

Ageing properties of polyamide-12 pipes exposed to fuels with and without ethanol

K.J. Kallio^a, M.S. Hedenqvist^{b,*}

^aVolvo Car Corporation, Polymer Centre, SE-40531 Göteborg, Sweden

^bSchool of Chemical Science and Engineering, Fibre and Polymer Technology, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

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ABSTRACT

The chemical and physical properties of polyamide-12 (PA12) fuel pipes/lines, aged for ≤ 2400 h at 110 °C, have been investigated. The pipes, containing fuel with or without ethanol, were either of a single PA12 layer, or of two PA12 layers surrounding a poly(vinylidene fluoride) barrier layer. The molar mass of the inner surface region obtained by size-exclusion chromatography was reduced during ageing, and optical microscopy revealed a surface that was partly dissolved in the presence of ethanol. Infrared spectroscopy revealed a rapid loss of plasticiser, especially in the presence of ethanol, and the fuel contained plasticiser and other polymer related components. Immersion tests at 60 °C showed that the swelling of the pipe and the amount of dissolved material were greatest for the fuels with intermediate ethanol content (50 vol.%). Aged samples experienced an increase in melting point, presumably, to a large extent, due to the loss of plasticiser and/or PA12-related components. In addition, for several samples, the crystallinity seemed to increase with ageing.

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1. Introduction

The design freedom and the high performance/weight ratio have led to the use of plastics even in fuel delivery applications. The main advantages in fuel systems are corrosion resistance, sound isolation, vibration damping and chemical resistance. However, one drawback is the normally strong temperature and time dependence of plastics; a fact that requires high skill when selecting materials for such a “demanding” application.

In this work, the behaviour of plastic fuel lines, aged in different environments, was investigated. Fuel emissions from fuel lines are dealt with in several studies, and they report a reduced emission by the use of different barrier layers [1,2]. The emissions are measured in both complete vehicle tests and as components in mini-sealed housing evaporation tests. The problem with these tests is that they require a long time for equilibration [3,4]. For the last 20 years, polyamide-12 (PA12) was and is used as fuel line material due to its relatively low cost and good mechanical properties. The barrier properties of polyamide-12 alone will not meet the required hydrocarbon emission levels set out in present legislation, and the pipes are now therefore produced with a barrier layer. Materials that are, or have been, used in the barrier layer include poly(vinylidene fluoride) (PVDF), copolymers of

tetrafluoroethylene and perfluoropropylvinylether (PFA) or hexafluoropropylene (FEP), terpolymers of tetrafluoroethylene, hexafluoropropylene and vinylidene fluoride (THV), and poly(butylene terephthalate) (PBT). These materials require tie layers, especially if more than two layers are involved [5,6]. Still, layer delamination may be a risk to consider.

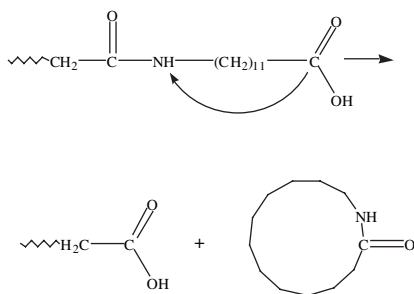
In order to understand what happens during ageing of PA12, it is necessary to understand its polymerisation mechanisms and overall properties. Since PA12 is polymerised from laurolactam by polycondensation, it is sensitive to hydrolysis. However, the water absorption is lower than for PA6, mainly due to its higher hydrocarbon-to-amide ratio [7]. The ageing behaviour of PA12 involves changes in crystallinity, extraction of plasticizers and low-molar mass PA12-related species. Reactions with oxygen and fuel components may cause chain scission or crosslinking [8].

Basically, three different mechanisms of PA12 thermal degradation in inert and oxidative environments have been proposed (Scheme 1). Lüderwald and Merz [9] suggested that the degradation of poly lactams at 170–400 °C using mass-spectrometry, occurred by ring-chain equilibration or basically through intramolecular exchange (Scheme 1.1), but cis-elimination with cleavage of amide bonds was also mentioned and favoured for diamines (Scheme 1.2). Also Ballistreri et al. [10] found intramolecular exchange and cis-elimination as degradation mechanisms, they suggested monomer and dimer lactams to be the primary products of thermal degradation of PA12, as determined by temperature-time resolved mass-spectrometry up to 500 °C. The main

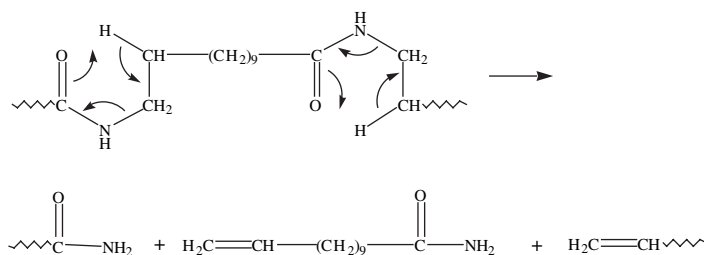
* Corresponding author. Tel.: +46 8 7907645; fax: +46 8 208856.

E-mail address: mikaelhe@polymer.kth.se (M.S. Hedenqvist).

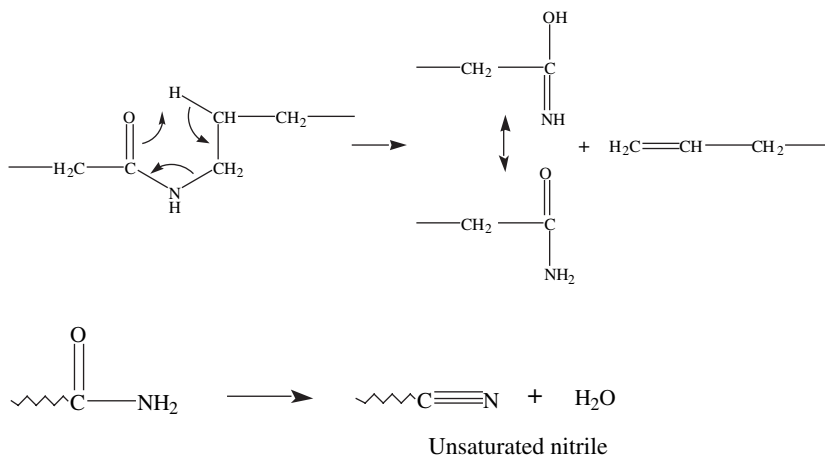
1.1 Intramolecular exchange



1.2 Cis-elimination with alkylamide bond splitting



1.3 Cis-elimination and dehydration



Scheme 1. The three mechanisms of thermal degradation in inert and oxidative environments of PA12 [9–12].

mechanism suggested was the intramolecular exchange between amide groups (Scheme 1.1). In contrast, Ohtani et al. [11], found unsaturated nitriles and lactams using pyrolysis-gas-chromatography mass-spectrometry at 550 °C. They proposed cis-elimination and dehydration to nitrile to be the main degradation mechanism (Scheme 1.3). Studies conducted on PA12, with flame-retardants by Mailhos-Lefiere and Sallet [12], suggested cis-elimination, homolytic cleavage and intramolecular exchange to be the main thermal degradation mechanisms in inert atmosphere up to 580 °C. Degradation products were mainly nitriles, lactams and hydrocarbons with favour of lactams for PA12. The degradation products

produced at 550 °C under a flow of nitrogen or air, identified by Levchik et al. [13], were lactams and unsaturated nitriles.

Hydrolysis is considered as a possible mechanism causing performance loss of PA11 when exposed, at 140 °C, to oil with a small amount (1 wt.%) of water [14]. In contrast to pure hydrolysis, the reversibility of the reaction: amide + water \leftrightarrow acid + amine, indicated a balanced reaction here. Results by Feldmann and Feinauer [15] showed that the hydrolysis-polycondensation equilibrium for PA12 in the molten state was temperature-dependent; an increase in temperature decreases the equilibrium water value. Jacques et al. [14] showed that the hydrolysis-polycondensation

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