Polymer Testing 46 (2015) 72–78

Contents lists available at ScienceDirect

Polymer Testing

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

Test method

Non-destructive condition monitoring of aged ethylene-propylene copolymer cable insulation samples using dielectric spectroscopy and NMR spectroscopy

E. Linde [a], L. Verardi [b], P. Pourmand [a], D. Fabiani [b], U.W. Gedde [a, *]

[a] KTH Royal Institute of Technology, School of Chemical Science and Engineering, Fibre and Polymer Technology, SE-100 44 Stockholm, Sweden
[b] Laboratory of Innovation Technology, Dept. of Electrical, Electronic and Information Engineering, University of Bologna, Italy

ARTICLE INFO

Article history:
Received 3 June 2015
Accepted 8 July 2015
Available online 11 July 2015

Keywords:
Ethylene propylene rubber
Radiation ageing
Thermal ageing
Dielectric response
Portable NMR spectrometer
Condition monitoring

ABSTRACT

The causes of changes in dielectric response as a result of thermal and irradiative ageing of cable insulation of ethylene propylene copolymer rubber containing 38 wt.% filler were investigated. Samples were aged in three different combinations of irradiation dose rate and temperature, 0.42 kGy h^{-1} at 85 °C, and 1.58 kGy h^{-1} at 55 and 85 °C, and subsequently studied by dielectric spectroscopy, NMR spectroscopy using a portable spectrometer, and tensile testing. The extractable mass fraction and density were determined and related to the imaginary part of the dielectric permittivity at 100 kHz. The ageing led to an increase in the dielectric permittivity, stiffness, density and degree of oxidation, together with a decrease in both strain-at-break and relaxation time, as revealed by NMR spectroscopy. Except for the strain-at-break, the properties changed in a linear fashion with increasing imaginary part of the dielectric permittivity at 100 kHz, with particularly good agreement with respect to the density. As these properties are affected by the degree of oxidation, the results show that both NMR using a portable spectrometer and dielectric spectroscopy can be used as condition monitoring techniques to detect the degree of oxidation in complex systems such as filled copolymers.

1. Introduction

This paper is a continuation of a series of papers [1,2] investigating the use of dielectric spectroscopy as a condition monitoring technique for cable insulations installed in nuclear power plants. Nuclear plants generate a significant part of the electrical power consumed in the world [3], but many of these power plants are nearing, or have even exceeded, their design lifetime, and significant effort is being put into ensuring that they can continue operation for an extended period of time. To ensure the reliable operation of a nuclear power plant, it is vital to show that all components related to safety and operation are able to fulfil their functions under both normal service conditions and in postulated accident conditions [4]. Therefore, this applies to all polymeric components present in the power plants, e.g. cable insulations, seals and membranes, which need to maintain their functionality over the service time [5]. Polymers subjected to higher temperatures and/or γ-radiation, both of which are possible within a nuclear power plant, deteriorate over time through irreversible processes, often caused by oxidation [6], leading to changes in their functional properties [7,8]. It has been found that components lose their functionality because of thermal degradation more often than from irradiation [9,10]. To verify the long-term performance of a safety-related polymeric component, several standards describe the formal so-called qualification process [11].

Due to the long lifetimes involved, which can be several decades, the ageing process in these tests is accelerated by increasing the temperature and irradiation dose rate in order to subject the sample to an ageing level corresponding to that which the component would have been subjected to during service. The accelerated ageing must mimic the real ageing in order to be effective, so the mode of ageing has to be unchanged and the rate-limiting properties should remain the same [7,12,13]. One such rate-limiting effect of the degradation is related to diffusion-limited oxidation, which may occur if the rate of oxygen consumption within a polymer is higher than the rate at which the oxygen can be resupplied through diffusion [14,15], and this occurs at high temperatures and/or high irradiation dose rates. Once the samples have

* Corresponding author.
E-mail address: gedde@kth.se (U.W. Gedde).

http://dx.doi.org/10.1016/j.polymertesting.2015.07.002
0142-9418/

been aged, they are subjected to tests to determine their level of degradation, and to evaluate their functionality. Differences in the mode of ageing between the accelerated and service conditions can have a major impact on the extrapolated lifetimes [16], so care must be taken when designing accelerated ageing experiments.

The functionality of a cable is often determined on the basis of mechanical data, in particular strain-at-break, with a critical minimum value often set to 50% engineering strain [7,17]. However, mechanical testing requires relatively large amounts of sample and is destructive, and therefore cannot be used on an installed cable. Other test methods have been proposed, using a smaller amount of sample, including measurements of oxidation induction time [18–20], soluble fraction [21,22], density [23,24], oxygen consumption [25] and the assessment of oxidation by infrared spectroscopy [19,26].

Several electrical techniques have been evaluated as non-destructive condition monitoring techniques, such as line resonance analysis (LIRA) [27] and the assessment of dielectric loss factor [28] and voltage return [29]. Dielectric response has also been studied for this purpose, and it has been promising for various systems, including cross-linked polyethylene [2,30], chlorosulphonated polyethylene [31], ethylene-propylene rubber (EPR) and ethylene-propylene diene monomer (EPDM) rubber [1,32–34]. This method has also been effective as a tool for the detection of water trees in medium- and high-voltage cable insulations [35–37]. This paper aims to extend the knowledge of the behaviour of the dielectric response of filled copolymer elastomers and to compare the data with results obtained by other methods, especially nuclear magnetic resonance (NMR) spectroscopy, which may also prove to be a useful tool for the lifetime management of polymeric components in nuclear power plants. NMR spectroscopy has shown promising results for monitoring the condition of ageing polymers [38–40]. The instrument used in this study was portable, required no special sample preparation and, in principle, can be used on site for measurements on cables and other rubber/plastic components.

2. Experimental

2.1. Materials

An ethylene-propylene rubber (EPR) insulation, obtained from an Alcatel C0 6249 04 cable, was studied. Before ageing, the two layers of chlorosulphonated polyethylene sheathing and the steel screen were removed, leaving only the insulation and copper conductor. The thickness of the insulation was 1.2 mm, and the inner radius was 3.5 mm. The insulation contained 41 wt.% EPR, 22 wt.% volatiles, 4 wt.% carbon black and 33 wt.% talc. The volatiles consisted of oil and presumably some low molar mass polymer.

2.2. Accelerated ageing

A 10 m long piece of the bare insulation with an internal copper conductor was aged in three different combinations of elevated temperature and simultaneous γ-radiation from a ^{60}Co γ-ray source; viz., 55 °C and 1.58 kGy h^{-1}, 85 °C and 0.42 kGy h^{-1}, and 85 °C and 1.58 kGy h^{-1}. The accelerated ageing was performed at the ROZA facility at ÚJV Řež, a. s., Czech Republic. The samples were aged for a maximum of 1000 h, and samples were withdrawn for analysis every 200 h. From earlier studies, some diffusion-limited oxidation effects were expected due to the high irradiation dose rates used [41–43].

2.3. Dielectric spectroscopy

The dielectric properties were measured at 50 °C, using a Novocontrol Alpha Dielectric Analyzer V2.2 over the frequency range 10^{-2}–10^{6} Hz with an applied voltage of 3 $V_{rms.}$ The input voltage was applied to the central conductor and the output signal was obtained from a copper wire braid placed around the surface of the sample.

2.4. Density assessment

The Archimedes principle was used to assess the density of aged and unaged samples. The samples, cut from the entire cross-section of the insulation, were weighed in both air and ethanol (96 vol.% ethanol, 4 vol.% water) using a Precisa XR 205SM-DR microbalance. Three replicates of each sample were used.

2.5. Determination of oil content by extraction

Samples with a mass of 200 ± 100 mg were cut from the entire cross-section of each sample and extracted in 20 mL *n*-heptane (CAS No. 142-82-5; ≥99% purity; VWR GPR Rectapur) at 60 °C in a ventilated oven (Memmert ULE-600) for 24 h. The extracted samples were dried at 60 °C for 12 h. The masses of the samples before and after extraction were obtained using a Precisa XR 205SM-DR microbalance, and the extractable amount was calculated as the mass difference relative to the initial mass. To confirm satisfactory extraction, the process was repeated on the extracted sample, to ensure that the mass difference between the first and second runs was less than 2%.

2.6. Tensile testing

Dumbbell-shaped specimens, with dimensions according to ISO 37-5, were cut from the insulation after removal of the copper conductors. The specimens were stored at 50 %RH and 23 ± 1 °C for 24 h prior to tensile testing in an Instron 5566 Universal Testing Machine, using an initial gauge length of 40 mm and an extension rate of 50 mm min^{-1}, on six replicates of each sample.

2.7. Nuclear magnetic resonance (NMR) spectroscopy

The NMR spectroscopy measurements were conducted using a portable permanent magnet NMR-MOUSE (ACT GmbH, Roetgen, Germany). The magnet had dimensions of 13 × 10 × 9 cm^3, which generated a magnetic field of 0.31 T parallel to the measurement surface and a constant gradient of 14 T m^{-1} in the perpendicular direction. At the working frequency of 13 MHz, the sensitive measurement spot was located 10 mm above the instrument surface. With a radiofrequency pulse length of 5 μs, the width of the sensitive slice was approximately 200 μm. The position of the magnet with respect to the sample surface and the position of the sensitive spot were monitored using a micrometre clock with an accuracy of 5 μm. A portable NMR console from Magritek recorded the ^{1}H NMR signal, and measurements were performed using the Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence [44].

2.8. Infrared (IR) spectroscopy

The oxidation profile of aged samples was obtained by IR spectroscopy. Samples, 60 μm thick, were cut parallel to the surface using a Jung Autocut 2055. The IR spectra were obtained using a Perkin–Elmer Spectrum 2000 (Norwalk, CT), equipped with a Golden Gate single reflection ATR crystal (Graseby Specac, Kent, England). The spectra were recorded from 600 to 4000 cm^{-1}, with