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A novel in-situ aging evaluation method by FTIR and the application to thermal oxidized nitrile rubber☆

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ABSTRACT

A novel in-situ aging evaluation method with high sensitivity was established. This method allowed simultaneous heating and UV irradiation of a sample under variable atmosphere, and in-situ Fourier transform infrared spectroscopy (FTIR) detection of the atmosphere change in a specially designed sealable cell. This method was applied to the evaluation of aging status of thermal oxidized nitrile rubber (NBR). In-situ FTIR signals of the atmosphere during heating of NBR samples were analyzed and the decrease of absorbances of characteristic bands with aging times were observed. The absorbances of the selected characteristic band (-N=C=S band) were correlated to the mechanical properties including recovery from bending (RFB), Young's modulus and elongation at break of the samples. Perfect linear relations between the absorbances of the characteristic band and mechanical properties were obtained. The method was extremely sensitive and had high sensitivity. Stability information or aging status of NBR could be obtained within several hours, and sample changes in very early stage (0–36 h) could be distinguished. The flexible and variable testing conditions provided the new method with great potential.

1. Introduction

Evaluation of ageing status is important to the analysis and development of polymeric materials. Understanding the material stability and degradation helps to make better choices and to avoid waste of products. Usually, this is accomplished by natural or accelerated aging test followed by the analysis of the structure and properties. Such aging tests are time-consuming and always lasts for months and in some circumstances even for years. Analytical methods such as Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), gel permeation chromatography (GPC), thermogravimetric analysis (TGA), pyrolysis gas chromatography-mass spectrometry (Py-GC/MS), nuclear magnetic resonance (NMR), scanning electron microscope (SEM), transmission electron microscopy (TEM), atomic force microscope (AFM), as well as tensile tests, compression tests, dynamic thermomechanical analysis (DMA) and so on, have been widely used for the detection of the structure and properties of aged materials but most of them are not sensitive to early aging [1–9]. Especially in industrial setting, when the development of advanced material requires prompt and fast analysis, the use of rapid and sensitive aging evaluation methods is highly desirable.

Investigators have made great efforts to establish new methods for rapid and sensitive aging evaluation. Chemiluminescence (CL), oxygen consumption and in-situ FTIR analysis are among the most effective ones.

CL method traced the early aging process by detecting the emitted light of oxidative reactions during thermal aging [10–12]. An instrument with two hot stages was set up to investigate thermal aging of hydroxyl-terminated polybutadiene (HTPB) [13–15]. It was found that CL maximum (t_{max}), initial rate or intensity (I_{ini}) and total CL emission (integrated inert CL peak) could be correlated to the relative tensile elongation of the rubber [16]. Since very weak emitted light could be detected by the photo multiplier tube, CL method was found to be really sensitive to early aging.

By means of oxygen consumption method, the remaining oxygen in a sealed chamber by gas chromatography (GC) was monitored to obtain its rate and amount during aging [17]. Thermal aging of different kinds of elastomers was studied via this method [18–24]. Due to the high sensitivity of GC, a detection of the oxygen consumption rate as low as 10^{-13} mol/(g s) has been reported, corresponding to decades of predicted lifetime for most elastomers

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[17]. The development of precise differential oxygen analyser would make further improvement of this method [25].

In-situ FTIR analysis was first applied to the investigation of photo-degradation of acrylic-emulsion paint films by measuring the evolution of carbon dioxide from samples under UV irradiation [26,27]. Information about the stability of different samples could be obtained within 3–5 h, and perfect linear relation between the generated carbon dioxide under UV irradiation for 10 h and the carbonyl index after accelerated QUV aging for 328 h of different samples was observed [28]. The effectiveness and convenience of this method were demonstrated by investigations about photo-degradation of different kinds of polymers like poly (vinyl chloride) (PVC), polyethylene (PE), polypropylene (PP), poly (ethylene terephthalate) (PET), and polycaprolactone/PVC blend [29–38].

All of these methods above offered convenient approaches to rapid and sensitive aging evaluation. However, only one or two of the test conditions, including heating, UV irradiation and atmosphere, could be realized in these methods. In this work, a novel in-situ aging evaluation method was developed, based on in-situ FTIR analysis and for the purpose of rapid and sensitive aging evaluation in various combined conditions. The new method allowed for simultaneous heating and UV irradiation of a sample under variable atmosphere, and in-situ FTIR detection of the atmosphere change related to the aging status or stability of the sample. Then the method was applied to the evaluation of aging status of thermal oxidized NBR compounds. NBR has been widely used as sealing materials in key positions of mechanical components, and it has been object of several ageing investigations [39–43]. In this study, we showed that, by using this method, the aging status of different NBR samples could be evaluated rapidly, conveniently and with high sensitivity.

2. Experimental section

2.1. Materials

Vulcanized NBR compounds sheets with thickness of 2 mm were supplied by SKF Engineering & Research Centre, the Netherlands. The original sheets were aged in an air-circulating oven at 125 °C for up to 1000 h to obtain thermal oxidized nitrile rubber samples.

2.2. In-situ aging evaluation method

2.2.1. Principle

The in-situ aging evaluation method was based on the in-situ atmosphere detection in a homemade airtight cell by FTIR. The atmosphere changed when a sample in the cell was heated and/or irradiated; volatile additives and/or small molecular weight degradation products were emitted. This change was related to the aging status or stability of the sample and could provide important information about the aging properties of different materials.

The schematic diagram of the cell is shown in Fig. 1. Through gas inlet and outlet, various initial atmospheres could be introduced into the cell. Infrared light passed through the cell via CaF_2 windows at two ends to monitor the atmosphere change in the cell. A sample was placed in the sample-holder and could be heated by the heating loops embedded in the plug and/or irradiated by UV light through the quartz glass window.

2.2.2. Apparatus

The in-situ aging evaluation system was composed of four subsystems, i.e. spectroscopy system, purge system, UV irradiation system and heating system. The layout of the system is shown in Fig. 2.

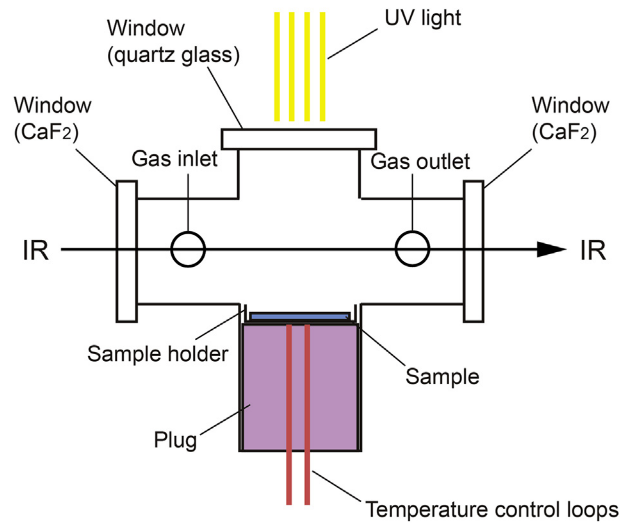

Fig. 1. Schematic diagram of the sealable cell.

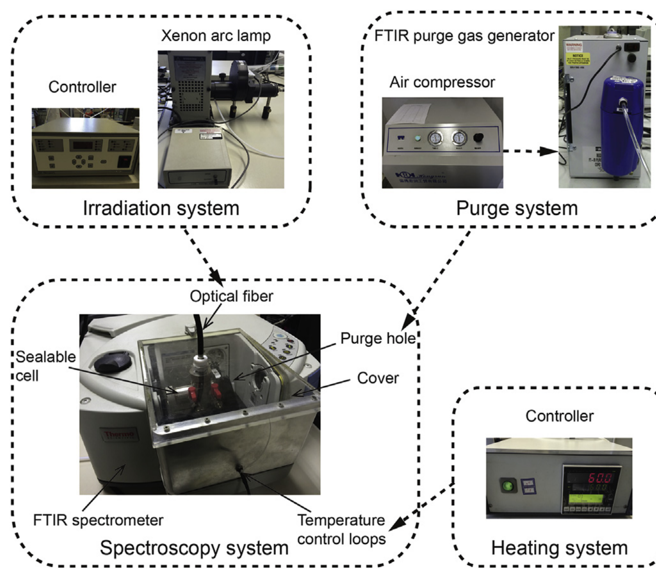

Fig. 2. The layout of four subsystems of the in-situ aging evaluation system.

The spectroscopy system was the core subsystem that included the cell and a FTIR spectrometer (Thermo-Nicolet iS10) equipped with an MCT detector to ensure high sensitivity. A new cover of the sample compartment was designed to enable the introduction of UV irradiation from the top and heating from the front. Infrared spectra were obtained by signal averaging 128 scans at the resolution of 4 cm^{-1} in the wavenumber range of 1111–4000 cm^{-1}.

The purge system was composed of an air compressor (Hongrun Industrial & Trading Co. Ltd., HYG-200) and a FITR purge gas generator (Parker, Model 75-45). Dry and clean air without carbon dioxide was supplied to purge the whole spectrometer and maintain a steady background signal.

The irradiation system was composed of a 150 W high-pressure Xenon arc lamp (Oriel, Model 6255), a controller (Oriel, Model 69907) and a shutter (Oriel, Model 71445), providing UV irradiation via a 1 m flexible light guide (Oriel, Model 77556). The shutter was used to control the irradiation on and off without frequently turning on and off the lamp. An AM 1.5 solar filter (Oriel, Model 81094) was used to remove the irradiation with the wavelength below 300 nm.