Spin-trapping and electron spin resonance of radicals produced by mastication of EPDM polymers

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The spin-trapping technique and electron spin resonance (e.s.r.) spectroscopy were employed to study radicals produced by milling ethylene-propylene (EPM) and ethylene-propylene-diene (EPDM) polymers. Mastication of EPDM polymers on a laboratory micromill at room temperature under nitrogen, and in the presence of 2,4,6-tri-tert-butylnitrosobenzene (TBNB), gave a spin adduct which was identified as an anilino type radical where the trapped radical is tertiary in structure. On the other hand, the milling of EPM copolymers in the presence of TBNB did not give spin-trapped radicals.

(Keywords: spin trap; e.s.r.; milling; EPM; EPDM)

Introduction

Ethylene-propylene-diene (EPDM) elastomers have a saturated backbone which accounts for their excellent weatherability and ozone resistance. It has been reported[1] that in blends of EPDM with natural rubber (NR), the presence of EPDM improves the ozone resistance of the blend. A possible application of these blends is in tyre components such as sidewalls, where ozone resistance is important. However, in general, these blends cannot be used in tyre sidewalls because of poor adhesion of the blends to other tyre components. In recent studies[2,3] of the properties of blends of EPDM and NR, it was observed that EPDM polymers with high ethylidene norbornene (ENB) as a third monomer and high molecular weight provided an elastomeric blend with improved adhesion and excellent ozone resistance, thus rendering it suitable for use in tyre sidewalls[2,3]. The work of von Hellens[3] and others[4] showed that mastication of EPDM rubber resulted in a molecular weight decrease and narrowing of the molecular weight distribution (*MWD*) as characterized by size exclusion chromatography (s.e.c.) and Mooney viscosity measurements. Furthermore, addition of antioxidants to the high molecular weight and high ENB EPDM resulted in a decrease in the adhesion of the masticated EPDM[3]. Consequently, it was suggested that the improved adhesion properties of the masticated EPDM could be attributed to free radical formation. Thus far, to our knowledge, no direct experimental evidence is available for radical formation during milling of EPDM polymers.

Electron spin resonance (e.s.r.) spectroscopy has been widely used to study free radicals produced by mechanical destruction of polymeric materials[5,6]. Moreover, a spin-trapping technique using 2,4,6-tri-tert-butylnitrosobenzene (TBNB) as a spin trap has been successfully applied for trapping radicals produced by irradiation, thermal degradation and ball-milling of polyethylene powder[7,8]. In this work we used TBNB and e.s.r. spectroscopy to determine whether radicals can be trapped during the milling of ethylene-propylene (EPM) and EPDM polymers on a laboratory micromill at room temperature, and to identify the type and class of radicals trapped.

Experimental

Characterization data for the EPM and EPDM polymers employed in this study are summarized in *Table 1*. All polymers were free of antioxidants.

The spin-trap TBNB was synthesized according to a published procedure[9]. E.s.r. spectra were recorded on a Varian E-3 spectrometer operating in the standard X-band and outfitted with a Varian V-6040 calibrated, variable-temperature controller. The operating conditions of the instrument were: scan range ±100 G, field set 3222 G, time constant 3.0 s, scan time 4 min, modulation amplitude 1.0 G, receiver gain normally in the range 2.0×10^5–2.5×10^6 and microwave power 3.2 mW.

Typical procedure for spin-trapping and e.s.r. experiments: the polymer sample (7 g) was dissolved in n-hexane (300 ml) and TBNB (77 mg) was added to the polymer solution and stirred for 1 h. The solvent was removed by a rotary evaporator. The resulting coevaporated polymer with spin trap was milled on a micromill with a nip setting of 0.8 mm for 30 min at

Table 1 Characteristics of EPM and EPDM polymers

Polymer	Ethylene (mol%)[a]	Third monomer (mol%)[a]	Molecular weight[b] ($\times 10^{-3}$)	*MWD*
EPM	62.0	0	334.0	2.1
EPDM-1	62.0	5.5 ENB	471.0	3.2
EPDM-2	71.5	1.1 ENB	378.3	3.2

[a] Measured by n.m.r.
[b] Measured by s.e.c. and reported as polystyrene equivalents

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room temperature under nitrogen. The milled polymer was sent immediately by courier for e.s.r. analysis at Mount Allison University.

The e.s.r. experiments were carried out with 100 mg of the milled polymer sample, which was placed in an argon-purged e.s.r. round cell and measurements were made from 25 to 145°C.

Results and discussion

Milling of the EPDM-1 polymer on a laboratory micromill resulted in a decrease in molecular weight from 471.0×10^3 to 250.6×10^3 and the *MWD* narrowed from 3.2 to 2.4. These results are consistent with the observations of von Hellens[3]. Under the same conditions, milling of EPM copolymers did not cause any noticeable changes in the molecular weight. Typical e.s.r. spectra of unmilled EPM containing TBNB are shown in *Figure 1a*. The same results were obtained with *milled* EPM containing TBNB. We found that milled and unmilled EPM did not exhibit e.s.r. signals, even at 125°C. On the contrary, milled terpolymer, EPDM-1, exhibited characteristic e.s.r. signals (*Figure 1b*). Moreover, the unmilled EPDM and TBNB was e.s.r. inactive, even at 125°C (not shown). Comparison between the e.s.r. spectra of milled EPDM-1 at various temperatures shows that temperature increases from room temperature up to 145°C cause a change from an anisotropic spectrum to a sharper and more symmetrical spectrum at 145°C. Higher temperatures, above 150°C, were not beneficial because the signal intensity decreased, probably due to decomposition of the spin adduct. Furthermore, milled EPDM-2, which has a molecular weight similar to EPDM-1 but ENB content 20% of that of EPDM-1, showed very weak e.s.r. signals (*Figure 2*). These results are in very good agreement with s.e.c. results which showed only a slight change in the molecular weight of EPDM-2.

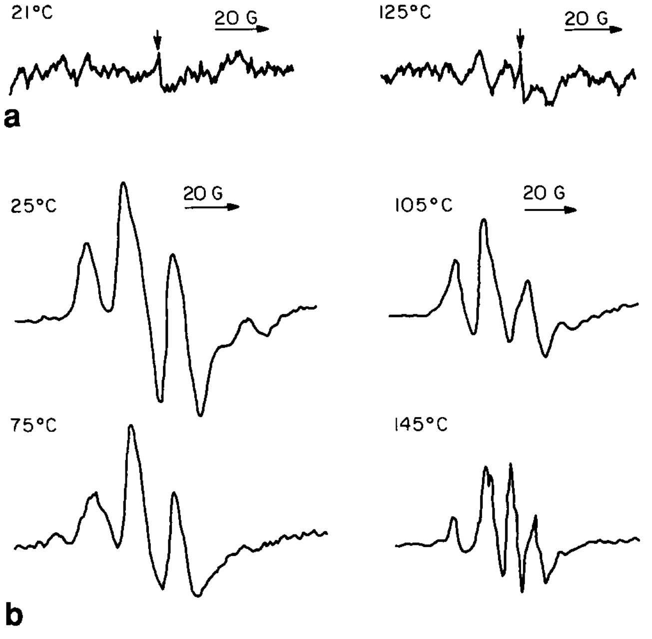

Figure 1 E.s.r. spectra of TBNB with (a) unmilled EPM and (b) milled EPDM-1. The spectra were recorded at a receiver gain of 6.2×10^5 and a modulation amplitude of 1.0 G. The cavity signal is denoted by an arrow

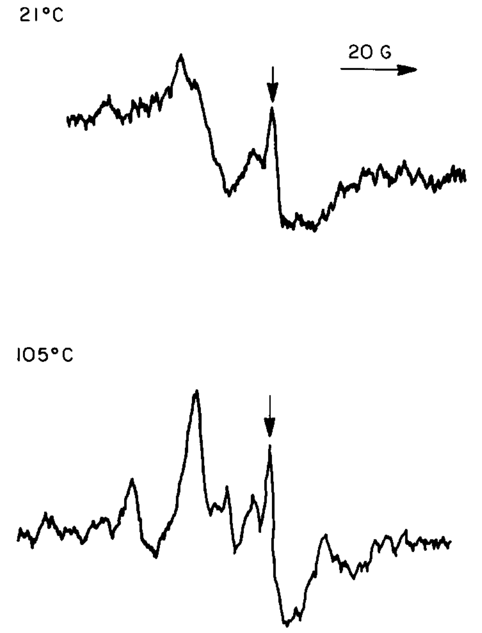

Figure 2 E.s.r. spectra of TBNB with milled EPDM-2. The spectra were recorded at a receiver gain of 2.0×10^6 and a modulation amplitude of 2.0 G. The cavity signal is denoted by an arrow

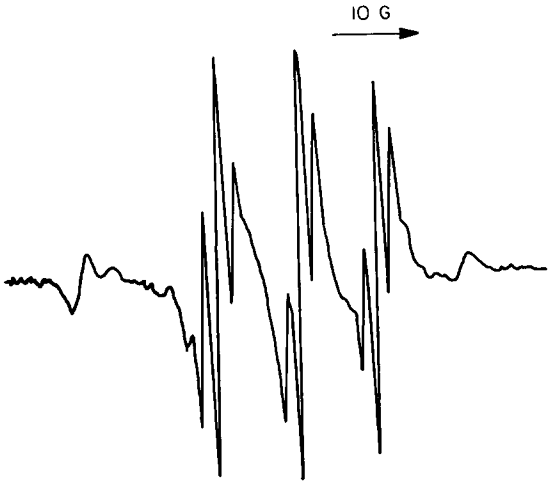

Figure 3 E.s.r. spectrum of TBNB with milled EPDM-1 in tert-butylbenzene

The characterization of the trapped radicals, from milled EPDM-1, was performed on a tert-butylbenzene solution of the EPDM. Thus, the polymer was dissolved in tert-butylbenzene and the e.s.r. spectrum was recorded at room temperature (*Figure 3*). It is clear that the signals are isotropic and the spectrum of the trapped radicals consisted of a 1:1:1 triplet of triplets with hyperfine couplings of $a_N = 10.25$ G and $a_H = 1.91$ G and $g = 2.004$. These couplings are similar to those known for tertiary radicals which are trapped at the oxygen of TBNB yielding anilino radicals[10,11]. Therefore, we can assign the observed e.s.r. spectra of the trapped radical from EPDM polymers to an anilino type radical where the trapped radical is tertiary in structure.

From this work, it can be concluded that, indeed, radicals are formed and trapped during milling of high molecular weight and high ENB EPDM polymers. On the other hand, milling of EPM copolymers in the presence of TBNB did not give spin-trapped radicals.

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