Artifacts in Transverse Proton NMR Relaxation Studies of Elastomers

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Introduction

Proton transverse NMR relaxation using Hahn echoes is a convenient and simple means to characterize polymer networks with respect to their cross-link density.[1,2] The principle governing the transverse magnetization decay is basically a dephasing, brought about by residual dipolar couplings (D_{res}) within nonisotropically fluctuating network chains.[3] The magnitude of these residual couplings is inversely related to the length of the network chains and is thus proportional to the density of cross-links. Hahn echoes are in principle well suited to study the dipolar dephasing mechanism, as effects of chemical and local susceptibility shifts should be refocused while dipolar couplings remain unaffected.

Using this technique at 400 MHz proton Larmor frequency, Schneider and co-workers[1] very recently analyzed the effect of silica and carbon black fillers on styrene–butadiene rubbers and could identify significant increases in the cross-link density with increasing filler content. Experimental data were fitted using the relation

$$\frac{M(t)}{M_0} = A \exp\{-t/T_{2A} - qM_2\tau^2[\exp(-t/\tau) + t/\tau - 1]\} + B \exp\{-t/T_{2B}\} + C \exp\{-t/T_{2C}\} \quad (1)$$

for the decay of transverse magnetization M_t. Term A represents the fraction of network chains fluctuating rapidly between constraints. In the framework of the Andersen–Weiss (A–W) model, the residual dipolar second moment (in units of rad^2/s^2)

$$qM_2 = \frac{9}{20} D_{res}^2 \quad (2)$$

is taken to be subject to exponential loss of correlation, with τ as an apparent slow rotational diffusion time of inter-cross-link orientations.[4] On top of that, network chains (A) as well as dangling chains (B) and liquidlike sol (C) are assumed to undergo additional (BPP-type) transverse relaxation described by $T_{2A,B,C}$. As in the work of Schneider, it is often customary to assume $T_{2A} = T_{2B}$.

In a collaborative effort,[5] we have later analyzed the same samples at 500 MHz using a recently devised proton double-quantum (DQ) method[6] and found essentially *no* influence of filler particles. The DQ method is intrinsically better suited to measure residual dipolar couplings, as it yields intensity build-up data related to DQ coherences, which are only excitable by means of dipolar couplings. The data are further normalized so
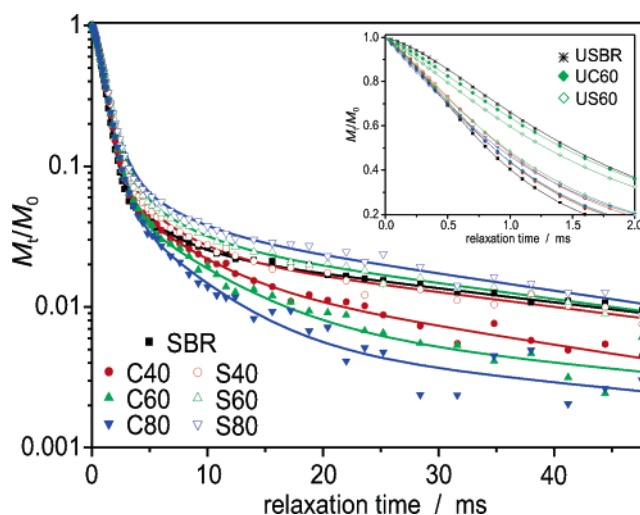
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Figure 1. Proton transverse relaxation of SBR, pure as well as filled with carbon black (C) and silica (S). The numbers indicate the filler loading in phr. The enlarged inset also shows results for unvulcanized (U) rubbers for comparison. The data were obtained on a Bruker minispec mq20 at 80 °C and are scaled to match the data shown in Figure 1 of ref 1. Lines correspond to the best-fit results.

as to remove any influence of experimental imperfections and of intermediate to slow motions occurring on the millisecond time scale. At that time, we could only speculate that strong local field gradients induced by a relatively large susceptibility contrast between network and filler might not be negligible and impose a trend on the relaxometry data.

Here, I show that, indeed, the magnetic field along with inadequacies of the fitting model plays a crucial role. Figure 1 shows relaxation data of samples from the same series, investigated at 20 MHz. The spread in apparent decay times among the cross-linked samples is seen to be rather small, in particular at short times, where the dephasing of the network chains manifests primarily. This immediately suggests minor differences in cross-link density, but this is not necessarily found upon fitting with eq 1. The analysis of the new data and implications for the feasibility of transverse relaxation experiments in general are discussed. These findings emphasize the use of more specific approaches such as DQ NMR, which is less biased by field-dependent as well as fitting artifacts.

Results and Discussion

The low-field relaxation curves of Figure 1 were fitted to eq 1 using the Microcal Origin 6.0 software, and the results are shown in Table 1 and compared with previous data in Figure 2. The most prominent finding concerns the stark discrepancy between results obtained at high and low field. While in the high-field study of ref 1, an increase in residual couplings (i.e., cross-link density) upon filling was indicated; the new data suggest a *decrease* when fitted to the same model (Figure 2b).

Both trends are considered artifacts related to parameter interdependencies, inadequacies of the model, and field-dependent susceptibility-induced changes in the shape of the relaxation functions. Results from a less model-dependent fitting approach and more reliable

Table 1. Results Obtained by Fitting of the Relaxation Data to Eq 1[a]

sample	$10^4 q$	D_{res}, $2\pi/s$	τ, ms	T_{2A}, ms	T_{2B}, ms	T_{2C}, ms	A, %	B, %	C, %
SBR	1.9	318	0.65	2.40	4.80	43.6	93.4	3.9	2.7
C40	1.4	274	0.77	2.16	5.38	34.7	92.4	6.1	1.6
C60	1.4	274	0.67	2.10	6.06	56.2	92.9	6.3	0.8
C80	1.0	231	0.64	1.77	4.91	54.6	92.6	6.8	0.7
S40	1.1	243	0.84	2.16	4.39	41.9	90.3	7.2	2.5
S60	0.7	193	0.99	1.81	4.86	38.7	90.6	6.2	3.1
S80	0.5	164	1.43	1.45	4.43	35.7	89.0	6.9	4.1
USBR	1.0	231	0.64	6.90	5.84	65.4	88.8	10.4	0.7
UC60	0.7	193	0.70	3.57	5.58	48.9	86.8	12.4	0.8
US60	0.6	179	0.72	2.63	7.03	54.6	90.0	8.1	1.8

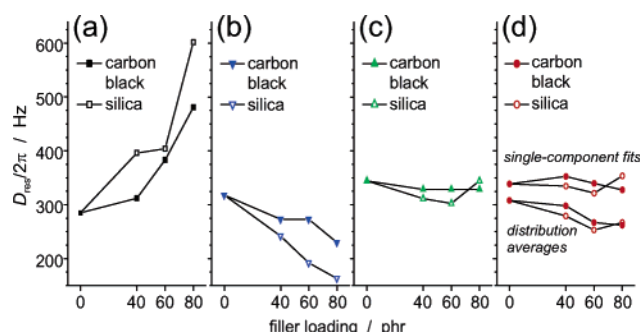[a] D_{res} and q are related through eq 2 with $M_2 = 9500/ms^2$.

Figure 2. Proton residual dipolar couplings measured in SBR as a function of filler content: (a) Hahn-echo relaxometry at 400 MHz, ref 1; (b, c) Hahn-echo relaxometry at 20 MHz (this work); (d) static DQ spectroscopy at 500 MHz, ref 5. The results in (a) and (b) were obtained by fits to eq 1, while data in (c) are the result of a single-parameter fit (eq 3) after subtraction of sol and dangling chain contributions.

DQ experiments agree in that the fillers do not seem to exert an appreciable influence on the rubber matrix (Figure 2, c and d, respectively). These issues are addressed in the following.

Fitting Procedure and Ambiguities. Generally, it proved advantageous to first determine the C component using a single exponential for data measured at $t \geq 50$ ms, where any other contribution has decayed beyond detection. As a second step, more data at $t \geq 7$ ms were included to determine first estimates of B and T_{2B}. Then, the whole range could be fitted provided good initial guesses for the parameters in the A–W term A. For some data sets, certain parameters converged to unrealistic values (e.g., when the sol content is low, T_{2C} may jump to a few milliseconds, which makes it effectively a contribution to the B part). Such behavior is avoided by holding C and T_{2C} fixed at their initial values, which are quite well determined. Figure 3 shows a sample decomposition into the three components, indicating that they appear well separated.

As mentioned, the authors of ref 1 used $T_{2A} = T_{2B}$. The new data are not well represented under this constraint, as indicated by the residuals shown in Figure 3b. Moreover, $T_{2A} = T_{2B}$ imposes a coupling between the A and the B part, which may lead to an unreliable separation. This was for example manifested in our results for the series S40–S80, where constrained fits lead to an increasing B between 0.17 and 0.43! Also, τ increased from 1 ms to unusually high values up to 5 ms. Generally, T_{2AB} assumed values between the two independent values, and D_{res} was increased by 30% at most under the constraint, preserving the trend of decreasing D_{res} with filler content.

All cross-linked samples show an almost universal B content of around 7% when the fit is not restricted, while
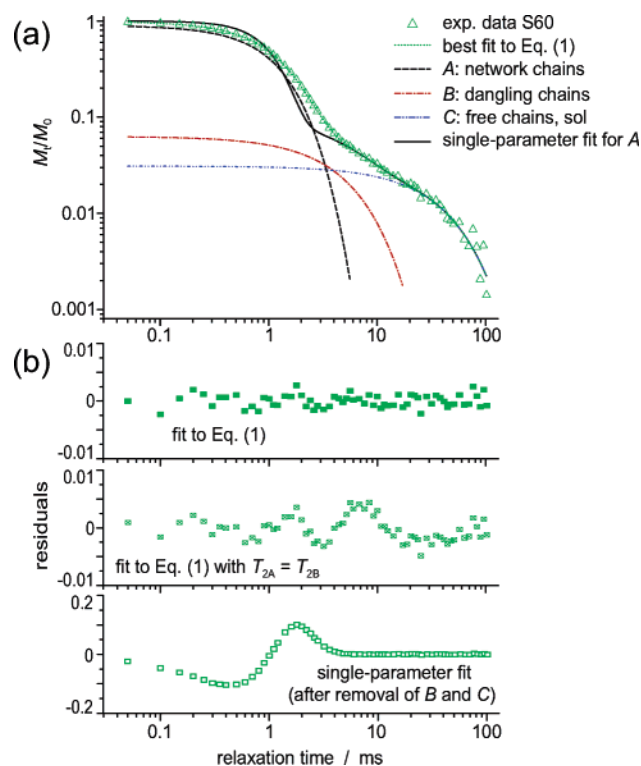

Figure 3. (a) Exemplary fitting and decomposition of sample data into its individual contributions and (b) residuals for different fitting protocols.

in ref 1, substantial variations with filler content are claimed. Again, the DQ results[5] corroborate the low-field data with uniform, albeit somewhat higher, values (~10%). Further, I see no a priori reason to assume that $T_{2A} = T_{2B}$. Fast polymer chain fluctuations, which in the BPP framework are responsible for T_1 as well as T_2 processes, cover wide ranges of frequency,[7] and the relaxation spectrum is greatly altered by the presence of constraints such as cross-links. This is for instance demonstrated by some recent computer simulations.[8] It is of course well possible that such differences in segmental relaxation spectra are more effective at low field, at which slower segmental processes contribute to spin relaxation.

Origin and Avoidance of Fitting Artifacts. This paper presents new evidence that the three parameters in the exponent of the A part do not necessarily reflect physically meaningful quantities but merely serve to parametrize a complex relaxation curve. The central question is in how far deviations of actual data from what is predicted by the rather strong A–W model become manifest in the fitting parameters. There are many reasons for the A–W model to be unrealistic, some of which are now addressed.

First, the significance of τ is not clear. Values from relaxometry as well as other methods,[9-11] all of which are based on the A−W model, yield values on the order of 1 ms irrespective of the type of network. If the model were correct, 1 ms would represent an isotropic (!) rotational diffusion time of the residual dipolar tensor. On the theoretical side, the validity of the A−W model as applied in the intermediate and slow regimes has seriously been questioned.[12,13] Experimentally, our previous work showed that rotational diffusion cannot possibly be isotropic in order to explain the DQ build-up on this time scale, as dipolar dephasing as well as DQ build-up also takes place within 1−3 ms.[11] Our ongoing work indicates that the "apparent" τ is related to a long-time tail of the primary segmental averaging process, as supported by our computer simulations.[8] Finally, spin alignment experiments suggested that reorientations of the residual tensor do not take place on a 100 ms scale even in highly mobile PDMS networks.[14] Therefore, it is proposed that an analysis of transverse relaxation data in terms of dipolar dephasing only is more appropriate. In the limit of $\tau, T_{2A} \rightarrow \infty$, term A of eq 1 reduces to

$$\frac{M_A(t)}{M_0} = A \exp\left\{-\frac{1}{2}qM_2t^2\right\} = A \exp\left\{-\frac{9}{40}D_{res}{}^2t^2\right\} \quad (3)$$

The limits and applicability of this equation are discussed further below.

Second, a uniform second moment is assumed, which is often justified by the central limit theorem and the joint effect of pairwise couplings in a many-spin system.[15] Yet, residual couplings in a network are not necessarily well represented by a Gaussian distribution of phase angles typical for a rigid solid, and the limited validity of the Gaussian assumption first and foremost rests on the powder average, which leads to an initial dephasing which is quadratic in t even for a single pair coupling. Simple relaxation experiments on rubbers show different behaviors for different chemical groups when these are resolved at higher field,[16] clearly proving the need to deal with *distributions of couplings*. Apart from varying interproton distances, the specific fast-motion averaging of differently oriented internuclear vectors within the different functional groups is important, as proven by DQ NMR under high-resolution conditions.[17] Finally, distributions occur naturally due to sample heterogeneities and distributions in end-to-end distances and mesh sizes.[6]

Such distributions can be analyzed with the DQ method (as it is compensated for slow-motional effects), and for SBR they were found to be quite broad, with a fwhm about as large as the average D_{res}.[5] This is not at all surprising, considering the chemical heterogeneity of SBR rubbers. In Figure 4, it is demonstrated that fits of eq 1 to a superposition of Gaussian-type decay curves (eq 3) with a moderate Gaussian distribution of D_{res} leads to completely ill-defined parameter values.

Third, the differences between high- and low-field results suggest an influence of susceptibility gradients. This was discussed in great detail by McBrierty and co-workers.[18] Note that not only the filler itself, but also micro- and nanoscopic voids, possibly introduced upon compounding, might play a role.[19-21] The effect is subtle, as spatial shift heterogeneity should be refocused by Hahn echoes; thus, molecular motions leading to exchange between different sites (or fluctuating internal
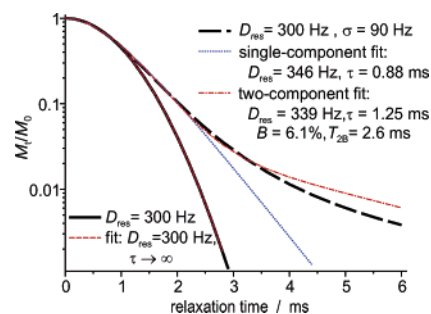

Figure 4. Influence of a Gaussian distribution of static residual couplings on the results of fits to eq 1. Thick lines represent the model functions, while the thin lines are from fitting. T_{2A} reaches infinity in all cases.

field gradients) must be present.[20] Therefore, such effects are restricted to length scales on the order of the cross-link separations, and only parts of a filled sample should be influenced. This can then lead to a faster initial decay, and in the work of McBrierty, this type of heterogeneity of the magnetization decay was indeed observed in terms of shape changes of the free induction decay as a function of the echo time.

As the A−W term demands homogeneous behavior, such deviations from the prediction can again seriously bias the fit to eq 1. For example, upon extending the realistic model case with the distributed D_{res} of Figure 4 by taking a 10% contribution to relax with $T_{2A} = 1$ ms (to mimic exchange effects), residual couplings of 360 Hz or higher are obtained irrespective of the fitting approach. Thus, small susceptibility-induced changes in the relaxation curves may indeed lead to artificially increased cross-link densities. A full investigation of this phenomenon is desirable, yet beyond the scope of this note. For example, McBrierty et al.[18] have performed pulse-spacing-dependent Carr−Purcell experiments, which should be sensitive to such exchange effects, but they have also discussed the serious caveats relating to cumulative effects of pulse imperfections which interfere with an exact quantification.

Piecing together all these arguments, it is not surprising that fits using eq 1 can yield incorrect results. As an alternative, eq 3 provides a means to circumvent interdependency problems. Obviously, this form cannot represent the data well (Figure 3), but it has the advantage of not being very dependent on the curve shape. The fit basically yields a result for D_{res} which parametrizes the overall decay time and of course represents an average over an unknown distribution. Note that the fit should be performed over the whole data range. Equation 3 can certainly provide a better fit to the *initial decay*, which would, however, bias the result toward the stronger couplings in the distribution. As another approach to achieve a better overall fit, an analytical result assuming quasi-static residual couplings and a Gaussian distribution of end-to-end distances may be used[22] but will probably yield a similar result representing a somewhat different type of average over the unknown distribution. It was further proposed to analyze data in terms of superpositions of eq 3 and extract the distribution,[23] but the result would probably be distorted to an unknown degree by the neglect of other factors.

Certainly, a bias must be expected due to the neglect of a relaxation contribution. As is apparent from Figure 2c,d, this systematic deviation is well within the range

of the different averages over the distribution provided by the DQ method. An improvement should be possible by including a *fixed T_{2A}*, to be obtained from a suitable echo experiment which provides full refocusing of the dipolar dephasing.[24] Ultimately, such a procedure would closely resemble what is done in the DQ approach, where the data used for referencing represents a kind of dipolar "multiple-quantum" echo.[6]

A few final comments should be added concerning artifacts related to experimental conditions. In spin systems characterized by substantial (residual) homonuclear dipolar couplings, deviations of the echo pulse from 180° lead to a partial refocusing of these couplings and thus to underestimated second moments as well as overestimated contributions of liquidlike components. This solid-echo-type effect is most pronounced when the two pulses have orthogonal phases but also gains importance in a 90_x-180_x sequence when a large frequency dispersion (background gradients, shim) is present. Most importantly, such artifacts *cannot* be removed by phase cycling (e.g., EXORCYCLE).

Experiments are therefore preferably performed on-resonance under well-shimmed conditions, using a $90_x-t/2-180_{\pm x}-t/2-acq_y$ sequence, and additional CYCLOPS comprising both pulses. Flip angle imperfections will then only lead to an immaterial loss of signal irrespective of t, but not to distortions of the relaxation curve. On the minispec mq20 used in our experiments as on other low-field equipment, spectral lines are usually dominated by the bad shim of the magnet. In such cases, special care must be taken to avoid flip angle deviations. A careful setup is then essential, and effects of rf inhomogeneity must be avoided by appropriate restriction of the sample size.

Conclusions

Hahn-echo relaxometry of rubbers and data analysis following eq 1 still enjoys great popularity. A number of caveats have been raised in the past, and the arguments presented here further suggest that the Andersen–Weiss model is not reliable, mainly due to the fact that the shape of relaxation functions is influenced by unknowns such as distributions of residual couplings arising from chemical variability within the monomer units or heterogeneity of the material and motions in local susceptibility gradients in the case of filled materials. Fits are then biased toward parameter values which are meaningless in a physical sense and might lead to severe misinterpretations.

As slow motions in rubbers appear to be of minor importance, data analysis in terms of dipolar dephasing due to quasi-static residual couplings appears more reliable. In the present case, this strategy gives quantitative agreement with proton DQ spectroscopy, which is compensated for effects of slow motions and therefore permits even the estimation of distributions of residual couplings.[6] Finally, it should be noted that the DQ method is robust, easy to set up, and can also be performed on cost-efficient low-field instrumentation without compromise in data quality.[25] The data treatment might appear more involved at a first glance but is certainly less challenging than reliable processing of transverse relaxation data.

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