Polyamide 66's (PA66) unique set of properties, most notably the ability to maintain its integrity in high heat, has made it a critical material in a variety of applications. Use of PA66 has grown three to four percent annually for the past decade; that growth is projected to continue.

Because of that increase and other market factors, supply of PA66 tightened in 2017 and 2018. One major reason for this tightening was the availability of adiponitrile (ADN), a key precursor of PA66. Ascend Performance Materials is addressing the situation by investing in ADN and PA66 polymerization capacity expansions.

As the world's largest fully integrated producer of PA66 resin, Ascend invests in capacity throughout the production chain for PA66. In 2017 and 2018, Ascend expanded production of ADN, hexamethylene diamine, PA66 resin and compounds. By 2022, Ascend will increase production to support an additional 100 kilotons of PA66. When complete, these expansions will represent the largest investment in PA66 capacity since the 1960s.

Ascend’s increased efforts are designed to keep pace with market growth and ultimately relieve the supply tightness of PA66 within two years. In spite of this, some processors and manufacturers are concerned about the near-term availability and cost of PA66 for their applications, leading some to search for substitutes to a polymer ideally suited for their applications.

Material selection is predicated on performance, processability and value. Finding alternative materials is a resource-intensive process that requires a thorough review across performance and processing characteristics. The challenge is to find a material that performs well over time, can be molded efficiently and consistently, and offers value beyond the cost per kilogram.

This paper will illustrate PA66's superior performance, processability and value relative to next-best materials. None of these alternatives, however, can match the unique mix of properties that makes PA66 the ideal material for applications in many industries.
The next-best materials

No single alternative exists to cover the variety of current PA66 applications, but a handful of engineered plastics have been suggested. The most commonly cited alternatives are polyamide 6 (PA6), polybutylene terephthalate (PBT) and polyoxymethylene (POM).

Comparing these alternatives to PA66 seems straightforward: melting temperature versus melting temperature or flammability versus flammability. Figure 1 illustrates that, when compared individually, these properties, with the exception of thermal performance, seem similar and may approximate the performance of PA66 in any given application.

Some in the industry even suggest designing around the substitute material’s shortcomings, as though that would be a trivial exercise. Take high-heat automotive applications, for example. PA66 has become a material of choice because as automakers create more efficient vehicles, the thermal load under the hood has increased dramatically. Able to withstand instantaneous and prolonged exposure to elevated temperatures, 30 percent glass-filled PA66 is used to create charge air coolers, ducts and cylinder head covers – all parts that need to operate in extreme conditions. Notably, PA66 performs reliably during the life of the vehicle.

The next-best materials in these applications are PA6 and PBT, which have a nearly 50°C heat-deflection temperature deficit compared to PA66. Switching to either of these materials would require automakers to design entirely new systems to reduce the heat under the hood.

“Some suppliers of thermoplastics are seeing an opportunity to move into applications specifically designed for PA66 with alternatives,” said Steve Manning, Ascend’s senior director of nylon product technology. “Unfortunately, they’re presenting some of these alternatives as drop-in replacements, and that is simply not the case.”

Part performance seldom relies on a single property. Cable tie molders, for example, are concerned not only with the impact resistance or weathering of the finished cable tie but also with how well the raw material behaves during molding and how quickly they can produce cable ties without defect. Replacing one material with another based on a single property is often not advisable.

So how does PA66’s unique mix of properties make it the preferred material for so many diverse applications?
How polyamide 66 performs against next-best resins

A unique mix of properties

Chosen primarily for its ability to maintain integrity after short-term and prolonged exposure to elevated temperatures and stress, PA66 has become the preferred material in demanding applications. Its strength, density, heat and chemical resistance, electrical properties and processability combine to make it the most appropriate material across applications as diverse as cable ties and electrical connectors.

This diversity results from the unique mix of properties that PA66 offers. PA66 offers the best balance of performance and overall system cost. Below are some of the applications where PA66 is ideally suited and why an alternative material would likely fail to meet the same performance requirements.

Automotive: Lighter, stronger and more reliable

Consumer expectations around performance and comfort coupled with regulations requiring greater fuel efficiency have automakers turning to solutions such as turbocharged internal combustion engines, hybrid drivetrains and vehicle lightweighting. Each of these solutions depend on materials that can reliably withstand the demanding conditions found throughout vehicles. Nowhere is this clearer than under the hood of turbocharged automobiles.

In order to make fuel efficiency gains without sacrificing performance, many automakers are downsizing engines and adding turbochargers. The consequence is higher operating temperatures under the hood. Metal manages the increased thermal load, but its heavy weight is a drag on fuel efficiency.

PA66 has become automakers’ material of choice because of how well it handles high temperatures and mechanical stresses while also reducing weight. PA66 has a higher specific strength than any of the next-best materials. Choosing 30 percent glass-filled PA6, for example, would require approximately 21 percent more material to match the strength requirements of PA66 at 60°C, a mild temperature under the hood of a vehicle. PBT and POM fair worse than PA6, requiring 56 and 59 percent more material respectively. The increase in material to meet the same strength performance would negate much of the weight savings sought by using a thermoplastic.

Matching PA66’s strength performance with any of the next-best materials would require more of that material and therefore reduce any possible weight savings.

Even if one is willing to forgo some of the weight savings, parts made with the next-best alternatives are often less reliable than those made with PA66. Looking at creep and fatigue performance, it becomes clear that PA66 handles constant and cyclical stresses better than the other materials, providing more reliable performance over the life of a vehicle.

PA66 exhibits better creep performance than PA6 or PBT at 120°C, a temperature well within all three materials’ heat-deflection temperature. Creep is a long-term measure of deformations of a material under constant load. Under a load of 40 MPa, PBT has a creep modulus of approximately 1,900 MPa after 10 hours. PA6 reaches that same modulus at little over 100 hours, while PA66 reaches the same modulus after 10,000 hours. This means that parts made with PA66 maintain their shape 100 times longer than PA6 and 1000 times longer than PBT. For applications such as oil pan or cylinder head covers, this higher creep resistance translates into reducing the likelihood of a fluid leak or other critical part failure.
Under persistent load and elevated temperatures, PA66 exhibits significantly better performance than either PA6 or PBT. POM's considerably lower heat-deflection temperature makes it poorly suited for applications at elevated temperatures.

Similarly, PA66 performs better than PA6 or PBT under cyclical stresses, or fatigue. Under alternating stresses of 25 MPa, PA6 fails at around 30,000 cycles. PA66 withstands over 100,000 cycles of the same stresses, providing a part lifespan nearly three times that of a part made with PA6. PBT fails to meet that stress load entirely at 120°C.

For automotive applications, where strength, reliability and light weight are important characteristics, it is easy to see why PA66 has become the material of choice. Parts made with PA66 carry more stress for longer periods without failure than any of the next-best alternatives.

“In the auto industry, polyamide 66 is primarily considered for its thermal properties, but its ability to withstand myriad stresses while reducing overall part weight is critically important as well,” said Vikram Gopal, senior vice president of technology at Ascend. “This is the reason we are seeing more and more application areas in vehicles, not just under the hood.”
E&E: Resistance is crucial

For electrical and electronic applications, PA66’s unique combination of properties give it a distinct advantage. Electrical current produces heat, and the connectors, wires and other infrastructure used to direct the flow of electricity must withstand persistent exposure to elevated temperatures. Furthermore, given the potential hazards should electrical systems fail, how a material behaves during a failure is vitally important.

A number of international standards ensure that materials used in electrical equipment meet critical safety thresholds. A material’s classification within these standards dictates its suitability.

For example, the United States Council for Automotive Research (USCAR) classifies electrical system components based on a material’s ability to withstand ambient temperatures. PBT’s USCAR temperature classification of T2 to T3 means it can withstand ambient temperatures up to 125°C, rendering it suitable only for use in the passenger compartment. PA66’s classification of T5 shows it can withstand ambient operating temperatures of 175°C, making it suitable for any automotive application, including under-the-hood connectors.

Another important standard is UL 94, which rates the flammability of plastic used to make electrical parts inside devices and appliances. PA66 has an inherent UL 94 rating of V2, meaning that in the event of critical failure, the material is less likely to produce a flame. The proposed next-best materials carry a rating of HB, which means they are more flammable. Flame retardant additives may boost the performance of those polymers, but they also will boost the cost.

Finally, dielectric strength measures the voltage a material can withstand before breaking down. As with thermal resistance, PA66 outperforms the next-best materials handily.

As a material for electrical components, PA66 possesses properties conducive to demanding applications. PA66 is inherently more flame retardant, a better insulator at higher voltages and better at withstanding high ambient operating temperatures.

“The energy trends are pointing toward a more electrified future, from high-voltage hybrid and electric vehicles to always-on smart devices,” said Dharm Vahalia, senior director of engineering plastics at Ascend. “PA66’s role in ensuring the safe and reliable transition toward electrification cannot be overstated. None of the next-best alternatives can perform the way PA66 does in electrical applications.”
Processability

Of course, none of these properties matter if a material is difficult to work with. A molder’s ability to make a part is contingent on processing polymer into that part reliably, consistently and economically.

What is often missing from the discussion about raw material costs is how that material behaves during processing.

None of the proposed alternatives to PA66 match its processability. With a low viscosity, higher crystallization rate and faster cooling, PA66 outperforms the next-best materials. That performance translates into faster cycle times, allowing molders to produce parts more quickly at a higher quality.

<table>
<thead>
<tr>
<th>Units</th>
<th>PA66</th>
<th>PA6</th>
<th>PBT</th>
<th>POM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spiral Flow</td>
<td>cm</td>
<td>76.7–101.4</td>
<td>39.1–106.9</td>
<td>17.0–35.0</td>
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<tr>
<td>Crystallization Rate @ T_{\text{max}}</td>
<td>sec^{-1}</td>
<td>1.64</td>
<td>0.14</td>
<td>0.05</td>
</tr>
<tr>
<td>Relative Crystallization Rate vs POM</td>
<td>82x</td>
<td>7x</td>
<td>2.5x</td>
<td>1x</td>
</tr>
</tbody>
</table>

The spiral flow test measures the flow of a molten material under a consistent force of 6.9 MPa through a spiral mold. The farther the material travels, the better that material is likely to perform when filling a part mold.

PA66 outperforms PBT and POM by a factor of three, and performs more consistently than PA6. In processing terms, this means that PA66 can fill a mold faster, more completely and more reliably than any of the alternatives.

Furthermore, PA6 is plagued by other factors in processing. During the production of PA6 from caprolactam, achieving 100 percent conversion is extremely difficult. The residual caprolactam adheres to the mold and causes deformities in the part. Addressing the issue of caprolactam residue reduces cycle time, thereby decreasing production.

Filling a mold quickly and consistently is the first step in reducing cycle times. The next step is crystallization and cooling of the material.

PA66 crystallizes 12 times faster than PA6, nearly 33 times faster than PBT and 82 times faster than POM. Rapid crystallization means that a part hardens faster and can be removed from its mold sooner.

Figures 5 and 6: PA66’s rapid crystallization rate and shorter cooling time mean that more parts can be produced in a given timeframe than any of the next-best alternatives.
Value

As outlined previously, PA66’s performance and processability are unmatched by any of the alternatives. When it comes to finished part performance, PA66 parts perform more reliably over the long term, withstand higher temperatures and have higher strength per kilogram.

Some of these attributes can be approximated by the alternatives. For example, PA66’s strength can be matched using more PA6, PBT or POM (21, 56 and 59 percent more material, respectively) but the raw material cost also increases.

Furthermore, the failure rate of finished parts made with the alternatives may be significantly higher than for parts made with PA66, depending on the application. Replacing failed parts increases the material need over the long term and can negatively impact the manufacturer’s reputation.

Each performance trade-off must be met with an increase in material or other cost. Any processing trade-off increases cycle time and necessitates retooling, thus increasing the cost of the finished part.

Just as isolating a single performance characteristic fails to provide a full picture of PA66’s benefits over the next-best materials, so too does a cost-per-kilogram comparison. Again, replacing PA66 will likely require costly changes and trade-offs, making the alternatives less economical.

Never settle for less

PA66’s superior thermal, strength, electrical and processing properties have made it a sought-after polymer. Its popularity coupled with market forces led to supply constraints in 2017 and 2018. However, with producers investing in capacity expansions for PA66 and key raw materials, those constraints are projected to be relieved in the near future.

Ascend continues to invest in research and development of new grades of PA66 – building on an already indispensable polymer’s capabilities. New higher heat, high flow and flame retardant grades are further increasing PA66’s performance, processability and value.

Of course, the push toward alternatives will persist beyond any capacity expansion. Producers of those alternatives have a financial stake in the success of their material, as do producers of PA66.

But isolating and comparing a single property between two or more materials provides an incomplete evaluation when choosing one material over another. The interplay of properties in PA66’s unique mix is central to its versatile performance, and that is hard to beat.
About Ascend

Ascend Performance Materials is the world’s largest fully integrated producer of nylon 6,6 resin. We manufacture and reliably supply world-class plastics, fibers and chemicals that are used in thousands of everyday applications such as car parts, electronics and cable ties.

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