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Evaluation of Improved Polyamides

By R. J. Hishaw

MASTER

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Topical Report
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Prepared by R. J. Hishaw

Three polyamides, nylon 11, nylon 12, and a transparent nylon, were evaluated by physical testing, characterization and analytical methods, and injection molding. None of the materials proved to be clearly superior to the others. Results of the evaluation will be used to determine applications for the materials in future production programs.

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CONTENTS

Section	Page
SUMMARY.	5
DISCUSSION	6
SCOPE AND PURPOSE.	6
ACTIVITY	6
<u>Physical Testing</u>	6
<u>Characterization</u>	6
<u>Moldability Evaluation</u>	9
ACCOMPLISHMENTS.	15
FUTURE WORK.	17

ILLUSTRATIONS

Figure		Page
1	Stairstep Flow Evaluation (P106298).	10
2	Molding Test Configuration 1 (P106300)	12
3	Molding Test Configuration 2 (P106299)	14
4	Molding Test Configuration 3, Under Polarized Light (P106419).	16

TABLES

Number		Page
1	Physical Properties of Tested Polyamides . . .	7
2	Flow Parameter Comparison.	13

SUMMARY

Concerns about sensitivity to moisture levels of most type 6 and 6/6 polyamides are deterrents to acceptance of those materials for many applications. Polyamides nylon 11 and nylon 12 were evaluated for potential use where temperature and strength requirements are not severe. These latter materials appear to offer few physical advantages, as compared to most other engineering thermoplastics. However, these polyamides, because of their toughness properties and lack of moisture sensitivity, together with good chemical and environmental stress crack resistance, could replace certain materials where operating temperatures are not severe. A third material (transparent nylon), advertised as an amorphous polyamide, offers heat deflection temperature comparable to polycarbonate and improved environmental stress crack resistance. Its hydrolytic stability is advertised as superior to other polyamides. Its amorphous structure, as opposed to the normal crystalline structure of polyamides, allows the characteristic of clarity. Because of these peculiarities of a polyamide material, an attempt was made to characterize this polymer through the use of solution studies, ash analysis, infrared spectral analysis, gel permeation chromatography, saponification, carbon hydrogen nitrogen analysis, thermomechanical and thermogravimetric analysis, long term heat aging, gas chromatography, and mass spectrographic analysis.

Moldability also was evaluated, using existing molds with demanding flow geometries. Flow properties appeared to be good, filling thick-thin sections and thin-wall moldings. Clarity appears to be the most sensitive property of transparent nylon, responding to changes in temperature of melt and mold. This characteristic also is responsive to low levels of contamination.

Physical testing of key characteristics was performed for all three materials. No single material is superior in all areas, suggesting that product requirements must be evaluated closely when considering these materials.

DISCUSSION

SCOPE AND PURPOSE

As part of an ongoing project to evaluate and categorize the many newer or improved engineering thermoplastics, this report deals with physical and moldability testing of polyamide materials known as nylon 11, nylon 12, and a material referred to as transparent nylon. Interest at Bendix Kansas City is greatest in the latter material because of its superior heat deflection and toughness properties. Also of interest is its predominantly amorphous molecular structure and clarity, which are not typical of polyamide materials. These characteristics make this material a likely replacement for polycarbonate, especially if exposed to high temperatures, certain solvents, or ultraviolet radiation. Interest in nylon 11 and nylon 12 is stimulated by their advertised hydrolytic stability and potential vegetable derivation.

ACTIVITY

Physical Testing

The physical properties of nylon 11, nylon 12, and transparent nylon were determined for those properties most pertinent to potential applications: tensile strength, elongation, flexural strength, flexural modulus (stiffness of flexure), heat deflection, and Izod impact (notched). Test results are given in Table 1. Also included are specific gravity and advertised values of moisture absorption which conform to documented values from recognized testing agencies. Advertised values of type 6/6 nylon and polycarbonate are included for comparison. All these characteristics are affected and most enhanced by grades containing various percentages of filler loadings; however, for comparative purposes only unfilled grades were evaluated.

In comparing the various characteristics, no single material appears superior in all categories. Like selection of most engineering thermoplastics, a thorough understanding of end product functions is mandatory.

Characterization

Attempts to characterize the transparent nylon were performed because of the peculiarities of this material in comparison with others of the polyamide family. Several analytic methods were

Table 1. Physical Properties of Tested Polyamides

Property	Type 6/6 Natural*	Polycarbonate Natural Unfilled*	Transparent Nylon	Nylon 11	Nylon 12
Tensile Strength (MPa)	82.74	62.05	68.879	43.34	44.82
Elongation (Percent)	40 to 60	110.0	114.0	116.67	240
Flexural Strength (MPa)	96.53	93.08	82.74	53.158	23.097
Flexural Modulus (GPa)	2.83 to 2.89	2.34	5.13	1.845	1.320
Heat Deflection (°C)	104	132.2	116.7	47	51
Izod Impact** (N·m/m)		749.3	58.72	42.17	69.79
Specific Gravity* (g/cm ³)	1.13 to 1.15	1.20	1.06	1.04	1.01
Moisture Absorption (Percent Weight Gain)					
Immersion for 24 h at 23°C*	2.0	0.15	3.2	0.3	0.25
Equilibrium at 65 Percent RH*	8.7	0.35	1.3***	1.1	1.5

*Advertised values.

**Sample thickness was 3.175 mm.

***Performed at 50 percent RH.

attempted, including solution studies; ash content; infrared spectral analysis; gel permeation chromatography (GPC); saponification; carbon, hydrogen, nitrogen (CHN) analysis; thermomechanical analysis (TMA); thermogravimetric analysis (TGA); differential scanning calorimetry (DSC); long term heat aging; and gas chromatography/mass spectrographic (GC/MS) analysis.

Solution studies were unsuccessful, as most common solvents had no effect on the polymer. Creosol, hot formic acid, and dimethyl formamide (DMF) did dissolve the material slowly, and the latter could possibly be used; however, none of these solvents is really suitable for solution properties of molecular weight studies. During these efforts, the blue coloration was found to be a surface dye removable by a methylene chloride rinse. The base polymer is a pale transparent yellow. The dye content is about 0.01 percent by weight and does not match the infrared spectra of known dyes. Ash analysis revealed no filler content. Moisture content at 50 percent relative humidity was 0.51 percent. Pyrolysis infrared spectra did not match that of common nylons, indicating this material is not a long chain aliphatic polyamide such as is commonly known.

GPC analysis of acetone extract showed major peaks at 23, 25.5, and 27 counts. Infrared spectra were prepared for fractions collected at each peak. The peak at 23 counts was an oligomer of molecular weight 500 and probably consists of two like monomers in conjunction with one dissimilar monomer, assuming typical polyamide structure. The peak at 25.5 counts was an oligomer of molecular weight 450 and theoretically consisted of one of each monomer. In neither case could these monomers be positively identified. The peak at 27 counts had a molecular weight of 180 and the spectrum of a nonaromatic amide, apparently related to the amine monomer. Attempts to match the spectrum to that of known amides were unsuccessful. Attempts to separate the two monomers through saponification with sodium hydroxide also were unsuccessful, even at high temperature.

CHN analysis revealed a composition content of 73.85 percent carbon, 9.39 percent hydrogen, 7.12 percent nitrogen, and 9.64 percent oxygen. From this information, several structures were theorized containing all aliphatic or all aromatic monomers. Comparisons of calculated CHN values for these structures to actual data showed that some combination of aliphatic and aromatic monomers was necessary. The polymer's resistance to saponification also rules out a purely aliphatic structure. The theorized structure of an aliphatic amine monomer with an aromatic acid monomer is best supported by the C:H ratio, the infrared spectrum of GPC peak 27, and the long chain amine detected at high temperature from GC/MS analysis. A speculative structure which nearly fits analytic data consists of a 14-carbon aliphatic amine and terephthalic acid as the two monomers.

Thermal analysis detected a small but repeatable glass transition from DSC analysis at 146°C. Loaded probe of TMA showed an actual softening point of 157°C. The lack of a sharp or free standing melt point is indicative of a predominantly amorphous structure. The gradual slumping over a wide temperature range should aid in material processability.

TGA scans in both air and nitrogen indicate stability to 400°C. Rapid decomposition was seen in both atmospheres above this temperature, with air being the more rapid of the two and leaving more residue.

Long-term heat aging trace shows a high degree of stability to 150°C, with minimal loss and stabilization patterns at increments of 165°C for 12 days, 180°C for 22 days, and 200°C for 31 days. At 220°C the material continued to lose weight for 30 days, and degradation was obvious from the carbonized appearance.

Moldability Evaluation

Molding characteristics of all three materials were evaluated in a stairstep configuration (Figure 1). This configuration increases flow restriction by reducing cavity thickness, in six increments, from 6.35 to 0.254 mm. Overall cavity length is 95 mm, with a generously drafted 25.4 mm width. Parts are gated into the thickest section. Mold temperature, melt temperature, injection pressure, and fill rate are monitored in this evaluation, as these parameters most enhance material flow.

These conditions are increased until the thinnest step is filled or detrimental results are obtained. Such detrimental results include degradation from excessive melt temperature or fill velocity, excessive flashing of thick sections from a combination of conditions, and sticking of part or sprue indicating excessive packing or inadequate gate size.

Nylons 11 and 12 were similar in responses to changes in parameters. Mold temperature yielded increased flow with warpage and sticking occurring around 70°C. Injection pressure was effective up to 138 MPa with little apparent gain above that level. Both materials exhibit a narrow melt band, permitting little manipulation of this parameter. Fast fill rates were used without adverse effects. Complete fill of the thinnest section was not attained with either material; however, fill was initiated and covered about 40 percent of this area. Degree of flow was nearly identical. This effort was terminated with both materials because of excessive flashing of thick sections.

Figure 1. Stairstep Flow Evaluation

Generally, molding characteristics of nylon 11 and 12 are identical and comparable to most other more common nylons; both have good flow properties with restrictive processing latitudes. A sizable plus for these materials is an apparent reduction to moisture sensitivity in processing. Predrying was not as critical or demanding as commonly experienced with nylons.

A 30-percent glass-filled grade of nylon 11 was run in this evaluation to establish comparisons of moldability for this physically superior composite. Nearly equal flow was established (about 30 percent of the thinnest area) with only minor increases in melt temperature and injection pressure. The higher heat deflection temperature of this grade facilitates a broader range of usable mold temperatures, thereby increasing processability.

The transparent nylon offered a wider range of all parameters in comparison to the other unfilled grades. Though greater enhancement was used, the degree of fill obtainable was less, filling only about 10 percent of the thinnest area before excessive packing in thick areas caused sticking problems.

Flow properties and processability of the transparent nylon were evaluated in three configurations: a thin walled molding edge gated, a thin walled molding center-pin gated, and a configuration requiring fill in alternating thick and thin sections.

Configuration 1 simulates a shallow (11.5 mm) panel with a 2.286-mm-thick surface area and a 1.016-mm-thick sidewall (Figure 2). Approximate surface dimensions are 102 by 127 mm. The part contains several thick bosses for locating and mounting purposes and a number of cutouts which act as flow restrictions in the molding process. The part is fan gated at one thin walled edge. Flow problems result from the necessity to feed in the thin edge, flow around twelve cutouts or through holes, and over numerous fixed pin restrictions in an approximate area of 107.30 cm^2 while maintaining sufficiently low viscosity to fill opposing thin walls and pack boss areas without sinks. Surface aesthetics also are critical. In production, alphanumeric characters, positional demarkations, and highlighting are incorporated through the use of inserted molded details of corresponding color and compatible material. These features were not included in parts for this evaluation.

Flowability of the material was responsive to changes in processing conditions, primarily because of the wide softening/melt range typical of most amorphous materials. Processing conditions for adequate molding were more demanding than the polybutylene terephthalate (PBT) material used in production, but were well within the range of most processing equipment. A comparison of the major flow parameters is given in Table 2. These conditions are necessary at the melt temperatures (263°C for PBT and 305°C

Figure 2. Molding Test Configuration 1

Table 2. Flow Parameter Comparison

Parameter	PBT	Transparent Nylon
Mold Temperature (°C)	Ambient to 65.5	110
Injection Pressure (MPa)	110	166
Fill Speed	Moderate	Fast

for transparent nylon) that provide the greatest fluidity of both materials. Although PBT is among the easiest flowing of engineering thermoplastics, the overall characteristics and visual quality of the transparent nylon part compare favorably.

Configuration 2 was a cylindrical part about 12.7 cm in diameter, closed on one end with a constant wall thickness of 1.02 mm (Figure 3). This part is center-pin gated on the closed end. In production, polycarbonate material is used and successful prototyping with polysulfone also has been performed. In both cases, cyclic molding was necessary.

Cyclic molding uses a mold temperature profile during the production cycle. The material is injected into the mold at a mold surface temperature approaching the softening or melt temperatures of the material. Cavity pressure then is held while the mold is cooled to temperatures below the material solidification point. This process has been successful in solving many common molding problems, in that it enhances material flowability for complex or thin cross sections; increases packing for producing sink-free thick sections; and, with an improved level of sophistication, allows a controlled cooling rate to reduce warp, control stress levels, and facilitate tighter dimensional control. This controlled cooling rate is both the chief asset and the major drawback of this system. The time required for mold heat transfer has adverse effects on the physical properties of the molded part because of extensive barrel residence time, which simulates the long-term heat aging tests. Depending on the several factors of heat transfer involved, these cycles typically run from 10 to 45 minutes. At Bendix, undersized shots, typically about 30 percent of barrel capacity, could result in materials being held in a molten state for more than 2 hours. This condition is undesirable for most materials, although some show negligible adverse effects. This material, however, was affected adversely even at minimal melt levels. Though cavity fill was attained, signs of the initiation of degradation were evident in the marginal visual quality and the highly brittle nature of the parts produced.

Figure 3. Molding Test Configuration 2

Configuration 3 (Figure 4) combines thick and thin cross section and, in many ways, is the most demanding of the three. The application was a protective cover for a compartment containing electrical connectors. This cover provides dust sealing with or without connections in place. Access to the connector is through holes molded in the cover. The hole plugs were molded as part of the cover on long flexible stringers. The part was gated into the main cover section with a constant thickness of about 5 mm and a surface area of approximately 97 cm². The attaching chords were ribbons approximately 13 mm long, 1.27 cm wide, and only 1.5 mm thick, flowing directly into the plug features, which were 2.8 cm in diameter by 12 mm thick.

This configuration was molded successfully with low viscosity materials such as polyethylene and polypropylene, but fills could not be attained with polycarbonate or polysulfone at constant mold temperatures. As optical clarity was desired, transparent nylon was a likely candidate for this application.

Flow characteristics in this configuration were excellent, providing easy cavity fill and good clarity even in thick sections. Normal processing conditions were sufficient for establishing adequate flow, indicating maintenance of viscosity over an extended flow period through retention of heat in thick sections. Excessive warping or high skin stress would be expected with this set of conditions; however, no excessive warpage was seen. Flexibility of stringers was not adequate for the extreme demands of this application, but all molding characteristics were favorable.

ACCOMPLISHMENTS

Physical testing of pertinent properties of nylon 11, nylon 12, and transparent nylon was performed. No one material was totally superior, but the transparent nylon was most impressive. Because little structural information was available for the transparent nylon, an effort was made to characterize this material through the use of several analytical methods. Although the exact molecular structure was not determined, the most probable composition has been hypothesized and will provide base information if more detailed work is necessary on future projects.

Molding evaluations were performed, but no unusual processing conditions were experienced with any of the materials. Most characteristics were predictable. No effort was made to evaluate shrinkage characteristics. General design and processing practices should suffice in any future production activities using these materials, with the exception of the transparent nylon's clarity sensitivity.

Figure 4. Molding Test Configuration 3, Under Polarized Light

FUTURE WORK

Wear testing of bearing grade materials is currently in progress. These materials include:

- Polyphenylene sulfide with MoS_2 ,
- Polyphenylene sulfide with SbO_2 ,
- Polyphenylene sulfide with TFE,
- Polybutylene terephthalate with TFE, and
- Polyamide 6/6 with 40 percent glass and MoS_2 .

Test fixturing is being fabricated to evaluate these materials in various functional situations simulating cams, rollers, and other metallic interfaces as well as wear against mating surfaces of like material.

Plans to pursue polyarylsulfone, aromatic copolyester, and polyphenylsulfone have been delayed.

Testing and evaluation of new or resurgent polymers is being conducted and includes two grades of polyethersulfone and polyethylene terephthalate. A new material, designated polyarylate, and an advertised low warpage polyester also will be evaluated.

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PLASTICS: Nylon

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