

Zytel® HTN PPA and Zytel® Nylon 6,6 and Nylon 6 Resins in High Temperature and Automotive Chemical Exposure Environments

John Gavenonis and Joshua E. McIlvaine

DuPont Engineering Polymers

ABSTRACT

As petroleum prices experience record volatility, automotive OEMs are seeking advanced materials that permit the development of more light weight, fuel efficient vehicles. Thermoplastics are a natural solution since they provide the combination of structural properties with lower material density, along with ease of forming geometrically complicated parts with rapid cycles and with minimal finishing operations. However, new automotive applications are becoming increasingly demanding with regard to chemical exposure, environmental exposure, thermal environment, and load bearing requirements. Addressing these challenges requires a thorough understanding of the application in order to identify appropriate thermoplastic resins and to develop novel resin technologies to extend the performance of structural engineering thermoplastics.

Herein, the authors review existing nylon 6,6, nylon 6, and polyphthalamide (PPA) technologies, laying the foundation for new resin innovations that may expand the design windows for engineers utilizing polyamide and PPA structural engineering thermoplastics. In particular, this paper investigates the effects of automotive coolant and engine oil exposure along with mechanical properties at elevated temperatures.

ABOUT THE AUTHORS

John Gavenonis is the Technical Consultant supporting Zytel® and Minlon® nylon resins with the DuPont Engineering Polymers business of E.I. du Pont de Nemours and Company in Wilmington, Delaware. John received an S.B. in Chemistry from the Massachusetts Institute of Technology (MIT) and a Ph.D. in inorganic/organometallic chemistry from University of California, Berkeley. Josh E. McIlvaine is a Senior Technical Specialist for the DuPont Engineering Polymers business of E.I. du Pont de Nemours and Company in Troy, Michigan. Josh received a B.S. in Mechanical Engineering from Virginia Polytechnic Institute and State University. Please direct any correspondence to john.gavenonis@usa.dupont.com. More information about DuPont Engineering Polymers can be found at <http://plastics.dupont.com>.



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INTRODUCTION

Poly(hexamethylene adipamide) (nylon 6,6) was invented by Wallace Hume Carothers at the DuPont Experimental Station in the 1930s.¹ The polymer is prepared by the condensation reaction of hexamethylenediamine and adipic acid. DuPont chose the trade name “Nylon” for this material and debuted it at the 1939 New York World’s Fair.² Since then, nylon has become the term to describe a class of polyamides prepared using a variety of reactions and monomers. Poly-(ϵ -caproamide) (nylon 6) was discovered by Paul Schlack of Aceta, an I.G. Farbenindustrie company, in 1938.³⁻⁵ This polymer, in contrast to nylon 6,6, is prepared by the ring-opening polymerization of ϵ -caprolactam. Polyphthalamide (PPA) polymers were invented more than 50 years ago⁶ and are prepared by the reaction of aromatic diacids with aliphatic diamines.^{7, 8} At least 55 molar percent of the carboxylic acid portion of the polyamide chain must contain terephthalic acid, isophthalic acid, or a combination of both for a polyamide to be classified as PPA.^{9, 10}

Initial polyamide automotive applications, including windshield wiper systems, wiring clips, bearings, and bushings, were exposed to relatively mild operating conditions.¹¹ However, formulation innovations resulting in glass-reinforced composite systems with antioxidant heat stabilizers permitted the use of nylon resins in the higher temperature, chemically-aggressive environments found in under-the-hood applications.¹² The inclusion of glass as a resin modifier resulted in parts featuring high mechanical strength and excellent dimensional stability, along with the light weight and molding ease characteristic of nylon materials. Radiator end-tanks in particular, are examples of high volume under-the-hood applications that require these properties and face demanding operating conditions. The purpose of the automobile radiator is to dissipate engine heat to the surrounding air via coolant, which is typically comprised of equal parts water and ethylene glycol along with much smaller concentrations of proprietary additives.^{13, 14} A typical radiator end-tank will be exposed to coolant temperatures of 90 – 130 °C, but can experience temperature extremes greater than 150 °C. Consequently, a nylon radiator end-tank is exposed to conditions that can promote polyamide hydrolysis.¹⁵⁻¹⁷ Even in the absence of aggressive hydrolysis conditions, nylon parts can be degraded via oxidation at elevated temperatures^{2, 18, 19} and in the presence of automotive lubricants.²⁰

In this report, we describe the mechanical property changes observed after aging nylon 6,6, nylon 6, and PPA test bars at elevated temperatures in the presence of commercial automotive radiator coolants and engine oils. These same materials are also examined for

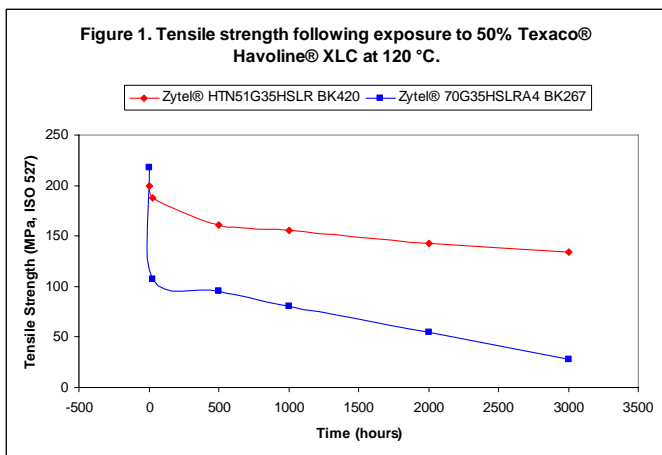
changes in mechanical properties at different measurement temperatures. The tensile strength, tensile modulus, and unnotched Charpy impact strength data obtained provide a useful guide for material selection for parts in high temperature, chemically-aggressive, under-the-hood environments.

RESULTS AND DISCUSSION

AGING WITH 50% AQUEOUS COOLANT – Test bars molded from several commercial nylon 6,6, nylon 6, and PPA resins were aged via immersion in commercial radiator coolants. Immersion testing is not a true reflection of the environment experienced by nylon and PPA resins used in radiator end-tanks. In the end-use application, only one side of a radiator end-tank wall is exposed to automotive coolant. However, immersion testing provides a reasonable approximation of the end-use application and is much simpler to implement than a single-side exposure, especially at elevated temperatures. Table 1 lists the PPA, nylon 6,6, and nylon 6 resins evaluated along with a description of each material.

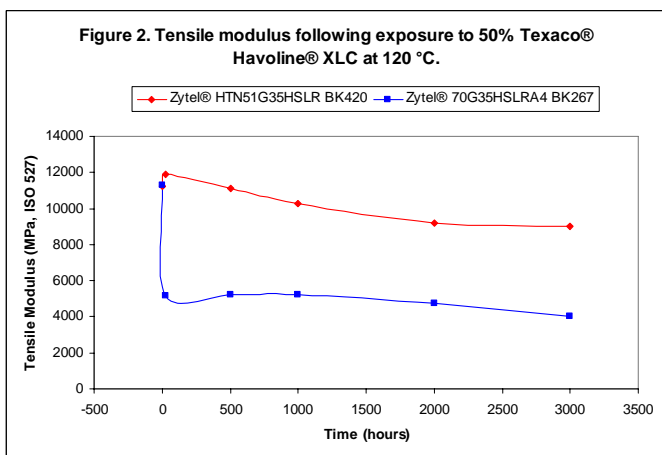
Zytel® Resin	Description
HTN51G35HSLR BK420	35% glass PPA, heat stabilized, hydrolysis resistant
70G35HSLRA4 BK267	35% glass PA66, heat stabilized, hydrolysis resistant
FE5105 BK083	33% glass PA66, heat stabilized, hydrolysis resistant
70G30HSLR BK099	30% glass PA66, heat stabilized, hydrolysis resistant
73G30HSL BK416	30% glass PA6, heat stabilized

Figure 1 shows the tensile strength properties for Zytel® HTN51G35HSLR BK420 and Zytel® 70G35HSLRA4 BK267 measured according to ISO 527 following 0, 24, 500, 1000, 2000, and 3000 h of exposure to 50% aqueous Texaco® Havoline® XLC at 120 °C.



Both materials feature a loss of tensile strength after 24 h, but the loss is much more significant for the nylon 6,6 bars. While the PPA bars lose only 6% of their tensile strength, the nylon 6,6 bars lose 51%. This is likely due to the ease at which nylon 6,6 is plasticized by aqueous coolant solution. The loss of properties continues over time for both materials, but at a faster rate for nylon 6,6 as compared to PPA. Ultimately, after 3000 h of exposure, the nylon 6,6 bars have retained only 13% of their tensile strength in contrast to 67% retention for the PPA bars. The superior tensile strength retention for PPA is due to slower hydrolysis kinetics associated with aromatic, as compared to aliphatic, polyamides in aqueous coolant.

Similar results were observed for tensile modulus measurements of Zytel® HTN51G35HSLR BK420 and Zytel® 70G35HSLRA4 BK267 test bars exposed to 50% aqueous Texaco® Havoline® XLC under the same conditions (Figure 2).



Much like for tensile strength, the nylon 6,6 test bars show an initial loss of 54% of tensile modulus after 24 h of exposure, which is likely due to plasticization by the aqueous coolant. The PPA test bars, in contrast, feature

almost no change after 24 h of exposure. In addition, whereas the nylon 6,6 test bars ultimately retain only 36% of their initial tensile modulus after 3000 h of coolant exposure, the PPA test bars retain 80% of their tensile modulus. The high tensile strength and tensile modulus retention in the presence of automotive coolant at elevated temperatures has led to the adoption of PPA resins for automotive thermostat housings (Figure 3).



Figure 3. The housing of the map-controlled thermostat by Behr Thermot-tronik, which is installed in BMW's N43 series four-cylinder petrol motors, is exposed to very high mechanical, thermal, and chemical stresses. Automotive coolant flows through the interior of the thermostat housing at temperatures up to 140 °C. The combination of high temperature coolant resistance, creep performance, and resistance to typical motor-compartment media (such as oils, greases, fuel, and road salts) contributed to the selection of Zytel® HTN51G35HSLR for this engine-mounted component.

In order to provide a direct comparison of how nylon 6 materials compare to nylon 6,6 and PPA, data from separate coolant exposure studies were added to the data described in Figures 1 and 2. Figure 4 provides a direct comparison of tensile strength retention for PPA (Zytel® HTN51G35HSLR BK420), nylon 6,6 (Zytel® 70G35HSLRA4 BK267 and Zytel® 70G30HSLR BK099), and nylon 6 (Zytel® 73G30HSL BK416) test bars. Figure 5 provides a comparison of tensile modulus for PPA, nylon 6,6 (Zytel® 70G35HSLRA4 BK267 only), and nylon 6 test bars. Note that the time scales of Figures 4 and 5 are 2000 h and 1200 h, respectively (instead of 3500 h), to highlight the differences observed for the resins that were part of shorter coolant exposure studies. Test bars of the added materials, Zytel® 70G30HSLR BK099 and Zytel® 73G30HSL BK416, were exposed to different 50% aqueous long-life coolant solutions (consistent with the Chrysler MS-7170 specification) than the test bars of Zytel® HTN51G35HSLR BK420 and Zytel® 70G35HSLRA4 BK267. However, the same exposure temperature (120

°C) was used. Tensile strength and modulus were measured according to ISO 527.

and modulus in automotive coolant exposure environments is PPA > nylon 6,6 > nylon 6.¹⁰

AGING WITH 100% COOLANT – The loss of tensile properties observed during aging with 50% aqueous coolant is due to polyamide hydrolysis.¹⁵⁻¹⁷ A more thorough understanding of the hydrolysis mechanism is achieved by comparing the loss of mechanical properties observed for test bars in 50% aqueous coolant and 100% coolant. Figures 6 and 7 show tensile strength measurements for test bars molded from PPA (Zytel® HTN51G35HSLR BK420) and nylon 6,6 (Zytel® FE5105 BK083) following exposure to 50% aqueous Prestone® DEX-COOL® LLC at 130 °C. While these resins contain different glass loadings (35% and 33%, respectively), the difference in mechanical properties for 33% and 35% nylon 6,6 is small enough (*vide supra*, Figure 4) such that meaningful comparisons can still be drawn about the polymers used.

Figure 6 reveals a loss in properties similar to that observed in Figures 1 and 4. In this particular case, over the course of 2000 h, PPA has 34% tensile strength retention and nylon 6,6 has 9% retention. The 34% tensile strength retention observed for PPA after 2000 h is approximately half the value observed in Figure 1 for the same PPA resin. The difference in tensile strength retention observed between Figures 1 and 6 is likely due to the higher temperature of the latter study (130 °C) and possible formulation differences between the coolants used in each experiment (Texaco® Havoline® XLC and Prestone® DEX-COOL® LLC, respectively).

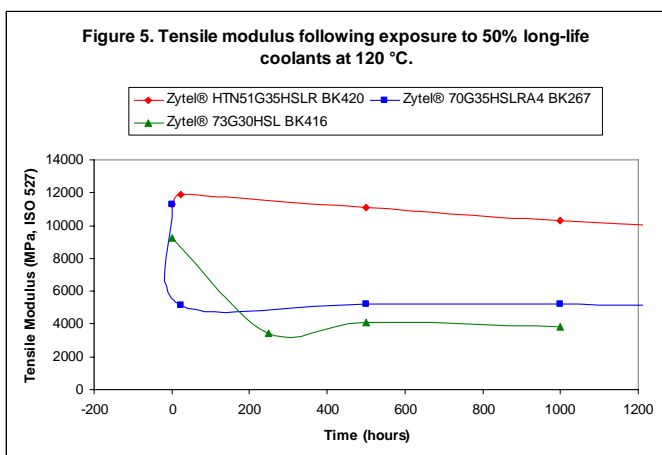
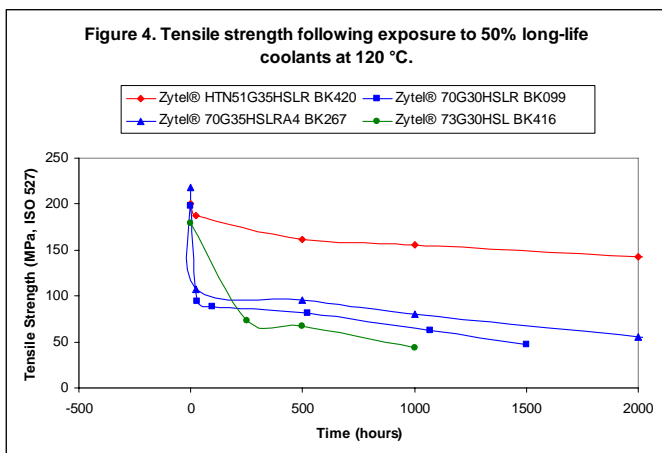


Figure 4 reveals several expected trends. The 30% glass nylon 6,6 material was found to have slightly lower tensile strength than the 35% glass nylon 6,6 material throughout the study. For example, the 30% glass nylon 6,6 material has 32% tensile strength retention after 1070 h exposure, which is slightly less than the 37% tensile strength retention observed for the 35% glass nylon 6,6 material after 1000 h exposure. In contrast, the nylon 6 resin has 25% tensile strength retention after 1000 h. All of these values are much lower than the 78% tensile strength retention observed for the PPA material following 1000 h coolant exposure.

Figure 5 shows the same trend for tensile modulus retention as was observed in Figure 4 for tensile strength retention. After 1000 h coolant exposure at 120 °C, the PPA material was found to retain 91% of its tensile modulus, the nylon 6,6 material retains 46%, and the nylon 6 material retains 41%. Collectively, the results described here indicate that the preferred choice of materials for maximum retention of tensile strength

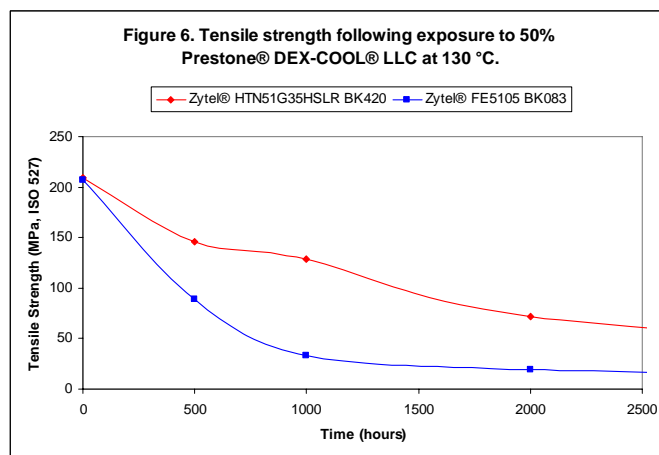
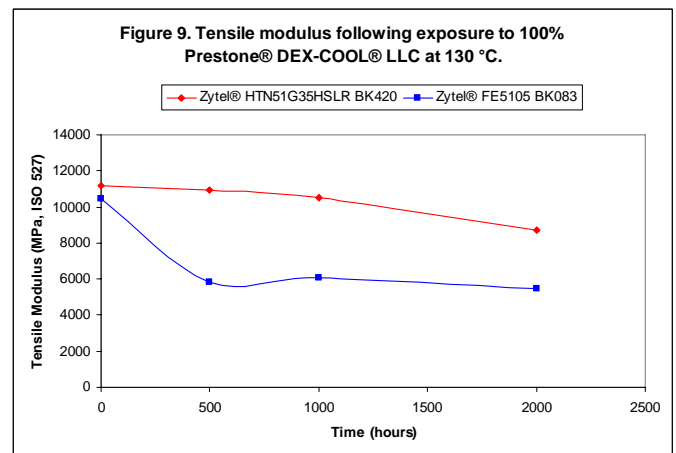
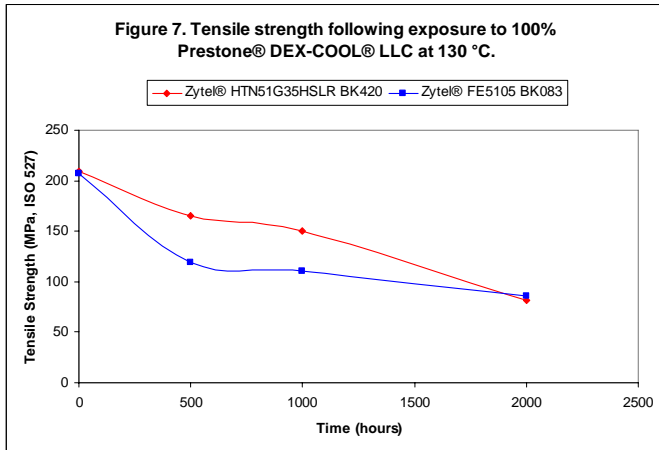
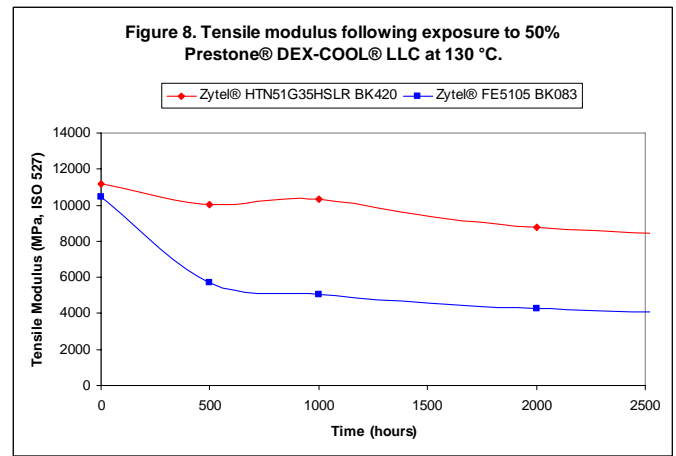


Figure 7 shows the tensile strength properties of the same two resins examined in the study described in Figure 6 and exposed at the same temperature, but instead with 100% Prestone® DEX-COOL® LLC. In this case, both the PPA and nylon 6,6 resins have approximately 40% tensile strength retention after 2000 h exposure at 130 °C. This is in contrast to 34% tensile strength retention for PPA and 9% retention for nylon 6,6

following 2000 h exposure to 50% aqueous Prestone® DEX-COOL® LLC at 130 °C (Figure 6). The greater tensile strength retention observed for the 100% coolant example is likely due to the minimal water present in the coolant solution. While the strongly hydrogen bonding 100% Prestone® DEX-COOL® LLC will absorb some moisture from the atmosphere, the water content is significantly lower than the amount in a 50% aqueous solution. Lower water concentrations result in less polymer hydrolysis, leading to greater tensile strength retention. In particular, nylon 6,6 has better tensile strength retention improvement in moving from 50% aqueous coolant to 100% coolant since this aliphatic polyamide is more susceptible to hydrolysis than PPA.



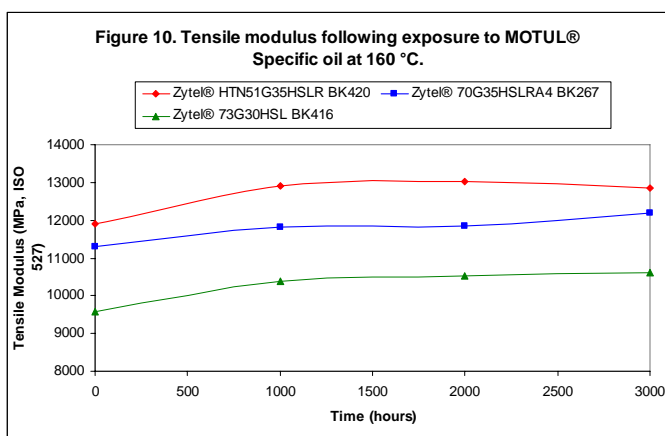
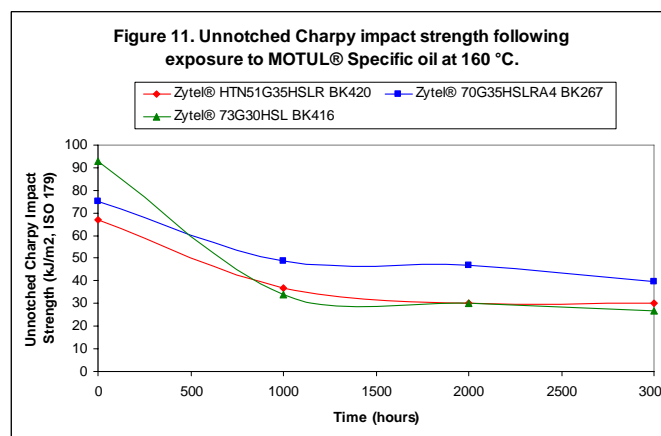
A similar pattern is observed for tensile modulus measurements recorded for PPA and nylon 6,6 (Zytel® HTN51G35HSLR BK420 and Zytel® FE5105 BK083, respectively) following exposure to 50% aqueous Prestone® DEX-COOL® LLC (Figure 8) and 100% Prestone® DEX-COOL® LLC (Figure 9). In Figure 8, exposure to 50% aqueous coolant for 2000 h gives 79% tensile modulus retention for the PPA test bars and 41% retention for the nylon 6,6 test bars. Recall that the data reported for Texaco® Havoline® XLC exposure (Figure 2) indicate 82% tensile modulus retention for PPA and 42% tensile modulus retention for the 35% glass nylon 6,6 resin. When exposed to 100% Prestone® DEX-COOL® LLC (Figure 9), PPA was found to have 78% tensile modulus retention and nylon 6,6 was found to have 52% retention. Much like tensile strength retention, tensile modulus retention does not vary much for PPA when the coolant is changed from 50% aqueous coolant to 100% coolant. However, tensile modulus retention for nylon 6,6 is significantly improved by aging in 100% coolant instead of the 50% aqueous coolant solution. This is likely due to the greater reactivity of water with nylon 6,6 than with PPA polymers.²¹

AGING WITH ENGINE OIL – Test bars molded from several commercial nylon 6,6, nylon 6, and PPA resins were aged via immersion in MOTUL® Specific 506.01-506.00-503.00 0W30 100% Synthetic engine oil at 160 °C. Similar to automotive coolant exposure testing, immersion testing is not a true reflection of the environment experienced by nylon and PPA resins used in under-the-hood oil exposure applications. However, immersion testing provides a reasonable approximation of the end-use application and is much simpler to implement than a single-side exposure, especially at elevated temperatures. One concern, though, is that immersion testing attenuates the effects of oxidation on the polymer, which is an important consideration since many end-use applications are exposed to a combination of environmental factors. The 160 °C test temperature is essentially an upper-limit temperature that may be encountered in demanding, under-the-hood automotive applications exposed to synthetic engine oil. Table 2 lists the PPA, nylon 6,6, and nylon 6 resins evaluated along with a description of each material.

Zytel® Resin	Description
HTN51G35HSLR BK420	35% glass PPA, heat stabilized, hydrolysis resistant
70G35HSLRA4 BK267	35% glass PA66, heat stabilized, hydrolysis resistant
73G30HSL BK416	30% glass PA6, heat stabilized

observed at 0 h. In a typical non-immersion environment, nylon 6 will absorb atmospheric moisture leading to plasticization and the increase in toughness that accompanies such conditioning. However, in the hot oil immersion environment, nylon 6 is unable to absorb moisture, which prevents plasticization / toughening. The net result is that after long term exposure (3000 h), the unnotched Charpy impact strength of Zytel® 73G30HSL BK416 is lower than Zytel® 70G35HSLRA4 BK267 and comparable to, though with overall lower retention than, Zytel® HTN51G35HSLR BK420 (45% retention for Zytel® HTN51G35HSLR BK420; 29% retention for Zytel® 73G30HSL BK416). This reinforces the importance of understanding both the temperature and chemical environment of an end-use application when selecting an engineering thermoplastic resin. The combination of properties observed for nylon 6,6 during hot engine oil aging makes it an attractive material for the new Mercedes-Benz C class oil pan (Figure 12).

Figure 10 shows the tensile modulus properties for Zytel® HTN51G35HSLR BK420, Zytel® 70G35HSLRA4 BK267, and Zytel® 73G30HSL BK416 test bars measured at room temperature according to ISO 527 following 0, 1000, 2000, and 3000 hours of exposure to MOTUL® Specific 506.01-506.00-503.00 0W30 100% Synthetic engine oil at 160 °C. Tensile modulus remains relatively stable for all three glass-reinforced resins. The slight increase in modulus over the course of 3000 h (8% for Zytel® HTN51G35HSLR BK420, 8% for Zytel® 70G35HSLRA4 BK267, and 11% for Zytel® 73G30HSL BK416) may be attributed to several factors. First, the high temperature and lack of moisture prevents polymer hydrolysis. Any moisture present in the test bars at 0 h is likely lost at elevated temperature, causing a slight modulus increase. Furthermore, extended time at elevated temperature could cause post mold crystallization or annealing in the test bars. The increased crystallinity would result in a higher tensile modulus.



Analyzing the changes in unnotched Charpy impact strength following exposure to hot oil (Figure 11) reveals trends similar to those observed for tensile modulus, along with some ductility loss due to thermal and chemical degradation. The relative change in impact performance as a function of time is particularly noteworthy. Specifically, nylon 6 is generally the toughest base polymer in the test group, which is



Figure 12. For the first time in automotive history, an oil pan module made from a thermoplastic polymer is now used for commercial production vehicles. The combination of modulus as a function of temperature, impact resistance, and relative compatibility with hot engine oil contributed to the selection of Zytel® 70G35HSLR for the oil pan module of the 4-cylinder diesel engines of Mercedes-Benz C Class vehicles.

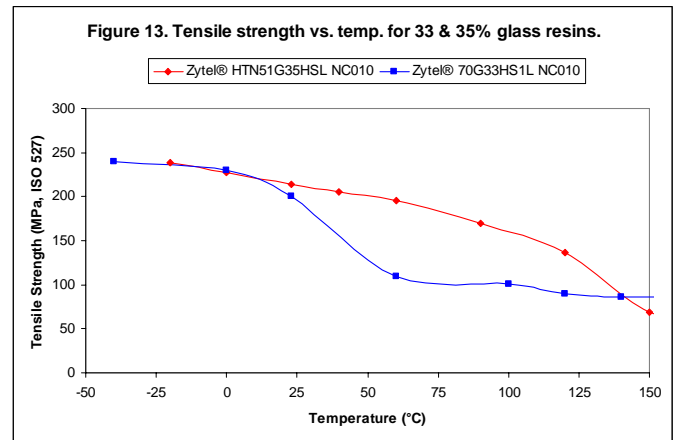
MECHANICAL PROPERTIES VS. TEMPERATURE –

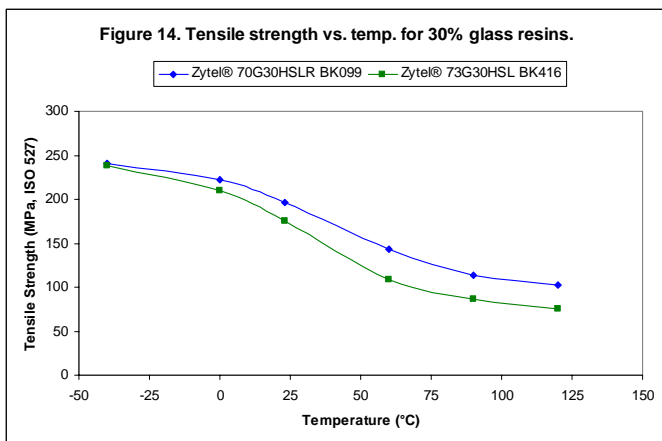
While coolant and engine oil aging studies provide insight into how the mechanical properties of a particular resin will change with temperature, time, and automotive fluid exposure, they do not provide insight as to how the resin will perform at a specific operating temperature. In order to gain a better comparative understanding of how the mechanical properties of nylon 6,6, nylon 6, and PPA resins change with temperature, tensile strength and modulus were measured over the range of -40 °C to 220 °C for test bars molded from 35% and 30% glass-reinforced resins (Table 3).

Table 3. Materials used to evaluate mechanical properties as a function of temperature.	
Zytel® Resin	Description
HTN51G35HSL NC010	35% glass PPA, heat stabilized
70G33HS1L NC010	33% glass PA66, heat stabilized
70G35HSLX NC010	35% glass PA66, heat stabilized

70G30HSLR BK099	30% glass PA66, heat stabilized, hydrolysis resistant
73G30HSL BK416	30% glass PA6, heat stabilized
73G35HSL BK262	35% glass PA6, heat stabilized

Figure 13 shows the change in tensile strength as a function of temperature for test bars molded from PPA (Zytel® HTN51G35HSL NC010) and nylon 6,6 (Zytel® 70G33HS1L NC010). The PPA resin contains 35% glass and the nylon 6,6 resin contains 33% glass. Nonetheless, the glass concentration is sufficiently close to allow a reasonable comparison of properties vs. temperature. Figure 14 shows the change in tensile strength as a function of temperature for test bars molded from nylon 6,6 (Zytel® 70G30HSLR BK099) and nylon 6 (Zytel® 73G30HSL BK416) reinforced with 30% glass. In both cases, while the measured tensile strengths tend to converge at lower temperatures, especially below room temperature, the tensile strength values tend to be separated by larger ranges at the intermediate temperature range of approximately 25 °C to 125 °C. In particular, for the resins with 35% and 33% glass reinforcement (Figure 13), PPA maintains 60% of its 0 °C tensile strength at 120 °C, while nylon 6,6 retains 39%. Similar tensile strength retention is observed for the resins with 30% glass reinforcement (Figure 14). The nylon 6,6 resin retains 42% of its -40 °C tensile strength at 120 °C whereas the nylon 6 resin retains 32%. Comparing both sets of data (Figures 13 and 14) reveals that PPA > nylon 6,6 > nylon 6 for tensile strength retention over the range of -40 °C to 120 °C.





data illustrate that PPA > nylon 6,6 > nylon 6 for tensile modulus over the temperature range evaluated.

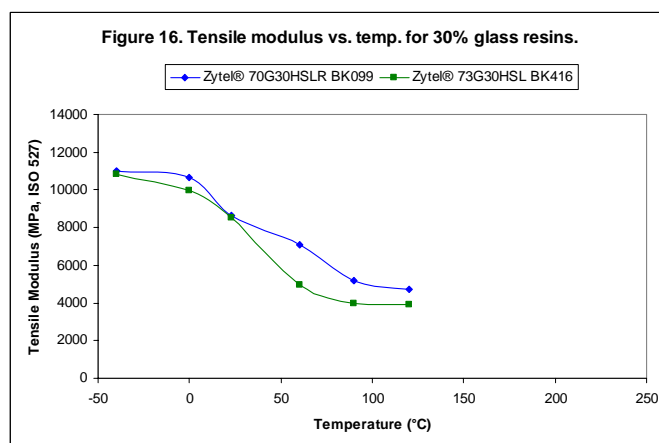
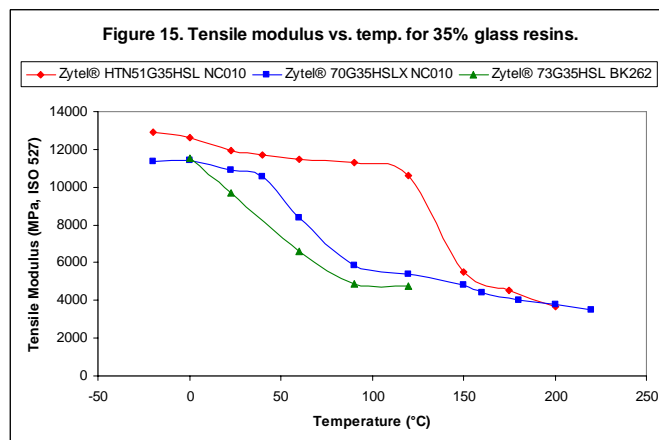


Figure 15 shows the change in tensile modulus as a function of temperature for test bars molded from PPA (Zytel® HTN51G35HSL NC010), nylon 6,6 (Zytel® 70G35HSLX NC010), and nylon 6 (Zytel® 73G35HSL BK262) reinforced with 35% glass. Figure 16 shows the change in tensile modulus over the same temperature range for test bars molded from nylon 6,6 (Zytel® 70G30HSLR BK099) and nylon 6 (Zytel® 73G30HSL BK416) reinforced with 30% glass. Examination of Figures 15 and 16 reveals that tensile modulus values for the three polymer types tend to be separated by the greatest margin at 60, 90, and 120 °C, which is likely due to the different T_g values for PPA, nylon 6,6, and nylon 6. Generally, the values tend to be closest at temperatures below 23 °C and above 120 °C. As is observed for the tensile strength data (Figures 13 and 14), the test bars molded from PPA have the greatest tensile modulus retention (84%) over the temperature range of 0 °C to 120 °C. The 35% glass-reinforced nylon 6,6 and nylon 6 resins have 47% and 41% retention, respectively, over the same temperature range. While the tensile modulus percent retention values for the 35% glass-reinforced nylon 6,6 and nylon 6 resins are relatively close to the tensile strength percent retention values for related resins (nylon 6,6 = 39%, *vide supra*), the PPA shows a much greater difference in percent retention from tensile strength to tensile modulus. While PPA has 60% tensile strength retention over the 0 °C to 120 °C temperature range (*vide supra*), the material has 84% tensile modulus retention over the same temperature range. Regardless, this demonstrates excellent property maintenance that clearly illustrates the benefit of this material relative to nylon 6,6 and nylon 6 for applications that experience a variety of temperatures. The tensile modulus property retentions observed for the 30% glass-reinforced nylon 6,6 and nylon 6 resins over the -40 °C to 120 °C temperature range (43% and 36%, respectively) are similar to those observed for tensile strength (42% and 32%, respectively). Collectively, the

CONCLUDING REMARKS

Automotive under-the-hood applications increasingly require thermoplastic materials capable of withstanding elevated temperatures and aggressive chemical environments. Nylon 6,6, nylon 6, and PPA resins modified for a variety of exposure conditions have been used for a number of under-the-hood applications with varying degrees of success. Evaluation of tensile strength and tensile modulus retention of nylon 6,6, nylon 6, and PPA test bars after aging with 50% aqueous coolant solutions at 120 °C reveals the trend PPA > nylon 6,6 > nylon 6, which is consistent with the kinetics of polyamide hydrolysis.¹⁵⁻¹⁷ Furthermore, a separate study comparing tensile strength and tensile modulus retention in 50% aqueous coolant and 100% coolant reveals that 50% aqueous coolant causes more rapid loss of mechanical properties for nylon 6,6 as compared to PPA. This confirms that the loss of mechanical properties, especially for nylon 6,6, is due to hydrolysis from water present in the automotive coolant.

Exposure of nylon 6,6, nylon 6, and PPA test bars to synthetic engine oil at 160 °C reveals a marginal increase in tensile modulus over the course of 3000 h. This is attributed to post mold crystallization, or annealing, at the aging temperature. In contrast, test bars for all three resins show a loss of unnotched Charpy impact strength under the same conditions. The absence of moisture in the hot engine oil environment prevents the plasticization that increases toughness, especially for nylon 6, leading to the loss of impact strength observed.

Evaluation of tensile strength and tensile modulus changes over the temperature range -40 °C to 220 °C reveals property retention following the trend PPA > nylon 6,6 > nylon 6. Collectively, the automotive coolant and engine oil exposure results, along with the mechanical property changes reported as a function of temperature, suggest that PPA is the preferred material for automotive applications that are simulated by these tests. Of course, material selection ultimately must be balanced with the process economics of part manufacture and the cost structure of each resin class.

EXPERIMENTAL PROCEDURES

GENERAL CONSIDERATIONS – Test bars of each commercial resin were injection molded according to ISO 294 following the recommended processing conditions. Tensile properties were measured according to ISO 527 using an Instron® Model 1125 Electromechanical Test System or an Instru-Met Corporation Model TTK-102/30 Multi-Head Tensile Tester. Unnotched Charpy impact strengths were measured according to ISO 179 using a CEAST® Resil Impactor Model Number 6956.000. Test bars for coolant exposure studies were immersed in 50% aqueous automotive coolant or 100% automotive coolant in a Parr vessel for the time period indicated. Test bars for oil exposure studies were immersed in engine oil in a test tube that was placed in a temperature controlled bath for the time period indicated. Test bars in the automotive coolant and engine oil aging studies were measured for tensile and impact strength properties at 23 °C. Test bars for the properties vs. temperature studied were analyzed as dry as molded (DAM) at the temperatures indicated. Automotive fluids (Texaco® Havoline® XLC, Prestone® DEX-COOL® LLC, and MOTUL® Specific 506.01-506.00-503.00 0W30 100% Synthetic) were purchased from retail sources.

ACKNOWLEDGMENTS

The authors acknowledge the laboratory staff of the DuPont Engineering Polymers Applications Technical Center in Wilmington, Delaware and the European Technical Center in Meyrin, Switzerland for molding test

bars and acquiring the experimental data reported. The authors thank Kimberly Lewis for organizing and coordinating the automotive coolant and properties vs. temperature testing, thank Norbert Adjadj for coordinating the engine oil testing, and thank Gary Kozielski, Edmund Flexman, and Rob Palmer for insightful discussions.

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