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MECHANICAL PERFORMANCE OF POLYAMIDES WITH INFLUENCE OF MOISTURE AND TEMPERATURE – ACCURATE EVALUATION AND BETTER UNDERSTANDING

Abstract

The wide use of thermoplastics has put higher demands on designers to conduct more accurate and increasingly sophisticated analysis of materials in order to ensure the performance of the molded parts under the end-use conditions characterized by varying humidity, temperature, and dynamic load or deformation. One of the key aspects in thermoplastic analysis is to apply correct material property parameters obtained using standard testing procedures and under end-use conditions. Previously we reported to SPE (AnTec'97, AnTec'98, and RETEC/ASTM'99) the short- and long-term mechanical properties of polyamides (nylon) with time and temperature effects under dry-as-molded conditions.

The current paper focuses on the two of the most influential factors on polyamides' properties and performance – moisture and temperature. The tensile properties of conditioned polyamides were obtained from – 40°C to 150°C, and the moisture content in the sample was examined immediately after test to ensure that the change in material properties is accurately reflected.

The results provided critical understanding on the impact of moisture and temperature on polyamides strength and ductility. The findings in this investigation will enable engineers and product developers to successfully design and evaluate the performance of injection molded nylon parts under end-use conditions.

Introduction

The plastic industry has no doubt witnessed in recent years an increase in interests and demands in using thermoplastics, such as polyamides, to replace certain metals and thermosets in manufacturing automotive air induction and power train systems, lawn / garden and other power tools. Technologies have also advanced to accommodate these demands by developing materials and products with higher performance, less weight, more time / cost savings, optimized welded joints, and better resistance to fatigue and environmental changes [1-3].

The important roles today's thermoplastic structures are designed to play have made it increasingly critical for the materials to perform, especially under adversary working and environmental conditions such as cyclic stress /strain, high and low temperatures, and changing humidity.

The short-term and long-term mechanical properties (tensile and fatigue) of polyamide (PA), or nylon, based plastics under dry-as-molded (DAM) conditions were analyzed previously [1-2]. Fatigue properties of unfilled nylon 6 and nylon 66 at room temperature conditions with the influence of absorbed moisture were also discussed [4]. The absorbed moisture (≤2.5 wt.%) decreased fatigue crack growth rates, which might reflect the ability of tightly bounded water to enhance chain mobility. Results on combined moisture-temperature effects on short-term and long-term properties of polyamides, on the other hand, were rarely found in the literature.

The current investigation has been focused on the combined effects of moisture-temperature on the short-term (tensile) properties of reinforced nylon 6. Specifics in nylon conditioning using ISO and ASTM procedures are discussed in [5]. The purpose of this investigation is to help designers of plastic parts and assembled product, material developers, and the database users to correctly interpret the data on tensile properties.

The Effect of Moisture

Despite its high performance and easy processing, Nylon's tendency and ability of absorbing moisture from the surrounding environment has made it a constant challenge for processing and design engineers alike. The moisture is known to affect a range of polymer properties, which in turn impact processability, dimensional stability, mechanical, acoustic, electrical, optical, and chemical properties, and ultimately the performance of products [6-7].

The moisture in nylon acts as a plasticizer that reduces the entanglement and bonding between molecules, therefore increases their volume and mobility [7]. The moisturized material exhibits lower glass transition temperature (T_g), which makes it easier for further crystallization. The increase in moisture may cause profound changes in a material's behavior under load; it reduces strength, stiffness, and natural frequency, while increasing energy absorption and ductility in the material. Practically, the best way to minimize the moisture uptake is to select plastics with low absorption rate or design products in ways to prevent excessive absorption.

Under dry-as-molded (DAM) conditions, polyamide, or nylon, usually contains 0.1 ~ 0.3% water. At room temperature and 50% relative humidity (RH), type 6 polyamide could eventually absorb 2.75% water. Every 1% moisture increase in nylon may result in 0.2 to 0.3% increase in its dimension [6]. This change in dimension would have to be accommodated by preconditioning parts prior to service.

Sample Conditioning – Method and Analysis

Realizing the fact that the properties of dry-as-molded materials often do not reflect their true behavior in service due to the changes in properties caused by the subsequent moisture uptake, sample conditioning is therefore applied to adjust the moisture content in the materials to a desired level so that their properties and performance can be properly tested and analyzed.

In this regard, ISO-291 defines the following two standard atmospheres for conditioning:

- "Atmosphere 23": 23/50 (temperature in °C/ relative humidity in %) as recommended for most applications;
- "Atmosphere 27": 27/65, as recommended for tropical regions.

For practical purposes it is very important to analyze the properties of thermoplastics conditioned under "Atmosphere 23" (23°C/50%RH), which is recommended for most industrial applications such as automotive, lawn & garden, power tools, appliances, and so on.

The rate of moisture absorption, however, is very low under "Atmosphere 23". In this environment, it would take more than a year for the moisture in an ISO-3167 multipurpose test specimen (4 mm thick) of PA 66 to reach equilibrium. To accelerate this process, one must increase the conditioning temperature, and /or the relative humidity. Several such conditioning procedures that may be applied to thermoplastics are shown in Table 1.

Table 2 lists the water absorption values for several plastics as determined by ASTM D-570 after 24 h immersion at 23°C. Equilibrium values for water absorption will be significantly higher for these materials. The water absorption will also be higher at elevated temperatures. For unfilled nylon 6, the moisture at equilibrium at 23°C and 50%RH is 2.75% (see Table 3).

Once conditioned, it becomes important for the moisture level to be determined accurately. Moisture analysis for pellets and parts is critical for manufacturing and other processes such as molding, testing, and end-use. Table 3 shows the equilibrium moisture levels at different RH for several commercial nylons, and Table 4 lists several methods of determining moisture for nylon based thermoplastics.

Materials and Experimental Procedures

Materials

The material used in this investigation was heat-stabilized nylon 6 with 33 wt.% glass fiber reinforcement. The material was injection molded into several configurations:

- 4 mm thick ISO multi-purpose tensile bars (ISO-3167);
- 3.2 mm thick ASTM Type I tensile bars (ASTM D638) and ASTM flex bars (ASTM D 790);
- 4 and 6.4 mm thick plaques.

The molded specimens were tightly sealed prior to conditioning and testing in order to preserve their dry-as-molded state while the moisture content remains at ~ 0.2%.

Procedure for Moisture Conditioning

The procedure for sample conditioning was based on ISO-1110. The molded specimens were loaded into an environmental chamber where the temperature and relative humidity were maintained at 70°C and 62%, respectively. The moisture uptake in the sample was periodically calculated by recording the weight gains using a Mettler balance. The water absorption was also determined on a small group of samples using a Karl-Fischer unit. The moisture content in samples with different thickness was plotted against the conditioning time, as shown in Figure 1.

Although the method in ISO-1110 can greatly accelerate the moisture absorption in nylon compared to the standard method such as "Atmosphere 23", prolonged exposure of samples under conditions specified in ISO-1110 (70°C and 62%RH) has been found to cause "over conditioning" in materials by injecting more moisture than what one can ever obtain when conditioned under "Atmosphere 23". For this reason, the conditioning was terminated once the moisture in the material was found to have reached the equilibrium level under "Atmosphere 23". Samples were then sealed tightly in moisture proof bags until tested or analyzed.

Procedure for Tensile Property Test

The tensile properties of reinforced nylon 6 used in this study was obtained by following ISO-527. Tests were conducted on ISO multipurpose specimens using an Instron 4505 universal testing system. Tests at high and low temperatures were conducted in an environmental chamber attached to the Instron frame. During the test, the temperature at the center of the chamber was maintained at ±2°C within the set point. The detailed description of test setup can be found in [1-2].

Results and Discussions

Figures 2a ~ 2c compare the tensile behavior (stress-strain curves) of DAM and moisturized nylon 6 at –40°C, 23°C, and 120°C, temperatures among those typically found in the end-use conditions. Changes in tensile strength, Young's modulus, and strain at yield versus moisture are shown in Figures 3 and 4.

The effect of temperature on tensile behavior can be found in Figures 5a and 5b for DAM and conditioned materials, respectively. The decrease in strength and modulus due to the rising temperature is shown in Figure 6.

Although it has been well known that the moisture in thermoplastics will in general serve as a plasticizer that reduces a material's strength and increases its ductility, the current study indicates clearly that the net impact of moisture on tensile properties of nylon depends also on temperature. At –40°C, change in tensile behavior was insignificant within the elastic limit of the material (Figure 2a). About 10% decrease was found in the ultimate tensile strength after conditioning, but the total elongation (or strain) at failure remained virtually unchanged.

The most significant change in tensile behavior due to moisture can be found at room temperature where the tensile strength was reduced by about 40% after conditioning, while the elongation at failure increased by 150% (Figure 2b).

At elevated temperatures (80°C and above) where considerable plastic deformation in nylon has been resulted from heat, it was found that the conditioned samples exhibited not only a further reduction in strength, but lower overall elongation as well (Figure 2c).

Figures 2a to 5b seem to suggest that an increase in temperature or moisture can each achieve similar results in nylon, which is to reduce the material's strength and increase its ductility. However, the combination of temperature and moisture did not result in more ductility in the material that would allow it to deform further before failure. Instead, the material failed sooner with lower strength, indicating that the high temperature and moisture together are able to cause deterioration in the reinforced nylon, and possibly other thermoplastic materials as well.

The tensile properties of nylon 6 at various temperature and moisture combinations are shown in Figures 7, 8, and 9. The values of these properties were obtained by measuring the moisture content in individual tensile bars immediately after each test using a Karl-Fischer analyzer described in Table 4. Each point on Figures 7 ~ 9 represents a single test. At each temperature (other than 23°C), the first test was conduced 1 hour after specimens were placed in the preheated chamber, and the subsequent tests were conduced approximately one every 20 minutes. One can see that, at each temperature, the tensile properties, especially the tensile strength and Young's modulus, correlate fairly well with the moisture measured individually from the test bars.

The results in Figures 7 ~ 9 also indicate that, in a hot and relatively dry environment, nylon can quickly lose its absorbed moisture, making the initial moisture level reported at the end of conditioning meaningless as a reference parameter to reflect the material's moisture state. The rise or fall in the material's properties (e.g., tensile parameters) following the change in temperature and relative humidity is something any design engineer must consider if he or she wishes to design and model structures or products made of thermoplastics.

Summary and Conclusions

The individual and combined effects of temperature and moisture on the tensile properties of glass fiber reinforced nylon 6 were investigated and characterized. The sample conditioning was performed in an environmental chamber at 70°C and 62% RH as specified in ISO-1110. The conditioning was conducted until the moisture in the samples reached the equilibrium level under the standard conditions, i.e. 23°C/50%RH. The tensile property tests were conducted between –40°C and 150°C on ISO multipurpose test specimens with moisture levels from 0.2% (DAM) to 2.6% (conditioned).

The following conclusions can be made as a result of the current investigation:

1. For nylon thermoplastics used in this investigation, both temperature and moisture can cause a decrease in strength and an increase in ductility. Among the selected temperatures, the moisture was found to cause the greatest change in tensile properties at 23°C. After conditioning, the material has lost 40% of its original tensile strength, and at the same time, the total elongation has increased by 150%.

2. At –40°C, nylon lost 10% of its tensile strength, but other characteristics such as tensile strain and Young's modulus remained largely unchanged, especially within the elastic limit.

3. At 80°C and above, the tensile strength and Young's modulus decreased further, while the elongation or strain to failure increased.

4. At elevated temperatures, the material properties have further deteriorated by adding moisture into the structure. Comparing to the dry-as-molded materials, the conditioned materials have lower tensile strength, and they also fail sooner.

5. Due to the rapid loss in moisture in a high temperature and low humidity environment, the initial moisture value obtained from a given nylon thermoplastic can quickly become meaningless once the material is exposed to such an environment. The rise or fall in the materials properties (e.g., tensile parameters) following the change in temperature and relative humidity is something one must consider in design, modeling, and manufacture of parts and products using moisture sensitive thermoplastics.

Acknowledgment

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Table 1. Methods of Moisture Conditioning for Thermoplastics

Standard	Procedure	Use / Comment
ISO-291; ASTM D618	Six conditions varying by atmosphere, temperature, water, duration, relative humidity	Standard procedure prior to testing; not a good choice for DAM nylons due to their sensitivity to moisture
ISO-62; ASTM D 570	Water absorption at 23 ± 1°C, 50 ± 1°C, 105 ~ 110°C between 0.5 and 24 h.	See Table 2 for data. The moisture at equilibrium varies between 1 to 14% depending on temperature & RH; the microstructure of polymers may be affected by high temperature and high RH (e.g. boiling water).
ISO 483; ASTM E 104	Conditioning done in saturated salt solutions with different RH and temperature.	See Table 3 for results.
ISO-1110	Conditioning performed at 70°C and 62% RH.	Materials tend to "over-saturate" under using this procedure, comparing to the "Atmosphere 23".

Table 2. Water Absorption Values for Selected Thermoplastics after 24 h. (ISO-62, ASTM D570) [6]

Material	Water Absorption
PP	< 0.01 %
PC	0.15 %
Nylon 11	0.25 %
Nylon 6	1.3 %
Cellulose Acetate	1.7 %

Table 3. Influence of Relative Humidity on Water Absorption in Non-Filled Nylons (at 23°C in air) [7]

Type of PA	30% RH	50% RH	62% RH	100% RH
PA 46	1.4%	3.8%	5.0%	15%
PA 6	1.1%	2.75%	3.85%	9.5%
PA 66	1.0%	2.5%	3.6%	8.5%

Table 4. Standard Methods of Moisture Analysis for nylon (PA) thermoplastics

Standard	Use / Comment
ASTM D789 (Karl-Fischer)	Analysis is based on titration with a Karl Fischer Reagent. It is sensitive to moisture from 0.1% to 0.2% with typical sample weight 20 ~ 30 g. Smaller sample size is preferred for higher moisture content.
ASTM D 4029	Analysis is based on release of water vapor, which is carried away by an inert gas into an electrolytic cell. It can determine moisture in nylon at a level < 0.1% from a sample 2 ~ 4 g in weight. In a "dry" state the moisture content in nylon based thermoplastics is between 0.05% (nylon 46) and 0.3% (nylon 612) (ASTM D 4066). For nylon 6 the number is ~ 0.2%.
ISO-1110, ASTM D 570	Analysis is based on weight gain. A precision of 0.001 g is required for the weight determining device.

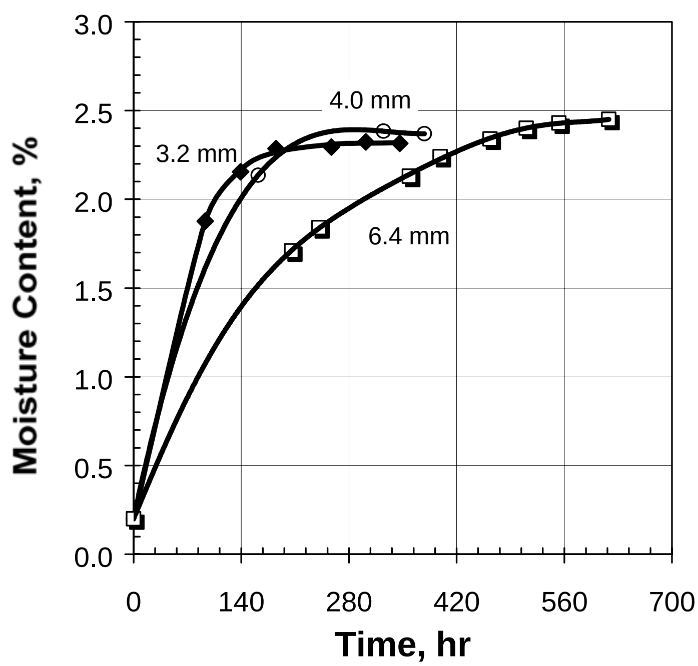

Figure 1. Moisture absorption vs. time for 33% glass fiber reinforced nylon 6. The number in mm by each curve indicates the thickness of the samples [5].

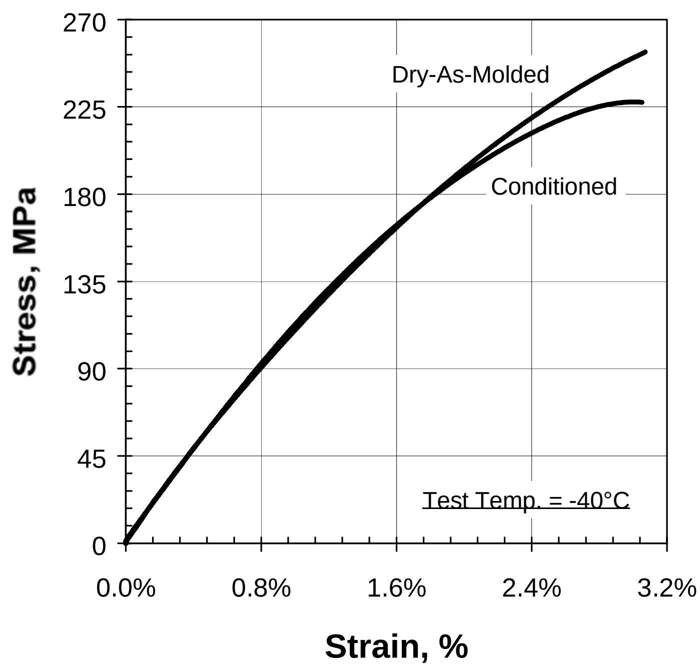

Figure 2a. Effect of moisture on tensile behavior of reinforced nylon 6 (33% glass fiber) at low temperature.

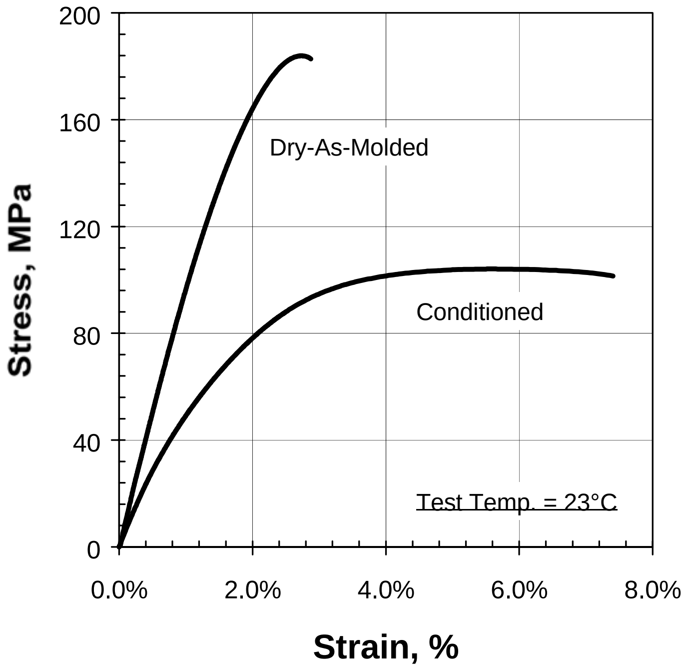

Figure 2b. Effect of moisture on tensile behavior of reinforced nylon 6 (33% glass fiber) at room temperature.

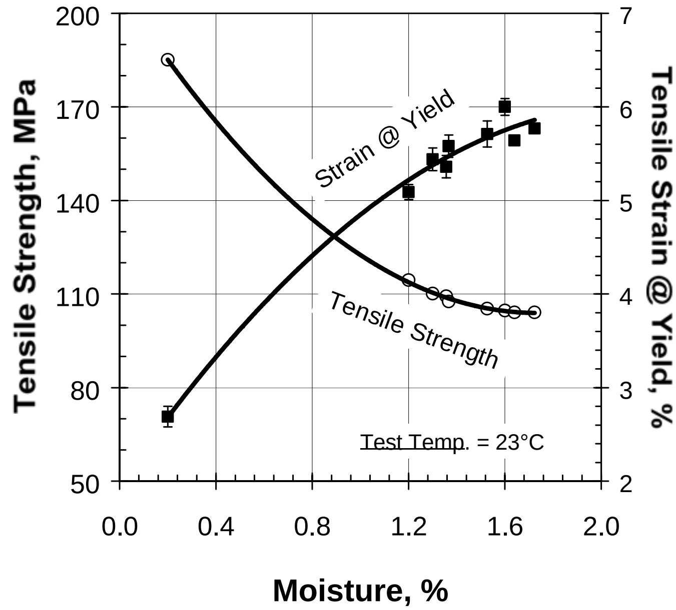

Figure 3. Effect of moisture on tensile properties of reinforced nylon 6 (33% glass fiber): tensile strength and strain at yield vs. moisture at room temperature.

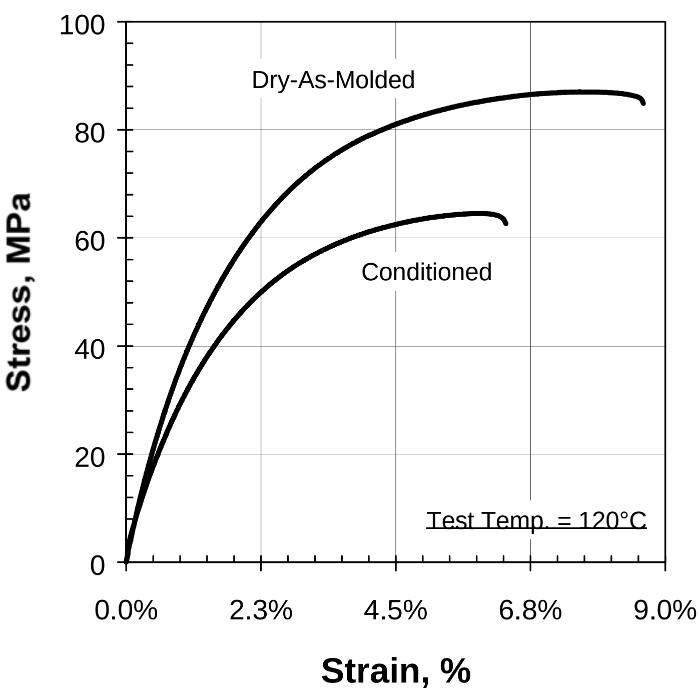

Figure 2c. Effect of moisture on tensile behavior of reinforced nylon 6 (33% glass fiber) at elevated temperature.

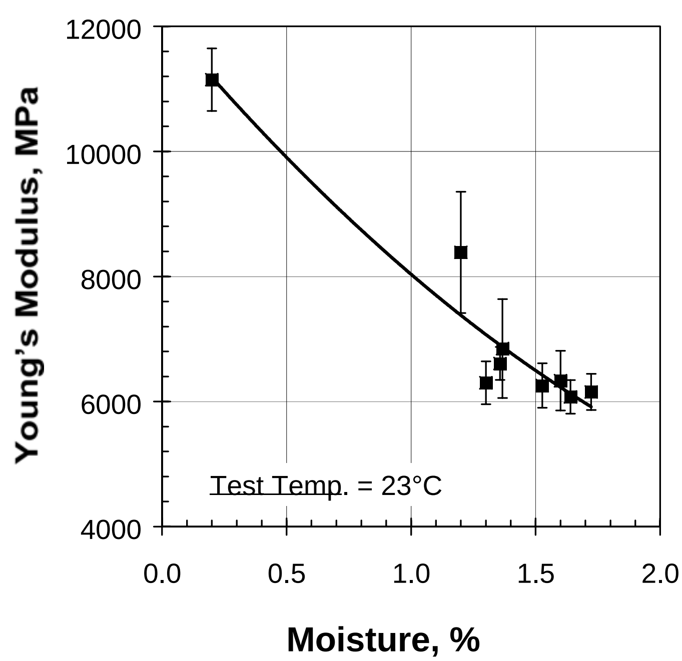

Figure 4. Effect of moisture on Young's modulus: 33% glass fiber reinforced nylon 6.

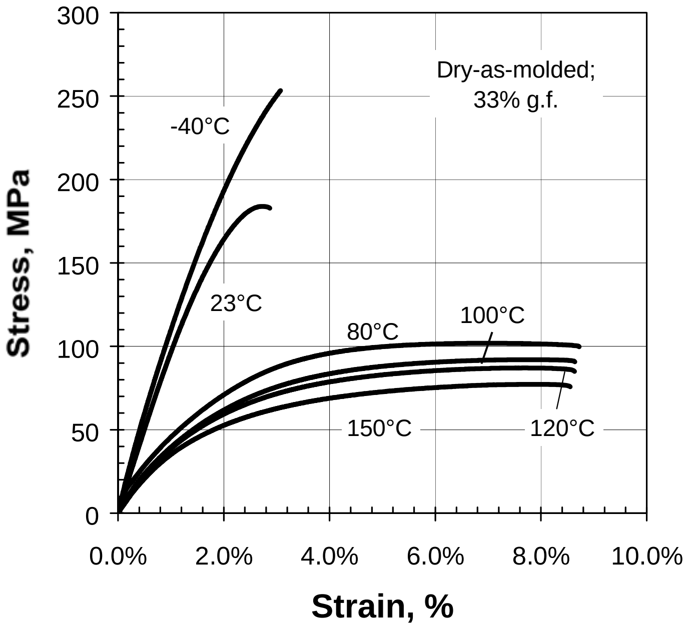

Figure 5a. Effect of temperature on tensile behavior of dry-as-molded nylon 6 (33% glass fiber).

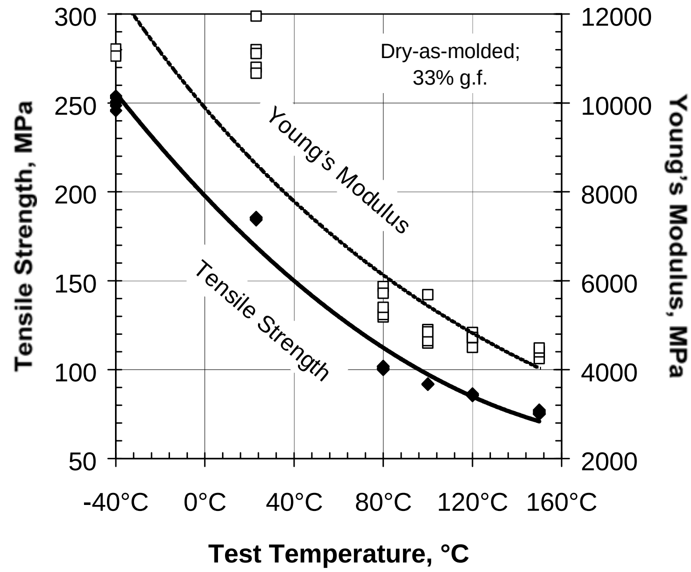

Figure 6. Effect of temperature on tensile strength and Young's modulus of dry-as-molded nylon 6 (33% glass fiber).

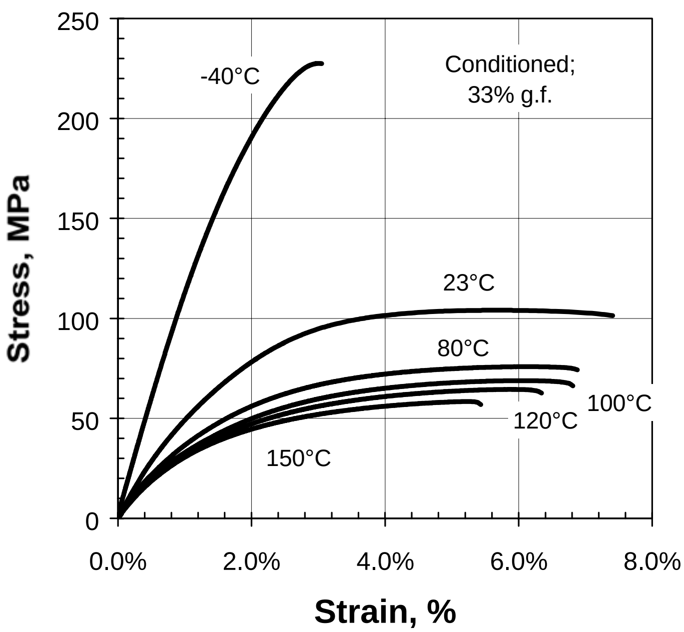

Figure 5b. Effect of temperature on tensile behavior of conditioned nylon 6 (33% glass fiber).

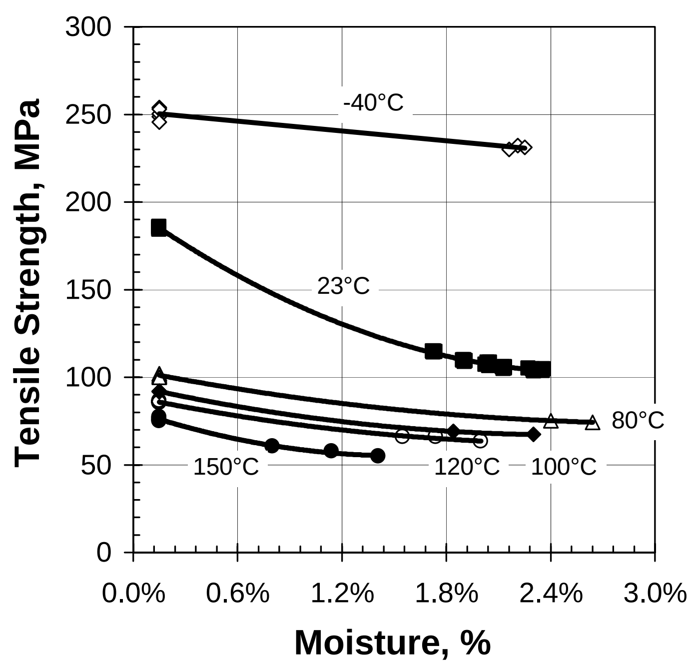

Figure 7. Impact of temperature and moisture on tensile strength of reinforced nylon 6 (33% glass fiber).

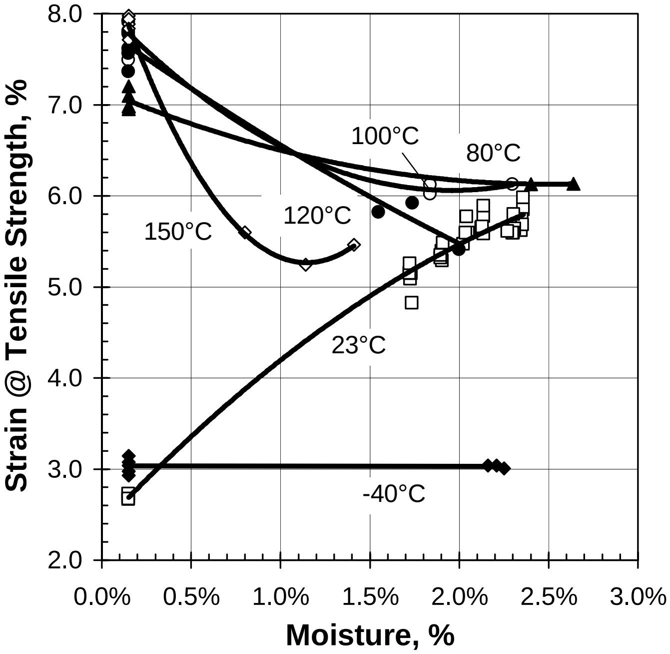

Figure 8. Impact of temperature and moisture on tensile strain @ tensile strength of reinforced nylon 6 (33% glass fiber).

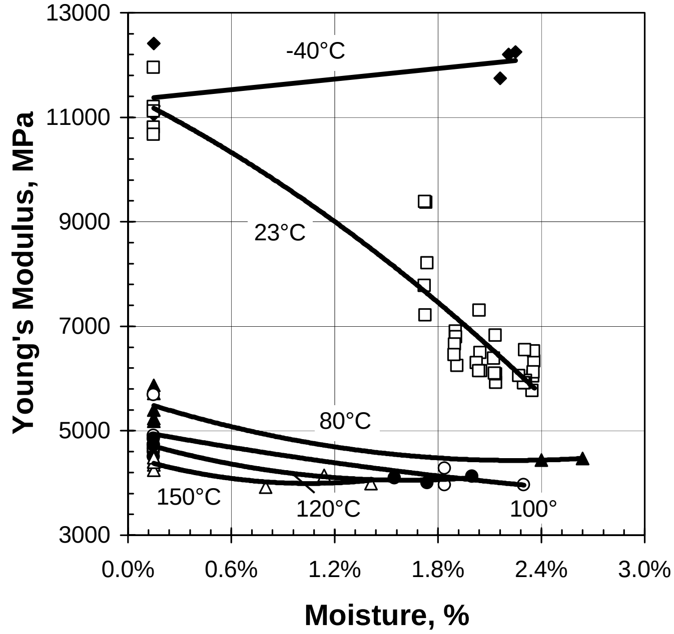

Figure 9. Impact of temperature and moisture on Young's modulus of reinforced nylon 6 (33% glass fiber).

Keywords

Polyamide, Nylon 6, moisture, temperature, relative humidity, tensile strength, ductility

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3000 Continental Drive - North
Mount Olive, New Jersey 07828-1234

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