SII NanoTechnology Inc.

TMA AS PROBLEM-SOLVING TOOL: CHARACTERIZATION OF BIAXIALLY ORIENTED FILMS

Problem

A scientist, working for a company which manufactures films, has a need to characterize the dimensional and elongational/shrinkage properties of biaxially oriented films. There is a specific desire to analyze and understand these properties with regards to orientation (machine and transverse) in order to optimize the production of the films and for quality assurance purposes

Solution

Thermomechanical analysis (TMA) provides an excellent means of determining the shrinkage and elongation properties of materials, including films. The technique operates by holding the sample at a constant load (or length) and monitoring the dimensional (or force) changes in the material as a function of temperature or time. TMA offers a wide range of modes and clamping fixtures to handle and accommodate various samples, which include:

- expansion
- penetration
- film and fiber extension or tension
- 3 point bending
- pin and cup for gels or uncured thermoset resins
- dilatometry for measuring bulk expansion properties

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The Seiko TMA/SS6000 offers some major and unique advantages for performing TMA characterization measurements, including,

- the highest force loading levels (6N or 600 gf) of any TMA instrument on the market
- the widest displacement range (± 5 mm travel) of any TMA for monitoring large sample dimensional changes continuously
- DMA operation in addition to standard TMA measurements
- high precision load generator with unsurpassed linearity (1%) for the best possible and most reproducible results
- auto length measurement feature for the automated determination of the sample thickness for ease of use
- automated probe initialization for ease of use and efficiency

Analysis of Biaxially Oriented Films

In this study, the dimensional properties of two different biaxially stretched films (Film 1 and Film 2) were characterized using the Seiko TMA/SS6100. The following experimental conditions were utilized to analyze the films:

Instrument:	Seiko TMA/SS6100
Probe:	Quartz film extension
Loading:	10 g force (constant)
Sample length:	20 mm

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Sample width: 4.2 mm
Sample thickness: 0.19 mm
Heating rate: 5°C/min
Initial temperature: -30°C
Final temperature: pre-set elongation limit of 4.0 mm
Purge gas: nitrogen at a flow rate of 150 mL/min

The TMA instrument was calibrated for temperature response using the penetration onset temperature of high purity indium metal (M.P. = 156.6°C).

The Seiko TMA features a user selectable sample fusion control protection option. With this feature, the operator can select a shrinkage or elongation limiting value, at which point the instrument will automatically terminate the experiment. This prevents the full melting of the sample, which makes it easier and less time consuming to remove the sample at the conclusion of the experiment.

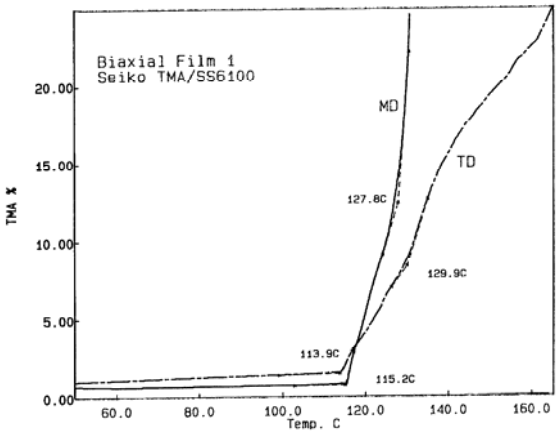

Figure 1

Displayed in Figure 1 is an overlay of the TMA results generated on Film 1 in the machine (MD) and transverse (TD) orientations. The plot shows the percent elongation and/or shrinkage as a function of temperature under the constant load of 10 g force. Up to 115°C, the film samples exhibit only a slight and reversible change in their shrinkage and elongational properties. At 115°C, the film specimens undergo a significant and irreversible elongation. The film in the machine orientation undergoes a more rapid increase in its elongation as compared to the transverse orientation. An additional significant increase in the elongational characteristics of the film specimens is observed at 128°C for the MD sample and at 130°C for the TD film. At 165°C, it may be seen that the MD sample has elongated to a much greater extent compared to the TD specimen. This

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reflects the differences in crystalline morphologies or structures in the MD and TD orientations due to the biaxial stretching of the film during production.

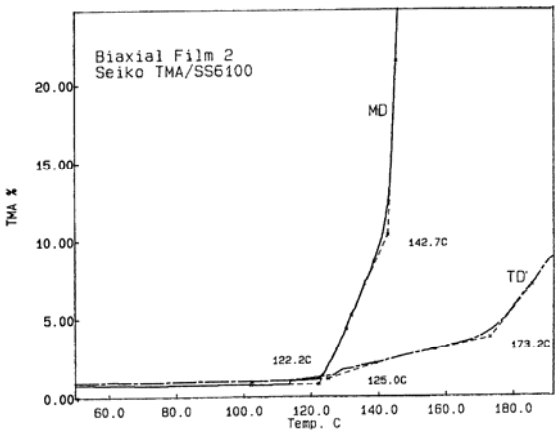

Figure 2

Displayed in Figure 2 are the TMA results obtained on Film 2 in the MD and TD orientations. This film is dimensionally stable up to approximately 122°C. At this temperature, the sample undergoes significant elongation, which is most apparent in the machine direction. The elongation in the TD orientation is only slight at a temperature of 125°C. A further significant increase in the rate of elongation occurs at 143°C in the MD orientation and at 173°C in the TD direction, with the rate of elongation being much less in the TD versus MD orientation. Film 2 shows a much greater difference in its TD and MD elongational characteristics as compared to Film 1. This reflects the development of different crystalline structures due to the given processing conditions for Films 1 and 2.

Creep and Recovery Testing

One additional powerful characterization measurement that can be conducted on samples using the Seiko TMA/SS6000 is creep and relaxation. Creep is the study of the deformation or 'cold flow' of the material as it is subjected to a constant load. The relaxation refers to the 'shrink back' of the sample after the load is removed and the sample tries to recover.

In this portion of the study, Film 2 was characterized using the creep and relaxation approach at a temperature of 87°C, which is above the material's Tg but below the melting temperature. In this test, the sample was heated from room temperature to 87°C at 5°C/min under a small loading of 5 g force. The sample was held at 87°C for 5 minutes

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under the 5 g load to permit it to thermally equilibrate. A higher load of 100 g force was applied and held for 15 minutes at 87°C and the resulting sample creep or elongation was monitored. After the 15 minute hold, the force was removed (0 g force) and the sample was permitted to cool down. The resulting sample shrink back or recovery was monitored.

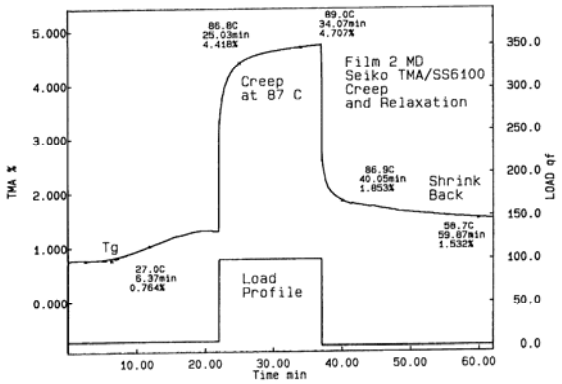

Figure 3

Shown in Figure 3 are the results of the creep and relaxation test conducted on Film 2 in the MD orientation. The plot shows the percent TMA and the load profile as a function of time. The Tg of the film is observed as a change in the rate of elongation (under a 5 g load) at 27.0°C. At 22 minutes, once the temperature achieved 87°C, the 100 g force load was applied and the film undergoes significant elongation. During the application of the higher loading, the sample continues to elongate from 4.42% at 25 minutes to 4.71% at 34 minutes. For polymeric materials, it is important to determine the degree of creep that they will undergo when subjected to a given loading, especially for materials which are subjected to a loading under real life applications. At the end of the 15 minute isothermal holding period, the force on the sample is removed (to 0 gram force) and the sample is permitted to undergo shrink back or recovery, as is seen in Figure 3. Some polymers will exhibit more complete recovery than others, depending on the chemistry of the polymer and the sample's particular morphology.

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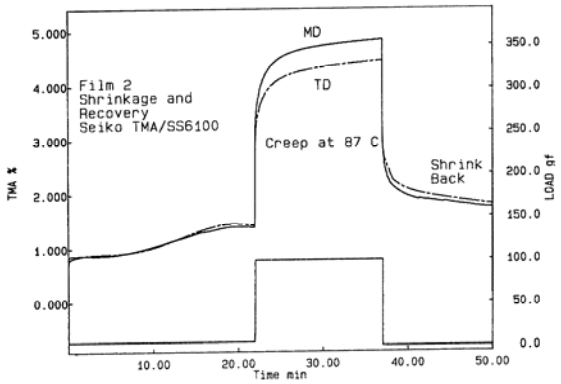

Figure 4

Displayed in Figure 4 is an overlay of the TMA creep and recovery results generated on Film 2 in the MD and TD orientations. It may be seen that the film in the MD orientation undergoes creep to a greater extent than in the TD orientation, at the test temperature of 87°C.

Summary

TMA provides excellent data concerning the shrinkage/elongational properties of films. With the TMA, samples can be cut and mounted in the machine and transverse orientations using the extension mode in order to study the differences which occur in the different orientations as the sample is heated. The temperature at which the film becomes dimensionally unstable is easily assessed from the TMA elongational data. Creep and recovery studies were performed on the films using the TMA in both the machine and transverse orientations. The Seiko TMA/SS6100 provides outstanding results on the shrinkage/elongation properties of films given its ease of use, wide displacement range, and unsurpassed linearity.

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