

Solid-state NMR characterization of cross-linking in EPDM/PP blends from ^1H – ^{13}C polarization transfer dynamics

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Abstract

A novel approach for solid-state NMR characterization of cross-linking in polymer blends from the analysis of ^1H – ^{13}C polarization transfer dynamics is introduced. It extends the model of residual dipolar couplings under permanent cross-linking, typically used to describe ^1H transverse relaxation techniques, by considering a more realistic distribution of the order parameter along a polymer chain in rubbers. Based on a systematic numerical analysis, the extended model was shown to accurately reproduce all the characteristic features of the cross-polarization curves measured on such materials. This is particularly important for investigating blends of great technological potential, like thermoplastic elastomers, where ^{13}C high-resolution techniques, such as CP-MAS, are indispensable to selectively investigate structural and dynamical properties of the desired component. The validity of the new approach was demonstrated using the example of the CP build-up curves measured on a well resolved EPDM resonance line in a series of EPDM/PP blends.

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1. Introduction

Thermoplastic elastomers (TPEs) present the service properties of elastomers and the processing properties of thermoplastics. They can be manufactured by dispersing milled rubber into a melt of an uncross-linked polymer. Such materials have special importance as they contain recycled rubber materials. Mechanical properties, and especially the level of elasticity, can be improved by dynamic cross-linking in situ of the elastomer during mixing with the thermoplastic material [1,2] resulting in a material called thermoplastic vulcanizate (TPV). To understand and fully control this process, adequate analytical methods are needed for fast and reliable estimation of the cross-link density, as well as related morphological and dynamical properties.

In this paper, we introduce investigations of TPV's consisting of a matrix of isotactic polypropylene (PP) and cross-linked EPDM rubber. The application of standard methods as swelling or dynamic-mechanical investigations is rather problematic as the contribution of the two phases to the measured data can be hardly quantified. The same problem is encountered also in the case of NMR methods widely used for determining cross-link density, such as proton transverse relaxation [3]: the ^1H resonances of PP and EPDM superimpose in a way which does not allow us unambiguous estimation of the EPDM structural parameters. The relaxation curves exhibit a multi-component behavior, so that it was not possible to fit that to a linear superposition of the relaxation curves of the single components; obviously interface effects play an important role [4].

The way out was the use of ^{13}C NMR because in ^{13}C spectra some EPDM resonances are well separated from the PP resonances, hence we have access to the EPDM

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phase of the vulcanizate. The cross-link density influences the NMR signal via residual dipolar coupling. Some experimental schemes are proposed to estimate this parameter [5], but in the present work we restrict ourselves to demonstrate the use of cross-polarization between the ^1H and ^{13}C spin systems.

In rigid organic solids CP was demonstrated to be useful not only for increasing sensitivity of ^{13}C (^{15}N) NMR spectra, but also for providing valuable structural information [6]. By contrast, cross-polarization techniques in elastomers were commonly considered as being not very quantitative, despite their advantage of providing chemical site resolution. For instance, the large CP scaling factor observed experimentally in the CP build-up curves of rubbers, and also the occurrence in some cases of transient dipolar oscillations, are inconsistent with the thermodynamic models [7] used to describe CP dynamics in the presence of fast molecular motion. However, the possibility of extracting quantitative information from the analysis of CP dynamics is more difficult when molecular motion has correlation times which lead to interference with the coherent evolution, but this is definitely not the case for elastomers at temperatures well above the glass transition temperature. In this regime, the coherent character [8,9] of the polarization transfer is assumed to be preserved, though at a much longer time-scale. Its order of magnitude is determined by the inverse of an average residual dipolar coupling induced by the motion of the polymer chains, which is anisotropic due to restriction imposed by cross-linking. Characteristic features of the residual dipolar coupling network in elastomers at high temperatures are exploited in the present work to elaborate a more rigorous description of CP dynamics, with the purpose of making the structural information encoded in the corresponding CP build-up curves more readily available.

2. Materials and methods

2.1. Sample preparation

The EPDM Buna EP G 5567 sample (Bayer AG, ML (1+4) $125^\circ\text{C}=46$, $M_w = 620\,000\text{g/mol}$) chosen for this study contains 66% propylene, 29% ethylene and 5% 2-ethylidenenorbornane (ENB). The ENB is used as termonomer making possible the conventional sulfur vulcanization by introducing 4–15 double bounds for each 1000 carbon atom chain length [1]. Because this is a low amount of unsaturation, sulfur vulcanization of EPDM is rather slow and therefore a relatively large amount of accelerators is needed. The EPDM was vulcanized using two different recipes (Table 1). The tetramethylthiuranium disulfide (TMTD) and dibenzothiazyl disulfide (MBTS) were used as accelerators.

Table 1
The recipes for the vulcanization of EPDM

Composition	EPDM_A (phr) ^a	EPDM_B (phr)
EPDM	100	100
Sulfur	1	1
TMTD	0.5	0.5
ZDEC	0.3	0.5
MBTS	0.3	—
ZnO	—	3
Stearic acid	—	1

^aper hundred rubber.

For development of the full activity of accelerators addition of ZnO and stearic acid is necessary. According to the vulcanization recipe, the EPDM_B sample is expected to present the highest degree of crosslink density.

Two series of blends were prepared, each of them composed of 30% isotactic polypropylene (PP—Huels AG Verstolen P7000, 46% crystallinity) and the two different ethylene propylene-diene terpolymers (EPDM_A and EPDM_B). The former (BL1_A and BL1_B) contain EPDM vulcanized powder (diameter < 80 μm) mixed at high temperature with PP, while the latter (BL2_A and BL2_B) were obtained by additional dynamic cross-linking in situ of EPDM during mixing.

All the PP/EPDM blends were produced through a melting mixing process in a 60 cm^3 Brabender Plastimeter, equipped with a pair of high shear roller-type rotors. The Brabender is connected to a computer to allow monitoring of mixing properties such as torque and temperature as well as control mixing parameters. The starting temperature of the electrically heated chamber was 190°C , the filling grade 0.67, the total mixing time 10 min and the rotor speed was set at 100 rpm. The polypropylene was introduced into the mixer during the first 2 min and after another 2 min the rubber powder was added. In the case of additionally cross-linked blends a vulcanization system was added. The vulcanization system used is Struktol 120 (Schill & Seilacher) and is composed by 83% soluble sulfur, 16% organic dispersing agent and 1% inorganic dispersing agent.

2.2. NMR experiments

Solid state ^{13}C NMR spectra were recorded at 100 MHz ^{13}C Larmor frequency with a Varian Inova-400 spectrometer. A Varian double-resonance MAS probe was used with 7 mm zirconia rotors and Torlon caps. For all NMR experiments the temperature was kept at 80°C , which corresponds to approximately $T_g + 120^\circ\text{C}$ for EPDM, and $T_g + 95^\circ\text{C}$ for the PP, respectively, where T_g is the glass transition temperature. This enhances the mobility of the polymer chains

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