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Effect of third monomer type and content on the UV stability of EPDM

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Abstract

Various uncompounded ethylene–propylene–diene (EPDM) elastomers were photo-oxidized using standard Weather-O-Meter (WOM) aging and oxygen absorption measurements during UV irradiation. The influence of the type and amount of diene on the UV stability was investigated. FTIR (ATR) measurements of the carbonyl absorbance after WOM aging were comparable with the outcome of the oxygen absorption tests. Both techniques showed a decrease in UV stability with increasing diene content. In addition, EPDM containing 5-ethylidene-2-norbornene (ENB) as the third monomer showed a higher UV stability compared to EPDM containing dicyclopentadiene (DCPD) as the third monomer. Furthermore, a linear relation was found between the carbonyl absorbance after WOM aging and the third monomer content for DCPD- and ENB-containing EPDM samples with comparable ethylene/propylene (C_2/C_3) ratio. The microhardness (International Rubber Hardness Degree) and the Young's modulus of the various EPDMs as function of the WOM irradiation time showed a maximum. This maximum is the result of parallel photo-crosslinking and chain-scission reactions, the latter being dominant in the later stages of the oxidation process. Combining the results from the FTIR measurements with the Young's modulus showed that DCPD-containing EPDM has a higher propensity to crosslinking reactions compared to ENB-containing EPDM.

Keywords: Ethylene–propylene–diene rubber; EPDM; 5-Ethylidene-2-norbornene; Dicyclopentadiene; Carbonyl; UV; Stability; Degradation

1. Introduction

Ethylene–propylene–diene elastomers (EPDMs) provide several beneficial properties, including high resistance to ozone and oxidation without the need of large quantities of anti-degradants, low temperature flexibility, and the ability to accommodate large quantities of filler and oil without creating processing instabilities and unacceptable loss of mechanical properties. The outstanding ozone and weathering resistance of carbon-black filled EPDM rubber and their composites make them well suited for many outdoor applications. This is inherent to hydrocarbon polymers with a fully saturated backbone.

EPDM elastomers are produced with variations in the ethylene/propylene (C_2/C_3) ratios, the amount and type of diene used, the molar mass and the amount of long-chain branching. The composition and structure of EPDM can greatly affect the degradation characteristics [1]. EPDMs with 5-ethylidene-2-norbornene (ENB) as third monomer are well known to be more sensitive to photo-oxidation when compared to ethylene–propylene copolymers (EPM) [2]. However, EPDM is more stable

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than highly unsaturated elastomers (e.g. styrene–butadiene and isoprene rubber) [3]. The choice for a particular type of EPDM depends on the final application [4,5]. The two most commonly applied diene monomers in EPDM are 5-ethylidene-2-norbornene (ENB) and dicyclopentadiene (DCPD). The structures of the EPDM polymers corresponding with the type of diene monomer used are presented in Fig. 1.

In recent years, there has been an increasing demand for light-coloured rubbers in outdoor applications. In traditionally used rubbers, the presence of carbon-black confers a very powerful UV screen. Replacement of carbon-black with various types of light-coloured inorganic fillers leads to a decrease in UV stability, since these fillers do not contribute significantly to the protection against UV irradiation [6,7]. Unfortunately, the fundamental knowledge regarding the UV stability of polyolefins is not easily translated to rubbers, due to the differences in composition and morphology [8]. In most applications of rubbers, stabilization is achieved by trial and error rather than a scientific approach. In order to understand the aging of a vulcanisate, it is necessary to first understand the aging characteristics of the pure polymer without addition of fillers, crosslinkers, processing oils and stabilizers. The present investigation focuses on the effects of the third monomer type and content on the UV degradation of EPDM.

2. Experimental

2.1. Materials and sample preparation

The EPDM samples studied are given in Table 1 and were selected to cover a wide range of third monomer content with comparable ethylene/propylene (C_2/C_3) ratios. These materials were purified to remove any stabilizer traces by dissolution in xylene (Merck, >98.5%) and subsequent precipitation in methanol (J.T. Baker, >99.8%). The materials were then dried in an oven at 50 °C for 72 h. Prior to WOM degradation, the EPDMs were hot pressed into plates (100 °C, 20 min) with a thickness of 1 mm and cut into rectangular bars of 70 mm × 4 mm. The EPDMs subjected to oxygen absorption were hot pressed under the same conditions into films having an approximate size of 50 mm × 20 mm × 0.15 mm.

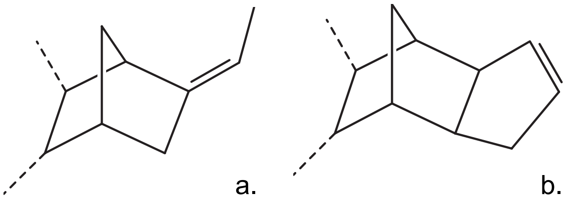

Fig. 1. Chemical structures of diene monomers incorporated in EPDM: a. 5-ethylidene-2-norbornene (ENB) and b. dicyclopentadiene (DCPD).

Table 1
EPDM samples used, where TM: type of third monomer, ENB: 5-ethylidene-2-norbornene, DCPD: dicyclopentadiene and C_2/C_3: ethylene/propylene ratio

Code	TM	wt.% TM	C_2/C_3	M_w [kg/mol]	M_w/M_n
ENB2.0	ENB	2.0	56.5/43.5	220	3.8
ENB4.3	ENB	4.3	52/48	225	2.7
ENB5.0	ENB	5.0	54/46	260	4.9
ENB9.0	ENB	9.0	48/52	245	3.4
DCPD1.4	DCPD	1.4	64/36	270	3.6
DCPD4.5	DCPD	4.5	58/42	240	5.3
DCPD8.0	DCPD	8.0	50/50	450	11.4
EPM50/50	–	–	50/50	150	1.9
ENB/DCPD	ENB/DCPD	4.3/2.0	49/51	195	3.8

2.2. Weather-O-Meter (WOM)

The WOM-degradations were performed in a Weather-O-Meter Ci4000 (Atlas Material Testing Technology BV) containing a borosilicate filtered xenon lamp (cut off < 290 nm). The test chamber temperature was 40 °C (black standard temperature: 65 °C), the intensity of the lamp at 340 nm was 0.5 W/m^2 nm, the relative humidity was 50% and a rain cycle of 108 min dry and 12 min wet was used.

2.3. FTIR spectroscopy

Attenuated total reflection (ATR) IR spectra were recorded at 25 °C on a Bio-Rad Excalibur Fourier Transform InfraRed spectrophotometer equipped with a horizontal Golden Gate single reflection diamond ATR cell. The IR spectra of the exposed side of the WOM samples were recorded with a resolution of 4 cm^{-1}, co-adding 30 scans. The absorption band at 1713 cm^{-1} in the IR spectrum is a measure of the degree of degradation; this band corresponds to the C=O band, resulting from oxidation of the polymer [9,10]. The relative carbonyl absorbance at 1713 cm^{-1} was determined relative to the CH_2 bending band at 1462 cm^{-1}, both after subtraction of the base line. The IR spectrum for a typical sample used in this study (ENB9.0) after 304 h of WOM aging is given in Fig. 2.

2.4. Microhardness

Microhardness (microIRHD) was measured on a standard FRANK Hardness Tester 38210 according to ISO 48:1994(E) at 23 °C on the exposed side of the WOM samples. The range of applicability is 30–95 microIRHD.