Purity Requirements for Fuel Lines

Development, Testing and Processing Low-Extractable Multilayer Tubes for Fuel Lines

Biogasoline fuels such as E10 and improved fuel injection systems to reduce consumption have changed the specifications for gasoline fuel lines. As a result, extractables from conventional components of the fuel system can clog injection nozzles in individual cases and lead to critical situations. To eliminate this, new low-extractable multilayer tubes for fuel lines were developed.

Changes in fuels and optimizations in injection systems require modified tubing systems. From specific OEM instructions, the MLT 4800 and 4900 multilayer tubing systems were developed for this purpose (© Evonik)

For plastic fuel lines, polyamide 12 (PA12) has a track record of decades because of its outstanding low-temperature impact strength, chemical resistance and the general mechanical behavior of this class of material. In the 1990s, the stricter laws for hydrocarbon emissions led to the introduction of fuel lines of multilayer tubes with a barrier layer, e.g., of fluoropolymer such as polyvinylidene fluoride (PVDF) or ethylene-vinyl alcohol (EVOH). Because of cost pressure, multilayer tube systems with an EVOH barrier layer saw the strongest growth, among others, on the European market through the 2000s. They include the 4000 multilayer tube (MLT) series with the designations of the individual systems MLT 4300, MLT 4500 and MLT 4540, which were developed by Evonik Industries AG, Essen, Germany (**Title figure**). This MLT series meets requirements such as very good low-temperature impact strength, low fuel permeation through the wall, high resistance to aggressive fuels, high stress-cracking resistance, good processing by co-extrusion and thermoforming and easy mounting of plastic quick connectors.

New Fuel Types Influence Extraction Resistance

With the introduction of alcohol-containing gasoline fuels, e.g. E10 in Europe, the situation has changed. Alcohol-containing fuel can extract or leach components out of the wall of the tubes, which, under unfavorable conditions, may become concentrated in the fuel volume of the first fueling of the car. In parallel, the need to reduce consumption and improve the fuel combustion in the combustion chamber has led to new injection nozzles. Older models with a few relatively large orifices were replaced by small-pored nozzles, which generate a fine mist of gasoline and air.

Under particular, unfavorable ambient conditions, both trends lead to a higher risk that the gasoline injection nozzles in new vehicles may be clogged and the vehicle might not start. Due to the low fueling level after the vehicle assembly and a longer time of nonuse, this risk is highest when the new vehicle is still the responsibility of the original equipment manufacturer (OEM), i.e. before it is delivered to the customer. Even if these phenomena only occur very rarely, modern quality specifications of many OEMs require that this risk be avoided. For this purpose, Evonik has developed a new product series of low-extractable multilayer tubes for gasoline lines.

In advance of the development, it was necessary to specify test conditions for assessing the degree of extraction. For the determination, a distinction is made between different processes (**Fig. 1**). They include methods concerning the compo-

Fig. 1. Set-up of a roll peeling test for determining the layer adhesion of a multilayer plastic tube with a tensile testing machine (© Evonik)

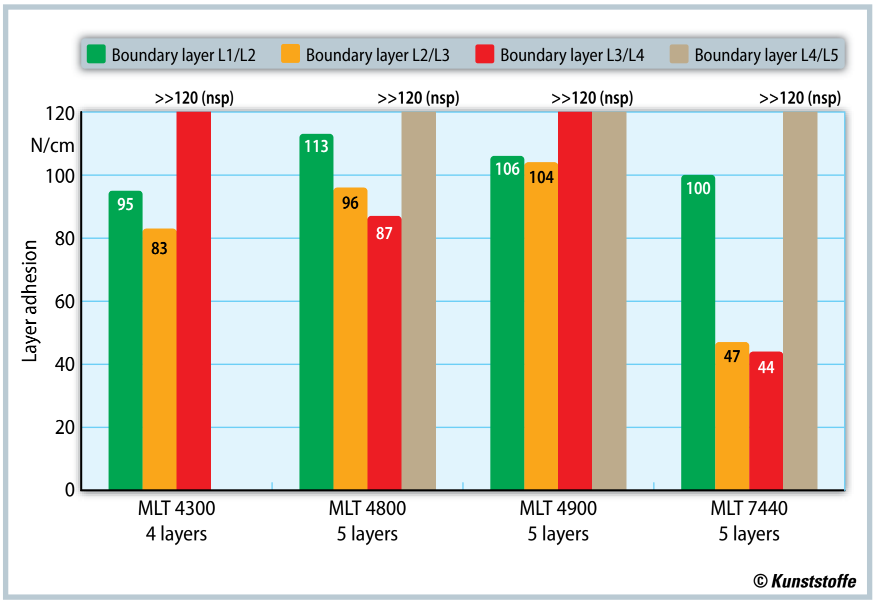

Fig. 2. The layer adhesion (from the outer layer to the inner layer) of the developed 8x1mm multilayer tubes exceeds the market requirements (SAE J2260: 10 N/cm, nsp = not separable) (source: Evonik)

nents that are extractable from the pellet stock of a molding compound (e.g. EN ISO 6427) and also processes for determining the extractions from co-extruded semifinished products, for example fuel lines. The extraction methods on co-extruded semifinished products are described in international standards such as SAE J2260 (11-2004) or else in OEM specifications such as the VW TL 52712 (08-2016).

The determination of the extractable components according to EN ISO 6427 takes place directly on the pellets. For this purpose, the polymer sample is extracted with methanol and re-weighed after subsequent drying. The complete extract content is determined from the weight decreases without distinguishing between soluble and insoluble extracts.

Determination of the Extract Content from Co-extruded Semifinished Products

In contrast to the extraction method on the pellets, multilayer tubing systems are used for the application-level tests as per SAE J2260 or as per VW TL 52712. To this end, a tube portion is filled completely with a defined test fuel, without bubbles, and tightly sealed and stored at 60 °C for 48 h (SAE J2260) and 96 h (VW TL 52712) respectively, depending on the method used. Then the extractant is emptied into a sealable glass vessel, the tube piece is rinsed with a defined amount of fresh test fuel and also filled into the glass vessel. After storage of 24 h at a given temperature (0 °C for SAE J2260 and 23 °C for VW TL 52712 respectively) , the soluble and insoluble components are separated from one another and are each gravimetrically determined. For reproducible results, the drying conditions must be precisely maintained.

In SAE J2260, CE10 is specified as test fuel. According to ASTM D471, CE10 consists of 90 vol. % Fuel C (50 vol. % toluene, 50 vol. % isooctane) and 10 vol. % ethanol). In contrast to this, in the test method described by Volkswagen, FAM B is used as test fuel. It consists of 84.5 vol. % FAM A (as per DIN 51604-1/-2: 50 vol. % toluene, 30 vol. % isooctane, 15 vol. % diisobutylene and 5 vol. % ethanol), 15 vol. % methanol and 0.5 vol. % water. Due to the high alcohol content, in particular the relatively large proportion of methanol, FAM B is considered as more critical than CE10 as regards extraction, permeation and swelling behavior.

In a multilayer fuel line, all inner layers as far as the barrier layer contribute to the extractions. Classification of the extracts according to their quantity and solubility is therefore significantly more complex than in the case of extraction from pellets, in which only one molding compound is generally tested, not all molding compounds of the entire system of a multilayer tube.

Parameters for Valid Test Results

The test method described by VW (TL 52712) and also the procedure described in SAE J2260 for determining the extraction resistance of a co-extruded fuel line represent a pragmatic approach. They allow a relatively quick statement about whether a co-extruded multilayer tube is suitable for use as fuel line. The focus here is on the applications-relevant qualification test and not the complete analytical statement about the quality and quantity of the extractable components. However, to generate reproducible, and therefore valid, test results in this way, some points in the test procedure must be looked at critically. Among the most important influencing parameters are the nature and amount of the solvents as well as the temperature used for extraction, and the precipitation of the extracted components. These influencing parameters also determine the steps for which, in the above-described test methods, a particular influence on the reproducibility of the test results can be observed.

Solvent: The nature and, first and foremost, the amount of the solvents used determine the extractability and the solubility of the substances extracted »

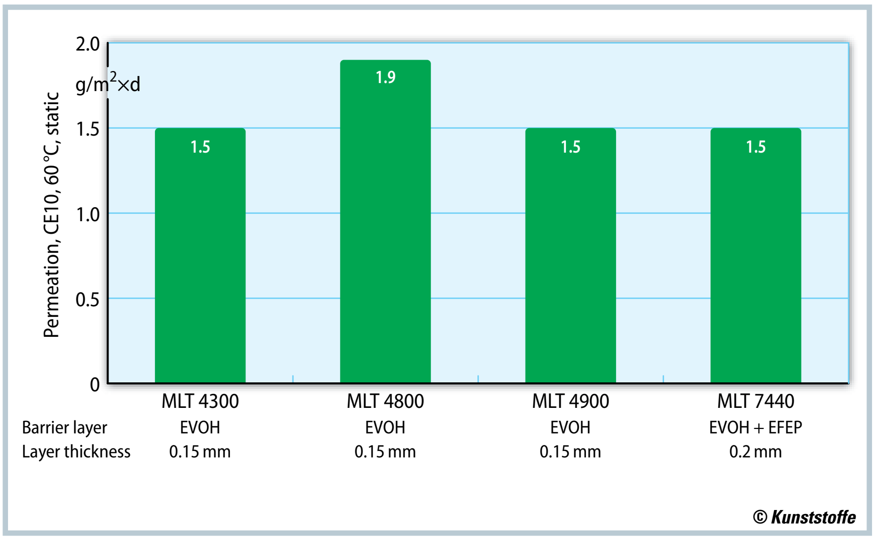

Fig. 3. The measured permeation (8 x 1 tubes acc. to SAE J30) confirms that the new multilayer tubes can be used for emission-critical applications (source: Evonik)

from the tubes. The solvent is determined by the test method, so that in the laboratory routine only different application quantities have an effect on the extractability and the solubility of the extracts. It is therefore necessary to use a defined amount of fresh test solutions for all steps of the analysis if possible, i. e. for filling the tubes, as well as for rinsing during draining the tubes and rinsing the filtered residues on the polyethersulfone (PES) filter. An influence on the concentration, and therefore the solubility of the extracts in the various test fuels can also be expected if no vacuum is used in the filtration of the insoluble components. Without vacuum, the filtration takes considerably longer and the highly volatile components of the test fuels can evaporate during separation on the filter and thereby increase the concentration of the extracts.

If the critical solubility concentration of an extracted component is exceeded in the process, elevated values for the content of insoluble components are systematically obtained. The proportion of soluble components is reduced correspondingly.

Temperature: The temperature is also a critical influencing parameter for the solubility of the extracted components. In general, the solubility increases with rising temperature. The solubility of the extracts into insoluble and soluble components is performed by filtration, as described above. Before filtration, the solution or suspension is kept at room temperature (VW TL 52712) or at 0 °C (SAE J2260). The influence on solubility is apparent in that more insoluble components are found at low temperatures, and less soluble components during further treatment. However, the totality of the soluble and insoluble components remains constant. Only the use of an alternative test fuel also has an effect on the totality of the soluble and insoluble components.

Consistent Development

When the above-described tests are performed on existing multilayer tube systems from Evonik, MLT 7440, which has been in use internationally for many years, shows very low extraction. This is a fuel line with an electrically conductive barrier layer of EFEP (ethylene-fluoroethylene copolymer).

In Europe, MLT 4300 with an EVOH barrier is predominantly used. Its structure served as the basis for developing a new generation of low-extractable fuel lines. A plasticized PA12 outer layer shows

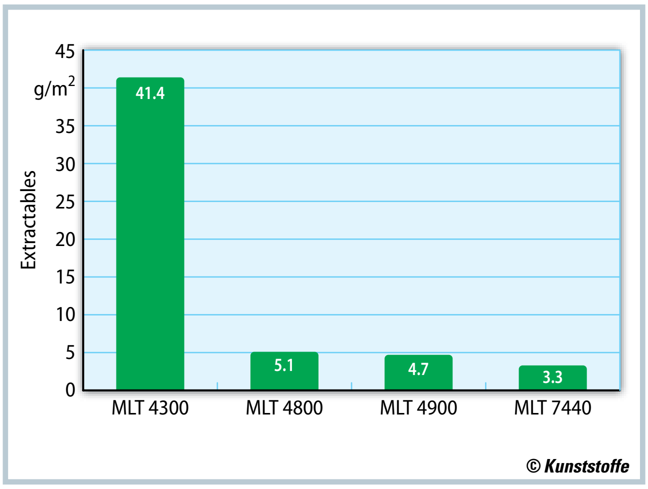

Fig. 4. The soluble extractables at 23 °C with FAM-B laboratory fuel as per VW TL 52712 in the case of 8 x 1 mm tubes show that the new MLT product range features significantly less extractables (source: Evonik)

The Authors

Dr. Jasmin Berger has been Senior Manager for compound development in innovation management at Evonik Resource Efficiency GmbH, Marl, Germany, since 2011, for the business field of high performance polymers; jasmin.berger@evonik.com

Dipl.-Ing. Olivier Farges is responsible for OEM marketing activities for the automotive field in the high performance polymers business filed at Evonik Resource Efficiency GmbH, Marl; olivier.farges@evonik.com

Dr. Jan Heimink has been Head of the polymer testing workgroup in the field of innovation management for high performance polymers at Evonik Resource Efficiency GmbH, Marl, since 2015; jan.heimink@evonik.com

Mario Resing is Extrusion Manager in innovation management at Evonik Resource Efficiency GmbH, Marl, for the business field of high performance polymers.

Service

References & Digital Version

- You can find the list of references and a PDF file of the article at *www.kunststoffe-international.com/3008432*

German Version

- Read the German version of the article in our magazine *Kunststoffe* or at *www.kunststoffe.de* a high chemical resistance and is of crucial importance for the mechanical properties such as elongation at yield and low-temperature impact resistance of the multilayer tube. It thus ensures the necessary flexibility for this application. The high performance of the entire system depends on the suitable incorporation of a permeation barrier by coextrusion using selected adhesion promoters (**Fig. 2**). EVOH was also used as a basis for the barrier layer in the newly developed fuel lines. The permeation is thus comparatively low, as with the MLT 4000 series systems that have been in use for about ten years (**Fig. 3**).

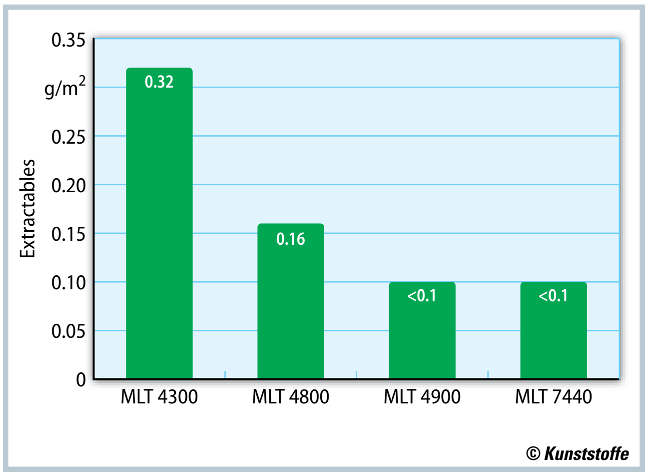

Fig. 5. Presentation of the insoluble extractables at 23 °C with FAM B laboratory fuel as per VW TL 52712 at 8 x 1 mm tubes. The insoluble extract concentration lies within the measurement accuracy range of the test method (source: Evonik)

Polymer Composition Is Crucial

As already mentioned for the test description, the extracts from a multilayer fuel line are principally determined by the layers lying within the barrier layer. This is determined by the basic polymer. The extractable oligomers are principally dimers and trimers, and, for lactam-based polyamides, also the monomers, such as caprolactam in the case of PA6. To an increasing extent, they are cyclic molecules. The tendency towards cyclization increases with the distance between the molecule ends; put in simplified terms, the oligomer content increases with reducing chain length (decreasing number of C atoms in the repetitive unit). Moreover, polymers with only one monomer, such as PA6, show higher oligomer contents than polymers with several monomers such as PA66. It is also critical whether the extracts occur as a precipitate in the fuel. Compared to polyamides based on lactams or amino acids, aliphatic PA612 shows a significant reduction in insoluble extracts after storage in fuel. If aromatic components are integrated into the polymer chain, the polyamide PA612 modified in this way shows reduced content of insoluble extract.

Besides the basic polymer, other additives in the polymer, such as plasticizers and stabilizers, also play a major role in the total extract content. Additives at different temperatures must be carefully chosen for long-term resistance during fuel contact. With the additional development of a low-extractable adhesion promoter, the two new systems MLT 4800 with an aliphatic PA612-based inner layer and MLT 4900 with a modified aromatic PA612-based inner layer were created. The content of insoluble and soluble extracts, as well as the total extracts, were significantly reduced (**Figs. 4 and 5**).

Processing with Dies without Thermal Separation

For manufacturing multilayer tubes, besides the extruders for melt treatment and the downstream ancillary units for calibrating the melt tube, the co-extrusion die is a particularly important component of a tube extrusion line. Dies with a spiral mandrel distributor have proven suitable for processing EVOH. Multilayer tube systems such as MLT 4300 and MLT 7440 can thus be produced in a stable process at high extrusion rates.

This also applies for the new series of low-extractable multilayer tube systems. Comparable commercially available material combinations are problematic because of the relatively large differences in melt temperature of the different polymer types during processing. The construction of the Evonik systems permits, besides a very low degree of extractables, also a precise temperature control across the layers, and reduces the melt temperature differences between adjacent melt streams. The use of dies with thermal separation is thus not necessary.

For finishing, the multilayer tubes 4800 and 4900 can be thermoformed using the temperatures and media that are conventional for PA12. Since fuel lines of PA12 are usually joined by means of plug couplings, the fitting disassembly force according to SAE J2044, besides the thermoformability, was another criterion in the development of these systems. All systems have already been successfully produced, while subjected to numerous customer tests with the support of Evonik, and met the required specifications.

Long-Term Tests for Series Use

In the approval procedure for multilayer plastic fuel lines, not only the static behavior of a line filled with fuel is determined over time, but the dynamic behavior of thermoformed, finished lines with series-fitted quick connectors was tested under defined temperature, pressure and movement cycle. The behavior of a typical line on the vehicle over several thousand hours is thus simulated realistically. The assessment and testing of the features of the aged lines are decisive for the approval of the materials. The three low-extractable multilayer tube systems MLT 4800, MLT 4900 and MLT 7440 presented above have withstood corresponding long-time aging and tests, or are currently undergoing corresponding aging tests.

Summary

As a result of changes in fuels and optimized injection systems, the demands on gasoline fuel systems have changed significantly, requiring the development of new, low-extractable multilayer tubes for lines. For this reason, a series of multilayer tube systems was developed, which, compared to the material systems previously available on the market, have very low extraction levels. Depending on the demand on the line on the vehicle, automotive manufacturers can choose between low-extractable multilayer tube systems MLT 4800, MLT 4900 and MLT 7440. ■