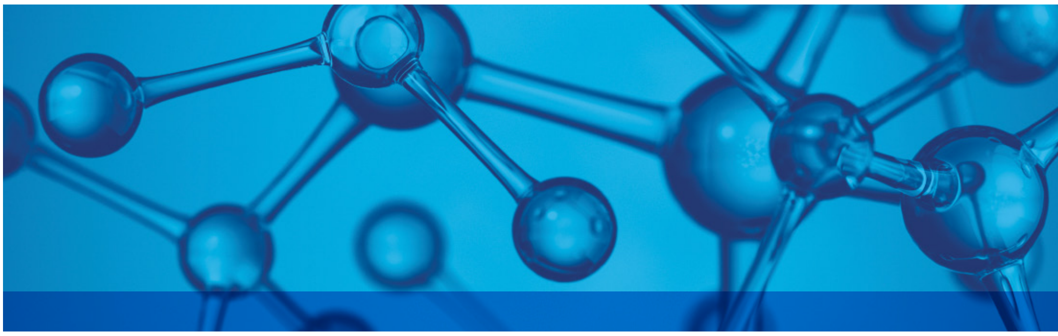

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The Importance of Mold Temperature on the Properties of PPS Parts

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Abstract

Polyphenylene sulfide (PPS) is a semi-crystalline engineering thermoplastic recognized for its unique combination of properties including chemical resistance, dimensional stability and thermal stability. The exceptional performance of this material in these environments has lead to extensive use in automotive "under the hood" applications. To maximize these material properties and make the high quality parts demanded by the automotive industry, it is very important that certain guidelines are followed in the molding process, failure to do so can result in premature part failure. This paper outlines one of the basic molding requirements, mold temperature, and the effect it has on the finished part.

Introduction

The failure of a part to perform in its intended function is always disappointing, but when this failure can easily be prevented by close monitoring of the molding process, it makes for an interesting case study on how to detect improperly molded parts and what the actual effect is going to be on the finished assembly. The thermostat housing in this case study is somewhat unique in that the arms that hold the thermostat in place are under tension from the initial assembly at room temperature (Figure 1). Only when the parts see the heated environment in which they operate do the problems of improper mold temperature come into play. This paper will explore the analytical methods used to determine if the appropriate mold temperature was utilized and how changes in mold temperature affect the critical properties of dimensional stability, thermal stability, and mechanical strength.

Figure 1: Thermostat housing, thermostat held by small tabs at the end of each arm

Materials

The material used in this investigation is a 40 percent glass fiber reinforced grade of PPS that was developed specifically for use in hot, wet environments such as the thermostat housing being discussed. This injection molding compound has a tensile modulus of over 15 GPa when properly molded and tested at room temperature. A complete table of mechanical properties is provided later in the paper for comparison.

The above PPS compound was molded at a range of temperatures to cover a spectrum from amorphous to fully crystalline. The temperatures and the reason for their selection are listed below:

- 135 °C, typically the minimum recommended molding temperature for PPS
- 100 °C, slightly above the glass transition temperature (T_g) and below the crystallization temperature (T_c)
- 90 °C, approximately the T_g for PPS when molded crystalline
- 60 °C, sufficiently cold to yield parts that are amorphous in structure

The mechanical testing was conducted at the following temperatures which were chosen for the reasons listed:

- 23 °C, the temperature where data sheet properties are generated
- 75 °C, a temperature slightly below the T_g of PPS
- 90 °C, the temperature approximately equal to the T_g of PPS
- 100 °C, a temperature slightly above the T_g of PPS
- 115 °C, a temperature slightly below the T_c of PPS above which crystallization takes place rapidly

Crystallinity

To obtain high levels of crystallinity in PPS components it's recommended to utilize hot mold conditions, greater than 125 °C [Ref 1] and 135 °C or higher is commonly recommended by material suppliers. Beyond the level of crystallinity, the advantages of utilizing hot molds includes improved high-temperature dimensional stability, increased heat deflection temperature (HDT), and improved mechanical properties at elevated temperatures.

Crystallinity content can be monitored by many analytical techniques, including x-ray diffraction, thermal analysis, infrared analysis, density measurements, and solid phase nuclear magnetic resonance measurement [Ref 2]. The most commonly practiced method of determining component crystallinity levels is through differential thermal analysis, more specifically differential scanning calorimetry (DSC). This method provides a quick pass/fail test with either the presence or absence of a T_c in the 120 °C range of the thermogram (Figure 2). Another method utilized to measure levels of crystallinity, which provides a greater level of precision, albeit at a greater cost and effort, is X-ray diffraction (XRD). Both methods were used in this investigation to study the effects of mold temperature on levels of crystallinity. When tested by DSC, parts molded with mold temperatures below 120 °C showed a definite T_c indicating low levels of crystallinity had been achieved. Conversely, parts molded with mold temperatures of 120 °C and above showed no T_c indicating relatively high levels of crystallinity. The XRD testing of these same parts indicates although no T_c was apparent in the DSC of parts molded at 120 °C, only mold temperatures of 135 °C and higher produced parts that had reached maximum levels of crystallinity (Figure 3).

Figure 2: DSC of amorphous (cold molded) PPS part illustrating the T_c associated with crystallization in the oval

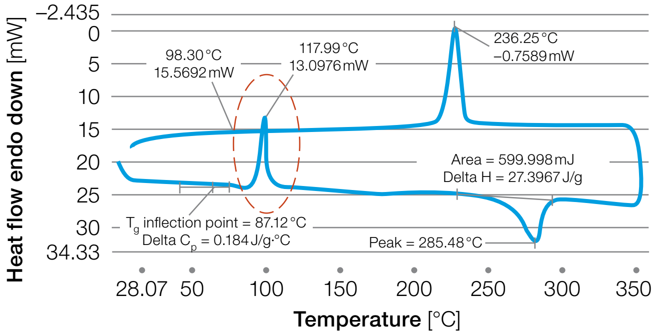
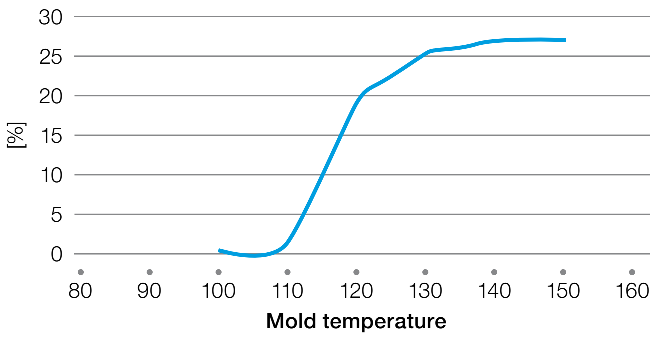


Figure 3: Crystallinity at various mold temperatures, as measured by XRD



Dimensional Stability

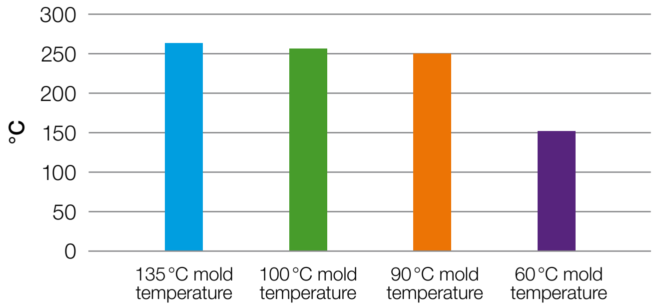
Any time a partially crystalline molding is exposed to temperatures above its T_g, it can crystallize more, and the resulting shrinkage can compromise dimensional accuracy. A study of shrinkage after thermal aging has shown test specimens molded with a mold temperature below 100 °C have greater shrinkage after thermal aging for 24 hours at 232 °C, than parts molded with a mold temperature of 135 °C. This is caused by the crystallization of the amorphous regions of the less crystalline parts that were a result of the lower molding temperatures. In this study fan gated plaques, 100 mm by 100 mm by 3 mm, were injection molded and then measured on a Mitutoyo model B504B coordinate measuring machine. The fan gate is designed to maximize fiber alignment so that measurements may be taken in both the axial and transverse directions. Results are shown in Table 1. Even though both hot and cold molded parts showed additional shrinkage after thermal aging the hot molded parts showed considerably less. In cases where maximum crystallinity is required to achieve the most dimensionally stable parts, heat treating at temperatures from 200 to 232 °C for 2 to 4 hours may be conducted [Ref. 2].

Table 1: Post mold shrinkage after 24 hrs. at 232 °C

Mold Temperature	Additional Axial Shrinkage	Additional Transverse Shrinkage
Cold < 100 °C	0.21 %	0.52 %
Hot > 135 °C	0.13 %	0.10 %

Another aspect of maintaining part integrity at elevated temperatures is Heat Deflection Temperature (HDT), ASTM D648. This test method utilizes a standard temperature increase of 2 °C per minute and measures the temperature where a deflection of 250 µm takes place with a pressure of 1,820 kPa. One of the major difficulties in obtaining results via this test method is the tendency of PPS to continue to crystallize at temperatures above the T_g. As a result, crystallization is taking place as the test is progressing. Therefore, even the relatively amorphous parts are increasing in crystalline structure the longer they are in the test bath. The lowest temperature molding, that should be predominantly amorphous, shows the greatest loss in HDT, only about 58 percent retention (Figure 4).

Figure 4: Heat Deflection Temperature of PPS test specimens molded at different temperatures



Mechanical Strength

What prompted this particular phase of the study is that plastic materials typically fail in one of two failure modes, ductile or brittle. PPS, having a tensile modulus of over 15 GPa for reinforced grades, fails in the brittle mode, that is, the part remains intact until the pressure exceeds the strength and then a catastrophic failure occurs rendering the part ineffective. Oddly, in this particular case, the parts were failing in a ductile mode. The objective was to determine how the molded parts could have a ductile failure as seen in Figure 4.

Perhaps the most critical component of this case study is the mechanical strength and how it is affected by crystallinity levels and when that effect takes place. To study these effects samples were tested at both room temperature (23 °C) and at elevated temperatures as outlined in the materials section of this paper.

A considerable amount of data has been available either in manufacturers' literature or on companies' internet web sites, comparing the mechanical properties of hot and cold molded PPS parts. As can be seen in Table 2, there is very little overall apparent advantage or disadvantage to either hot or cold molding. Cold molding does provide an advantage in the areas of Izod impact strength and a slight advantage in tensile strain. However, not an advantage so great as to overcome the disadvantages observed in dimensional stability. Surprisingly, neither mold temperature had an advantage in modulus when tested at room temperature as might have been anticipated by the failure mode of the thermostat housing.

Figure 5: Unusual ductile failure of tab on thermostat housing

Testing tensile strength at elevated temperature also presents its challenges. Again, because of the tendency of PPS to continue to crystallize at temperatures above the T_g (90 °C), it's difficult to maintain the same level of crystallinity throughout the test range. As was discussed in the materials section, the test temperatures were strategically chosen in an attempt to avoid rapid crystallization of the test specimens. It was also important to consider the finished item and failure mode in selecting the test temperatures. Being a thermostat housing, the part would be subjected to coolant temperatures that wouldn't normally exceed 125 °C, a temperature well below the HDT and the melting point of PPS (282 °C), where one might expect to see ductile failures.

The elevated temperature testing exposed a steady decline of tensile strength as the temperature increased. This is not an unexpected result, as previous testing has indicated losses in mechanical strength of thermoplastic materials as the test environment increases in temperature. However, this testing proved the cold molded parts' decline in tensile strength was much more severe than that of the hot molded parts. Because of the time required in the test chamber for the parts to reach test temperature, crystallization started to take place in the cold molded parts as the test temperature exceeded the T_g of the material.

This crystallization took place slowly at temperatures up to 100 °C, and the difference in tensile strength between hot and cold molded parts was exacerbated. However, at a test temperature of 115 °C the crystallization took place so rapidly that the tensile strength decline was reversed and values actually increased and started to approach those of the hot molded parts as can be seen in Figures 6 and 7. The test specimens molded at 60 °C retained only 38 percent of the initial tensile strength when tested at 100 °C, while the specimens molded at 135 °C retained 64 percent of the initial value.

Table 2: Room temperature mechanical properties of the material in this study molded at the temperatures outlined in the materials section

Material Property	Unit	135 °C	100 °C	90 °C	60 °C
Flexural Strength	MPa	246	243	241	246
Flexural Modulus	GPa	12.8	12.5	12.5	13.0
ISO Izod Notched	kJ/m²	7.3	8.0	8.4	8.8
ISO Izod Unnotched	kJ/m²	30.5	40.0	48.7	53.4
Tensile Strength	MPa	172	170	170	170
Tensile Modulus	GPa	15.1	14.5	14.5	14.8
Tensile Elongation	%	1.48	1.61	1.62	1.67
HDT	°C	263	256	249	152

Figure 6: Tensile strength tested at elevated temperatures

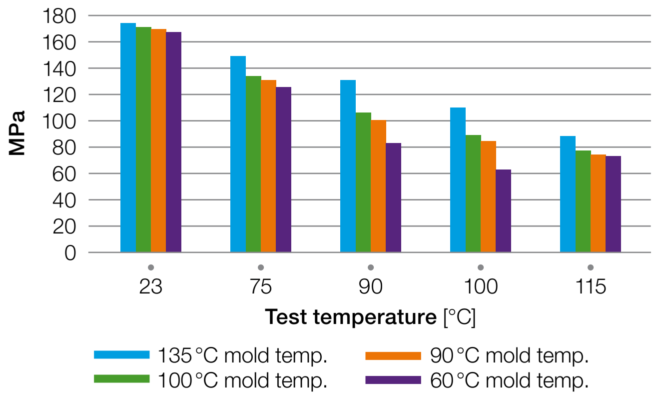
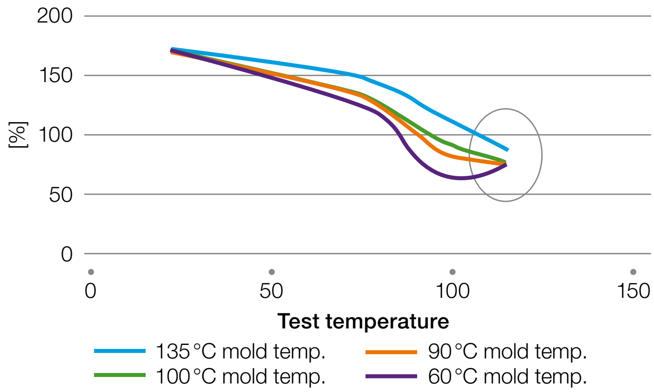


Figure 7: Tensile strength tested at temperature, note the convergence of the test results in the circled area, as the test temperature exceeds the T_g and crystallization takes place



The effect of the level of crystallinity in the molded test specimens could also be seen in the tensile elongation and tensile modulus. The elongation increased sharply at 90 °C, just above the T_g for the amorphous, cold molded parts. Compared to the hot molded test specimens, the least crystalline parts, molded at 60 °C, had 30 percent more elongation at 90 °C (Figure 8). Tensile modulus decreased as the test temperature increased and once again the greatest effect was observed when the test specimens were cold molded. At a test temperature of 100 °C the difference in tensile modulus between hot and cold molded specimens was 40 percent. Once again, as the test temperature increased to 115 °C, the test specimens began to crystallize and the modulus increased (Figure 9).

Figure 8: Tensile elongation tested at temperature, note the difference between hot and cold molded samples at 90 °C in the circled area

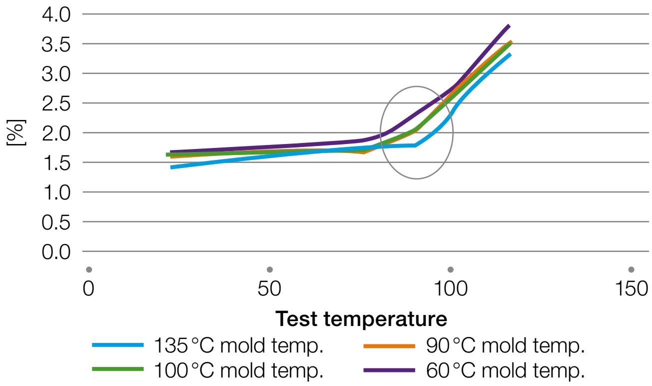
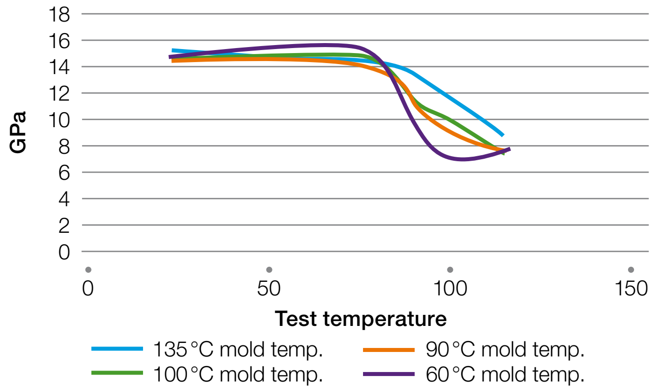


Figure 9: Tensile modulus tested at temperature, note the difference in hot and cold molded values at 100 °C



Discussion

The observations of tensile strength, elongation and modulus when tested at temperature provided insight into the failure mode of the thermostat housing. Although parts are designed to withstand loads beyond those expected in service, the basic premise is that parts will be properly molded and have the mechanical properties commensurate with those reported. In this case study, the lack of crystallinity in the molded thermostat housing was the root cause of the part failure. The lack of following proper molding procedures caused the parts to be less crystalline, therefore reducing critical mechanical strength properties when the part was at elevated temperatures in its end use environment.

This investigation also revealed another problem in evaluating the failed parts. Testing the parts by the normal method of DSC, the failed parts appeared to be crystalline. As was evident in the analysis of the experimental data, PPS will crystallize in the service temperature range of the thermostat housing. It was only after testing parts from the same production batch that had not been in service, that we were able to determine the parts were not properly molded. Once this observation was made, we were able to develop experimental methods to test molded parts and test specimens, to determine the effect this would have on the finished part. This led to the discovery that even though there was little if any difference in mechanical properties at room temperature, there was a considerably greater loss of mechanical properties at elevated temperatures when the parts were not fully crystalline. This differential in mechanical strength, of 30 to 40 percent at elevated temperatures, was enough to cause premature part failure.

Conclusions

The use of properly heated molds when molding parts from PPS is extremely important to the ultimate performance and durability of the part. Hot molded parts achieve enough crystallinity to withstand most end use temperatures. Hot molding also eliminates most shrinkage due to additional crystallization of the part while in service. As was determined by this investigation, hot molding is required to achieve the best mechanical properties when the part will be exposed to stress at temperatures above the glass transition temperature. Always check your mold temperature and be sure it falls within the recommended range provided by the material supplier.

References

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