SII NanoTechnology Inc.

TMA AS PROBLEM-SOLVING TOOL: MEASUREMENT OF HEAT SET TEMPERATURES OF FIBERS

Introduction

Thermomechanical analysis (TMA) measures linear or volumetric changes in the dimensions of a material as a function of temperature, time and force (or stress). The data provides valuable characterization information on samples including: coefficient of thermal expansion, glass transition temperatures (Tg), softening temperatures, heat deflection temperatures, gel times, tack times or temperatures, composite delamination temperatures, creep characteristics, stress relaxation properties and fiber heat set temperatures. In addition, the TMA can be operated in a dynamic force mode, similar to dynamic mechanical analysis (DMA), which provides additional viscoelastic data, including: storage modulus (E'), loss modulus or damping (E") and tan delta.

TMA is a powerful technique for the characterization of a wide range of materials, including thermoplastics, thermosets, gels, adhesives, fibers, films, coatings, seals, gaskets and elastomers. The technique offers a wide range of modes and clamping fixtures to handle and accommodate samples, which include:

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

In addition to its ability to handle a wide range of test specimens, TMA offers an advantage over other thermal analysis techniques, such as DSC, in that it offers significantly higher sensitivity for the detection of weak transitions. For example, TMA offers about a **10 fold increase in sensitivity** over standard DSC for the measurement of glass transition temperatures.

Features of Seiko TMA/SS

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

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- the highest force loading level (6 N or 600 g) of any TMA instrument on the market providing maximum sample handling capability ranging from single fibers to composites
- the widest displacement range (± 5 mm) of any TMA for monitoring large sample dimensional changes
- 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

Analysis of Nylon 6 Heat Set Fibers

In this study, the dimensional characteristics of two nylon 6 yarns, used to manufacture carpets, were characterized using the Seiko TMA/SS6100. During the production of the yarns, the nylon 6 fibers are exposed, briefly, to an elevated heat set temperature to stabilize the properties of the fibers. The heat set step alters the structure or morphology of the fibers, which can then be observed by TMA as the fibers are heated.

In this study, two nylon 6 yarns, Lots 1 and 2, were analyzed by TMA under constant force conditions. Lot 1 was considered to be 'Bad' based on its dye uptake performance, whereas Lot 2 was judged to be 'Good' based on its better dyeing propensity.

The following conditions were utilized to characterize the TMA properties of the nylon 6 yarns:

Instrument:	Seiko TMA/SS6100
Probe:	Quartz tension
Sample configuration:	bundle of fibers
Sample length:	20.0 mm
Tensile force:	15 g
Initial temperature:	- 40°C
Heating rate:	5°C/min
Purge gas:	nitrogen at 150 mL/min

The TMA instrument was calibrated for temperature response using the onset melting temperature of high purity indium metal.

Displayed in Figure 1 are the TMA results generated for the Lot 1, nylon 6 yarn sample. The plot shows the percent change in the TMA original length as the sample is heated. An increase reflects elongation and a decrease is due to shrinkage. Sample Lot 1 yields a linear change in expansion between -40 and -10°C. At about 0°C, the yarn begins to

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elongate most likely due to the occurrence of the glass transition temperature (Tg). Nylon 6 fibers

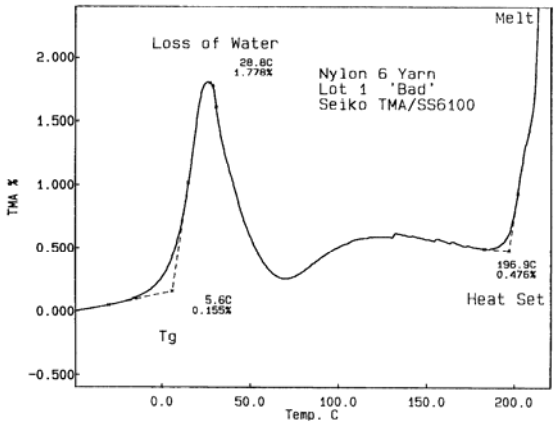

Figure 1

absorb moisture and this absorbed water functions as a plasticizing agent reducing the glass transition temperature of the nylon. At about 25°C, the drying effects of the nitrogen purge gas begins to remove the absorbed water from the fiber surfaces and this drying results in the yarn shrinking between 20 and 55°C. The small 'steps' observed in the TMA data between 100 and 180°C represents the crimp coming out of the yarn during heating. At a well-defined onset temperature of 196.9°C, the yarn undergoes significant elongation and this reflects the heat set treatment that the fibers received during production. Above 210°C, the sample undergoes extensive and continuous elongation due to the complete destruction of the crystals as the fiber melts.

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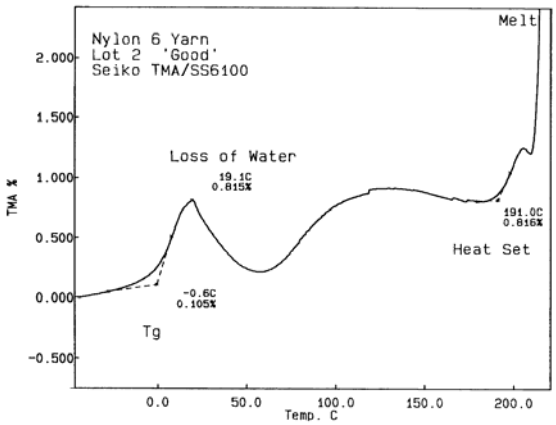

Figure 2

The TMA results obtained for the 'Good' nylon 6 yarn, Lot 2, are shown in Figure 2. The yarn exhibits the sample characteristics between 0 and 55°C reflecting the glass transition event along with the loss of absorbed water. The Lot 2 yarn yields its heat set onset at a temperature of 191.0°C which is significantly lower than that obtained for the 'Bad' yarn (196.9°C).

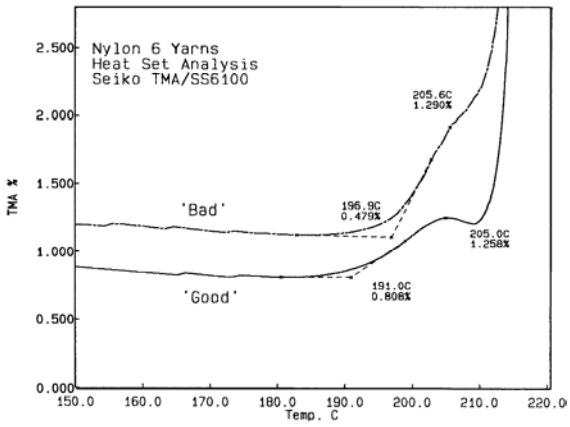

Figure 3

A direct overlay of the TMA results generated for Lots 1 and 2 are displayed in Figure 3. It may be seen that the 'Good' and 'Bad' fibers exhibit significantly different TMA responses in the temperature regions before the melt, reflective of the different heat set properties that the fibers received during production. These differences became apparent when the yarns were dyed.

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Analysis of PET Heat Set Yarns

Two samples of PET textured fibers (Lots 2 and 3 with different heat set temperatures), used to manufacture carpeting, were characterized using the tensile mode of the TMA. PET yarns exhibit significantly different dimensional changes during heating as compared to nylon 6 due to the differences in polymer chemistries and in the morphologies of the fibers. In addition, PET does not absorb moisture unlike nylon 6, so plasticizing effects due to moisture do not occur at Tg with PET fibers.

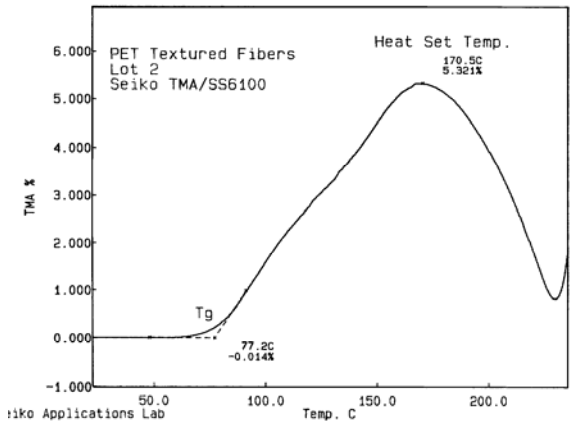

Figure 4

Shown in Figure 4 are the TMA results obtained for the PET Lot 2 yarn sample. The fiber yields essentially no significant dimensional changes until 77°C, where the yarn then begins to undergo elongation as it goes through the glass transition event, Tg. The yarn continues to elongate, under the applied load of 10 g force, until a maximum is reached at 170.5°C. At this point the yarn begins to shrink and the maximum represents the effective heat set temperature to which the PET fibers were exposed during production.

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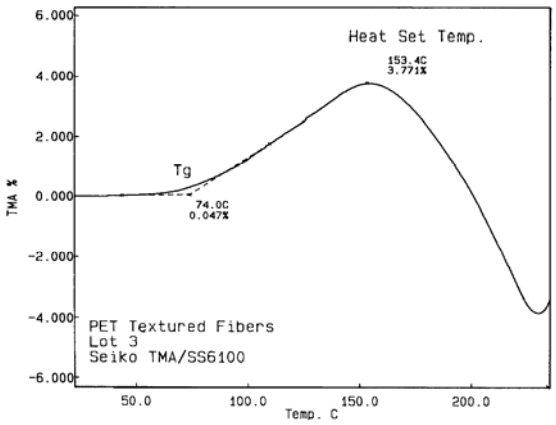

Figure 5

The TMA results generated for the PET Lot 3 yarn sample are displayed in Figure 5. This fiber specimen yields an effective heat set temperature of 153.4°C and it is known that the Lot 3 yarn was produced under more mild heat set conditions as compared to Lot 2.

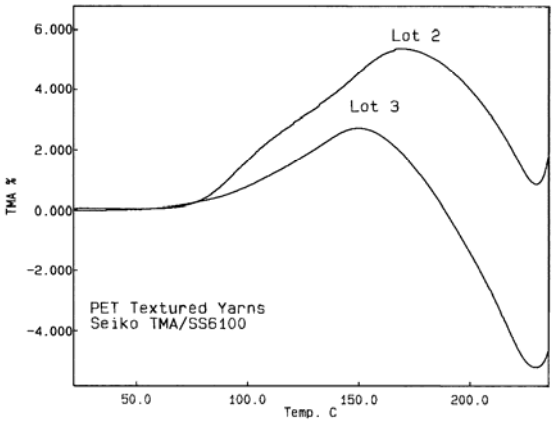

Figure 6

A direct overlay of the TMA results generated for PET Lots 2 and 3 are shown in Figure 6. The differences in the elongation/shrinkage and effective heat set characteristics of the two yarn samples are readily apparent in this figure.

Summary

TMA provides valuable information on the dimensional properties of a wide range of materials as a function of temperature, time and loading. For fibers, TMA is beneficial because the technique provides enhanced sensitivity (over standard DSC) for the

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measurement of the glass transition event as well as the heat set temperature used in the manufacture of the fibers. The heat set temperature is a critical measurement for fibers and yarns since the heat set conditions affect key properties such as shrinkage or elongation and dye uptake and dye uniformity. The Seiko TMA/SS6000 can detect the heat set conditions used to generate synthetic fibers, such as PET and nylon 6.

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