Failure Modes of Aramid Fibers as Knitted Reinforcements to Elastomeric Low Pressure Automotive Hoses

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Abstract

Increasing fuel efficiency standards for automobiles has driven choices by auto-manufacturers to downsize and boost internal combustion engines by turbocharging or supercharging to optimize performance per fuel consumption. The turbocharged system involves several new hose applications not typical to an un-boosted system. High heat, impulse, engine vibration, and chemical resistance requirements will influence the materials chosen including the aramid fiber for hose reinforcement. This paper will examine the failure modes and limitations for use of aramid yarn products for knitted hose applications. Modes discussed are compression and abrasion related failures in Kevlar® para-aramid differences to modes of Nomex® meta-aramid failures as they relate to knitted reinforcements for hose.

Introduction

The trend in automotive engineering and styling continues to impose increasingly severe requirements on hose products as internal combustion engines are continuously designed to have greater power in smaller spaces to achieve higher fuel efficiency ratings. Turbocharging direct injection gasoline engines has become a common choice among automotive manufacturing companies as technology to provide a means for engine-downsizing and raising fuel efficiency without sacrificing the consumer’s sense of performance. The result is that typical engine compartment air temperatures have increased within the possible range of 130-150 °C, while in higher performance engines and heavy duty vehicles temperatures could reach 200 °C or higher. Polymeric organic materials referred to as poly-aramids are well suited for high temperature applications.

A rubber automotive hose being constructed in the sequence of a cylindrical rubber inner tube, a reinforcement layer, and a rubber cover layer constitutes a basic definition. A hose is shaped to convey fluids through necessary units to enhance engine performance and typical hose routing involves a complex path past sources of heat. Accessibility is increasingly problematic with a tortuous path, and hose life is expected to last the lifetime of the engine. Radiator outlet and inlet hoses, heater core inlet and outlet hoses, engine coolant by-pass hoses, and charge air cooler hoses (i.e. turbocharger hoses) particularly for diesel and gasoline passenger vehicles and some heavy duty vehicle...
applications are a few examples of these hose applications and also ones that use knitted reinforcements. Figure 1 shows a schematic of the basic hose with knitted reinforcement.

Today’s automotive hoses must be highly heat resistant, dimensionally stable, vibration resistant, and durable. In terms of the hose reinforcement needed to meet the above requirements and to provide the specified resistance to hose working pressure, aramide based continuous filament yarns such as Kevlar® para-aramid and Nomex® meta-aramid fibers by DuPont are well suited for these demanding hose applications. Aramide filament yarns combine the excellence in processability and reinforcement properties with high heat resistance, dimensional stability, and fatigue tolerance.

Hose failures of the yarn do occur in product development and an examination of the failure modes of the two fibers will aid the investigation in determining a likely root cause of the failure. Hose failures due to combinations of rubber and reinforcement wear may also occur in the field during service, and a complete failure analysis with reference to the construction and performance specifications can provide the most information on the origin of the hose failure. To limit the scope of this paper to failures due to the fiber reinforcement, the assumption will be made that the rubber chemistry has been chosen to match the specified conditions or service. Additionally, the yarn reinforcement may vary in type of fiber chemistry and in the type of pattern laid on the inner tube. To further refine the scope of this paper, para-aramid and meta-aramid continuous filament yarns will be examined in knitted reinforcement geometries.

This paper will review the key fiber properties of para-aramid and meta-aramid continuous filament fibers as Kevlar® and Nomex® by DuPont, a methodology for yarn failure analysis, and an examination of each fiber’s failure in hose in order to provide hose engineers with a clearer picture of the environmental limitations of each fiber for knitted reinforcement patterns in molded automotive hose. A successful failure analysis during the product development cycle will increase the speed to market of new hose products.

Review of Kevlar® and Nomex® yarns by DuPont for Low Pressure Automotive Hose

Production of Kevlar® by DuPont began in 1972 in Richmond, Virginia (USA), and as demand grew for this high performance fiber additional capacity was added. In 2011, a new facility, built using the culmination of advanced DuPont technology of Kevlar® manufacturing, will be opened in the United States. This new Kevlar® facility is capable of providing customers with higher performing Kevlar® yarns such as Kevlar® Advanced Performance (Kevlar® AP) to enable cost savings or greater strength to be obtained in articles made by various industries, including low and high pressure hose. For automotive hose, the greater specific strength of Kevlar® AP creates possibilities to redesign parts for a reduction in yarn weight required to reinforce a length of hose. Nomex® by DuPont began production in 1966 also in Richmond. All plants use state of the art technology for efficient production and optimal environmental protection with a large commitment to total quality and highest safety standards of all personnel.

Kevlar® yarns is composed of several filaments each composed of linear rigid polymer chains of poly(paraphenylene terephthalamide). These molecules readily pack into highly ordered structures of hydrogen bonded sheets, which in turn align to a high degree along the axis of the filament’s length. The regularity of this semi-crystalline
structure is responsible for the high specific modulus and breaking strength of Kevlar®. Additionally, the high thermal and chemical stability of Kevlar® is due to the presence of aromatic rings linked by the conjugated amide bonds.

Nomex® yarn, like Kevlar® is composed of several filaments each consisting of long polymer chains of aromatic rings linked by amide bonds, but unlike Kevlar®, the linkages in Nomex® are in the meta-position relative to positions on the aromatic ring. Therefore, the polymer chains in Nomex® are not linear and rigid in their arrangement, which imparts significantly more amorphous phase presence than in Kevlar®. This arrangement does not promote high strength of the fiber but does promote high elongation at break of the fiber giving it high toughness. Although the specific strength of Nomex® is lower than Kevlar®, Nomex® fibers have higher thermal stability of strength at greater temperatures and higher chemical resistance, particularly with regard to hydrolysis.

The high tenacity (defined as the ultimate strength of the yarn divided by its linear density) and initial modulus in straight tensile mode of Kevlar® allows for the fabrication of economical and comparatively thin wall hose (the reinforcement is low weight and has a small cross-section), capable of withstanding high pressures with low volumetric expansion. For knitted hose applications, the loop tensile properties (as opposed to the straight tensile properties) of the yarn are the determining factor for hose performance at rupture pressure. The high orientation factors of polymer chains along the fiber’s longitudinal axis for para-aramid yarns tends to limit the residual strength of the yarn in a loop geometry to values of nearly 50% of the straight strength. However, loop tenacities of para-aramid yarns are greater than loop tenacities of meta-aramid yarns and common thermoplastic fibers such as nylon and polyester. Nomex® yarn has relatively less strength than Kevlar®, but has significantly higher toughness in loop testing and yarn on yarn abrasion resistance, making Nomex® ideal for heavy duty and high temperature applications. A combination of Kevlar® and Nomex® as a single end of twisted yarn provides an interesting balance in desired properties. Some property comparisons are made in Table 1.

Molecular degradation leading to strength loss of the fiber and early failure of the part can be caused by mismatching the thermal limits of the hose and the fiber or the chemical resistance of the rubber to the working fluid or exposure of harmful chemical through contact with the outside cover layer. Both Kevlar® and Nomex® have excellent thermal properties, including low heat shrinkage, which aids in improving the prediction of cured part length helping to reduce waste after vulcanization. Neither fiber is affected by long term temperatures ranging from cryogenic to 130°C. Exposures of the fibers in air at 160°C results in only minor changes in the characteristics of Kevlar® with less of a change in Nomex® (figure 2 and 3).

With regard to chemical exposure, both fibers are susceptible to hydrolysis when exposed to strong acids and bases, but most inorganic salts and organic solvents have minimal or no effect on Kevlar® or Nomex®. To some, exposure of the fibers to ethylene glycol based antifreezes is an important consideration for yarn selection. After 100 hours of exposure to 95% ethylene glycol at 140°C, Kevlar® yarn retains 50% of its original straight tensile strength and is stronger than Nomex® and common thermoplastic fibers. However, the rate of degradation is highly variable and can be minimized by avoiding high pH mixtures (see figure 4 for residual strength retention of Kevlar and
Nomex at 114°C). Yet, these experiments are direct exposures of these chemicals to the fiber, and in the application for knitted hose this interaction would occur through diffusion of the chemicals in the rubber wall. As a matter of good design, rubber chemistries are specifically chosen to prevent diffusion of the interior fluid through the wall.

Review of Kevlar® and Nomex® yarn Failure Analysis and Methodology

Failure of knitted hoses can occur in the inner rubber tube, the textile reinforcement, or in the cover layer. The tensile reinforcement part of these hoses is in a basic sense a form of Kevlar® or Nomex® twisted yarn. A reinforcement failure analysis consists of examining both the filament bundle and the individual filaments near the point of failure and comparing their behavior to those in the un-failed sections. In addition, a benchmark comparison is made by examining similar components of in an untested hose, i.e. a hose that has not been subjected to service. The actual investigation falls into three areas: visual/optical observation, measurement of physical properties, and measurement of chemical properties. Most observations and these properties can be determined only after the cover layer has been removed from the hose. Care must be exercised in cover removal as to not introduce defects into the yarn or the rubber (for a subsequent rubber failure analysis.)

The visual/observations include appearance of the surface of the fibers to the naked eye, followed by microscopic examination in transmitted or reflected light, and/or polarized light. In some instances, scanning electron microscopy techniques are called for at high magnification (2000X). Likely physical properties measured would be filament modulus, tenacity, and elongation, while the chemical characterization would include inherent viscosity or size exclusion chromatography for the isolation of strength loss due to a loss in yarn molecular weight. Additional chemical analysis can be run to determine the presence of contaminate substances leached through the rubber interior or exterior walls. A simple test for exposure to acid or base is to soak the filaments over night and then check the pH of the water. Another method is to heat age the yarn at elevated temperature and compare to base yarn. This method also enhances the color change (mentioned above).

Examination of Fiber Defects and Failure Modes Analysis

The most common mechanisms which cause failure or damage to Kevlar® and Nomex® filaments fall into the following categories:

- Tensile failure – due to fiber overloading
- Abrasion – caused by mechanical damage or abuse which could be internal or external
- Compression and shear fatigue – induced either by sharp, bend torsion, or actual compression.
- Chemical degradation – due to interaction with chemicals or heat

Microscopic examination of damaged yarns may identify the reasons for the damage. Five typical examples are shown in schematic drawings (Figure 5) as...
representatives of the following types of damages: fibrillation, twisted fiber, kink band, crushed fiber and axial crack. The term kink band requires some clarification. The crystal structure of a drawn Kevlar® yarn is such that the crystals are packed parallel to each other, with their ends forming a rather well defined plane. This plane is not perpendicular to the fiber axis but at an angle. When the fiber is compressed under circumstances where the fiber cannot bend to take up the length change, then the molecular structure wants to slip along this “fault line.” When the compression is minor, no real slippage takes place but heavy strain is put onto this fault line. The resulting change can be seen only as a faint line, although it can be made more pronounced visually in polarized light.

When the compression is substantial, actual physical movement takes place causing actual displacement. When the stress is removed, the molecules rearrange themselves so as to heal the damage, but the physical evidence remains in form as a distinct hump. Repeated stress and/or increased compressive stress eventually will cause complete filament rupture at this point in the filament. Progression of this phenomenon is shown in figure 6. Some researchers differentiate in nomenclature between the first two steps in this process by calling the first phenomenon Luder’s lines (Figure 7) and the second phenomenon kink bands (Figure 8); others lump both under the term kink bands.

For Kevlar®, tensile failure usually results in an irregular, elongated fracture zone. In a yarn or filament bundle, this manifests itself in irregular lengths of failed filaments (instead of each filament breaking at an imaginary transverse fracture plain). In addition the individual filaments separate in such a manner that splitting of filament ends is not uncommon (figure 9). Also a lack of the other features, discussed later, points to a simple tensile failure. Primary kink bands may appear near the failure due to the snap back energy released on breaking. In some circumstances, the tensile failure is hastened by fatigue, which weakens the filaments. Yet the occurrence of irregular fracture zone and split filament ends identify these as tensile failures.

For Nomex® tensile overloading is more granular in texture at the fractured ends, as opposed to the fibrillar, multi-axial splitting of a Kevlar® fiber break. This granular fracture is typical of low crystallinity solution spun fibers, and the fracture plane is generally perpendicular to the fiber axial direction (figure 10). Occasionally, tilting of the fracture plane can occur from the formation of relatively short and relatively axial splits. The absence of a large content of crystalline phase and inherent void content are two likely contributing factors to muted axial crack elongation during fracture.

Abrasion failures are precipitated by the fiber(s) rubbing on each other in the knitted loop in a plain and lock stitch, over each other in a lock stitch, and/or on the rubber inner tube or outer cover. The internal abrasive wear manifests itself by fibrillation (figures 11 and 12), powdery appearance as if the filament has been ground, general debris with the yarn bundle, lighter color, or distortive flattening of the filament bundle. This kind of wear is due to movement of yarns under high radial loads and manifests itself to significantly greater effect in Kevlar® versus Nomex® yarns.

For compression and shear fatigue, repeated loading is required to induce significant strength loss. A first compression cycle may cause strength loss only if it is extremely severe. To find the failures, one should look for kinked (buckled) regions in the filaments. For filaments, 500X magnification and an optical microscope are sufficient, but scanning electron microscopy is also useful. Since fatigue weakens the
filaments, a fatigued area will become the locus of failure in any subsequent tensile overload. Kinked areas are also more susceptible to chemical and hydrolytic attack and oxidation.

Degradation, caused by chemicals, heat or oxidation, changes the molecular entity of the filaments. The change for a cause of failure in hose would be large enough to significantly decrease the number average molecular weight to negatively affect tensile strength of the fiber. Chemical degradation may be highly localized to a zone along the length of the hose. Wicking action of the filament bundle may carry low viscosity fluids along the yarn bundle and accelerate strength loss to a tensile failure in local areas of the hose where stresses have weakened the filaments to a greater degree. Strong acids, bases and certain other chemicals, especially at elevated temperatures, can cause degradation in the filaments of both Kevlar® and Nomex®. Discolored yarns (brown or green), as well as streaks throughout the filament bundles, are a good leading indication of such chemical degradation.

Failures of hoses with knitted reinforcements of aramid fibers commonly occur in two zones along the hose length, at or near the smallest bend radius of largest curvature and at or near the hose connections. Under the assumption in this paper of a dominant yarn contribution to the hose failure, the hose failure is typically a rupture (burst), where the hose no longer supports the working pressure. Given this postulate, the ultimate failure mode of the yarn in knitted hose is by tensile overloading. But more relevant information to determine the root cause is drawn from observations and conclusions of the contributing modes.

For knitted hose, the modes of mechanical deformation leading to a decrease in strength of the yarn are transverse and axial compression and yarn-to-surface displacement, while chemical deformation or scission of the polymer chain is accomplished through mechanisms of hydrolysis at temperature. For the latter case, a record of the environmental conditions would point the analysis toward a cause. In a case where the hose midline wall temperature (i.e. the physical location of the yarn in the hose wall) is greater than the recommended upper limit of continuous use of the fiber, there is an expectation for the thermal environment to be a root cause. A simple estimation of the midline temperature can be made by taking the mean average of the interior fluid temperature and the temperature of the surrounding medium outside of the hose. For the former points to the mechanical nature of the fatigue within the limits of temperature, the specific causes may be due to a confounding of factors, such as knit tension and knit design, hose shape and hose coupling performance relative to the specified testing.

In a case for coolant hoses comparing the performance of Kevlar® versus Nomex®, there is a substantial difference in hose lifetime to failure in fatigue testing by a pressure-vibration-temperature (PVT) protocol due to the significant advantage of Nomex® in yarn and surface wear character. Yet within Kevlar®, strength loss due to compression related defects (both axial and transverse) can be overcome to an extent by modifying the fiber’s microstructure to achieve a lower modulus and higher elongation at break. The adjusted microstructure accommodates greater compressive strains and longer life of the hose is achieved in PVT. This data is displayed in figure 13 for 19mm inner diameter EPDM heater hoses. Kevlar® 119 is a lower modulus and high elongation at break (at standard twist levels) Kevlar® fiber useful for more demanding Kevlar® knitted hose applications, such as heater hose.

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Considering the advantages to compressive and wearing modes, Nomex® yarn is suited for heavier duty applications in low pressure knitted hose. A failed yarn bundle of Nomex® from a turbocharger hose is shown in figure 14. The fracture surface of the fiber observed is one in which the filaments have splits at their ends due to a tensile overload. The lengths of the cracks are not widely distributed, and the bundle appears to have broken completely, in that all filaments at the location have seen a relatively similar deformation mechanism. In this case, the mechanism appears to be one in which flex fatigue weakened the filaments by creating axial cracks likely developed from residual and inherent voids in the fiber, which in turn fractured to tensile overloading. By examining the hose section at the failure (shown figure 15), the failure is close to the end termination of the hose, which is a high strain area for the yarn in the hose as the yarn is subjected to transverse shear stress in the hose wall of the hoop load transitioning to an axial load at the coupling. In this case, an adjustment of the knit density (needle and course spacing) of the yarn on the hose to optimize cover factor of the yarn over the tube per strikethrough adhesion could have balanced the transition loads at the coupling.

Summary:

As vehicle engine compartment temperature requirements continue to climb above 130°C to 200°C and charged air temperatures from turbocharging reach as high as 220°C, the demands on the stability of rubber hose materials will continue to increase. For hose reinforcement at these temperatures, Kevlar®, for temperatures below 165°C, and Nomex®, for temperatures below 220°C, fibers are well suited when used in an appropriate knit design. However, determination of exact root causes for hose failure during fatigue testing by PVT in the hose product development cycle is a complex task that involves contributions from both the rubber matrices and reinforcing yarn. Under the assumption of failure of the hose during fatigue due to the yarn, strength loss of the yarn due to exposure to temperatures greater than the continuous use limit begins with the examination of the record of the temperature during manufacturing (i.e. vulcanization) and at the hose midline through the length of the hose and determination of fiber molecular weight. Subsequent evaluation of the physical modes of defect formation in fatigue in knit patterns with Kevlar® focuses around the relative amounts of kink banding (for axial compression) to crushed filaments (for transverse compression) to the degree of fibrillation throughout the hose length and particularly at the smallest bend radius of largest continuous curvature and the hose end terminations (coupling). Various types of Kevlar® (Kevlar® 29, Kevlar® 29AP, and Kevlar® 119) and a combination of Kevlar® and Nomex® yarns as a twisted ply may be used to achieve the desired level of hose life in particular knit design. Physical modes for Nomex® fiber failure in fatigued hose involve the development (through flexing) of axial cracks extending through the fiber length initiated by inherent micro-structural voids and eventual tensile overloading to the weakened structure of the fiber. Including the examination of the yarn, to the whole hose failure analysis can save considerable time and expense in the hose development cycle by avoiding unnecessary rubber compound reformulation, and consultation with the fiber manufacturer to the hose application for the best first estimate for fiber properties and type will further increase speed to market of new hose products.
Figure 1: Low pressure automotive hose with knitted reinforcement, cover layer removed between clamping regions at hose ends

Table 1: Physical property comparisons of Kevlar® and Nomex® yarns at 1.1 twist multiplier

<table>
<thead>
<tr>
<th></th>
<th>Kevlar® T-956</th>
<th>Nomex® T-430</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tenacity (cN/tex)</strong></td>
<td>203</td>
<td>45</td>
</tr>
<tr>
<td>(N/mm²)</td>
<td>2925</td>
<td>-</td>
</tr>
<tr>
<td><strong>Modulus (N/tex)</strong></td>
<td>44</td>
<td>8.4</td>
</tr>
<tr>
<td><strong>Elongation at break (%)</strong></td>
<td>3.6</td>
<td>28</td>
</tr>
<tr>
<td><strong>Loop-tenacity (cN/tex)</strong></td>
<td>95</td>
<td>43</td>
</tr>
<tr>
<td><strong>Loop-elongation (%)</strong></td>
<td>2</td>
<td>18</td>
</tr>
<tr>
<td><strong>Heat shrinkage (%)</strong></td>
<td>&lt; 0.2</td>
<td>0.4</td>
</tr>
<tr>
<td><strong>Density (g/cm³)</strong></td>
<td>1.44</td>
<td>1.38</td>
</tr>
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Heat shrinkage in dry air at 285 °C.

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Figure 2: Kevlar® breaking strength in the form of tenacity as a function of time at temperature.

Figure 3: Nomex® breaking strength in the form of tenacity as a function of time at temperature.
Figure 4: Kevlar® and Nomex® resistance to ethylene glycol at temperature as a function of time in days.

Figure 5: Common Kevlar® fiber damage types

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Figure 6: Process of yarn break at a kink band

Figure 7: Luder’s line of primary kink bands indicating compressive load on the fiber.
Figure 8: Kink bands – showing a dislocation of the filament cross section at shear planes.

Figure 9. Axial splits from tensile overloading.

Figure 10. SEM image of fracture Nomex® filaments in tensile mode.
Figure 11. Fibrillation of the Kevlar® filaments from abrasion fatigue optical micrograph.

Figure 12. Fibrillation of the Kevlar® filaments from abrasion fatigue scanning electron micrograph.

Figure 13. Burst pressure of 19mm heater hoses reinforced with Kevlar® and Nomex® yarns before and after PVT testing.

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Figure 14. SEM image of fracture Nomex® filaments from hose.

Figure 15. Section of failed hose as received

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