Zeotherm® TPVs for Automotive Boots, Bellows, and Air Duct Applications

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Abstract

Thermoplastic vulcanizates (TPVs) and copolyesters have found broad use in automotive boots, bellows, and air ducts. However, the limited long-term heat resistance of conventional TPVs, those based on EPDM rubber//polypropylene or copolyester, has limited their use in parts requiring sustained exposure to temperatures above 135°C and has forced the use of high-cost alternative materials (e.g., thermoset rubber, heat shields).

This paper presents a class of high-performance TPVs – Zeotherm® -- based on a continuous phase polyamide (PA) thermoplastic matrix and dynamically vulcanized polyacrylate (ACM) elastomer (ACM//PA). Recent advancements in blow molding and functional testing of Zeotherm TPVs for automotive boot and air duct applications will be shown. Additionally, a comparison will be made of Zeotherm TPVs versus conventional materials on the basis of elevated temperature and grease resistance.

Introduction

Automotive boots, bellows, and air ducts have largely been converted from thermoset rubber to TPVs and copolyesters over the past twenty years. This conversion can largely be attributed to the favorable economics of blow molding that TPVs/copolyester allow and improved part performance/life versus rubber.

TPVs based on EPDM and polypropylene (EPDM//PP) have become the industry standard for steering system rack-and-pinion boots and 3D blow molded air ducts. Copolyesters have largely replaced rubber for constant-velocity joint (CVJ) boots.

The dominance of EPDM//PP and copolyester, however, is threatened by new design changes and environmental regulations to automobiles and heavy trucks (e.g., turbo-diesel engines; more aerodynamic hood/grill designs; 2007 diesel engine emission regulations[1]) that exceed the limits of EPDM//PP and copolyester. Sustained ("continuous") underhood automotive temperatures are creeping above 135°C and more aggressive (e.g., low-friction) greases are being utilized.

Conventional Toolbox

The engineer's toolbox to address underhood heat excursions in excess of 135°C has often relied on: (1) installation of a metal heat shield; (2) switching the part to thermoset rubber; (3) utilizing nylon; and (4) changing the copolyester to a more heat resistant grade. Unfortunately, each of these options imparts cost or part functionality limitations.

Metal heat shields introduce concerns of noise transmission (rattling) and cost. While the cost of the heat shield may be low, on an installed basis it is often a considerable expense as it adds an additional step, and often headcount, to the vehicle assembly operation. At best, a heat shield can be considered a "band-aid" (Photo 1).

Thermoset rubber parts can be designed to survive high-temperature and aggressive fluids. The downsides of using thermoset rubber are long cycle times and the inability to take advantage of cost-effective blow molding processes. This often equates to higher part cost.

In air ducts, nylon is increasingly being used in place of polypropylene to meet 150°C temperature requirements. However, in using nylon, EPDM//PP TPVs cannot be used for co-ex blow molding or be welded to the nylon ducts due to the adhesion incompatibility of PP to nylon. Additionally, EPDM//PP TPVs melt with prolonged 150°C exposure. Rubber//nylon has been the only viable option to date, albeit with considerable cost associated with manual assembly and metal clamps.

The heat resistance of copolyester, in duct applications, can be improved by utilizing higher durometer (>50 ShD) grades. With these high hardness grades, the heat resistance can be improved to 140°C continuous. There are, however, considerable drawbacks to increased hardness. Namely, loss of flexibility, softness, and sealability expected with a thermoplastic elastomer.

In short, engineers have been left with few favorable options for addressing the increasing underhood temperatures.

High-Performance TPV Solution

Zeotherm® TPVs (ACM//PA) from Zeon Chemicals are designed to expand the boundaries of traditional TPV utilization – short-term ("spike") temperatures to 175°C; resistance to low-friction greases – while retaining the blow moldability of EPDM//PP and copolyester. They were introduced commercially in 2003 [2,3].

ACM//PA TPVs are based on a plastic phase of PA6 combined with vulcanized polyacrylate (ACM) rubber. The nylon phase is responsible for imparting flex resistance, chemical adhesion to rigid nylon[4] (e.g., welding, overmolding, co-extrusion), and heat resistance. ACM is well-known in the automotive arena to impart long-term oil and grease resistance at temperatures to 175°C and is commonly used in transmission and engine sealing parts[5].

As an evolution of the Zeon's ACM//PA TPV product line, new grades have recently been introduced that are optimized for blow molding processes (e.g., extrusion, co-extrusion, and press-blow) commonly used to produce boots, bellows, and air ducts. These new grades have found broad interest among leading OEMs and Tier 1 suppliers as performance upgrades to EPDM//PP and copolyester and as a cost-down versus more expensive thermoset rubber and metal heat shields.

Objective and Criteria

The objective of this paper is to compare the physical properties of ACM//PA TPVs to EPDM//PP and copolyester after exposure to temperatures up to 175°C and aggressive greases found in air duct, CVJ and rack-and-pinion applications. Further, the blow moldability of ACM//PA TPVs will be demonstrated and actual applications will be shown.

The criteria followed in this paper to confirm the performance of ACM//PA TPVs compared to conventional materials include:

1. Retention of at least 50% of original tensile and elongation properties after long-term 150°C and short-term, 175°C, temperature aging in air.
2. Retention of at least 50% of original tensile and elongation properties after exposure to common axle greases.
3. No visible loss of lubricity to the greases after aging grease-covered materials at elevated temperatures.
4. Low-temperature performance at –40°C.
5. Blow moldable via extrusion (mono and co-ex) and press-blow processes.

Experimental

Six materials were selected for evaluation:

1. Zeotherm® 120-90B, a TPV based on polyacrylate (ACM) rubber and polyamide. (Zeon Chemicals L.P.)
2. Hytrel 3078, a low-durometer copolyester resin. Designated COPE-1 (E.I. DuPont).
3. Hytrel HTR 8105, a blow moldable copolyester resin commonly used in CVJ boots. Designated COPE-2 (E.I. DuPont).
4. Arnitel EB463, a blow moldable copolyester resin commonly used in CVJ boots. Designated COPE-3 (DSM).
5. Santoprene 201-73, an EPDM//PP TPV. Designated EPDM//PP-1 (Advanced Elastomer Systems).
6. Santoprene 101-87, an EPDM//PP TPV. Designated EPDM//PP-2. (Advanced Elastomer Systems).

Original Properties

The original properties of ACM//PA TPV are summarized in Table 1. With the exception of COPE-2 and COPE-3, the polymers have hardnesses on the Shore A scale. Each has been selected to have elongation at break values in excess of 200%.

All stress/strain testing was conducted in accordance with ASTM D471 and D473.

Resistance to Elevated Temperatures

To simulate the environment that a real part would be subjected to underhood, physical properties of the selected materials were measured "at temperature" (i.e., the sample was considered to be "at temperature" when the physical properties were recorded). This is often a more severe test, especially for materials that soften or melt near the testing temperature.

As shown in Figure 1, ACM//PA TPVs have better retention of physical properties between 100°C and 150°C than either the COPE or EPDM//PP samples. Whereas the other materials demonstrated a significant drop in mechanical strength between 125° and 150°C, Zeotherm 120-90B was stable.

Further, ACM//PA TPVs have a higher softening point and melt point than the COPE-1 and EPDM//PP-1 samples (Figure 2). In application, this equates to a larger safety margin specific to deformation due to heat when utilizing ACM//PA TPVs.

Air Aging

Copolyester is often considered for applications requiring a heat upgrade versus EPDM//PP. However, as shown in Figure 3, blow moldable copolyester grades suffer severe loss of mechanical properties after relatively short-term (336-hour) exposure to 150°C. This makes copolyesters unsuitable for parts expected to see continuous exposure to temperatures above 140°C or requiring the use of a metal heat shield with the copolyester – at an added expense.

To simulate the long-term performance of ACM//PA TPVs to 150°C, air aging was continued to 1008 hours (Figure 4). As shown, ACM//PA TPVs retained approximately 50% of their original tensile and elongation at break. On the basis of the SAE J2258 continuous use temperature definition, ACM//PA TPVs can be deemed suitable for long-term 150°C exposure.

For the automotive engineer, spike temperature capability of materials must also be considered. For example, temperatures on boots and ducts can see higher temperatures during abnormal vehicle operation, stop-and-go traffic, and alpine driving. To simulate the effect of spike-temperature exposure to ACM//PA TPVs, a comparison was made between 168 hours of exposure to 175°C and 1008 hours of exposure to 150°C. It was found (Figure 5) that short-term exposure to 175°C was not catastrophic to ACM//PA TPVs and that the short-term exposure approximated the effects of long-term 150°C aging.

Grease Aging

Rack-and-pinion and CVJ boots must resist hot grease exposure in addition to hot air. The greases are selected on the basis of their lubricity in application (e.g., low friction greases), commonly without regard to the boot material. The greases are commonly lithium or polyurea based.

Figure 6 illustrates the impact of hot grease exposure to COPE-2 as compared to ACM//PA TPVs. In this test, one side of the material was covered in grease and the other side left exposed to air. The two greases are commercial grades utilized on CVJs supplied by a leading domestic Tier 1. ACM//PA TPV is shown to have superior resistance to the hot greases whereas COPE-2 has significant loss of mechanical properties.

The resistance of Zeotherm ACM//PA TPVs to grease is further illustrated in Figures 7 and 8 using Evolube 232 and Castrol Optitemp XBT1LF greases, respectively. While the XBT1LF grease is quite aggressive towards ACM//PA TPV, it is noted that copolyester and HNBR thermoset rubber have been found, in previous studies, to be destroyed by this grease whereas ACM//PA TPV retains 45% of its original elongation at break.

In application, it is expected that the boot material will not change the lubricity of the grease over time. That is, the boot material must not extract components from the grease nor bleed components into the grease that would result in the grease "drying out". This phenomenon has been reported on multiple occasions by the automotive Big 3 and European OEMs.

To simulate the condition of grease "drying out", a polyurea grease (Polyrex EP-2 grade) was exposed to ACM//PA TPV, EPDM//PP-2, and COPE-3 for 168 h, 150°C. Figure 9 shows that the polyurea grease was significantly altered and lost lubricity after exposure to EPDM//PP-2 and COPE-3, while it was minimally affected by ACM//PA TPV.

Low-Temperature Performance

The requirement for automotive boots and ducts is that they must function at low temperatures as well as high temperatures. The commonly stipulated low-temperature requirement is –40°C.

ACM//PA TPV was evaluated via multiple techniques (e.g., brittle point, DSC, DMTA) to confirm functional compliance at –40°C. See Table 2.

To simulate the effects of road debris impact at –40°C, low-temperature Izod impact testing is being conducted. It is anticipated that ACM//PA TPV will pass the notched Izod impact test at –40°C.

Splash Fluid Resistance

While boots and air ducts would not be expected to survive continuous exposure to hot coolant, gasoline, or diesel fuel, it is expected that the parts can resist casual, "splash" contact.

Figures 10, 11, and 12 depict the resistance of ACM//PA TPVs to the above noted fluids. For example, even under relatively long-term (1008 hours) full immersion exposure to diesel fuel at 40°C, ACM//PA TPVs swell less than 9% and retain in excess of 95% of the original tensile strength and 60% of the original elongation at break.

Resistance to fuel is important in air duct applications where blow-by can occur and where vaporized fuel can be expected to contact the duct.

Blow Moldability

The processability of ACM//PA TPVs has been proven using the dominant blow molding techniques and machines utilized for air ducts (mono and dual-layer) and automotive boots. These include Kautex co-extrusion sequential blow molding, Placo extrusion-blow, and Ossberger press-blow machines.

Table 3 details the typical machine set-up parameters for extrusion-blow molding with ACM//PA TPVs.

Compared to EPDM//PP and copolyester, it is found that ACM//PA TPVs require higher processing temperatures in the extruder and die. This is attributed to the PA6 plastic phase of ACM//PA TPV. Cycle times are similar to EPDM//PP and copolyester.

Application Specifics

ACM//PA TPV was blow molded into rack-and-pinion and CVJ boots and turbo air ducts to confirm its processability on commercial equipment and its functional performance on rig and vehicle testing.

Rack and Pinion Boots

Photo 2 depicts a rack-and-pinion boot that was blow molded on an Ossberger press-blow machine with Zeotherm 120-90B. The tooling design was developed for copolyester.

The use of ACM//PA TPVs allow for the elimination of a metal heat shield (Photo 1) needed to protect the existing EPDM//PP boot due to close proximity with the engine exhaust and steering hydraulic pump.

CVJ Boots

Utilizing copolyester tooling on an Ossberger press-blow machine, ACM//PA TPV was successfully molded for an inboard CVJ boot (Photo 3).

Inboard, exhaust-side CVJ boots require resistance to severe flex (45° angle of bend), high-speed (i.e., high heat) rotation, and heat in excess of 150°C. ACM//PA TPVs allow for the elimination of a heat shield needed to protect copolyester.

Turbo Air Ducts

Intercooler ducts on compact turbo-diesel engines and large air intake ducts, connecting air cleaners to turbos on Class 6-8 heavy trucks, are increasingly being forced away from EPDM//PP and copolyester due to heat.

So-called "short" ducts of ACM//PA TPV as a mono-layer have successfully been blow molded using Kautex machines.

Dual-durometer (i.e., 3D sequential) blow molding of ACM//PA TPV with nylon allows for elimination of rubber cuffs and attachment by clamps, while also providing for 150°C sustained heat resistance and the desirable rigid/flexible sections.

Photo 4 shows a ACM//PA TPV duct made on a Placo machine utilizing ACM//PA TPV and a rigid PA6. The ACM//PA layer and the PA6 layer were found to be completely fused together.

Conclusions

Multiple conclusions that can be drawn from the data presented in this paper:

1. ACM//PA TPVs provide elevated heat resistance as compared to EPDM//PP TPVs and copolyester.
2. ACM//PA TPVs retain in excess of 50% of their original tensile and elongation properties after 1008 hours, 150°C as well as short-term exposure to 175°C.
3. ACM//PA TPVs are capable of functionally performing at –40°C.
4. The resistance of ACM//PA TPVs to hot grease is superior to COPE-2 and EPDM//PP-2.
5. The blow moldability of ACM//PA TPVs on commercial grade machines has been proven for rack-and-pinion boots, CVJ boots, and turbo air ducts.
6. ACM//PA TPVs are commercially available under the Zeotherm® trade name from Zeon Chemicals.

References

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4. S. Harber, B. Cail, C. Smith, "150C Capable TPVs for Demanding Polyamide and Polyester Over-Molding",

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5. A. Anderson, R. Bruner, P. Manley, " Advances in Heat Resistant ACM Compounding Technology for Under-the-Hood Applications", American Chemical Rubber Division, Fall Meeting, Paper 34.

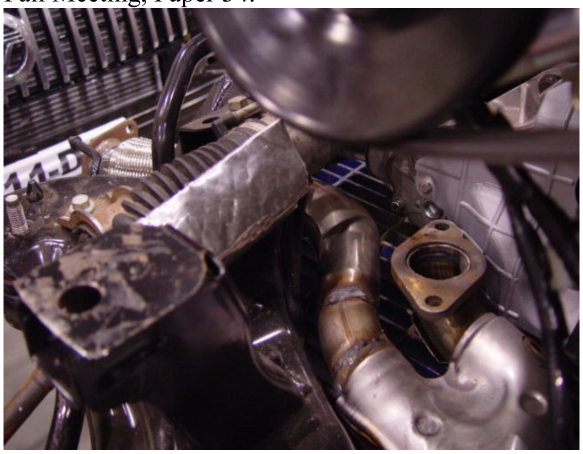


Photo 1, Rack and pinion boot with installed heat shield.

Zeotherm® 120-90B	
Hardness A, pts.	95
M100, MPa	8.7
Tensile at Break, MPa	11
Elongation at Break, %	200
Density – Specific Gravity	1.100

Table 1, Original physical properties – ACM//PA TPV.

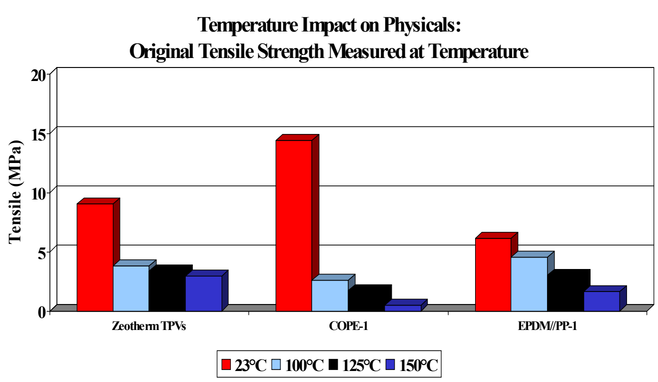


Figure 1, Tensile strength measured at temperature.

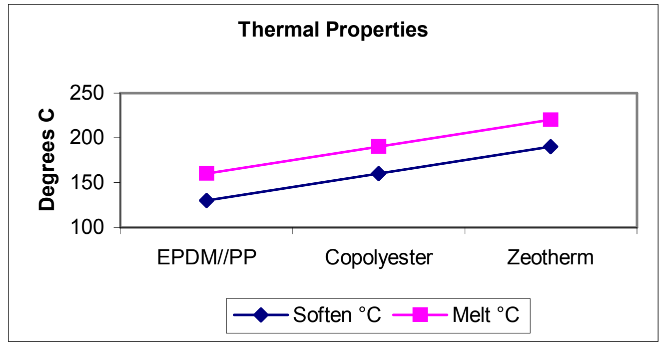


Figure 2, Softening and melting point comparison.

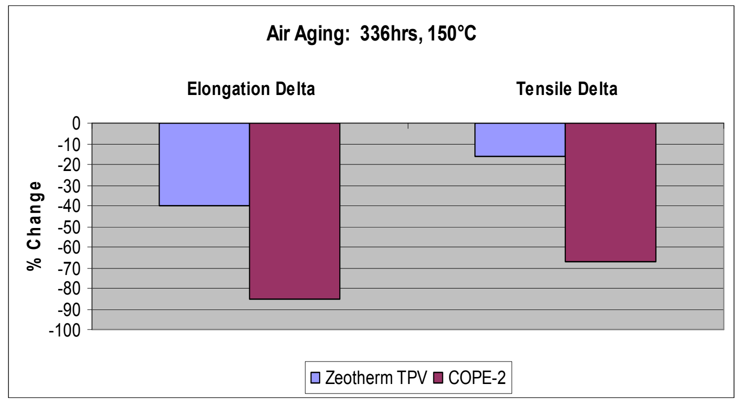


Figure 3, Retention of tensile strength after heat aging at 150°C, 336h.

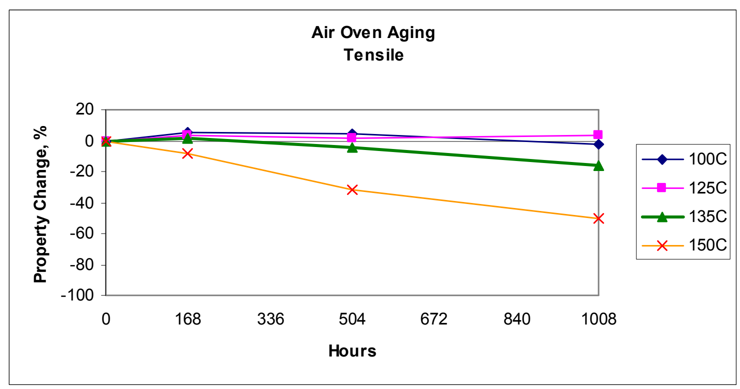


Figure 4, Retention of mechanicals after air aging of Zeotherm TPVs at various temperatures.

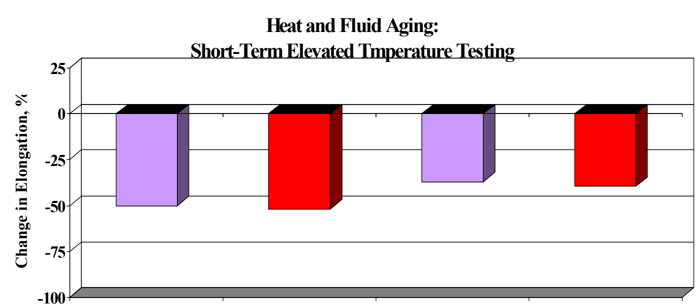


Figure 5, Short-term elevated temperature aging of ACM//PA TPVs.

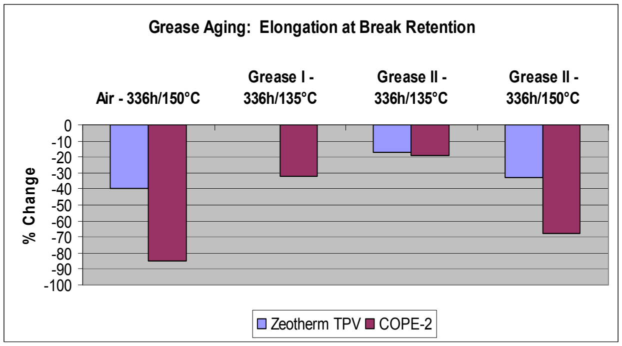
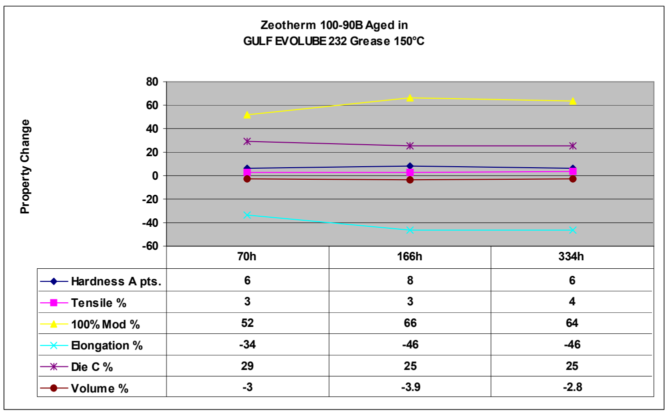
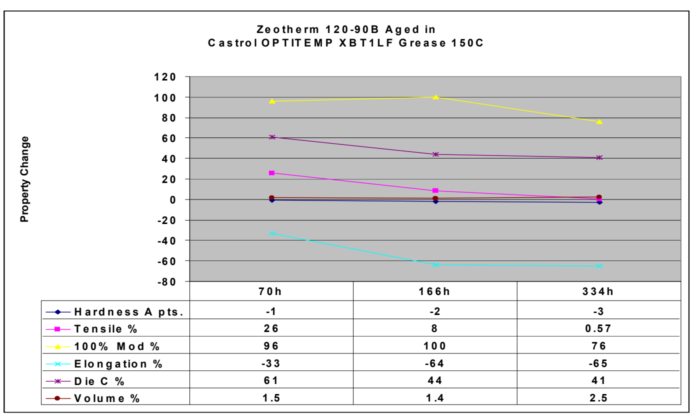


Figure 6, Grease aging mechanical property retention comparison.



	70h	166h	334h
Hardness A pts.	6	8	6
Tensile %	3	3	4
100% Mod %	52	66	64
Elongation %	-34	-46	-46
Die C %	29	25	25
Volume %	-3	-3.9	-2.8

Figure 7, Grease aging of ACM//PA TPVs in Evolube 232 grease.



	70h	166h	334h
Hardness A pts.	-1	-2	-3
Tensile %	26	8	0.57
100% Mod %	96	100	76
Elongation %	-33	-64	-65
Die C %	61	44	41
Volume %	1.5	1.4	2.5

Figure 8, Grease aging of ACM//PA TPVs in Castrol Optitemp XBT1LF grease.

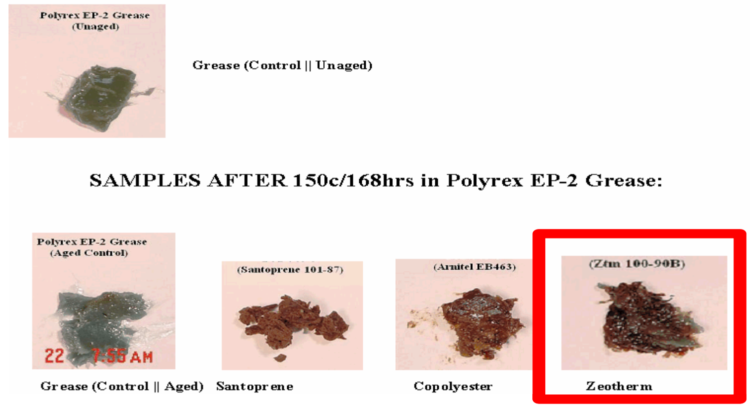


Figure 9, Grease lubricity after contact with various TPVs.

PROPERTY	Zeotherm
	120-90B
Low Temp	
T50	-71 C
T10	-48 C
T5	-38 C
Brittle Point	-50 C

Table 2, Low-temperature properties of ACM//PA TPVs.

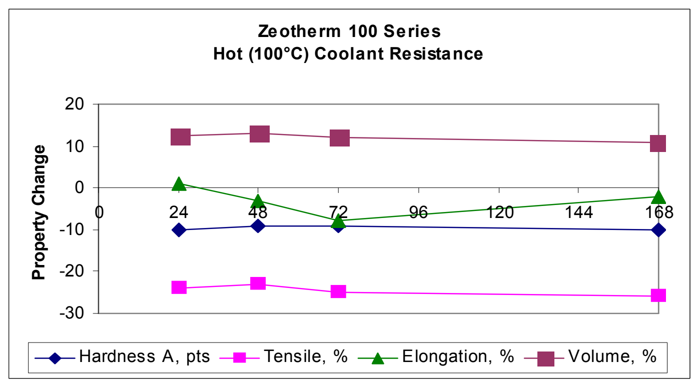


Figure 10, Impact of hot coolant exposure to ACM//PA TPVs.

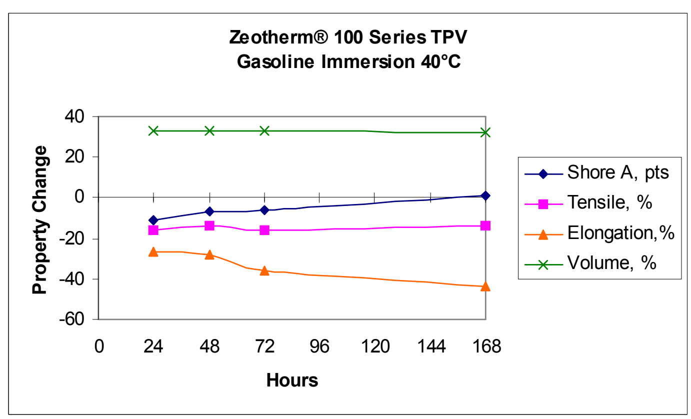


Figure 11, Impact of gasoline exposure to ACM//PA TPVs.

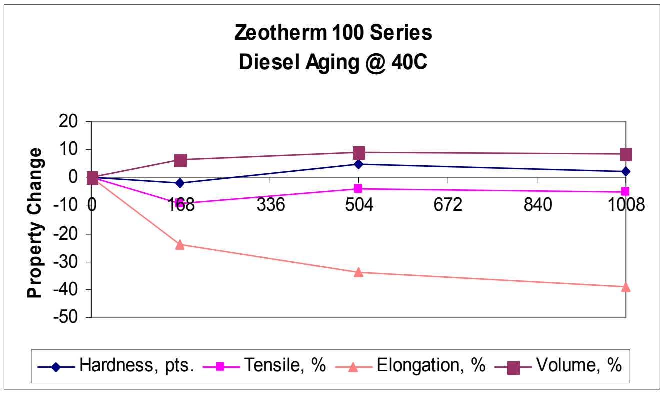


Figure 12, Impact of diesel fuel exposure to ACM//PA TPVs.

Temp. profile (°F):	set	act.
Feed:	460	460
Trans.:	470	470
Metering	470	470

	set	act.
Accumulator upper	470	470
Accumulator lower	470	470
Die tip:	465	465

Table 3, Processing conditions for extrusion blow molding with ACM//PA TPVs.

Photo 2, Rack and pinion boot made of ACM//PA TPV.

Photo 3, CVJ boot made of ACM//PA TPV.

Photo 4, Dual-durometer air duct made of ACM//PA TPV.