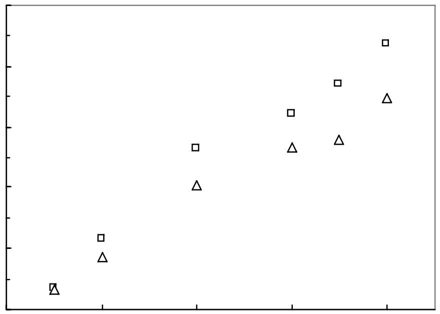

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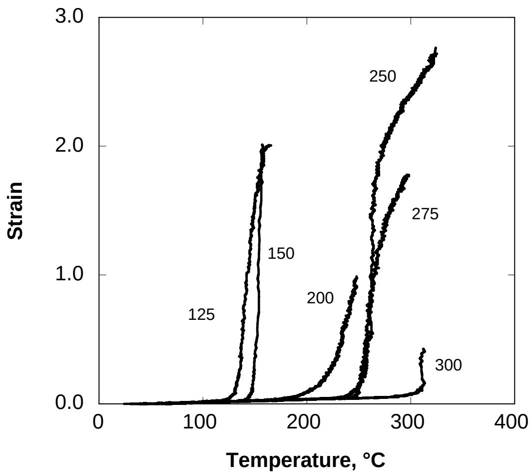

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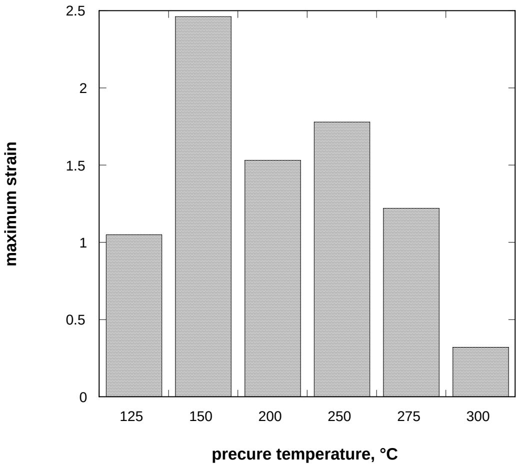

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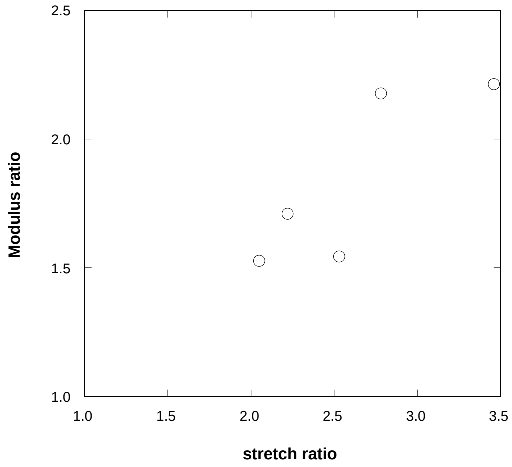

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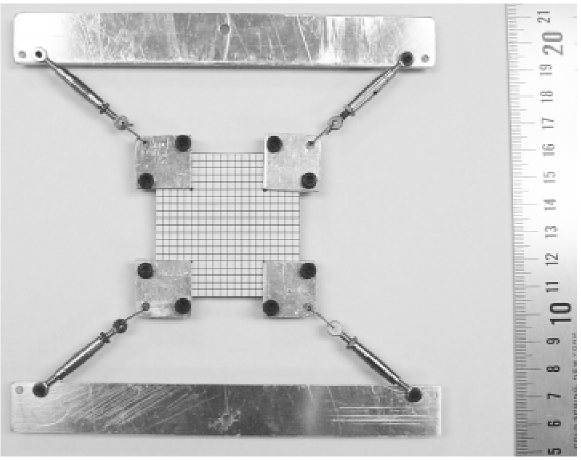

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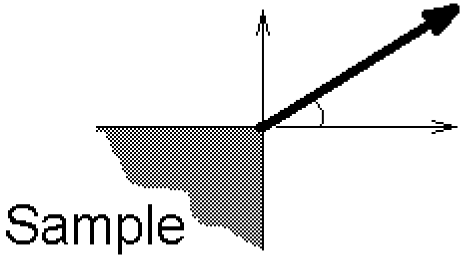

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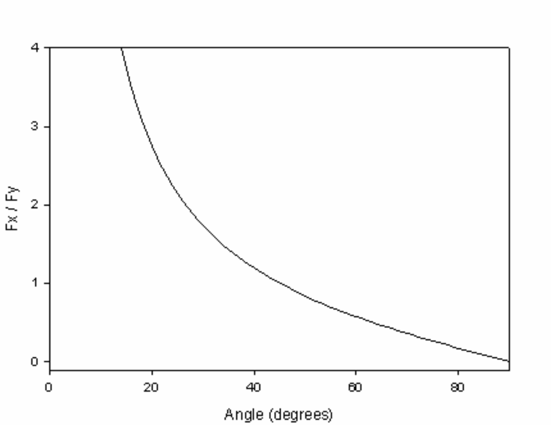

Figure 8. Ratio of horizontal and vertical forces versus angle of turnbuckle relative to horizontal