Polymer Degradation and Stability 111 (2015) 7–19

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Monitoring the effect of chlorine on the ageing of polypropylene pipes by infrared microscopy

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A R T I C L E I N F O

Article history:
Received 5 August 2014
Received in revised form
4 September 2014
Accepted 7 October 2014
Available online 16 October 2014

Keywords:
Chlorination
Polypropylene
Degradation
Ageing
Antioxidant
IR microscopy

A B S T R A C T

The effect of hot water and chlorinated water at 95 °C on differently nucleated random polypropylene pipes was analysed with respect to the chemical changes occurring to the polymer and antioxidants (AOs). Infrared microscopy (μFT-IR) was used to monitor the loss of the AOs as well as to identify their degradation products during ageing. For the quantification of the primary AO, 1, 3, 5-Tris (3, 5-di-tert-butyl-4-hydroxybenzyl)-2, 4, 6-methylbenzene (AO-13) in a mixture with Pentaerythritol tetrakis (3-3, 5-di-tert-butyl-4-hydroxyphenyl) propionate (AO-18) and the processing stabiliser tris(2,4-di-tert-butylphenyl) phosphate (PS-2) in PP-R, a new μFT-IR method has been developed and the results were supported by extraction → HPLC. Degradation products of phenolic AOs were profiled for the first time across the pipe wall using μFT-IR. Time and space resolved content of AO-18 and AO-13 left in the pipes with time was quantified. For both ageing conditions, AO-18 and AO-13 exhibited a bilateral loss from the wall of PP-R1 whereas in PP-R2, the loss was mainly unidirectional. Oxidative induction time (OIT) measurements of mechanically prepared samples across the pipe wall also validate the bilateral and unidirectional loss profiles of AOs. The loss in average molar mass of the polymer as a result of chain scission was analysed by gel permeation chromatography. The linear relations drawn for molar mass against the relative content of AOs explain that the deterioration of the pipes was accelerated with chlorinated water. From the substantial differences in the AO loss coefficients which were calculated using μFT-IR, it can be speculated that nucleation of the PP-R exerts an influence on the depletion of AOs.

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1. Introduction

PP is a highly versatile thermoplastic used for both short term and durable applications. A very important one in the latter category is pipes and fittings which are used to transport diverse liquid media. Transportation of water through polyolefin pipes spans a history of more than fifty years [1,2]. Depending on the final application of the transported water various disinfection methods have been used which can be classified as physical (UV radiation, solar disinfection, thermal etc.) and chemical (chlorine, chlorine dioxide, ozone etc.) [3]. A widely used disinfectant to treat both drinking water and waste water is chlorine because of its strong oxidising effect, widespread availability, and storability [4]. However, from previous studies it is evident that the chlorinated water has the potential to initiate the degradation of polyolefins [5].

Studies on the degradation of polyolefins by chlorinated water were mainly carried out on polyethylene (PE) using moulded plates, dog bones or thin films as test specimen, and immersing them in chlorinated water [6,7]. Sealed PE pipes containing pressurised chlorinated water as inner medium were aged as described by WIS 4-32-08 [8,9]. Even though, control of crucial testing parameters such as pH, chlorine concentration and temperature of the ageing medium throughout the experiments was not maintained.

As a rule, polyolefins can only be used in durable applications when compounded with stabilisers which ensure the longevity in different environmental conditions where oxidation of the polymer accompanied by chain scission is the typical process reducing the life time. The loss of AO activity which can be the result of either extraction into the inner medium or chemical consumption by reaction with various active species formed in the ageing medium is a prevalent step during ageing [5]. Subsequently the polymer undergoes chain scission which then leads to a loss in mechanical strength and ultimately a reduction in the life time of pipes as shown for PE pipes exposed to chlorinated water [6,8,10]. From an

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http://dx.doi.org/10.1016/j.polymdegradstab.2014.10.006
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Table 1
Content of AOs present in PP-R1 and PP-R2.

Sample	AO-18 (wt.%)	AO-13 (wt.%)	PS-2 (wt.%)
PP-R1	0.23 ± 0.01	0.25 ± 0.01	0.08 ± 0.005
PP-R2	0.17 ± 0.01	0.43 ± 0.03	0.07 ± 0.003

analytical point of view the effect of chlorine on the deterioration of PE pipes was assessed by studying the AO depletion. For this purpose the AO content across the pipe wall was profiled by measuring the oxidative induction time (OIT) of samples mechanically prepared. In the same sense the reduction in average molar mass was studied by analysing material scraped from the inner surface of the pipes [5,6].

When pipes are exposed to liquid media from the inside the degradation of the polymer initiates from the inner surface and then progresses into the wall. In order to understand the effects of ageing media on pipes in a quantitative manner it is therefore stringently necessary to analyse the changes occurring with a high spatial resolution.

The molar mass distribution can be determined by gel permeation chromatography while the chemical changes inferred to the polymer as a result of oxidation can be determined from IR spectroscopy [5,11,12]. However, a quasi-spatial resolution can only be achieved by mechanical preparation of samples and analysing them individually. IR microscopy (μFT-IR) which combines the optical information available from light microscopy with the chemical information from IR-spectroscopy has found entrance into material science in the early 1980s [13]. The high spatial resolution and reproducibility of results make μFT-IR an attractive analytical technique to study the effect of inner media on polyolefin pipes, and its scope in compiling information such as the distribution of additives or spectral crystallinity across the wall of PP pipes with high spatial resolution has been demonstrated recently [14].

In this paper we show how μFT-IR can be used to monitor the effect of chlorine and hot water on commercial PP-R pipes. Particular attention will be given to the aspects of extraction and chemical consumption of additives.

2. Experimental part

2.1. Ageing test

Two grades of differently nucleated commercial PP pipes, PP-R1 (alpha nucleated) and PP-R2 (beta nucleated), stabilised with hindered phenolic AO of different contents were tested with hot water containing chlorine in a test system constructed by IPT Todtenweis, Germany. The flow rate of the medium was 0.5 L/min, the chlorine concentration was set to 4.0 mg/L and the pH value was adjusted to 6.8. The resulting oxidation reduction potential (ORP) was in the range of 900 mV. These testing conditions are in accordance with ASTM F 2023 [15]. The consistency of the testing parameters such as pressure, temperature, flow rate of the medium oxygen concentration, pH chlorine concentration was continuously monitored and a high stability was found. The chlorinated water was prepared by dissolving the chlorine gas which was generated at the anode of the electrolytic cell. The chlorinated water was removed from the circulation loop at certain time intervals and the amount was compensated by adding fresh chlorine water. Testing with hot water was done by hydrostatic pressure testing according to DIN EN ISO 1167-1 with deionised water inside and outside the pipe [16]. Both ageing tests were carried out at a temperature of 95 °C. The samples taken from the ageing medium was dependent on the ageing time or fracture of the material.

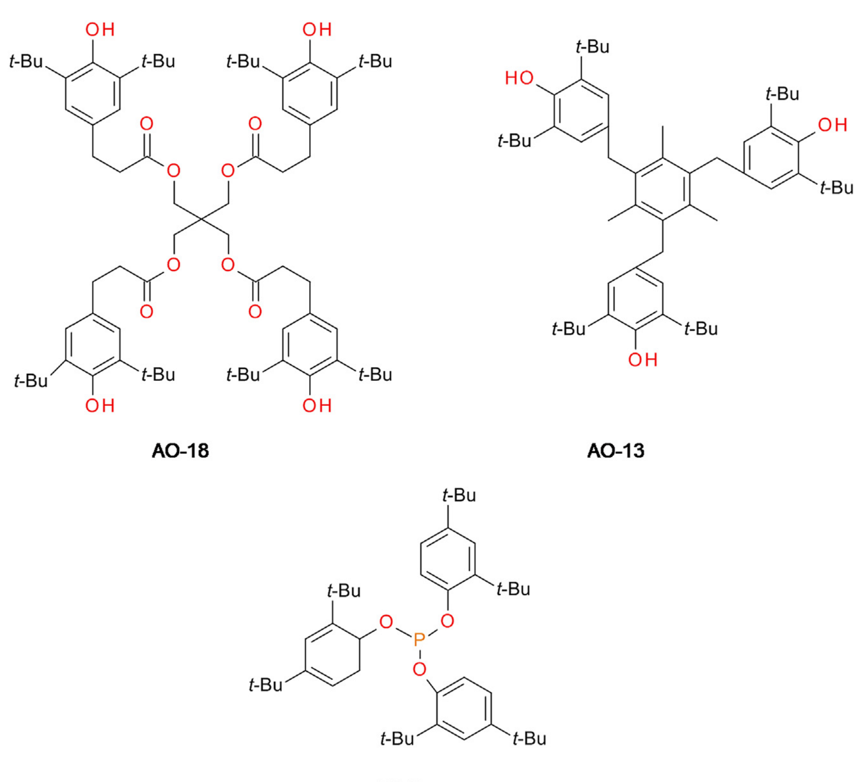

Fig. 1. Chemical structure of the AOs.

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