Chemical Engineering Science 64 (2009) 4684–4692

Contents lists available at ScienceDirect

Chemical Engineering Science

journal homepage: www.elsevier.com/locate/ces

Modeling ^{1}H NMR transverse magnetization decay in polysiloxane-silica composites

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ARTICLE INFO

Article history:
Received 31 August 2008
Received in revised form 9 January 2009
Accepted 15 January 2009
Available online 23 January 2009

Keywords:
Polymers
Soft solids
NMR
Residual dipolar coupling
Mathematical modeling
Parameter identification

ABSTRACT

Nuclear magnetic resonance (NMR) spectroscopy has been used effectively in the analysis of elastomeric, soft materials and has been proven to be both sensitive to micro- and macroscopic changes associated with "aging" mechanisms. Traditional analyses, however, rely on empirical formulae containing a large number of (often arbitrary) independent variables. The resulting ambiguity can be circumvented largely by developing models of NMR observables that are based on basic polymer physics. We compare two such models, one previously published and one derived herein, along with two empirical expressions that describe the proton transverse magnetization decay associated with complex polymer networks. One particular extracted parameter, the proton–proton residual dipolar coupling (RDC), can be directly related to network topology, and a comparison of the extracted RDCs reveals high consistency among the models. An expression derived from the properties of a static Gaussian chain can minimize the number of parameters necessarily to describe the solid-like, networked proton population to a single independent parameter, the average RDC, D_{avg}. The distribution of RDCs derived via this methodology is qualitatively similar to those derived from previously published multiple quantum techniques, although quantitative differences between the derived RDCs persist, suggesting that further analysis is necessary.

1. Introduction

Polysiloxane-based composites have been particularly attractive as structural materials due to a relatively large, tunable range in shear modulus upon milling with fumed silica, even at relatively low filler mass fractions. In practical application, however, these materials are often exposed to harsh chemical, physical, mechanical, and radiological environments that ultimately limit useful device lifetimes through irreversible changes in constituent components. The assessment of damage, particularly for elastomeric materials, is often done be monitoring changes in macroscopic structural properties (e.g., shear and storage moduli). These methods are often inherently destructive and typically afford an average measurement over the entire sample. In situations where these materials are scarce, sensitive, or otherwise difficult to attain in any quantity, there exists a need for analytical techniques to be sensitive to subtle changes in a non-destructive, non-invasive capacity. Perhaps most essential for engineering applications is the development of intuitive analytical methodologies from which one can extract physically meaningful parameters from experimental data yet are simple to implement in practice while containing significant scientific rigor in their foundation.

Nuclear magnetic resonance (NMR) spectroscopy has been utilized effectively over the last few decades for both fundamental and applied studies of polymer-containing materials. Elastomeric materials form one case study for the efficacy of NMR in addressing fundamentals issues of polymer physics. Elastomeric composite materials exhibit both physical and chemical junctions (from e.g., surface-polymer interactions and chain crosslinking, respectively) that form a long-range network topology. This physical structure imposes restrictions on individual polymer segment motions, enhancing the inherently anisotropic dynamical nature of these materials. NMR exploits the anisotropic nature of various intra- and internuclear interactions to quantify local chain fluctuations over a wide range of motional time scales, from discrete monomer motions to reptation and bulk diffusion. One observable that is particularly relevant is the *transverse decay* of the proton NMR signal. This decay, usually measured by stroboscopic sampling of the proton NMR signal during a repeating cycle of pulses, is governed by the residual proton–proton homonuclear dipolar coupling (hereafter referred to as the RDC) between protons on polymer chains. This magnetic dipole–dipole interaction between protons is partially averaged by molecular motion; in network elastomers, the entanglements between chains and chain interaction with filler surfaces act as tethers so that the residual couplings form an indirect measurement of entanglement density.

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doi:10.1016/j.ces.2009.01.020

We have used previously proton transverse magnetization (T_2) decay to develop a correlation of a particular NMR derived quantity, the proton homonuclear dipolar second moment, to the shear modulus in PDMS-silica composites and have demonstrated its use in the spatial resolution of macroscopic heterogeneities via NMR imaging techniques (Mayer et al., 2007). In analyzing our previous NMR data, several proton populations were spectroscopically identified, but it remains unclear if these populations correspond to any physically meaningful proton domains. Ultimately, the functional form chosen to describe proton T_2 decay, from which dipolar second moments were derived, became an ansatz chosen for simplicity and apparent fidelity to the data. Considering the heterogeneity of proton dynamics in networked polymers, one surmises that there exists a continuum of dipolar second moments, in contrast to the assertion of a distinct second moment for bulk network protons, a different second moment for protons on tightly silica-adsorbed chains, and others, perhaps, for weakly bound species. While a continuum model may be more physically appealing, the latter scenarios provide excellent fits to experimental data.

Previous workers have developed expressions for the transverse decay of protons on polymer chains, in polymer networks, etc., based on well-established ideas common in polymer physics. Most notably is a function that was applied to poly(styrene-co-butadiene) elastomers well above the glass transition temperature, T_g (Sotta et al., 1996). These workers recast the spatially dependent terms of the homonuclear dipolar Hamiltonian in terms of the Gaussian distribution of the polymer end-to-end vector. The transverse decay associated with solid-like domains represents inhomogeneous line broadening of the proton lineshape, and though these interactions are weak, the investigators are able to correlate them to structural moduli of these elastomers.

In this article we seek to assess several expressions for the transverse decay of proton magnetization for a complex PDMS-based elastomer subjected to a range of γ-irradiation exposures. These materials have been examined in several other studies but in a more phenomenological fashion (e.g., Maxwell and Balazs, 2002; Maxwell et al., 2005; Mayer et al., 2007). Here we apply the function mentioned above (Sotta et al., 1996), a similar function derived herein, and an expression derived assuming an ansatz distribution of dipolar couplings. The extracted parameters will be compared to each other and to trends published previously in the literature. The utility and efficacy of these expressions in describing T_2 decay in complex elastomeric materials is considered.

2. Theory

We first present an abbreviated summary of the derivation of Eq. (8) from Sotta et al. (1996), which we will refer to as $M_S(t)$, which represents the total ^{1}H transverse magnetization of the spin system. Note that the subscript S refers to the initial of that main author's last name. The authors take the inhomogeneous component of the time evolution of the free induction decay (FID) and recast it in terms of the Gaussian distributed squared end-to-end vector of a static polymer chain. Convolution of the FID (neglecting homogeneous T_2 terms) with the Gaussian distribution yields a normalized, closed-form expression for transverse magnetization evolution

$$\frac{M_S(t)}{M_0} = \mathrm{Re}\left[\left(1-\frac{2}{3}i\frac{k}{N}Dt\right)^{-1/2}\left(1+\frac{1}{2}i\frac{k}{N}Dt\right)^{-1}\right], \tag{1}$$

where M_0 is the initial transverse magnetization, N is related to the number of repeat units between crosslinks (i.e., a measure of interjunction segment length), k is a geometrical factor (equal to, e.g., $\frac{3}{5}$ for a freely jointed chain, Sotta and Deloche, 1990), and D is the homonuclear dipolar coupling strength given by

$$D = \frac{\mu_0}{4\pi}\frac{\gamma^2\hbar}{r^3}, \tag{2}$$

where γ is the proton gyromagnetic ratio, and r is the internuclear distance. Note that since D represents the *static* dipolar coupling strength (a constant for a given distance, r) from known monomer geometry, the sole parameter determining $M_S(t)$ is N, the effective mesh length of the network. This parameter can also be thought of as a scaling factor by which the dipolar coupling is reduced as a result of motional averaging over that length scale. This reduced coupling is referred to as the RDC constant and represents the coupling strength after averaging by fast, local segmental chain motions (i.e., those motions experienced by polymer chains despite the presence of the network topological constraints).

A similar expression can be derived that employs the so-called second moment approximation (Kimmich, 1997), where $D^2N^2t^2 \gg 1$, equivalent to the idea that strong dipolar couplings dominate the decay at short times. In this case we can write the basic transverse decay of proton magnetization as

$$\frac{M(t)}{M_0} = \exp\left(-\frac{9}{20}\left(\frac{k}{N}D\right)^2 t^2\right). \tag{3}$$

Following the derivation of Eq. (1), convolution of Eq. (3) with the predicted RDC distribution, Eq. (A.3), yields (see Appendix A)

$$\frac{M_M(t)}{M_0} = \frac{5^{3/4}}{2\sqrt{2}\left(\frac{k}{N}Dt\right)^{3/2}}\mathrm{U}\left(\frac{3}{4},\frac{1}{2};\frac{5}{\left(2\frac{k}{N}Dt\right)^2}\right), \tag{4}$$

where $\mathrm{U}(a,c;x)$ is the confluent hypergeometric function of the second kind, and the subscript M refers to the present author's name. Note that as a direct result of recasting the squared end-to-end vector distribution in terms of the quantity D/N, the distribution of residual couplings, P_M, can be now represented by a gamma distribution of D_{res}, or

$$P_M(D_{res}) = \frac{2}{\sqrt{\pi}}\left(\frac{3}{2\frac{k}{N}D}\right)^{3/2}\sqrt{D_{res}}\exp\left(-\frac{3}{2}\frac{D_{res}}{\frac{k}{N}D}\right) \tag{5}$$

for $D_{res} \geqslant 0$ (Saalwächter, 2007). We will return to this important result below. Additionally, we will now refer to the quantity $(k/N)D$ as D_{avg} for notational simplicity.

Lastly we derive an alternative expression that assumes that the NMR observables of the network are governed by a Gaussian distribution of RDCs. This function is derived in the same manner as Eq. (4), but results instead from the normalized distribution

$$P_G(D_{res}) = \sqrt{\frac{2}{\pi}}\frac{1}{\sigma}\left[1+\mathrm{erf}\left(\sqrt{\frac{D_{avg}^2}{2\sigma^2}}\right)\right]^{-1}\exp\left(\frac{-(D_{res}-D_{avg})^2}{2\sigma^2}\right) \tag{6}$$

for $D_{res} \geqslant 0$. Following Appendix A the expression for the decay transverse magnetization (with subscript G for "Gaussian") is

$$\frac{M_G(t)}{M_0} = \exp\left(\frac{-\frac{9}{20}D_{avg}^2t^2}{1+\frac{9}{10}\sigma^2t^2}\right)\left(1+\frac{9}{10}\sigma^2t^2\right)^{-1/2} \times\left[\frac{1+\mathrm{erf}\left(\sqrt{\frac{5D_{avg}^2}{10\sigma^2+9\sigma^4t^2}}\right)}{1+\mathrm{erf}\left(\sqrt{\frac{D_{avg}^2}{2\sigma^2}}\right)}\right]. \tag{7}$$