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^{129}Xe-NMR of Carbon Black Filled Elastomers

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Neste trabalho é mostrado que a RMN de ^{129}Xe é uma ferramenta poderosa para investigar negros de fumo e elastômeros recheados com negro de fumo. Para os negros de fumo puros, os deslocamentos químicos do ^{129}Xe adsorvido na superfície de agregados deste material fornece informações sobre o tamanho médio dos poros destes agregados.Os resultados experimentais de RMN de ^{129}Xe obtidos para terpolímeros de etileno-propileno-dieno (EPDM) recheados com negro de fumo podem ser explicados quando se assume que os átomos de xenônio na fração de EPDM ligada ao negro de fumo troca rapidamente, na escala de tempo da RMN, entre o estado em que está adsorvido na superfície do negro de fumo e o estado em que está adsorvido nas camadas do EPDM. Isto leva a crer que os agregados de negro de fumo não estão completamente recobertos com cadeias de EPDM.

It is shown that ^{129}Xe-NMR is a powerful tool to investigate carbon black and carbon black filled elastomers. For the carbon black material itself the ^{129}Xe chemical shift of xenon adsorbed at the surface of carbon black aggregates yields information about the relative average pore size of the carbon black aggregates.
The experimental ^{129}Xe-NMR results of carbon black filled ethylene-propylene-diene (EPDM) can be explained when it is assumed that the xenon atoms in the bound EPDM fraction exchange rapidly on the NMR time scale between a state where they are adsorbed on the carbon black surface and a state in which they are absorbed in the EPDM layer. This would imply that the carbon black aggregates are not completely covered with EPDM chains.

Keywords: *carbon black, elastomers, filled elastomers, ^{129}Xe-NMR*

Introduction

^{129}Xe-NMR spectroscopy has proven to be a valuable tool for the study of microporous solids. Xe atoms with their diameter of 4.4 Å can be sorbed in many porous materials, ranging from crystalline materials like silicates to amorphous polymers[1]. The advantage of Xe as a NMR probe is the extraordinary sensitivity of the Xe chemical shift to the interaction between the Xe atoms and the material in which they are adsorbed. For most materials the Xe chemical shift varies between 0 and 250 ppm, when the resonance of free Xe gas is taken as 0 ppm. A strong Xe-wall interaction results in high chemical shifts, a weak interaction in small shifts.

In rigid microporous materials with pores of which the diameter exceeds the Xe atom diameter, the Xe atoms are thought to rapidly exchange between an adsorbed and a pseudo-gas state in which the atoms are more or less free. In such a situation the experimentally found chemical shift δ results from the equilibration of the Xe atoms between the adsorbed state with shift $δ_a$ and free state with a shift of 0 ppm.

In most amorphous polymers the situation seems to be different. The Xe atom usually is not small compared to the local free volume and the mobility of the Xe atoms is largely determined by the polymer chain mobility.

Here we want to report experimental ^{129}Xe-NMR results of elastomers filled with carbon black fillers. In filled polymers, rigid microporous materials like carbon blacks are combined with amorphous polymers and we were interested to see how the ^{129}Xe-NMR parameters of Xe in filled polymers are related to those parameters in the unfilled polymers and in the filler itself.

Experimental

The ^{129}Xe-NMR experiments were performed on a Bruker CXP200 (^{129}Xe frequency 55.345 MHz) using 30° rf pulses (pulse length 4-5.5 μs) and between 10000 and 32000 scans. The NMR tubes, filled with the sample, are first evacuated for two hours at a pressure below 5×10^{-9} bar.

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In case of the pure carbon black samples, the tubes and their content are heated at 200 °C during evacuation, in case of the filled and unfilled polymer samples no heating is applied. After evacuation the tubes are filled with Xe gas with a pressure of 10 bar.

The ethylene-propylene block copolymers consisted of a polypropylene (PP) sequence (80 weight %) and a statistical ethylene-propylene (EP) sequence with a ethylene-propylene weight ratio which varies from 50:50 to 10:90. The EP elastomer has the composition ethylene-propylene 50:50. Finally, also a blend of PP and EP was investigated with the composition of 80% PP and 20% of a 50:50 EP statistical copolymer.

Several commercial carbon black samples have been investigated by [129]Xe-NMR. The samples with their commercial names and specific surface area are shown in Table 1. Carbon black filled EPDM samples were prepared with the carbon blacks N110, N330 and N550. These carbon blacks consist of aggregates with the average size of 18, 30 and 56 nm, respectively.

The elastomer was thoroughly mixed with the carbon black at 100 °C. The composition and characteristics of these samples are shown in Table 2. The bound polymer fraction was extracted from the masterbatch material with a mixture of o-xylene with 2 weight % acetonitrile. The percentage of carbon black in the bound elastomer material is also shown in Table 2.

[129]Xe-NMR of Unfilled Ethylene-Propylene Copolymers and Blends

Ethylene, propylene and ethylene-propylene copolymers and blends are ideal systems for Xe-NMR investigations. They strongly absorb xenon and the [129]Xe-NMR lines at room temperature are narrow[2]. Fig. 1 shows the room temperature [129]Xe-NMR spectra at a Xe pressure of 10 bar of (a) low density polyethylene (PE), (b) PP, (c) a statistical EP copolymer (50% ethylene, 50% propylene) and (d, e, f, g) of four blockcopolymers consisting of PP and EP (80% PP and varying ethylene/propylene content).

Several conclusions can be drawn from Fig. 1. First, Fig. 1c shows that in the statistical EP copolymer only one line is found at a shift (205 ppm) in between the chemical shifts of PP (219 ppm) and PE (197 ppm). Due to the mobility of the Xe atoms, the EP material is homogeneous for Xe on
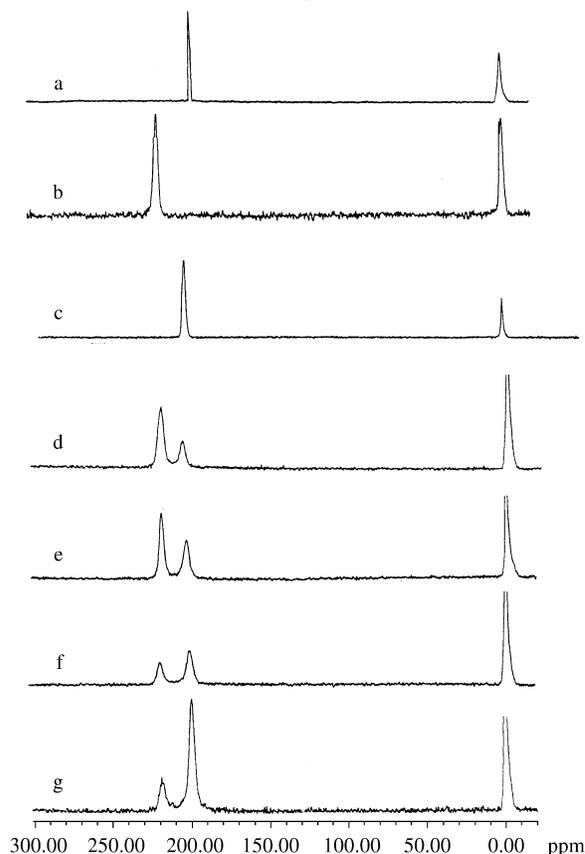
Figure 1. Room temperature [129]Xe-NMR of (a) very low density polyethylene (PE), (b) polypropylene (PP), (c) a statistical ethylene/propylene (EP) copolymer (50% ethylene, 50% propylene), (d) a blend of 80% PP and 20% EP (50:50), (e) a blend of 80% PP and 20% EP (60:40), (f) a blend of 80% PP and 20% EP (75:25) and (g) a blend of 80% PP and 20% EP (90:10).

**Table 1.** The various investigated carbon blacks.

carbon black #	Carbon black commercial name	Specific area (m^2/g)	Chemical shift at 298 K (ppm)	ΔE (kJ/mol)	$\dfrac{r}{R-r}$	R in Å when r = 4.4 Å
1	Raven 410	28	33.2	13.5	55.6	244
2	N550	30	44.7	12.9	50.0	220
3	N330	83	56.8	10.1	40.0	176
4	N110	143	64.0	8.7	33.3	146
5	Corax L	150	72.2	7.9	31.3	139
6	Monarch 1300	560	122.1	7.4	19.2	84
7	Printex XE2	1000	125.3	5.6	16.7	73
8	Conduktex 40-200	1075	119.0	6.0	8.7	38

Table 2. Characteristics of the carbon black filled EPDM samples.

Carbon black	phr	volume % carbon black	weight % bound rubber	volume % carbon black
		Masterbatches		Bound rubber
N110	40	0.157	22.7	0.451
	85.5	0.284	40.6	0.495
N330	85.5	0.284	29.6	0.573
N550	85.5	0.284	-	-

the time scale of the NMR experiment. On the other hand, from Fig. 1 d-g it is clear that the copolymer material PP+EP is heterogeneous from the view point of Xe-NMR. Two separate NMR lines are found at around 205 and 218 ppm, showing that the Xe diffusion is not fast enough to average the chemical shift difference of Xe in the PP matrix and in the EP domains. The intensity changes in Fig. 1 make clear that especially the ethylene content of the EP copolymer determines the amount of absorbed Xe. As reported before[2], in addition there is an approximately linear relation between the ethylene content in the EP polymer and the chemical shift of Xe in the EP copolymer domains (Fig. 2).

In Fig. 3 the Xe spectra of the PP+EP copolymer and of the PP/EP blend, both consisting of 80% PP and 20% EP (50% ethylene, 50% propylene), are shown. Although in many respects the two spectra are very similar, two differences can be noted. First, the intensity of the EP line in the blend is stronger than in the copolymer and, secondly, the EP line in the blend is narrower than in the copolymer. Further investigations are needed to establish whether these differences are a consequence of a difference in domain size.
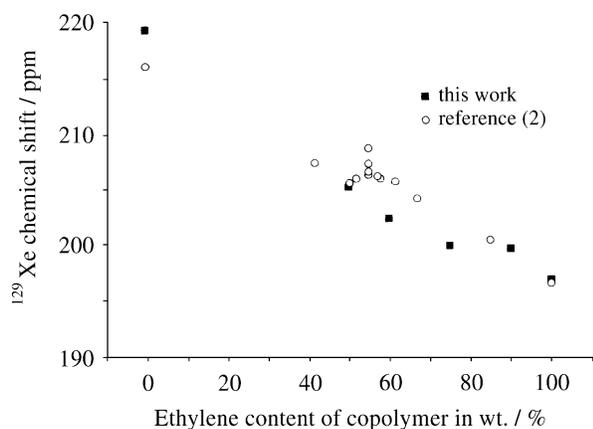
Figure 2. The [129]Xe chemical shift of xenon in EP copolymers as a function of the ethylene content; the data of Ref. 2 (open circles) are also included.
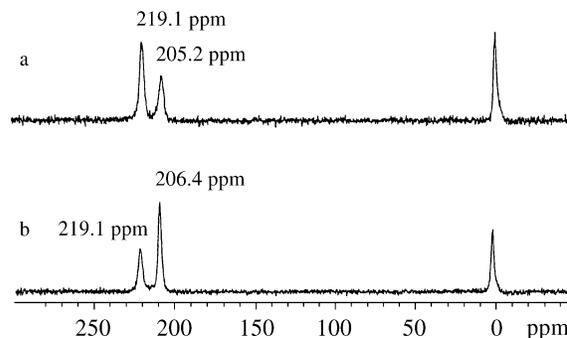
Figure 3. The room temperature [129]Xe spectra of an PP/EP blockcopolymer and a PP/EP blend of the same composition: 80% PP, 20% EP (50:50).

[129]Xe-NMR of Carbon Black

Carbon black consists of practically pure carbon, as in graphite and fullerenes. In comparison to graphite and fullerenes, however, the degree of structural organization in carbon blacks is greatly inferior. Carbon black is built of almost spherically shaped particles (diameter in the nm range) which agglomerate to form complicated three-dimensional aggregates[3] with high surface areas. The structure of the individual particles is characterized by graphitized zones and by amorphous interregions.

In ^{13}C magic angle spinning NMR spectra of carbon black filled polymers no signals of the carbon black are found[4]. This is most probably due to the susceptibility changes in the aggregates. In the literature susceptibility differences are often quoted to be responsible for line broadening. To show how serious this is, let us consider a small carbon black spherical particle with relative magnetic permeability μ_1 in a polymer matrix with relative permeability μ_2. At the interfaces between the carbon black particle and the polymer which are not perpendicular to the external magnetic field (Fig. 4), the magnetic field inside the particle $\vec{B_1}$ is not parallel to the field outside of the particle $\vec{B_2}$. From the relation between the angles α_1 and α_2[5]:

$$\frac{tg\,(\alpha_1)}{tg\,(\alpha_2)} = \frac{\mu_1}{\mu_2}$$

we find that not only the direction of the field changes at the interface, but also the magnitude of the field:

$$|\vec{B_1}| = |\vec{B_2}|\sqrt{[\frac{\mu_{r2}}{\mu_{r1}}\sin(\alpha_1)]^2 + \cos^2(\alpha_1)} \qquad (1)$$

Eq. (1) shows that even when the relative magnetic permeabilities of carbon black and the polymer matrix would differ by only 1%, this has enormous implications for the magnetic fields inside carbon black particles. Suppose the operating external magnetic field $B_0 \equiv B_2 = 9.400$
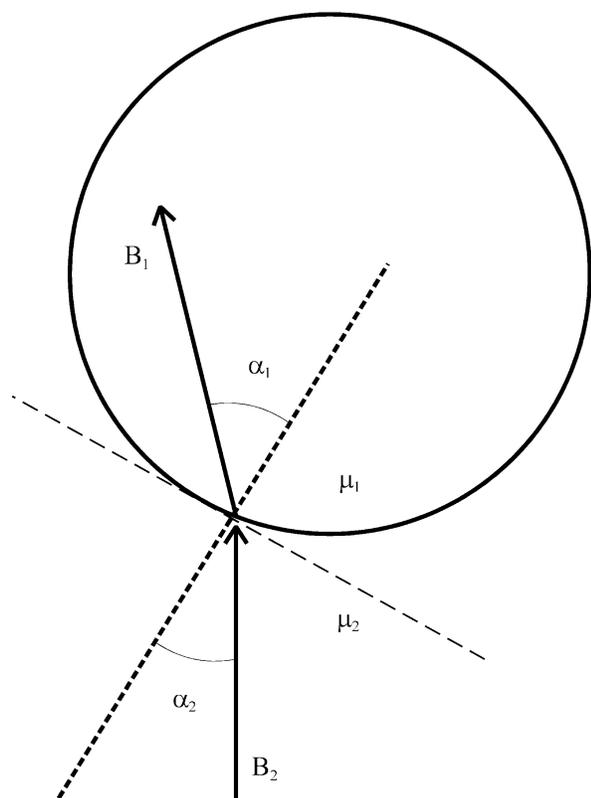
Figure 4. The refraction of the magnetic field at the surface of a hypo-
thetical carbon black sphere with relative magnetic permeability μ_1 in a
matrix with relative permeability μ_2.

Tesla, then B_1 inside the particle ranges from 9.4 T for α_1
= 0 to about 9.3 T for α_1 = 90°. The ^{13}C resonance frequency
inside the particle will range from about 100 MHz to 99
MHz, corresponding to a line width of 1 MHz. Of course
magic angle spinning will break up the line in many spin-
ning side bands, because this line broadening can be con-
sidered an inhomogeneous line broadening but the intensity
of the center and nearby sidebands will be strongly reduced.

As the ^{129}Xe-NMR results will show, the situation for
Xe-NMR of carbon blacks is much better. First, the Xe
atoms are located at the surface of the carbon black particles
where theoretically the refraction of the magnetic field
should have no effect. In addition, the Xe atoms are mobile
and sample during the NMR characteristic time ($\approx T_2$) very
many sites and local differences in the value of the static
magnetic field are averaged. Therefore, ^{129}Xe-NMR may be
the best NMR method to investigate filler materials like
carbon black.
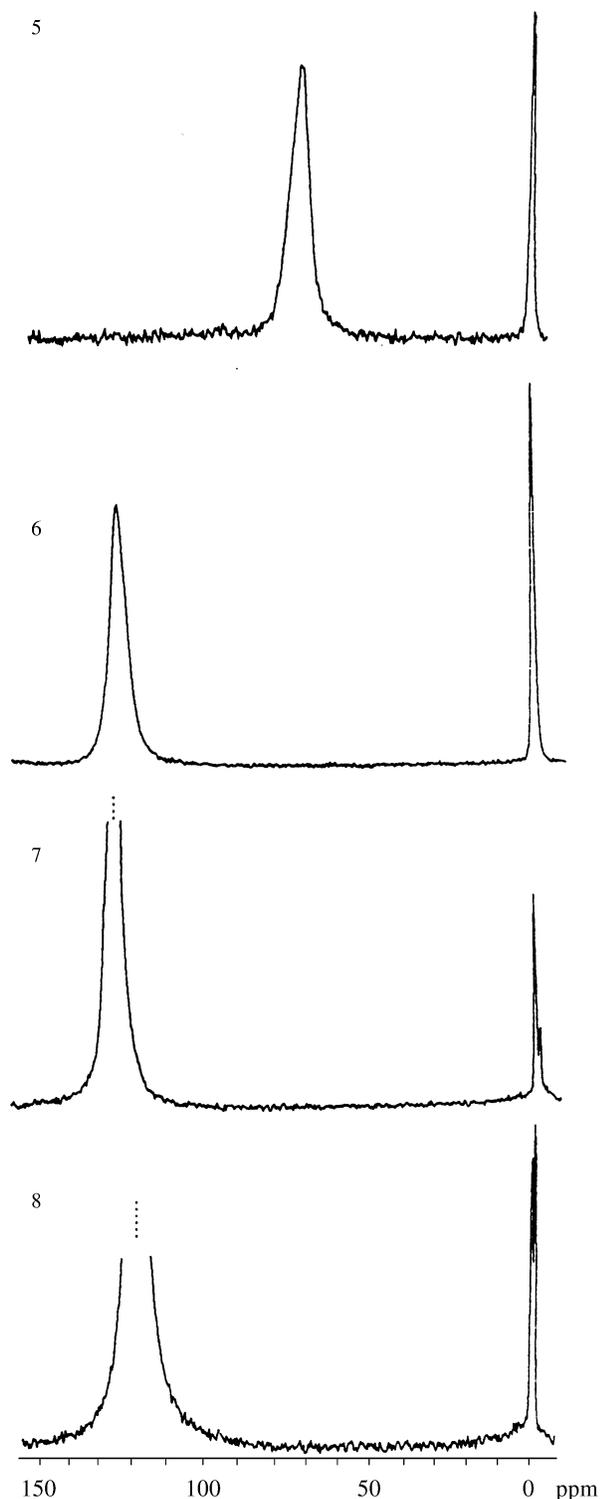
The ^{129}Xe-NMR spectra of 8 commercial carbon blacks
with increasing specific areas are shown in Fig. 5. Table 1
shows the corresponding Xe chemical shifts and the spe-
cific areas, which increase from 28 m²/g to 1075 m²/g. The
relation between chemical shift and specific area is shown
in Fig. 6. Clearly, the larger the specific area, the larger the
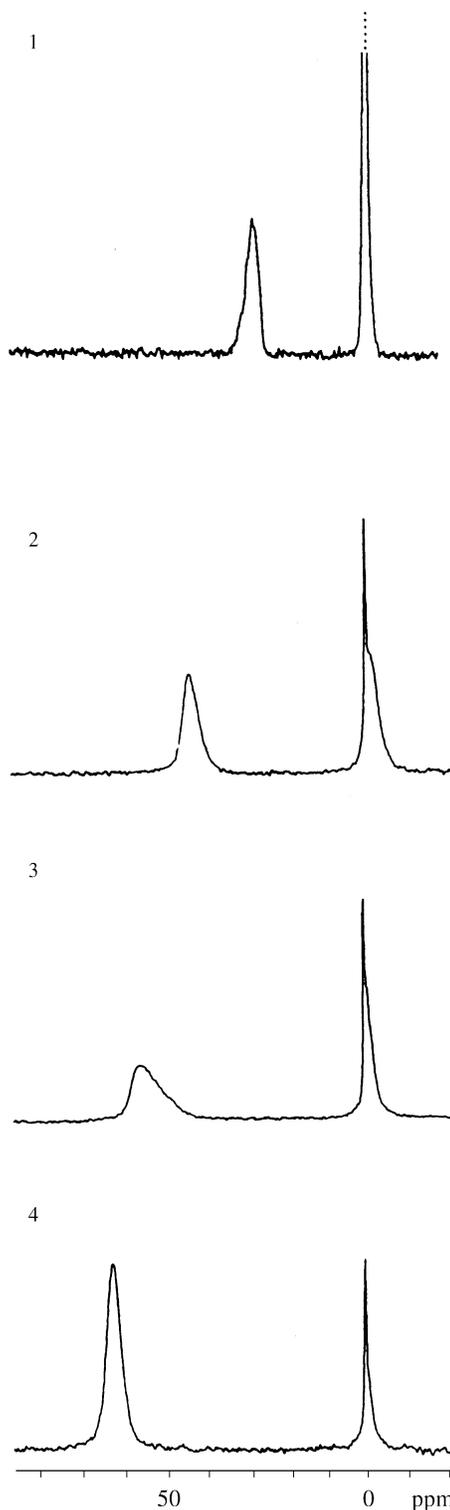
Figure 5. The room temperature ^{129}Xe-NMR spectra of the 8 commercial
carbon blacks of Table 1.

chemical shift. In a simple model this can be explained as
follows: aggregates of carbon blacks with small surface
areas have relatively smoothly curved surfaces on which

the interaction between adsorbed Xe atoms and the wall is relatively weak[6]. The chemical shift of the Xe atom is then also small. Carbon blacks with high surface areas probably contain many narrow pores in which the interaction Xe-

wall is much stronger, resulting in large chemical shifts. As discussed above, for rigid microporous materials it is expected that the Xe chemical shift is strongly temperature dependent. The variable temperature spectra for one of the carbon blacks are shown in Fig. 7. Over a temperature range of only about 50 K the chemical shift increases from 64 to 131 ppm. All carbon blacks show a similar temperature behaviour, see Fig 8. Several models have been proposed to explain the temperature dependence of the Xe chemical shift in porous media. In a model proposed by Ripmeester
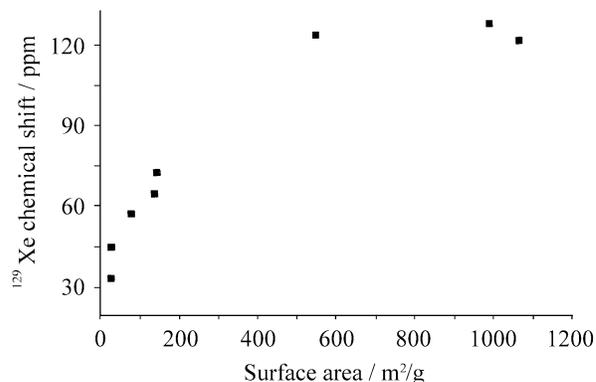
Figure 6. The relation between the ^{129}Xe room temperature chemical shift of the eight commercial carbon blacks and their specific surface area.

Figure 5 (cont). The room temperature ^{129}Xe-NMR spectra of the 8 commercial carbon blacks of Table 2.
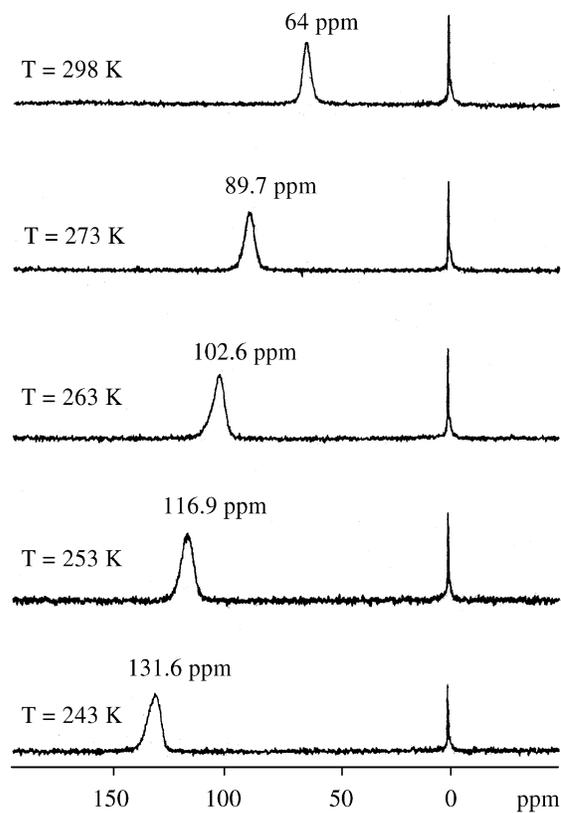
**Figure 7.** Variable temperature ^{129}Xe-NMR spectra of the carbon black N110 between 298 and 243 K.
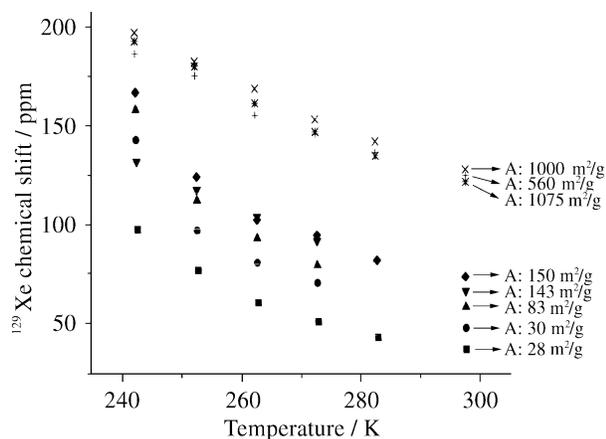
Figure 8. The temperature dependence of the ^{129}Xe chemical shift in the carbon blacks.

and Ratcliffe[7] an approximately spherical pore is considered with radius R. The interaction between a xenon atom and the walls of the pores should depend on the distance between the center of the xenon atom and the center of the pore . Therefore a simple rectangular potential is defined in such a way that the energy of a xenon atom at a distance smaller than R-r from the wall is ΔE lower than in the middle region with radius r (Fig. 9). By assuming a fast exchange of Xe between all positions in the pore and by applying Boltzmann's law, Ripmeester and Ratcliffe derived for the chemical shift δ of Xe in such a situation:

$$\delta = [\, 1 - \frac{r^3\, e^{-\frac{\Delta E}{kT}}}{R^3 - r^3 + R^3\, e^{-\frac{\Delta E}{kT}}}\,]\delta_a \tag{2}$$

where δ_a is the chemical shift of the xenon atom adsorbed on the pore wall.
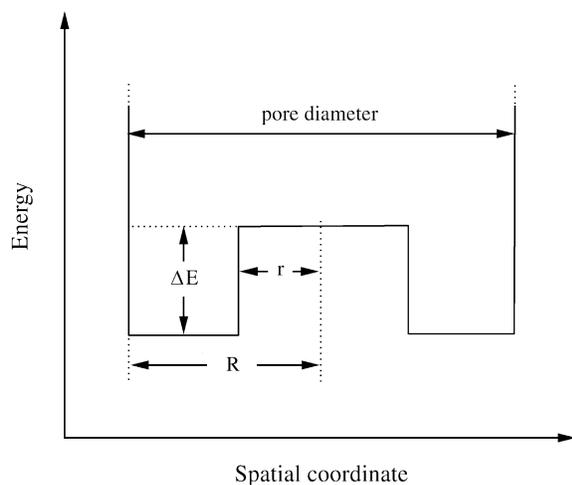
Figure 9. The potential energy of a xenon atom in a spherical cage of radius R[7].

The temperature dependence of the xenon chemical shift for all carbon black samples can be well fitted with Eq. (2). Table 1 shows the fitted parameters ΔE and r/(R-r). The results show, as expected, that, for carbon blacks with low specific area, r is very much larger than (R-r) ("large pores") and that, for materials with high specific area, r becomes more comparable to (R-r) ("small pores"). Using the fact that (R-r) will be of the order of the diameter of the xenon atom (R-r ≈ 4.4 Å) we can estimate the average pore size R in the carbon blacks (Table 1). The activation energy ΔE determined in this way shows that for decreasing pore size the energy difference of a xenon atom at the pore wall and in the center of the pore decreases. This can be explained qualitatively by considering the Lennard-Jones potential curves for a xenon atom in a spherical cage as a function of the cage radius. The calculations by Ripmeester and Ratcliffe[7] show that the energy difference for the xenon atom located at the center of the pore or at the pore wall is larger for large pores than for small pores.

^{129}Xe-NMR of Carbon Black Filled Ethylene-Propylene-Diene-Copolymer (EPDM)

After the discussion of the ^{129}Xe investigations of ethylene-propylene copolymers and carbon black we now want to show the results of such experiments on the carbon black filled elastomer EPDM. Fig. 10 shows the ^{129}Xe spectra of three EPDM samples filled with the carbon blacks N110, N330 and N550, which have aggregate sizes of 18, 30 and 56 nm, respectively. In these spectra no xenon resonances in the carbon black region are found. In spite of the high concentration of carbon black (85 phr) the only observable effect of carbon black in the spectra of Fig. 10 is a slight broadening of the EPDM line at 205 ppm. The line width increases from 164 Hz for pure EPDM to 250 Hz for EPDM/N550. The temperature dependence of the EPDM chemical shift and line width, however, are slightly dependent on the presence and the type of carbon black (see
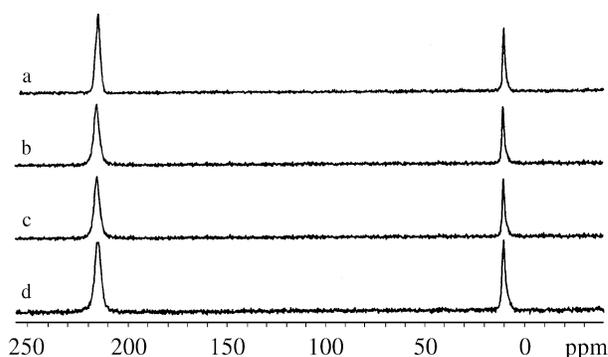

Figure 10. Room temperature ^{129}Xe-NMR spectra of xenon in (a) unfilled EPDM, EPDM/N110 (phr 85.5), (c) EPDM/N330 (phr 85.5) and (d) EPDM/N550 (phr 85.5).

Fig. 11). The larger the size of the carbon black aggregates, the slower the increase of the EPDM chemical shift at lower temperature. The temperature dependence of the Xe line width is less clear. At room temperature the largest line
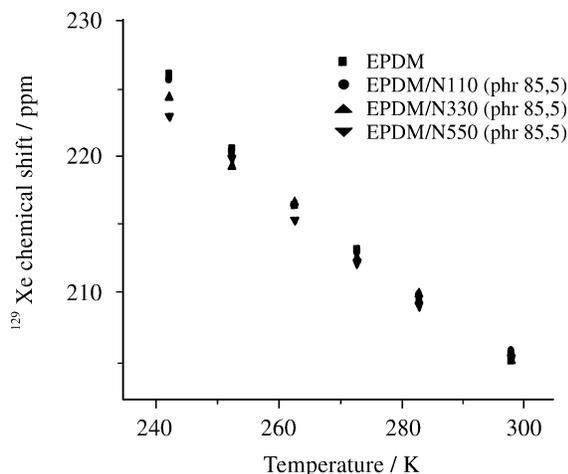
Figure 11. The temperature dependent chemical shift of Xe in the masterbatches of EPDM, EPDM/N110 (phr 85.5), EPDM/N330 (phr 85.5) and EPDM/N550 (phr 85.5).
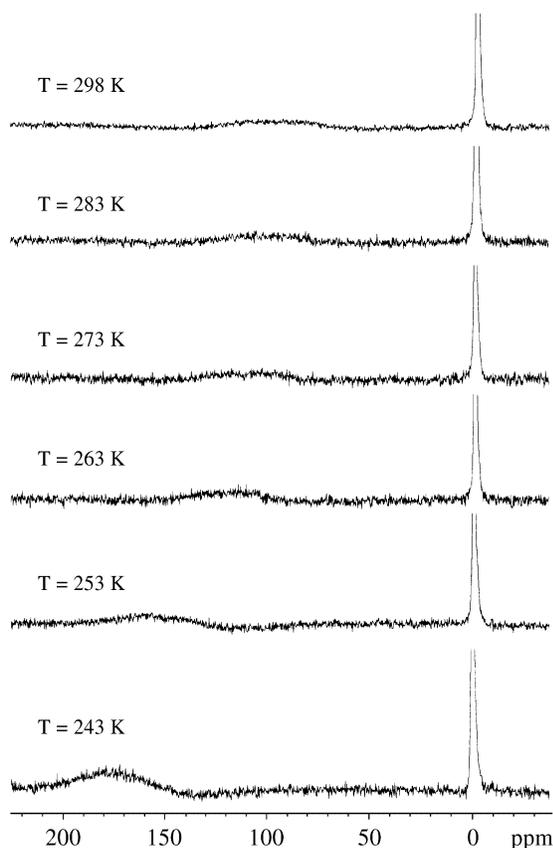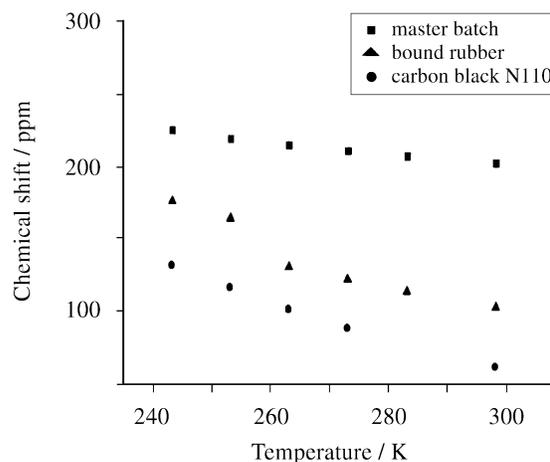

Figure 12. Temperature dependent [129]Xe spectra of xenon in the bound EPDM fraction of EPDM/N110.

width is found for N550 with the greatest aggregate size. At around 240 K the sample filled with N110 with the smallest aggregate size has the highest line width. In spite of the high concentration of carbon black no direct evidence of xenon adsorbed at the carbon black aggregates is found in the spectra of Fig. 10. We therefore extracted the EPDM that is not directly bonded to the carbon black with o-xylene. The bound rubber part is then again brought in a xenon atmosphere at 10 bar and the resulting spectra are shown in Fig. 12. It is very clear from these spectra that unperturbed EPDM has been removed by the extraction procedure, there is no EPDM Xe signal at around 205 ppm. Instead a very broad resonance is found centered around 100 ppm. This resonance shifts to higher frequency and becomes somewhat narrower at lower temperature. The temperature dependent shifts for this sample have been compared to that of the corresponding carbon black and to the master batch of filled EPDM material in Fig. 13. From the last figure it is very clear, that at all temperatures the chemical shift of the broad resonance in the bound rubber sample is inbetween those of the EPDM Xe resonance in the masterbatch and of the xenon adsorbed on the carbon black.

Of the last two spectra Fig. 14 shows the spectra of the bound EPDM fraction for increasing amounts of carbon black and Fig. 15 the [129]Xe chemical shift in the bound EPDM/carbon black fraction for the three carbon blacks as a function of the carbon black content.

Discussion

The appearance of a single, although broad, [129]Xe resonance from the bound rubber fraction of the carbon black filled EPDM elastomer shows that for the xenon atoms the surface layer of EPDM bound to the carbon black aggregates forms a more or less homogeneous material. The

Figure 13. The temperature dependent [129]Xe chemical shift of xenon in the masterbatch EPDM/N110, in the bound EPDM fraction and in the carbon black N110.
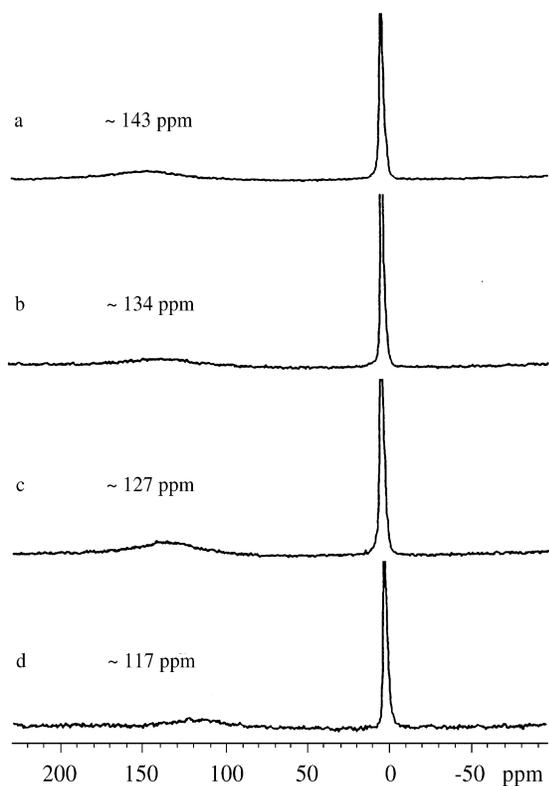
Figure 14. Room temperature ^{129}Xe spectra of xenon in the bound fraction of EPDM/N330 as a function of the carbon black content: (a) phr 40, (b) phr 60, (c) phr 85.5 and (d) phr 100.
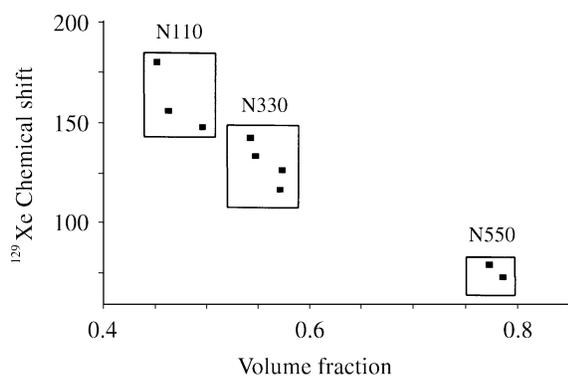
Figure 15. The room temperature ^{129}Xe chemical shift of the bound fractions EPDM/N110, EPDM/N330 and EPDM/N550 as a function of the carbon black content.

chemical shift of ^{129}Xe in this layer at various temperatures is inbetween the shift in pure EPDM and in the pure carbon black aggregates. This can be explained in two possible ways. In the first model, the EPDM chains completely cover the carbon black surface, no adsorption sites for Xe at the aggregate surface are left. When this model would be correct, then the high field shift of the ^{129}Xe resonance in the bound EPDM relative to the shift in unperturbed EPDM, would imply that in the bound EPDM fraction the

free volume has increased. This model, where the xenon atoms are surrounded by EPDM chains, seems to contradict the results of Figs. 14 and 15, which show a direct influence of the amount of carbon black and the aggregate size of the carbon black.

A second and more likely possibility is that the bound EPDM leaves many carbon black adsorption sites accessible for xenon atoms. An average chemical shift for ^{129}Xe, between EPDM and carbon black, then implies that the xenon atoms are so mobile that they can, on the NMR time scale, quickly exchange between an adsorbed state on the carbon black surface and an absorbed state in the EPDM layer. Adding more carbon black shifts the resonance in the direction of the resonance of pure carbon black (*i.e.* to lower frequency, Fig. 14) and replacing carbon black N110 by N330 or N550 with smaller surface area also shifts the resonance to lower frequencies (Fig. 15).

Conclusion

Of the experimental results reported above two aspects are new. First our results show that ^{129}Xe-NMR is a good technique to characterize carbon blacks. With the model of Ripmeester and Ratcliffe an average pore size can be derived from the experimental ^{129}Xe chemical shifts as a function of temperature.

The second novelty is the investigation of carbon black filled EPDM terpolymers with ^{129}Xe-NMR. Clearly further work is needed to quantify the conclusions, but the results obtained sofar show the potential of ^{129}Xe-NMR to study the interaction between a polymer and a filler material.

Acknowledgment

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