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Product Performance

Ageing properties of car fuel-lines; accelerated testing in "close-to-real" service conditions

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ABSTRACT

The use of ethanol-based fuels and tougher restrictions on fuel emissions put a higher demand on car fuel-line (pipe) systems. In this context, it is important to be able to establish and predict properties based on measurements on pipes exposed to real or "close-to-real" environments. This paper presents a new method to age pipes in accelerated "close-to-real" conditions. In this method, the pipe is exposed to circulating fuel on the inside and to air on the outside. The method/equipment allows for non-destructive mechanical testing on "continuous" pipes. The usefulness of the ageing method/system was illustrated on polyamide-12 (PA12) pipes exposed to fuels with varying ethanol content at 50 °C and 110 °C for a maximum of, respectively, ca 3 years and 100 days. "Non-destructive" three-point bending as well as tensile testing was used to assess the ageing-induced changes in mechanical properties. The most conclusive information was that the lowest pipe extensibility (ductility) of dried, previously fuel-exposed pipes was observed at the end of the ageing periods and at the higher ethanol contents. In fact, optical microscopy showed that the tensile fractured pipes, exposed to 25/30 vol. % ethanol at 110 °C (100 h), showed no signs of macroscopic yielding. The trends were interpreted, based also on findings from previous work, as being due to the loss of plasticiser (possibly also PA12 monomers/oligomers) and material "degradation/annealing" processes, the latter involving possibly stabiliser issues.

1. Introduction

There is a need to understand and predict both short- and long-term behaviour of plastic pipes in vehicle fuel-line systems. The reasons are obvious; it is possible to obtain vehicles with improved long-term behaviour as well as minimum emissions of fuel-related species. Today, the most restrictive legislation is set by the California Air Research Board (CARB) and the Environmental Protection Agency (EPA). According to these legislations, emissions from passenger cars should not exceed 2 g (LEV I) of hydrocarbons during a 24 h simulation of a typical vehicle running condition, and even more restrictive legislations exist (LEV II (0.5 g/car/24 h) and PZEV (0.054 g/car/day)) [1,2]. The actual legislations in use is decided by the local authorities, and it is up to the manufacturers whether they will deliver cars that fulfil the required level or even more restricted levels. Since local authorities will probably require lower emission limits in the future, plastic pipes are facing a real challenge.

This challenge lies in manufacturing pipes with sufficient time-stable mechanical and barrier properties. The pipe performance is closely related to the chemical and physical properties of the pipe material; this includes, for example, the molar mass of the polymer and the polymer-plasticiser interactions. In fact, it has been shown in

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a previous paper that chemical/physical polyamide-12 (PA12) pipe properties do change with time, and new types of fuel containing ethanol have a negative effect on the pipe performance [3].

Accelerated testing at elevated temperature is a must due to the long service times. A standard, such as SAE J2260, does not consider ageing at higher temperatures in a satisfying way. Both the testing and evaluation methods for non-metallic pipes in fuel systems have to be improved. Vehicle conditions vary mainly with the environment and driving styles, and to include these variations in an improved extrapolation test method requires a good knowledge of ageing factors.

This paper describes a new technique to age fuel pipelines in accelerated/elevated temperature "close-to-real" environments/conditions. The properties of the pipe specimens aged with this technique are evaluated with mechanical tests. Few investigations have been published prior to this paper, and usually with fully immersed material samples [4]. Here, however, the specimens are exposed to an environment close to which the fuel lines will experience in a vehicle, that is, with flow of fuel on the inside and air on the outside. The present tests highlight the effects of several factors, including outside environment (air), fuel type (ethanol content) and temperature, on the mechanical properties during ageing. Tests have been conducted on PA12-based "state of the art" multi-layer pipes as well as on single layer PA12 pipes. However, to limit the number of parameters influencing the pipe properties, the work presented here has been performed on the single layer pipe. The multi-layer pipes are designed to improve the barrier properties [5,6] using, for example, a poly (vinylidene fluoride) (PVDF) layer. It should be mentioned that the main part of the mechanical analysis is made on dried pipes and not on pipes under fuel exposure. In this way it was easier to correlate, e.g., plasticiser loss with the mechanical performance; in the wet state (fuel-swollen pipe) the effect of this loss may be masked by any eventual fuel-induced plasticisation.

The most common temperature range in standard ageing tests for fuel lines is 38 °C to 60 °C [1,2]. In the present fuel tests a high (110 °C) and a low (50 °C) temperature was chosen. The low temperature condition will simulate the ageing of a material close to its glass transition temperature [7,8], and where the "mechanical" ageing is probably dominated by the loss of plasticiser [9]. The loss may also involve other volatile/extractable species including PA12-related material (monomers and oligomers). However, we believe that they play a minor role relative to that of the plasticiser and these are consequently not discussed further in the following. A high temperature (110 °C) was chosen primarily to accelerate the testing to allow e.g. for the analysis of mechanisms that are slow at lower temperatures. However, it is also possible that the vehicle fuel-system will experience this high temperature during service [3]. During the high-temperature testing, as shown previously [3], ageing is also influenced by chemo-physical changes of the pipe material. It should be noted that 110 °C is well above the glass transition of the dry plasticised PA12 polymer [10,11] and that the supplier does not recommend continuous exposure to temperatures above 90 °C for this material.

The first step here was to understand the material behaviour in air at short times/accelerated conditions. Material property changes were expected due to e.g. loss of plasticiser. In the second step, pipes were exposed to fuels and the methodology here was based on the following criteria: 1) the "real" service-temperatures had to be considered, 2) the fuel had to be circulated to simulate "real" running conditions and 3) a fuel composition corresponding to "real" conditions had to be used.

2. Experimental

2.1. Materials

PA12 pipes were supplied by Cooper Standard, Coventry, United Kingdom. The pipe material had a mass-average molar mass of $\overline{M}_{w} = 126\ 000$ g/mol, a number-average molar mass $\overline{M}_{n} = 72\ 200$ g/mol and a polydispersity = 1.8 (according to the producer). The pipes consisted of one layer plasticised PA12 (mono). Our analysis of extracts [3] indicated a content of ca. 10 wt. % of N-(n-butyl) benzenesulfonamide (BBSA). The actual plasticiser was determined by mass spectroscopy.

2.2. Ageing test procedure

2.2.1. Conditioning before testing

Prior to the accelerated tests, pipe samples were conditioned at 23 °C and 50% relative humidity. When the samples had achieved equilibrium weight, they were transferred to the testing facility. In the case of the fuel tests, the pipes were connected to a fuel-line system with fuel mixtures. Specimens were removed for mechanical testing at various times during the exposure period.

2.2.2. Ageing in air, method A

Pipes were aged for 24–1500 h at 80 °C, 100 °C, 120 °C, 130 °C and 140 °C in a hot air circulating oven (Weiss WT11 180). A 1500 h ageing time was chosen since it is a standard ageing time in industry [12]. At least 2 pipes were removed at each specified time, conditioned at room temperature for one week and then tested with respect to bending resistance (vide infra) at two positions.

2.2.3. Ageing in contact with fuels at 110 °C, method B

By using authentic car components, including fuel tanks with valves and pumps, the internal flow and pressure could easily be adjusted to "correct" values. To compensate for the loss of fuel due to permeation through the pipe, the fuel was frequently replaced. Since a loop was long, incorporating several pipe samples, the start-up and shut-down times were long, implying also a slow change between the room and target temperature (110 °C). Fuel lines with quick connectors and stainless steel pipes formed closed circuits. These circuits, containing different fuels, were connected to a reservoir, a pump and valve systems in order to simulate "in car" conditions (Table 1, Fig. 1). Each circuit consisted of several test objects, which could, due to quick connectors, be dismantled easily during a fuel change or removal. Each circuit, which consisted of ca. 200 m of plastic pipes, was used for a specific combination of pipe and fuel system,