

Thermal Analysis Application Brief

Measurement of Moisture Effects on the Mechanical Properties of 66 Nylon

Number TA-133

SUMMARY

66 Nylon is one of many polymers known to be hydroscopic and to have its physical properties significantly influenced by absorbed moisture. Dynamic Mechanical Analysis (DMA), which measures the modulus (stiffness) and damping properties of materials, provides a convenient method for rapidly quantifying the adverse effects of absorbed moisture.

Observations from the DMA analysis can be used to correlate with specific end-use properties of the material to permit:

- Selection of optimum in-use environment
- Prediction of mechanical stability as a function of humidity
- Correlation of impact stability with damping and humidity
- Quality control of incoming raw materials

INTRODUCTION

66 Nylon is a polyamide formed by condensation of adipic acid with hexamethylene diamine. The physical properties of 66 Nylon are strongly dependent upon hydrogen bonding forces between the carbonyl oxygen and the amide hydrogen atoms within the polymer chain. Absorbed moisture has a very dramatic effect on these hydrogen bonding forces, and as a result, significantly modifies the physical properties of the 66 Nylon. Since polyamides are extremely hygroscopic, exposure to any humidity level above zero for an extended period of time will result in absorption of moisture, e.g., equilibration of 50% Relative Humidity (RH) will produce a moisture level of 2.5% by weight. It is therefore important to understand the effects of absorbed moisture on the physical properties of 66 Nylon. The technique of Dynamic Mechanical Analysis permits the rapid observation of these effects in a quantitative manner.

Dynamic Mechanical Analysis (DMA) measures the modulus (stiffness) and damping (energy dissipation) properties of materials as the materials are deformed under periodic stress. DMA is particularly useful for evaluating polymers which exhibit time, frequency, and temperature effects on these properties because of their viscoelastic nature.

EXPERIMENTAL

In dynamic mechanical analysis, a rectangular piece of material (nominally 19mm (L) x 13mm (W) x 3mm (T)) is clamped between two parallel arms and oscillated either at a fixed (operator-selected) frequency or at the natural resonant frequency of the material. In this case, the 66 Nylon samples were allowed to oscillate at their resonant frequencies while heating at 5°C/minute from -150 to 150°C. The oscillation amplitude chosen was 0.2mm.

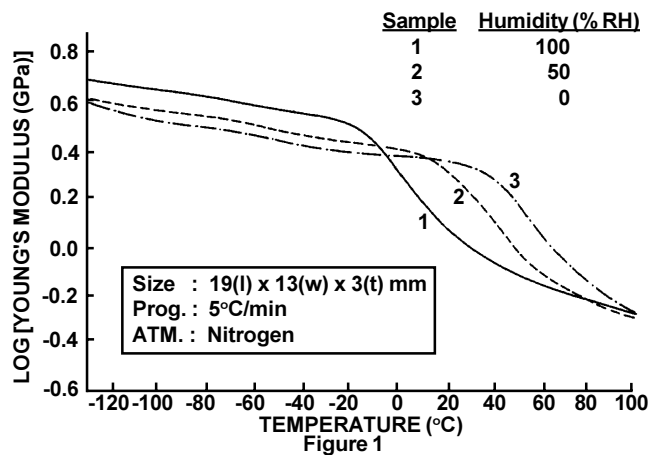
RESULTS

Figures 1 and 2 show comparative modulus and damping plots respectively for three 66 Nylon samples exposed to different humidity levels prior to DMA evaluation.

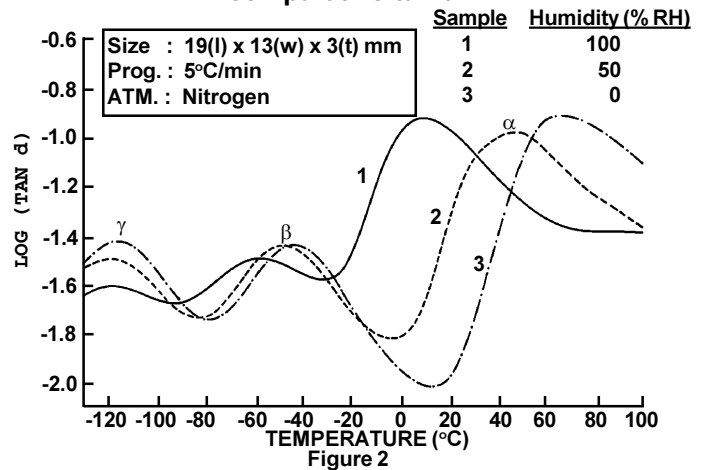
The large modulus decline in each sample (Figure 1) in the range between -10° and 80°C is associated with the glass transition of the amorphous state of 66 Nylon. The occurrence of this modulus decline is noted to move to lower temperatures as the humidity level is increased from the "dry as molded" case (curve 3) to the case where the Nylon had been conditioned at 100% relative humidity (curve 1). This lowering of the glass transition from 70 to -10°C in going from the dry to the high humidity conditioned Nylon can be explained in terms of the lowering of the hydrogen bonding forces, allowing greater chain mobility and more efficient packing, resulting in a large decrease in the glass transition temperature. Moisture also acts as a plasticizer and will lower the glass transition with increased concentration; however, this effect is much less significant than the effect of moisture in breaking the intermolecular hydrogen bonds of the polyamide.

At temperatures below the glass transition, Sample 1, conditioned at 100% humidity, is noted to have a higher modulus than those conditioned at 50% and 0% relative humidity. This increase in modulus below the glass transition is associated with the crystallization of absorbed moisture and, as a result of the high modulus of crystalline water, the higher humidity material has the higher Young's modulus.

**EFFECTS OF MOISTURE ON 66 NYLON
comparative modulus**



**EFFECTS OF MOISTURE ON 66 NYLON
comparative tan δ**



The log (tan δ) versus temperature curves (Figure 2) show three distinct peak maxima. These are designated as the alpha, beta, and gamma transitions, in order of decreasing temperature. The alpha transition is the primary glass transition of the amorphous phase and is attributed to long chain segmental motion within the main polymer chain. The beta transition, occurring between -60 and -40°C, is attributed to local motion within the amide segments of the polyamide. Finally, the gamma transition, occurring between

-120 and -110°C, is attributed to local segmental motion of the (-CH₂-) methylene groups between amide functions in the amorphous regions. The primary effect of moisture is in changing the position and intensity of the damping transitions observed for each of these specific relaxations. The most pronounced influence of absorbed moisture is on the position of the alpha or glass transition temperature. A shift of 60 to 70°C is observed in increasing the moisture content from the "dry as molded" case to that of Nylon conditioned at 100% humidity. As discussed earlier, this temperature shift is primarily the result of water breaking intramolecular hydrogen bonds, thus allowing greater chain mobility and resulting in a large decrease in the glass transition temperature. The lowering of the beta transition temperature is due to water molecules weakening interaction between the chains, shifting the beta transition to lower temperatures. The gamma transition is influenced by water/polymer interaction; increase in water content increases the fraction of hindered segments with a corresponding decrease in gamma intensity.

The most significant properties of 66 Nylon contributing to its use as an engineering plastic are toughness, impact resistance, mechanical stability, temperature stability, and weatherability. Moisture is known to have a pronounced influence on each of these physical properties, and DMA offers a means of correlating these end-use properties with a readily measurable scientific parameter. For example, the impact stability of 66 Nylon at room temperature for polymer conditioned at 50% relative humidity is approximately double that of the "dry as molded" material (see Table 1). It has been shown that the impact behavior of some amorphous materials can be determined by viscoelastic energy dissipation. High damping values can be correlated directly with impact strength in those cases where molecular motion within main polymer chains acts to dissipate a portion of the impact energy, thereby enhancing the stability of the material. Such a correlation is shown to exist in Table 1 where the tan delta value recorded at room temperature for material conditioned at 50% relative humidity is significantly higher than that of the "dry as molded" 66 Nylon. In this case, the enhanced stability is a result of the lowering of the glass transition temperature. The damping properties associated with this relaxation assist in dissipation of impact energy, thereby decreasing bond cleavage during impact.

**Table 1
66 NYLON IMPACT STABILITY
VERSUS MOISTURE**

	0% R.H.	50% R.H.
Impact Strength (23°C) (cm • kg cm ⁻²)	175	334
DMA Tan d (23°C)	0.010	0.059

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