BASF Corporation

BASF

OPTIMIZING THE MECHANICAL PERFORMANCE IN SEMI-CRYSTALLINE POLYMERS: *Roles Of Melt Temperature And Skin-Core Crystalline Morphology Of Nylon*

Abstract

Crystalline texture and mechanical (tensile and flexural) properties of injection molded nylon 6 were evaluated to understand the influence of one of the key-processing variable, the melt temperature (T_{mlt}). We find that mechanical properties are sensitive to T_{mlt} only below ~ 250°C. Rapid quenching of the surface produces a skin with lower crystallinity than the core, which cools more slowly; this difference in the rate of cooling produces γ crystalline form in the skin and α crystalline form in the core. Higher tensile strength at yield, lower elongation at break and higher flexural strength were observed in specimens molded at lower T_{mlt}. These characteristics are associated with thicker and less ordered skin, and a lower crystallinity core. The role of the T_{mlt} on micro-structure and mechanical properties of injection molded nylon 6, the development of skin and core morphologies, and the role of the residual stresses in the core are discussed.

Introduction

End-use performance of injection molded thermoplastic components strongly depends on the part design, thermoplastic composition, processing conditions and the microstructure [1-3]. By understanding the correlation between various polymer structural features and the mechanical performance of nylon 6 based plastics, it is possible to optimize injection molding conditions such as melt and mold temperatures, injection and hold pressures. Several aspects of polymer morphology influence the mechanical performance of the injection-molded nylon 6. These structural features are determined in a quite complex manner by the injection molding processing conditions. In this study, we report on our an effort to understand some of these issues by evaluating the influence of melt temperature (T_{mlt}) on tensile and flexural properties and microstructure for injection molded nylon 6. Specifically, we address the issue of measurement and evaluation and significance of skin-core homogeneity in plastics [4,5].

Experimental Procedures

Material and Specimens

Commercial available nylon 6 based plastic - Capron®[1] 8202 HS (an unfilled, heat stabilized nylon 6 with

molecular weight M_w = 22,900) was injection molded into standard ISO multipurpose tensile specimens (ISO 3167). Prior to injection molding, nylon pellets were

dried according to ASTM/ISO requirements. ISO (or ASTM, type 1) multipurpose specimens were injection molded using the standard practice (ISO 294-1, ISO 294-2, ASTM D 3641 and ASTM D 4066) and published recommendations for processing parameters [3,6].

Mechanical and Analytical Measurements

Static tensile tests were conducted according to ISO 527 (ASTM D 638) at crosshead speed of 50mm/min. Flexural tests were conducted according ISO 178 (ASTM D 790). Both tests were done at –40, 23 and 150°C (± 1°C) on an Instron Universal Tester (Model 4505) with an environmental test chamber. Five specimens were tested at every injection molding conditions.

X-ray diffraction data (XRD) were collected on a Philips diffractometer (PW3710) in reflection geometry. Data from as received specimens are labeled as skin-data. The specimens were cut lengthwise through the middle of the thickness, and the scan from this cut-surface is labeled the core-data. The results of the profile analyses of these scans were used to calculate a measure of crystallinity in the form of a crystalline index (CI), an index of crystalline perfection (ICP), and the ratio of the amount of α and γ crystalline forms. The CI is the ratio of the area under the crystalline peaks and the total area over the angular range of the data. This angular range (5° to 35°) was selected so as to cover all the intense crystalline peaks. ICP is the difference in the 2θ angle (in degrees) of the two α crystalline peaks, and this is a measure of the crystalline density and hence crystalline perfection.

---

[1] Capron® - is a registered trademark for BASF Corporation nylon plastic products.

Micro IR was done on a Nicolet Magna 550 spectrometer. Sections of ~20 μm in thickness were made from the 1/8 in. thick specimen using microtome at ambient conditions. The data were analyzed by measuring by the peak heights of the various bands using second derivatives of the spectra.

Results

Mechanical Tests

Tensile test data (Figure 1) show that as the melt temperature is decreased, the tensile stress at yield remains essentially unchanged up to ~260°C, and then increases at lower T_{mlt} (Figure 1a). Changes in elongation (strains) at break are opposite to that of tensile stress at yield: it increases with T_{mlt} up to 260°C and then remains essentially unchanged at higher melt temperatures (Figure 1b).

Flexural tests data (Figure 2) show that at room temperature (20°C), flexural modulus (*E*) decreases with increase in melt temperature (Figure 2a). However, at test temperatures of 150°C, the flexural modulus goes through a minimum at 260°C (Figure 2b). Similar results were obtained at -40°C.

X-ray Diffraction

Figures 3a and 3b show examples of the XRD scans from the skin and the core areas, respectively, of the injection-molded specimen. The crystallinity in the skin is mostly due to well-crystallized γ and poorly crystallized α. In contrast, the core has well formed α crystals. These XRD scans were used to determine the crystallite index (CI), ratio of α to γ crystalline fractions, and an index of crystalline perfection (ICP) of the skin and the core. Influence of the T_{mlt} on these parameters is shown in Figures 4 and 5.

The crystallinity of the skin is 23-27% and is significantly lower than the 31-35 % near the core. Whereas the crystallinity of the core increases with the melt temperature (Figure 4a), and the γ fraction decreases with increasing melt temperature (Figure 4b), the crystalline composition near the skin remains unchanged. Surprisingly, the expected increase in ICP with T_{mlt} is seen only in the skin; ICP in the core in fact decreases (Figure 5). As will be discussed below, this can be attributed to residual stresses in the core of the sample because of constrained shrinking.

Infrared Spectroscopy

An example of the IR scan as a function of depth (thickness of injection molded specimen) is shown in Figure 6. The heights of the peaks at 1200 and 1170cm^{-1} were taken as measures of the α crystalline fraction, and γ + amorphous fraction, respectively. Although it is difficult to separate the γ crystalline fraction and the amorphous fractions in IR spectra, in combination with the XRD data, IR data can be used quite effectively for determining the phase composition.

The heights of the α crystalline fraction, and combined γ + amorphous fraction are plotted in Figure 7

for one of the injection molded nylon 6 specimen. The IR data confirm the presence of larger fraction of γ near the skin than in the core. The transition from the skin to core is gradual at higher melt temperatures and show a relatively sharp transition at the lowest temperature used in these measurements. At higher melt temperatures (T_{mlt}), the core structure is constant only over a short distance (400 μm) and then changes toward the skin morphology. In contrast, at lower T_{mlt}, the core structure remains unchanged over a longer part of the core (1600 μm) and then rapidly increases towards the γ crystal-rich skin. The skin depths were obtained from the point at which the microstructure begins to change dramatically from the core and were measured from a plot of the changes in the slope of the curve of the relative content of the α crystalline fraction. The skin depth was found to decrease monotonically with increase in T_{mlt}.

Discussion

Our motivation was to understand how the micro-structural features of nylon 6 that change with molding conditions affect the mechanical performance of nylon 6 and to use this to develop information for determining the optimum molding conditions.

Tensile properties of our samples change significantly at lower melt temperatures (T_{mlt}) and are essentially unchanged above 245°C. Flexural modulus (*E*) at ambient temperatures decreases with increase in T_{mlt}, but at test temperatures of 150°C and -40°C appear to go through a minimum at T_{mlt} ~ 260°C. The question is what micro-structural features can explain these changes, especially those at T_{mlt} below 260°C.

Although, thickness of the skin appears to decrease monotonically with increase in melt temperature, we see that the lowest temperature sample is different from the rest: its skin is thicker and its ICP is lower. It has been previously suggested that thicker skin is obtained at lower molding temperature, i.e., of the quench surface [5]. In contrast, we find thicker skin at lower melt temperatures. All these parameters affect the mechanical behavior. In general, it appears that higher yield stress is accompanied by lower elongation (at yield and break), and is the result of thicker skin.

A significant observation from our mechanical test results is that the flexural and tensile properties do not change monotonically with T_{mlt}. Rather, there is a minimum in the flexural modulus, both at initial (3.5% strain) and final elongation (strains at break) and there is a maximum in the elongation to break at about 260°C. An equally significant observation is that the skin and core structures, which are known to exist in molded specimens, change differently with T_{mlt}. With increase in T_{mlt}, the ICP near the skin increases where as that in the

core decreases. Implications of these observations will be discussed below.

The skin cools rapidly from a melt at higher temperature, and therefore, the resulting nylon 6 crystals are γ. The core cools more slowly than the skin. Hence the core crystals are α. Because it takes longer to cool the melt from a higher temperature (T_{mlt}), there is a marginal increase in the core crystallinity from ~ 32% to 35% with increase in melt temperature. The increase in crystallinity is mostly due to the crystallization of the α crystals from the melt in the core.

There are two factors that affect the cooling rate. During the initial stages, a polymer melt at a higher temperature (T_1) cools faster than the one at a lower temperature (T_2). But after a time Δt_1, once the polymer has reached a temperature T_2, it will cool at about the same rate as the polymer at T_2. However, as the polymer crystallizes during cooling, the heat of crystallization given off from the crystals formed between T_1 and T_2 will reduce their cooling rate after T_2 .

Rapid initial cooling at higher melt temperatures results in a thinner skin. But because the crystallization occurred at a higher temperature (even if this crystallization temperature T_{cr} is not constant) and because it takes a longer time to cool the once formed crystals to the constant mold temperature, the crystals near the skin formed at higher T_{mlt} will have larger crystallites and ICP.

Since the skin solidifies before the core, the still molten polymer in the core is under strain as it crystallizes under constant volume conditions. The residual stresses that are created in this process will affect the core crystals. Higher ICP in the core at lower melt temperatures (T_{mlt}) could be because the thicker skin at the lower T_{mlt} reduces the rate of heat loss given off during crystallization and thus the core cools more slowly at lower T_{mlt}. As the molten polymer takes longer time to cool from a higher temperature, the skin-core transition becomes more diffuse, and this could also contribute to lower ICP.

The thickness of the skin appears to have a large influence on a host of mechanical properties such as yield stress, elongation at yield and flexural strength. Thicker skin results in higher yield and flexural strength, and lower elongation at yield. Note especially that these properties remain essentially unchanged in specimens molded at higher temperatures (T_{mlt}) and which have about the same skin thickness. It appears that the tensile strength at yield is high and elongation at yield are low, when skin is thick, and the skin-core interface is sharp. A stiff core and a soft skin, as indicated by high core ICP and low skin ICP, might account for the improved flexural performance of bars molded at lower melt temperatures.

Despite the large errors in the data, the correlation between one of the structural parameters, the degree of perfection (ICP), and the properties show that ICP in the skin and core have opposite effects on the measured mechanical properties (Figures 1, 2 and 5), and that these parameters change monotonically with melt temperatures. The opposing effects of the skin and the core are most clearly seen n the flexural data obtained at test temperature equal to 150°C. This suggests that it is necessary to trade off the effects of the skin and the core to achieve the desired mechanical performance. In general, melt temperatures between 260 and 280°C appears to the optimum for this particular formulation.

Concluding Remarks

There is an optimal melt temperature (T_{mlt}) to achieve the desired mechanical performance. This is because microstructure near the skin and core change in opposite directions as the T_{mlt} is changed: as T_{mlt} is increased, the ICP at the skin increases and that in the core decreases. This, for instance, gives rise to a minimum in flexural modulus and a maximum in the elongation at break.

Acknowledgments

References

1. Kohan, M., *Nylon Plastic Handbook,* Hanser/Gardner Publications, Inc., New York (1997).

2. *Plastics Handbook* Vol. 4, Polyamide, Hanser Publishing, Munich (1998).

3. *Injection Molding Processing Guide for Capron® Nylon*, Honeywell International, Engineered Applications & Solutions, Morristown, New Jersey, (1998).

4. Wenig W. and Herzog, F. *J. Appl. Polym. Sci*. 50 2163 (1993).

5. Oswald T.A. and Menges G., *Materials Science of Polymers for Engineers*, Hanser Publishing, Munich, pp.211-249 (1995).

6.   Kagan, V., A., *Optimizing Welding Temperatures of Semi-Crystalline Thermoplastics – Memory Effects of Nylon*, ANTEC'2000, SPE - Society of Plastic Engineers, Orlando, Fl, Proceedings of the 58th Annual Conference and Exhibits, pp. 1288-1301, (2000).

Key Words

Polyamide, injection molding, microstructure, mechanical properties.
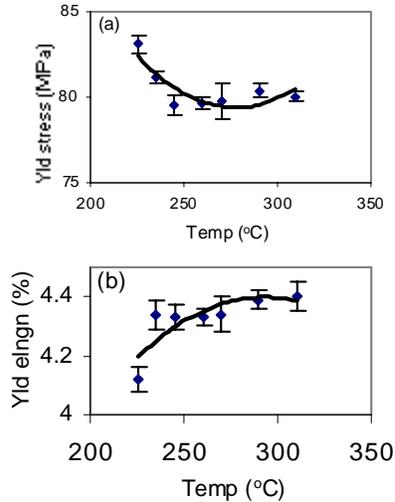
Figure 1. Influence of melt temperature (T_{mlt}) on the tensile properties of injection molded nylon 6. Legend: **a** – Tensile stress at yield; **b** – Strains (elongation) at break.
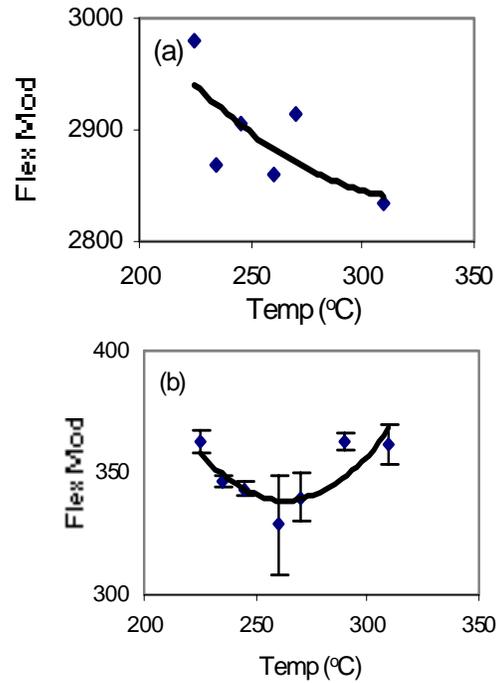
Figure 2. Influence of melt temperature (T_{mlt}) and test conditions on the flexural modulus (**E**) of injection molded nylon 6. Legend: **a** – at 23°C; **b** – at 150°C.
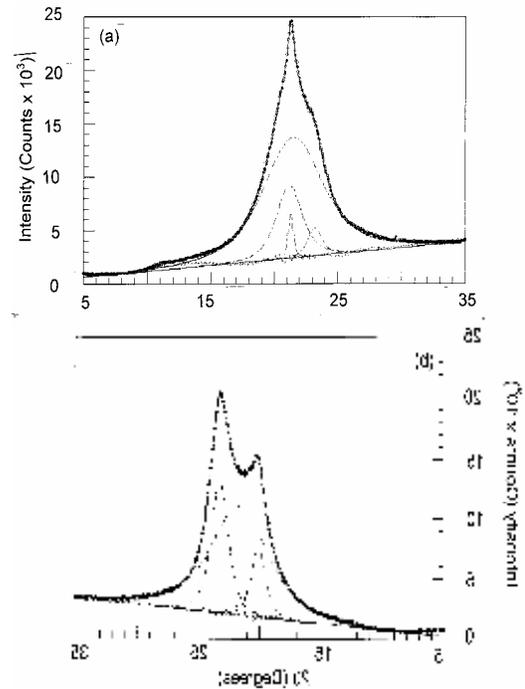
Figure 3. Typical X-ray diffraction for injection molded nylon 6. Legend: **a** – Skin area; **b** – Core.

Figure 5. Roles melt temperature (T_{mlt}) on the index of crystalline perfection (ICP). Legend: **a** - Skin; **b** – Core.

Figure 4. Influence of melt temperature (T_{mlt}) on microstructure in core for injection molded nylon 6. Legend: **a** – Ratio of the α to γ crystalline fraction; **b** – Crystallinity index (CI).
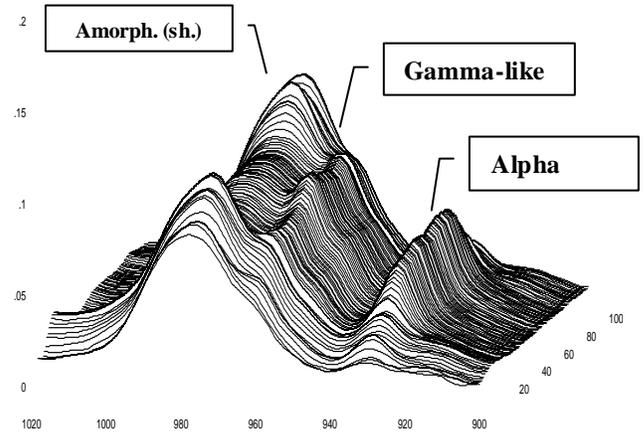
Figure 6. Typical IR scans for injection molded ISO specimen.
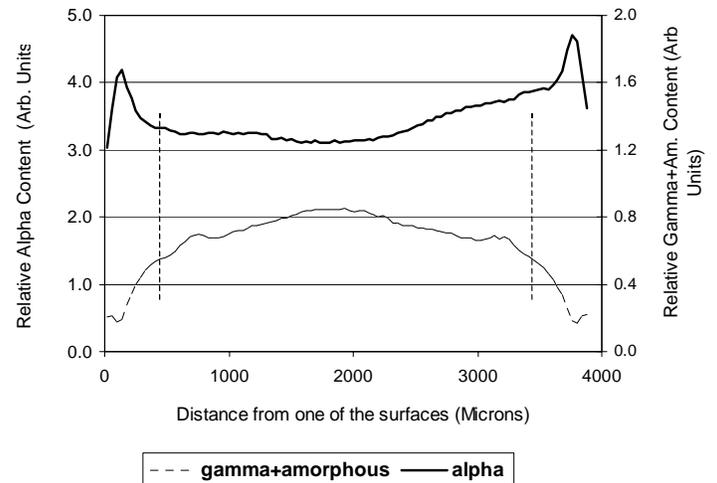
Figure 7. Plot of heights of the α and γ +amorphous peaks trough the thickness (Δ) of the ISO specimens molded at 310°C.
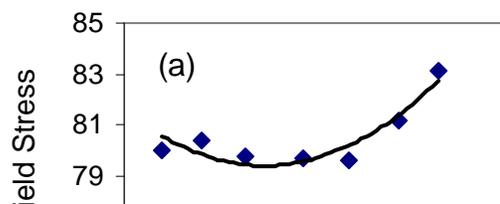
Figure 8. Correlation between mechanical performance
and skin depth for injection molded nylon 6.

HELPING MAKE PRODUCTS BETTER™

BASF