150°C Heat- and Oil-Resistant TPVs- Long-Term Fluid and Spike Temperature Comparison

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Abstract

New families of thermoplastic vulcanizates (TPVs) were commercially introduced in early 2003 offering 150°C heat and oil resistance in excess of 3000hrs. These TPVs are based on a continuous phase polyamide thermoplastic matrix and dynamically vulcanized polyacrylate (ACM) elastomer. Applications have a broad interest from underhood automotive to industrial applications.

The heat and oil resistance of a commercialized TPV from this family will be compared at 150°C to conventional and silicone-based TPVs in addition to an ethylene-acrylate (AEM) thermoset elastomer, all of similar initial physical properties. Degradation after 175°C spike temperature exposure to air and an assortment of automotive fluids will also be compared. Finally, an overall comparison will be made to qualitatively measure the equivalency of these materials in manufacturing and end use application.

Introduction

Design changes to automobiles to improve efficiency and appeal to regional preferences (e.g., turbo-diesel engines) are creating challenges for material and design engineers[2]. These changes have led to increased temperatures, the shift to synthetic long-life fluids, and the need for polymers capable of handling these extremes[3]. Industrial components have experienced a similar trend for extended service life expectations.

Whereas thermosets and TPVs capable of withstanding 125°C environments have been specified previously, many automotive underhood and industrial components are being required to withstand long-term exposure to 150°C in air and fluid immersion for the life of the vehicle or component. As a result, many part specifications have been written to require materials to withstand 2000h or longer continuous exposure to 150°C hot air and oil. Spike temperatures of up to 175°C can also be experienced under extreme underhood conditions.

Traditional Thermoset Elastomers

Thermoset elastomers have been the traditional material of choice for underhood and industrial applications when temperature/fluid resistance is required. Applications include air/fluid transport, vibration isolation/dampening, and sealing. Among the thermosets, silicone (VMQ), polyacrylate (ACM), and ethylene-acrylates (AEM) have traditionally been used for 150°C exposure due to their cost-performance balance. However, VMQ suffers severe volume swell and weeping when exposed to hot oils and cannot be considered an oil resistant material. ACM and AEM suffer from long overall cure cycle, often involving off-line post-curing, and high specific gravity after compounding. Additionally, thermoset elastomers are not readily recyclable – in-process or post-consumer[2].

Thermoplastic Vulcanizates (TPV)

Thermoplastic vulcanizates (TPVs) have several advantages over traditional thermoset elastomers. They offer the functional performance similar to that of thermoset elastomers but have the processing ease and recyclability of thermoplastics resulting in lower overall cycle times, elimination of internal mixing operations and the ability of overmolding with chemical adhesion to many thermoplastics. Unlike most thermoplastics, TPVs also retain desirable lower hardness with compressive behavior of elastomers[1].

Due to poor long-term heat and oil resistance, conventional (EPDM//Polypropylene) TPVs have found limited use in underhood and industrial applications requiring continuous use temperatures exceeding 135°C.

New Developments

Zeon Chemicals commercialized a new family of TPVs in early 2003, which provide dramatically improved resistance to heat and oils[4]. The resulting TPVs are capable of withstanding long-term exposure to high temperature (150°C) air and oils.

The initial grades from the new class are based on dynamically vulcanized ACM and polyamide (ACM//PA). The composition is “rubber-rich” resulting in low hardness, good dampening characteristics and physical properties comparable to thermoset ACM and AEM while retaining the favorable processing characteristics of thermoplastics.

Objective and Criteria

The objective of this paper is to compare the long-term heat and oil resistance of an ACM//PA TPV to other so-called heat and oil resistant TPVs as well as an industry-standard AEM thermoset elastomer. Conventional EPDM//PP TPVs have been excluded from this study and they are known to degrade after 135°C continuous air and oil exposure.

The criteria followed in this paper to confirm heat and oil resistance include:

1. Retention of at least 50% of initial tensile and elongation properties after long-term 150°C and short term, 175°C, spike temperature fluid aging.
2. No significant change of hardness (15 points Shore A) difference that would negatively impact sealing, dampening or flexibility characteristics
3. Less than 10% change in volume upon long-term oil exposure.

Experimental

Four materials were selected for evaluation, three TPVs and a representative thermoset rubber:

1. Zeotherm™ 100-80B, a TPV based on polyacrylate (ACM) rubber and polyamide. Designated ACM//PA (Zeon Chemicals L.P.)
2. Hytrel 3078, a low-durometer copolyester resin. Designated COPE (E.I. DuPont).
3. TPSiV 3040-65A, a low-durometer proprietary copolyester resin // silicone elastomer TPV. Designated Si-TPV (Dow Corning/Multibase).
4. Vamac AEM, an ethylene-acrylic thermoset elastomer compound. Designated AEM (E.I. DuPont).

Original Properties

The original properties of the four polymers are summarized in Table 1. The polymers are in the mid to upper range of the Shore A hardness scale and claim to have 150°C air and oil resistance under continuous use conditions. The original properties of the polymers are comparable to that of typical industrial and automotive materials targeted for applications such as hose covers, air-ducts, bellows and seals, requiring elastomeric or rubber-like flexibility.

Resistance to Environmental Exposure

Percent retention of physical properties was measured on the four polymers after long-term heat and oil immersion according to standard testing methods ASTM D471 and D473.

Two service temperatures were selected for sample aging: 150°C and 175°C. The three mediums selected for testing were: Air, ASTM Service Fluid 105 (SF105) and PetroCanada Dexron III transmission fluid (DEX III). Air exposure evaluates thermal and oxidative effects. SF105 is considered an aggressive test fluid designed to simulate modern semi-synthetic engine oil and accentuate differences in materials for sealing applications in a relatively short period of time. DEX III is transmission / power steering fluid picked for its presence in most vehicles across the automotive market, primarily General Motors.

Material Evaluations and Comparisons

1008-Hour Exposure at 150°C

Physical testing was performed on the four polymers after 1008-hour exposure to three mediums at 150°C.

Figures 1 and 2 display the percent change of tensile strength and elongation after 1008 hours of exposure at 150°C. The ACM//PA TPV and the AEM thermoset elastomer both retain better than 50% of their original properties in air, SF105 oil and DEX III. The COPE was destroyed in air and DEX III. It lost more than 50% of its properties in oil. Si-TPV performed poorly and was completely destroyed in fluid.

ACM//PA TPV shows excellent retention of hardness with less than 7-points change (Figure 3). The COPE was either destroyed or softened with more than a 30-point drop in hardness. Si-TPV displayed similar results to the ACM//PA TPV in air and was destroyed in fluid. The AEM thermoset elastomer sample performed comparably to the ACM//PA TPV in air and showed an approximate 10-point drop in SF105 and DEX III.

Figure 4 displays the percent swell of the polymers after 1008 hours exposure at 150°C. The ACM//PA TPV again shows excellent resistance to swell with less than an 8% loss in air and less than 4% loss in fluid. The COPE sample was severely degraded in all environments. The Si-TPV and AEM thermoset elastomer displayed comparable results to the ACM//PA TPV in air; however, Si-TPV swelled over 18% and AEM over 20% in SF105 and DEX III.

In summary, ACM//PA TPV shows: 1. significantly higher overall performance as compared to COPE and the Si-TPV; 2. comparable performance to the

AEM thermoset elastomer in regard to tensile and elongation percent retention; 3. the least degree of hardness change and volume swell of materials tested.

168-Hour Exposure at 175°C (Spike Temperature)

A spike temperature of 175°C was selected to simulate extreme underhood conditions for a short duration of time. Both COPE and Si-TPV were tested, but were excessively degraded in all environments such that adequate data was not produced to merit further discussion. The aggressive nature of the test mediums should quickly display the ability of ACM//PA TPV and AEM materials to perform in these extreme conditions.

Figures 5 and 6 display the percent change of tensile strength and elongation after 168-hour exposure at 175°C. Both ACM//PA TPV and AEM performed quite well and show similar degradation behavior.

Figure 7 displays the hardness change in points after 168-hour exposure to 175°C. The ACM//PA TPV has less than a 10-point gain in hardness in the three environments. The AEM thermoset elastomer performed comparably to the ACM//PA TPV in air but softened over 15 points in SF105and DEX III.

ACM//PA TPV shows excellent resistance to swell with less than a 10% loss in air and less than 4% loss in fluid (Figure 8). The AEM displays similar results in air, but swells over 20% in fluid.

ACM//PA TPV showed comparable retention of physical tensile strength and elongation to AEM. However, AEM suffers from softening and excessive volume swelling which make it questionable for applications requiring long-term oil resistance. With the exception of applications requiring low compression set, ACM//PA TPV can be considered a good substitute for thermoset AEM[5].

Processing

TPVs have significant advantages in process cycle, part cost and quality control when compared to thermoset elastomers. Thermosets require multiple steps from processing to the end-use part. They require in-house or toll mixing, calendering, both in and out of mold curing and post process trimming. TPVs, however, are process ready from the manufacturer. TPVs have no cavity to cavity cure state variability and require no post cure. More typical of thermoplastics, TPVs have cycle times on average less than 30 seconds whereas rubbers can take several minutes. TPV in-process (scrap, trim or reject) and post-consumer parts can easily be ground and recycled. These advantages afford potential significant cost savings per part versus a thermoset rubber.

Conclusions

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

1. COPE and Si-TPV did not pass the minimal requirements to be considered a material suitable for industrial and automotive applications requiring 150°C and oil resistance.
2. ACM//PA TPV has superior heat and oil resistance compared to COPE, Si-TPV and comparable performance to the AEM thermoset elastomer at 150°C in prolonged exposure to air, SF105 and DEX III.
3. The ACM//PA TPV has comparable performance to the AEM thermoset elastomer in 175°C short-term spike temperature exposure to air, SF105 and DEX III. The exception is compression set.
4. The ACM//PA TPV and the AEM thermoset elastomer were the only materials to retain over 50% of their original properties during long-term 150°C evaluation.
5. Due to its balance of properties and processability, the ACM//PA TPV can be considered a lower-cost, recyclable option to replace thermoset AEM and a definite performance upgrade from COPE and Si-TPV in automotive and industrial applications requiring 150°C and oil resistance.

References

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	ACM//PA	COPE	Si-TPV	AEM
Tensile (MPa)	9.30	14.20	7.50	19.10
Elongation (%)	200	650	563	372
Hardness	84A	81A	62A	64A
Specific Gravity	1.15	1.07	1.20	1.35

Table 1, Original physical properties of evaluated polymers.

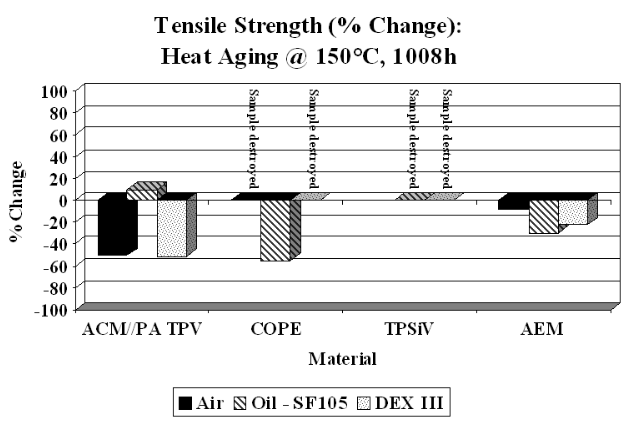

Figure 1, Tensile strength after 150°C, 1008h aging.

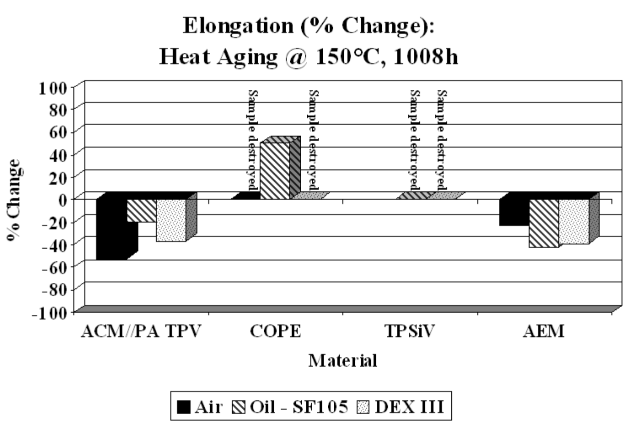

Figure 2, Elongation after 150°C, 1008h aging.

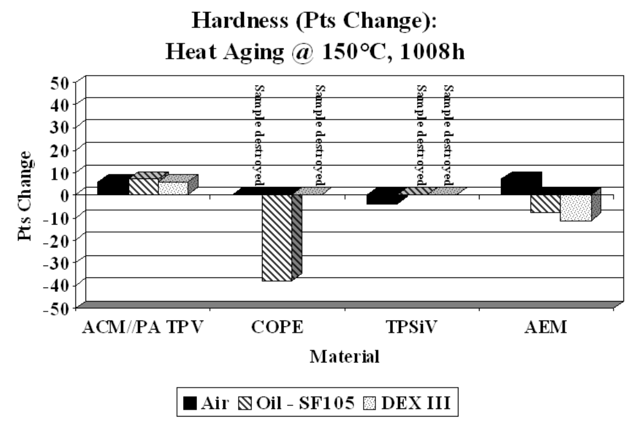

Figure 3, Hardness after 150°C, 1008h aging.

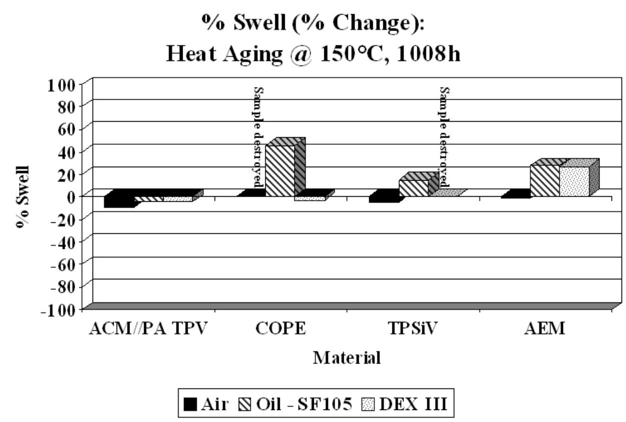

Figure 4, Volume swell after 150°C, 1008h aging.

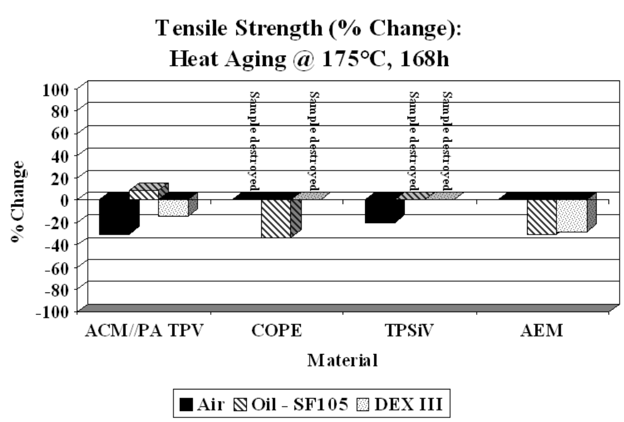

Figure 5, Tensile strength after 175°C, 168h aging.

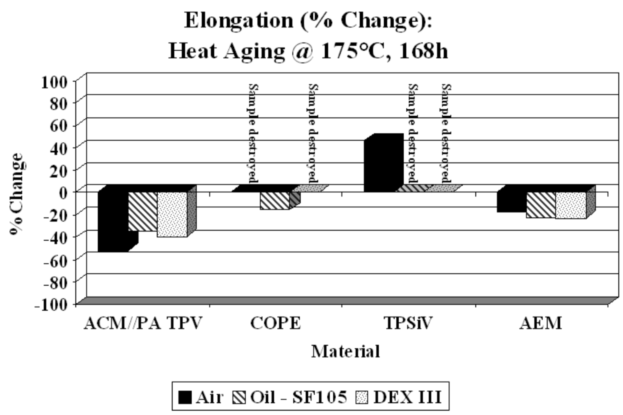

Figure 6, Elongation after 175°C, 168h aging.

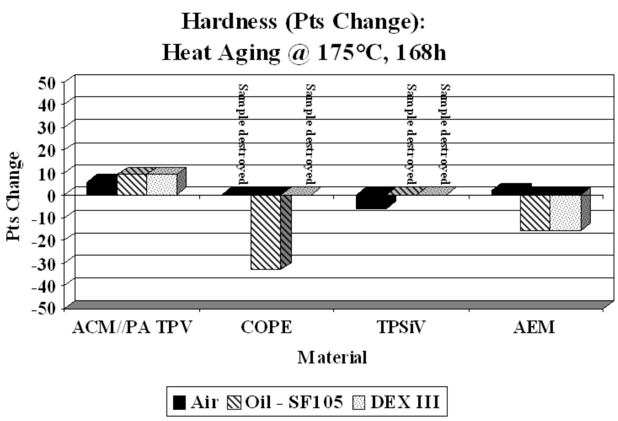

Figure 7, Hardness after 175°C, 168h aging.

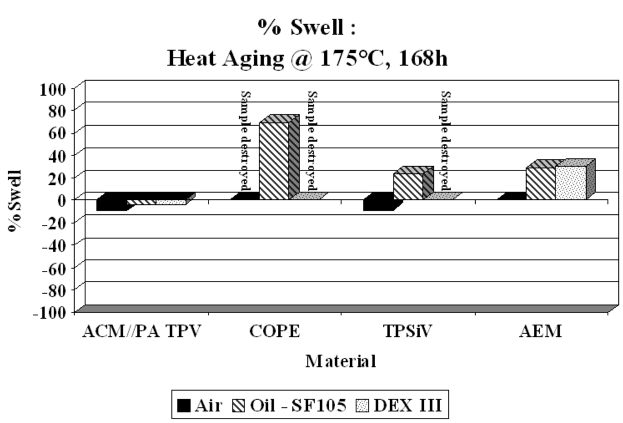

Figure 8, Volume swell after 175°C, 168h aging.