

Uncertainties in the Determination of Cross-Link Density by Equilibrium Swelling Experiments in Natural Rubber

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ABSTRACT: Equilibrium swelling is a feasible and simple experiment to determine the cross-link density of networks. It is the most popular and useful approach; however, in most of the cases, the given values are highly uncertain if not erroneous. The description of the complex thermodynamics of swollen polymer networks is usually based on the Flory–Rehner model. However, experimental evidence has shown that both the mixing term described by the Flory–Huggins expression and the elastic component derived from the affine model are only approximations that fail in the description and prediction of the rubber network behavior. This means that the Flory–Rehner treatment can only give a qualitative evaluation of cross-link density because of its strong dependence on the thermodynamic model. In this work, the uncertainties in the determination of the cross-link density in rubber materials by swelling experiments based on this model are reviewed. The implications and the validity of some of the used approximations as well as their influence in the relationship of the cross-link densities derived from swelling experiments are discussed. Importantly, swelling results are compared with results of a completely independent determination of the cross-link density by proton multiple-quantum NMR, and the correlation observed between the two methods can help to validate the thermodynamic model.

Introduction

Rubber is an important kind of material with many practical applications and is characterized by a long-range elasticity. This property is obtained after the vulcanization process, where a *plastic* polymer is transformed into an *elastic* material by formation of a three-dimensional network of cross-links that connect the different polymeric chains. For this reason, it is not surprising that the most important properties of rubbers depend on the network structure, and its study allows us to reach a better understanding of the correlation between the microstructure and the macroscopic properties of the rubber.^{1–3}

The network structure is defined by several parameters, i.e., the number of cross-links, their functionality and distribution, network defects (dangling chains and loops), and entanglements. However, the difficulty to study the vulcanization reaction *in situ*, further complicated by the complexity of the polymeric system itself, makes even the number of junctions, which appears to be a rather directly measurable parameter, a hardly accessible quantity.

There are many different experimental approaches to the analysis of cross-linked polymers,⁴ such as inverse gas chromatography,⁵ osmometry,⁶ dynamical mechanical analysis,⁷ neutron scattering,⁸ or dielectric measurements.⁹ However, the most common techniques to determine the cross-link density are mechanical measurements,^{10–15} NMR spectroscopy,^{16–23} and equilibrium swelling.^{24–28}

Although some of the previously mentioned techniques give some extra information about the structure of the network, the equilibrium swelling experiment is nowadays the most widely used approach in rubber science and technology. The technique allows the determination of the average molecular weight between cross-links, M_c , commonly also expressed as cross-

link density $\nu = 1/2M_c$ in moles of cross-links per gram of rubber, or $\nu' = \rho_r/2M_c$ when it is defined per volume of rubber using the rubber density, ρ_r .

The thermodynamics of swollen polymer network are usually based on the Flory–Rehner model^{24–26} or, more correctly, the Frenkel²⁹–Flory–Rehner treatment. They postulate that, in the swollen state, the mixing and elastic components of the free energy are additive and separable, i.e., $\Delta G_{\text{tot}} = \Delta G_{\text{mix}} + \Delta G_{\text{elas}}$. Then, it can be expressed in terms of change in chemical potential of the solvent, $\Delta\mu_s^{\text{total}}$, by differentiation with respect to the number of moles of solvent

$$\frac{\Delta\mu_s^{\text{total}}}{RT} = \frac{\Delta\mu_s^{\text{mix}}}{RT} + \frac{\Delta\mu_s^{\text{elas}}}{RT} \quad (1)$$

In equilibrium, the elastic forces compensate the dilation of the network caused by the mixing contribution. Consequently, the total change in the chemical potential vanishes:

$$\frac{\Delta\mu_s^{\text{mix}}}{RT} = -\frac{\Delta\mu_s^{\text{elas}}}{RT} \quad (2)$$

R and T are the ideal gas constant and temperature, respectively.

It is generally accepted that the Flory–Huggins expression^{30,31} is most appropriate to define the mixing term

$$\frac{\Delta\mu_s^{\text{mix}}}{RT} = \ln(1 - \phi_r) + \left(1 - \frac{V_s}{V_r}\right)\phi_r + \chi\phi_r^2 \quad (3)$$

For a cross-linked polymer, the molar volume of the polymer (V_r) tends to infinity, whereby the expression is simplified to

$$\frac{\Delta\mu_s^{\text{mix}}}{RT} = \ln(1 - \phi_r) + \phi_r + \chi\phi_r^2 \quad (4)$$

where χ is the Flory–Huggins polymer–solvent interaction parameter and ϕ_r is the volumetric fraction of rubber (or polymer fraction) at swelling equilibrium.

On the other hand, the elastic contribution to the chemical potential is expressed in terms of a molecular theory.^{3,11,12} In

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the original Flory–Rehner expression, the affine deformation model,³² which is defined by eq 5 for a swollen network, was assumed

$$\Delta G_{\text{elas}} = \frac{1}{2} \frac{RT}{M_c} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) - \frac{2}{f} \frac{RT \ln(V/V_0)}{M_c} \quad (5)$$

where λ_i represents the elongation in three dimensions, V and V_0 are the total volume of the polymer–solvent system and the pure polymer, respectively, and f is the functionality of the cross-links.

Taking into account the equilibrium requirements (eq 2) and the mixing part defined in eq 4 and deriving eq 5 with respect to the number of moles of solvent, the classical Flory–Rehner equation is obtained

$$\ln(1 - \phi_r) + \phi_r + \chi \phi_r^2 = - \frac{\rho_r}{M_c} V_s \left(\phi_r^{1/3} - \frac{2\phi_r}{f} \right) \quad (6)$$

However, in the past years some works proposed that the phantom network model^{33,34} should be more adequate to represent the behavior of the swollen networks. In that case, the expression is written as

$$\ln(1 - \phi_r) + \phi_r + \chi \phi_r^2 = - \frac{\rho_r}{M_c} V_s \left(1 - \frac{2}{f} \right) \phi_r^{1/3} \quad (7)$$

Obviously, the real behavior of the swollen network is between the two extremes represented by affine and phantom models. This fact was incorporated in the later Flory–Erman model^{35,36} which, by using a variable K parameter, was able to interpolate between the different behaviors of the two models, giving a more realistic picture of the process.

Therefore, and according to the above reasoning, the calculated M_c values from swelling experiments are subject to a large uncertainty, such as the adopted model to define the elastic term. Furthermore, and no less importantly, the parameters that determine the average molecular weight between cross-links, i.e. ϕ_r , χ , or f in eqs 6 and 7, further increase the ambiguity.

Accepting the proposed models, maybe the most important factor which limits the range of confidence is the Flory–Huggins interaction parameter χ . It is usually assumed to be constant for a given polymer–solvent pair. However, this assumption was generally proven incorrect by different experimental and theoretical works^{37–45} that showed a dependence of χ on the volumetric fraction of polymer. In addition, the ϕ_r dependence of χ in cross-linked and star polymers is different in comparison with the corresponding linear polymers under the same conditions.^{46–61} The quantitative evaluation of M_c from swelling experiments is thus highly uncertain.

Other sources of ambiguity stem from the determination of the volumetric fraction of rubber in the swollen gel at equilibrium. In earlier works, the measurement of the volume of the swollen samples was the most widely used approach,⁶² as it represents the most direct and accurate method to determine ϕ_r . However, nowadays the gravimetric method is the most popular, since it is quick and simple.^{63–68} As to the gravimetric approaches, the most remarkable point concerns corrections that must be made in order to obtain meaningful results. For instance, it is necessary to take into account the fraction of insoluble ingredients and the “real” rubber density as well as some corrections due to the time dependence of the amount of imbibed solvent observed during the swelling process (as it was pointed out by Ellis and Welding,^{63,64} the swelling degree is continually increasing with time of immersion). This again adds another source of considerable uncertainty.

A detailed description of the experimental procedure and the associated accuracy in the determination of the cross-link density is thus not a trivial problem, and revising the scientific literature

on the topic, it appeared to us that a unified approach is still missing. On one hand, many of the mentioned ambiguities are not at all addressed in previous work, making it almost impossible to compare data from different sources. On the other hand, and more seriously, it appears that many of the above-mentioned problems have not even come to the attention of a considerable section of the scientific community using equilibrium swelling as a standard tool. This is an important but long neglected problem in rubber science and technology.

This paper reviews the most widely used approaches and approximations to determine the cross-link density via Flory–Rehner swelling experiments and tries to delineate the limitations and errors associated with each one as clearly as possible. We explicitly discuss the range of uncertainty of the obtained M_c values and finally suggest the best approach from our point of view in order to improve the application of this useful methodology.

In order to assess the validity of a method, it is obviously desirable to include results from independent methods. Different combined studies have been published,^{69–75} and many of them use NMR. It is in fact well-known that a linear relationship exists between the network parameters determined by equilibrium swelling and by NMR. This suggests that the models used to establish the relationship between the actual NMR observable (an apparent, i.e., averaged residual dipolar coupling, D_{res}) and the cross-link density are at least qualitatively correct. In our previous work,⁷⁵ we have identified proton multiple-quantum NMR (rather than the more common measurement of transverse relaxation times) as the most quantitative and reliable method for the measurement of residual dipolar couplings,⁷⁶ and we have presented a molecular model that relates D_{res} with M_c . This, as any other model for NMR data interpretation, is also based on a number of assumptions (e.g., the validity of the Kuhn and Gr n argument for the calculation of the order parameter S_0 of a network chain, the rescaling of the chain based on the known characteristic ratio, etc.). Therefore, the re-evaluation of the validity of our NMR model is another important purpose of this paper. It should be noted that the model uncertainties only pertain to a prefactor, implying that the observation of a linear correlation between swelling and NMR results is an important diagnostic criterion.

Experimental Section

Materials, Preparation of Samples, and Characterization.

The aim of this work is to check the confidence limits of the most popular and useful approach to determine the cross-link density, i.e. swelling experiments, using common rubber samples. The studied compounds, based on standardized natural rubber kindly supplied by Malaysian Rubber (SMR-CV60), were prepared in an open two-roll mill using standard procedures. Sulfur cure systems are nowadays the most useful vulcanization method and therefore the main subject of this work. A conventional cure system was used, increasing the amount of reactive species but maintaining the accelerant/sulfur ratio (0.2) constant. All the details about the composition of the different samples are showed in Table 1.

In some cases, NR samples were also vulcanized with different contents of dicumyl peroxide (DCP) as well as with a different sulfur/accelerant ratio (more information about these samples will be given in following sections). All specimen were cured in a laboratory press at 150 °C at their respective optimum times (t_{97}), deduced from the rheometer curve (Monsanto moving die rheometer, model MDR 2000E).

Determination of the Volumetric Fraction of Rubber, ϕ_r . The volumetric fraction of rubber was determined following different approaches (see the Discussion section), but always on the basis of equilibrium swelling experiments (72 h at 21 °C) using toluene (molar volume $V_s = 106.2$ mL/mol and density $\rho_s = 0.87$ g/cm³) as solvent. In addition, some complementary experiments were

Table 1. Composition and Density of the Studied Compounds

sample	recipe ^a (phr)		density (g/cm ³)			
	sulfur	CBS ^b	compd before swelling ρ_c^b	compd after swelling ρ_c^a	rubber network ρ_r	weight fraction f_{ZnO}
C-1	0.7	0.14	0.949 ± 0.004	0.955 ± 0.005	0.912	0.0464
C-2	1.3	0.26	0.958 ± 0.002	0.959 ± 0.002	0.922	0.0461
C-3	1.9	0.38	0.961 ± 0.004	0.9605 ± 0.0009	0.924	0.0458
C-4	2.5	0.50	0.967 ± 0.007	0.965 ± 0.001	0.929	0.0455
C-5	3.1	0.62	0.965 ± 0.005	0.966 ± 0.001	0.930	0.0452
C-6	3.7	0.74	0.970 ± 0.001	0.970 ± 0.001	0.934	0.0449

^a Ingredients in parts per hundred of rubber (phr): natural rubber 100; zinc oxide 5; stearic acid 2; CBS; sulfur. ^b *N*-Cyclohexyl-2-benzothiazolesulfenamide.

carried out using methyl ethyl ketone (MEK) as solvent ($V_s = 90.2$ mL/mol and density $\rho_s = 0.805$ g/cm³).

In all the samples, the procedure to obtain the experimental gravimetric data was the same: Five weighed test pieces of rubber (w_i) were immersed in toluene at 22 °C for a period of 72 h, renewing the solvent every 24 h. Finally, the samples were blotted with tissue paper to remove the excess of the solvent and immediately weighed on an analytical balance with an accuracy of $\sim 10^{-5}$ g (w_s). Finally, the samples were dried in a vacuum oven for ~ 24 h at 60 °C until constant weight (w_d). It is important to note that in order to obtain a correct ϕ_r the time dependence of this quantity due to gradual network degradation needs to be taken into account. This very important point will be described and discussed in the next section.

To obtain ϕ_r by using gravimetric methods is necessary to know the rubber density in the cross-linked sample. It appears to be common in the literature to approximate this parameter as a constant, $\rho_r^{\text{const}} = 0.92$ g/cm³. However, it is well-known that this quantity depends on the cross-link density in sulfur-vulcanized samples (in the case of NR vulcanized with DCP, no deviation from 0.92 g/cm³ is observed). Ellis and Welding^{63,64} suggested that an estimated rubber density could be calculated assuming that the volumes of polymer and sulfur are additive, with a fictitious density of 6 g/cm³ for the combined sulfur

$$\rho_r^{\text{E-W}} = \frac{w_{\text{rubber}} + w_{\text{sulfur}}}{\frac{w_{\text{rubber}}}{0.92} + \frac{w_{\text{sulfur}}}{6}} \quad (8)$$

where w_{rubber} and w_{sulfur} are the nominal weights of rubber and sulfur tabulated in Table 1. The main problem of this approach is the dependence on the density of the pristine rubber. In the literature,^{40,41,45} density values for pristine rubber range from 0.906 to 0.9132, with 0.908 g/cm³ as the most commonly used. The difficulty arrives in the a priori estimation of this value, without any other experimental data. However, it is a good approximation when the real rubber density can not be measured experimentally.

Obviously, the latter approach is the most recommended. In this work, the compound density, ρ_c , was determined via the hydrostatic weighing method, which is one of the best known density measurement techniques.⁷⁷ In this method, the apparent weight $\bar{W}$ of a specimen is measured in two different media, e.g. air and water, and the density is obtained from

$$\rho_c = \frac{\bar{W}_{\text{air}}\rho_{\text{water}} - \bar{W}_{\text{water}}\rho_{\text{air}}}{0.99983(\bar{W}_{\text{air}} - \bar{W}_{\text{water}})} \quad (9)$$

where ρ_{water} (0.9977 g/cm³ at 22 °C) and ρ_{air} (0.0012 g/cm³) are water and air densities, respectively, and 0.99983 is a geometric balance correction.

All measurements were performed on a Sartorius balance, model Kern 770, with a resolution of ± 0.1 mg. It is important to point out that the sensitivity of the weighing balance becomes the limiting factor in precision because the specimens are rather small (around 0.11 g).⁷⁸

The average density of at least three samples per compound (each sample is also measured two times) is summarized in Table 1. The density of the compounds was calculated after (ρ_c^a) and before (ρ_c^b)

swelling in toluene in order to established the contribution of all the soluble compounds present in the sample. According to the results in Table 1, the mass loss during the swelling process does not produce any appreciable change in the density value.

With known density of the compounds (values obtained after swelling were used), it is possible to calculate the experimental density of the rubber matrix after the swelling experiments as follows:

$$\rho_r = \frac{w_d - f_{ZnO}w_i}{\frac{w_d}{\rho_c^a} - \frac{f_{ZnO}w_i}{\rho_{ZnO}}} \quad (10)$$

where w_d and w_i are the weight of the dry sample after and before the swelling, respectively, ρ_{ZnO} is the zinc oxide density (5.0 g/cm³ according to the technical data given by the supplier, Lanxess), and f_{ZnO} is the weight fraction of zinc oxide calculated as $f_{ZnO} = (\text{ZnO weight})/(\text{recipe weight})$.

With eq 10 it is assumed that, after the swelling process, all the remaining ingredients in the sample are part of the rubber network, with the exception of the ZnO. We confirmed that both stearic acid and CBS (*N*-cyclohexyl-2-benzothiazolesulfenamide) are soluble in toluene. Moreover, the weight loss during the swelling process is close to the calculated amount of these ingredients (except for the lowest cross-linked sample C-1). Although sulfur is insoluble in toluene, we assume that it is part of the rubber network and therefore must be included in the calculation of the density.

The influence of the rubber density on the obtained M_c values will be discussed in the Results and Discussion.

Determination of M_c by Equilibrium Swelling. The average mass of network chains between cross-links was determined on the basis of the previously described equilibrium swelling experiments and assuming the formation of 4-functional cross-links during the vulcanization reaction. The given M_c values are the average of five samples per compound, and their associated standard deviation is around 2.5% on average, with a maximum value close to 6.6% and the minimum around 0.7%. These latter values are incorporated in figures of this work as error bars for the x -axis. The different approaches used to calculate the M_c value from the swelling experiments, i.e., corrections in the calculation of the volumetric fraction of rubber, different Flory–Huggins interaction parameters, and the use of affine and phantom models, will be further described in the Discussion section.

Determination of M_c by Proton NMR Spectroscopy. Proton NMR spectroscopy is an attractive and powerful tool to study the structure and dynamics of elastomers.¹⁶ The existence of cross-links and other topological constraints in rubber matrices renders the fast segmental fluctuations of the polymeric chains nonisotropic, and as a consequence, residual dipolar couplings (D_{res}) persist.^{18,79,80} Many NMR techniques have been used to estimate D_{res} , e.g. Hahn echoes⁸¹ (although the quantitative results obtained from this method have been seriously criticized,^{19,82,83} it is still used), combinations of Hahn and solid echoes,^{18,84,85} stimulated echoes,⁸⁶ and two-dimensional (2D) magnetization exchange spectroscopy.²⁰ However, the most recent and quantitative approach for the measurement of weak residual dipolar coupling is the double-

quantum (DQ) or, more generally, multiple-quantum (MQ) NMR technique.^{21–23,87–90}

The essential advantage of MQ spectroscopy is that, in the same experiment, two qualitatively different sets of data, a buildup curve (I_{DQ}) dominated by spin-pair double-quantum (DQ) coherences and a decay curve (I_{ref}), are measured. They can be used to independently analyze residual couplings and the chain dynamics. I_{ref} contains not only the signal from half of the quantum orders of the dipolar-coupled network chains but also the signal from uncoupled components. This uncoupled fraction is characterized by isotropic motion and rather slow relaxation and is formed mainly by network defects, i.e., loops and/or dangling chains. The corresponding long-time tails of I_{ref} can therefore be determined quantitatively and subtracted. In this way, the experimental I_{DQ} can be normalized by point-by-point division by the corrected sum of the two components in order to obtain a buildup function (I_{ndQ}) that is largely independent from the time scale of the segmental motion and is therefore related only to the network structure (i.e., D_{res}).

¹H MQ experiments were carried out in a Bruker minispec mq20 operating at 0.5 T (90° pulses of 1.7 μs length). The experiments and the data analysis were performed following the previously published procedures.^{22,23,75,76} All samples characterized by NMR were not extracted after the vulcanization, yet we have checked that the extractable content is minor; thus, its removal has virtually no effect on the results (data not shown).

It is important to note that, apart from the fixed segmental time scale, the required time to sweep out the whole conformational space between topological constraints (related to the longest tube-constrained Rouse time), and thus the time required to achieve full averaging, becomes rather long for less cross-linked systems, leading to a residual temperature dependence.⁸⁹ Normalized DQ buildup data (I_{ndQ}) of common rubbers can be safely taken to be temperature-independent at 353 K or higher (around 140–145 K above the glass transition, T_g). Only the lowest cross-linked sample of our series (C-1) was evaluated at 373 K (the sample starts to degrade at 393 K). The variations of D_{res} with temperature in the range from 283 to 373 K (i.e., around 75 and 165 K above T_g , respectively) are briefly discussed in the next section.

In all the studied samples, distribution effects of D_{res} (related to different end-to-end separations and polydispersity of network chains) do not play any role. This somewhat surprising finding is explained by cooperativity of the reorientational dynamics on the length scale of a few network chain lengths, which averages the observable.⁹⁰ Therefore, the normalized DQ buildup curves were analyzed in the quasi-static limit in terms of a single D_{res} .^{22,23,75}

$$I_{\text{ndQ}}(D_{\text{res}}) = \frac{1}{2} \left(1 - \exp \left[-\frac{2}{5} D_{\text{res}}^2 \tau_{\text{DQ}}^2 \right] \right) \quad (11)$$

The obtained apparent coupling constant is directly proportional to the cross-link density, $\sim 1/M_c$, and the derivation of the proportionality factor was the subject of a previous paper.⁷⁵ In order to clarify that this is in itself a highly model-dependent procedure, we here give some of the details. D_{res} , which represents an average over different internuclear pair couplings, can be divided by its static counterpart, D_{stat} , in order to obtain the dynamic order parameter of the polymer backbone, S_b

$$S_b = k \frac{D_{\text{res}}}{D_{\text{stat}}} = \frac{3}{5} \frac{r^2}{N} \quad (12)$$

where k is a constant required by the model in order to rescale D_{stat} (determined by fixed proton–proton distances) in order to account for averaging effects that occur on the level below the segmental (Kuhn) length. Therefore, k represents the local coupling topology and intrasegmental motions. From previous spin dynamics simulations, and assuming a reasonable model for the intrasegmental motions, an apparent reference coupling for natural rubber was obtained: $D_{\text{stat}}/k = 2\pi \times 6300$ Hz (see ref 75 for a detailed account).

Equation 12 relates the NMR observable with r , i.e., the ratio of the end-to-end vector to its average unperturbed melt state ($r^2 =$

$r^2/\langle r^2 \rangle_0$), and with N , which represents the number of statistical (Kuhn) segments between constraints. The prefactor only reflects the assumption of Gaussian statistics for $\mathbf{r}$. In addition, N provides the link to calculate the molar mass between constraints, M_c .

The latter magnitude is defined as the molar mass of the monomer unit ($M_0 = 68.1$ g/mol for NR) multiplied by the number of monomer units, n , which is in turn related to N via an expression that defines the contour length $L = Nl_K = c4nl$ as a projection length of the fully stretched chain. Therefore

$$M_c = nM_0 = \frac{Nl_K}{c4l} M_0 \quad (13)$$

The ratio between the Kuhn segment length, l_K , and the root-mean-square bond length, l , can be substituted by the known characteristic ratio C_∞ (defined as $C_\infty = Nl_K^2/4nl^2$ with an average value of 4.7 for NR), leading to the expression

$$M_c = \frac{NC_\infty}{4c^2} M_0 \quad (14)$$

The factor c is the ratio between the projection length l_p of the bond onto the backbone at its maximum extension with respect to l and takes on a value of 0.7 for NR (according to the crystal-structure-based model discussed in ref 75). By the use of eq 12, M_c is finally related with the NMR observable, D_{res} , by the following expression:

$$M_c = \frac{3 \times 6300 \text{ Hz}}{5D_{\text{res}}/2\pi} \frac{4.7}{4 \times 0.7^2} M_0 = \frac{617 \text{ Hz}}{D_{\text{res}}/2\pi} \text{ kg/mol} \quad (15)$$

In order to obtain a clear picture on the variation of the results from the different approaches to the swelling experiment, we take these NMR values as an independent reference and always plot their inverse (which reflects cross-link density) vs the different values obtained from swelling. Note that very good linear relationships between NMR-based cross-link density determinations, and elastic moduli have been reported for different polymer systems,^{91,92} demonstrating the qualitative validity of the models used for the interpretation of NMR results (mainly eq 12) and supporting the use of NMR as a proper reference. Correlating NMR with swelling results, we also found good linear dependencies in most cases. In fact, we hoped to observe more decisive deviations from linearity for certain models (e.g., constant vs ϕ -dependent χ parameter) and thus to be able to even judge the validity of the different thermodynamic models. However, in the investigated M_c range and the limitations set by the (low) experimental error, all models turned out to be linearly related for the common case of the NR–toluene system. However, the possibility of using NMR (that characterizes the bulk unswollen network completely independently from its thermodynamics) to test (and possibly falsify) thermodynamic models is certainly an important strategy for other polymer network–solvent systems. We demonstrate it below for a less common swelling solvent, MEK.

Results and Discussion

The aim of this work is to identify the range of confidence for a given M_c value using the most often used methods in rubber science and technology. For this reason, eq 6 will be used as reference of the Flory–Rehner theory in the following section. In addition, these results will be compared with those obtained by means of NMR, paying particular attention to deviations from this relationship caused by the different thermodynamic models.

We group the problem into three categories, that is, (i) determination of volume fraction of rubber, (ii) the polymer/solvent interaction parameter (χ), and (iii) the applied model of elasticity.

Initially, we will briefly discuss some NMR results that show the D_{res} dependence on the number of cross-links and polymer dynamics. Then, we will present the variations of the average

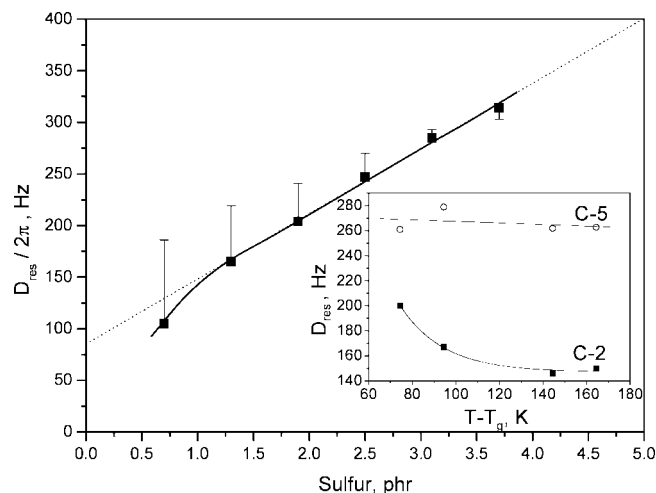


Figure 1. Relationship between the apparent dipolar coupling constant (always measured at the temperature where a constant D_{res} is reached) and the amount of sulfur added to the sample. The dashed line represents a linear fit of the last five points, whereas the solid line is only a guide to the eye. Error bars indicate the temperature dependence of D_{res} , which is also shown in more detail in the inset for the samples C-5 (plateau at $T = T_g + 75$ K) and C-2 (plateau at $T = T_g + 145$ K).

molecular weight between cross-links caused by the application of different corrections to evaluate the volumetric fraction of rubber from the gravimetric data. Once the best approach to study our system is identified, the role of the Flory–Huggins polymer–solvent interaction term in the estimation of M_c will be analyzed. Finally, the phantom network approach will be tested in order to delineate the limiting situations established in the Flory–Erman theory, realizing that the true behavior may be somewhere in between. The whole procedure will give us a confidence interval associated with the calculated cross-link density via swelling method. Finally, the significance of the relationship between the results obtained from swelling and NMR techniques will be discussed.

M_c Obtained by NMR. The NMR-determined residual dipolar constant obviously increases with the number of topological restrictions (mainly cross-links), as is shown in Figure 1. We stress the surprisingly good linear relationship between D_{res} and the amount of sulfur, which implies a constant yield in the vulcanization reaction. Only a small deviation is observed in the lowest cross-linked sample C-1, probably because it is a network just above the percolation threshold. Note also the intercept value in the y-axis, which is indicative of the fact that NMR is sensitive not only to the cross-links but also to topological constraints, i.e., entanglements, which are equally important restrictions to the segmental motion (and of course contribute to the elasticity). Further explanations on this point will be given in the next sections.

In previous work, we have demonstrated⁸⁹ that a residual temperature dependence of normalized DQ data can possibly lead to an overestimated D_{res} and thus cross-link density, in particular for lowly cross-linked systems. The (Rouse) relaxation time of the longest chain between topological restrictions (which roughly corresponds to the entanglement length at low cross-link density) is tied to the segmental relaxation time, which in turn is related to T_g . Therefore, the complete segmental averaging over all possible chain conformations on the time scale of the NMR experiment, and therefore a temperature independence of D_{res} , is only expected far above T_g .

As is obvious from the y-axis error bars in Figure 1, the temperature dependence is indeed a very important factor in the less cross-linked samples. This dependence is of course stronger in non-cross-linked samples, where the signal is only

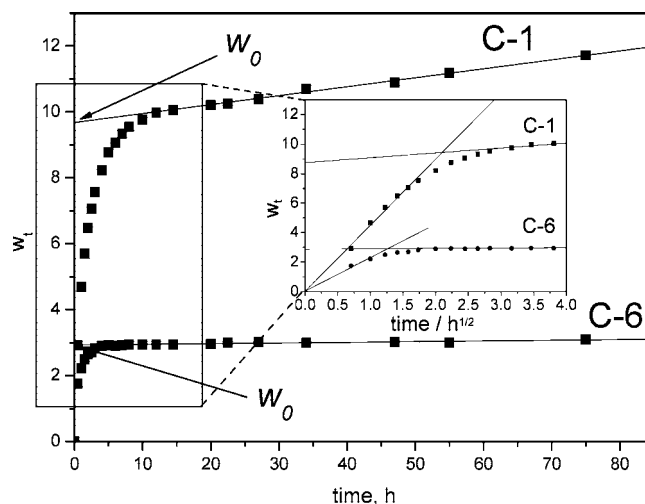


Figure 2. Degree of swelling vs immersion time for the samples C-1 and C-2. Each curve is a representation of the average behavior of three samples. At short times, the process is controlled by diffusion (see inset, where an initial linearity is apparent in a plot vs the square root of time), while at longer times of immersion, a further increase of swelling is caused by network degradation.

due to the entanglement restrictions and further decays due to reptation motion; thus, it never reaches a plateau. For instance, in sample C-1, D_{res} obtained at $T = T_g + 75$ K is 46% higher than the value obtained from the plateau beyond 165 K above T_g . For intermediate samples, D_{res} reaches a plateau at temperatures around $T_g + 95$ K, and $T_g + 75$ K is sufficient for the samples with the highest cross-link density. To take properly the temperature dependence into account and use D_{res} values from the plateau range was particularly important for the present study. Thus, all the measurements were performed at 353 K, which is far above the T_g of all samples (they vary from -65 to -56 °C) and ensures that the segmental dynamics is fast enough in order to average over all the possible conformations (thus reaching the plateau regime). Repeated measurements show that at the measuring temperature of 353 K and the required experimental time around 45 min; therefore, the degradation of the network is not an important factor.

Finally, from the experimental D_{res} and using eq 15, it is possible to obtain the average molecular weight between cross-links. More precisely, the inverse result, reflecting the overall cross-link density, is of course the sum of the density of actual chemical cross-links ($1/M_c$) and entanglements ($1/M_e$), taking into account that the latter also includes trapped entanglements ($1/M_{\text{te}}$).

M_c Obtained from Equilibrium Swelling. *1. Swelling Kinetics.* In order to obtain M_c from equilibrium swelling experiments, the first step is to study the swelling kinetics of the networks in order to estimate the most accurate equilibrium weight of solvent, w_s^{eq} . It is common to define the equilibrium weight of liquid as the difference $w_s^{\text{eq}} = w_s - w_d$ after 3 days of swelling, which is considered a time long enough to reach the equilibrium. However, according to Figure 2, which shows the degree of swelling (defined as $w_t = (w_s - w_i)/w_i$) as a function of time, an additional slow process appears.

At short times, swelling is dominated by a diffusive process, characterized by a linear behavior when w_t is plotted vs the square root of time (inset in Figure 2). This fast process seems to reach saturation in a rather short time, around 20 h. After that, a continuous but slow increase takes place as a consequence of the degradation of the network, as was stressed by Ellis and Welding.^{63,64}

This behavior was also studied by NMR (Figure 3), where a conventionally sulfur-cross-linked sample is compared with a

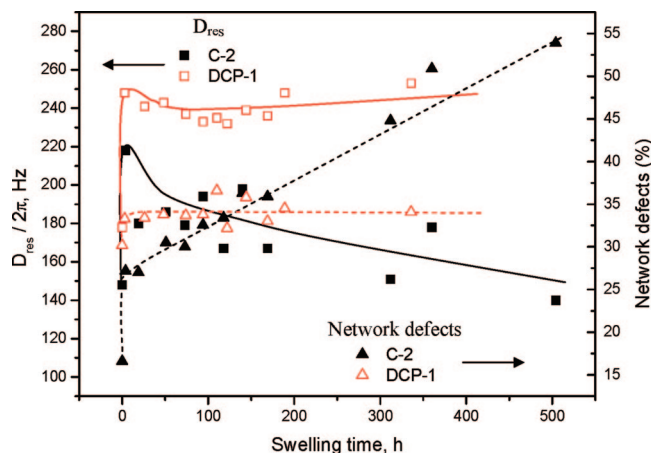


Figure 3. Evolution of D_{res} and the NMR-determined fraction of noncoupled network defects with swelling time for samples vulcanized with a conventional sulfur cure system (C-2) and an organic peroxide (DCP-1). DCP-1 is an NR sample vulcanized with 1 phr of dicumyl peroxide at 150 °C at its optimum cure time (t_{95}). Lines are only guide to the eye.

peroxide-cured sample. In the first stage of swelling, an abrupt increase in both D_{res} and the noncoupled fraction (network defects) as compared to the dry state is observed. This behavior is related to the nonhomogeneous nature of the swelling process in rubber networks.^{93,94} More highly swollen areas take on higher chain order parameters, and less swollen can even exhibit reduced order parameters due to relief of entanglements (“des-interpersion”), subaffine local deformation, and genuine excluded-volume effects (on details of which a publication is submitted), whereby the average value of D_{res} increases nonaffinely, while its distribution is strongly broadened (not shown). Moreover, the relief of entanglement constraints by topological reorganization is retarded in time due to its complex nature, which leads to a small local maximum of D_{res} at around 10 h.

After approximately 20–30 h, the system reaches the equilibrium swelling. The uncoupled fraction (defects such as dangling chains and loops) also reaches a plateau, since these structures become increasingly unentangled, with significantly decreased relaxation times (for arm retraction, etc.).

However, while the DCP-cross-linked sample (where the cross-links are carbon–carbon bonds) reaches a plateau for both observables, the sulfur-cured sample shows an increasing amount of defects as well as a decreasing tendency for the residual coupling. This is clearly indicative of a network degradation process. We also note that the large variations in both D_{res} and the uncoupled fractions result from some fitting ambiguities, related to the fact that the system develops a third fraction with higher molecular weight. This fraction does not have a residual coupling (i.e., it is isotropically mobile), but it has a short relaxation time comparable to that of the network fraction.

Obviously, the degradation process is related exclusively with the sulfur bridges. In order to clarify the origin of the degradation, the swelling process in sulfur-cured samples was carried out under different conditions. According to the results shown in Figure 4, the breakdown of the network is caused by a photo-oxidative process, reaching even complete dissolution of the network at longer times (around 1 month at room temperature). The exclusion of light or oxygen considerably reduces the destruction of the sulfur bridges, but in both cases a minor increase of the swelling degree with time is still observed (samples under inert atmosphere but exposed to light even showed an exponential increase of the swelling degree at longer times of swelling). Only under a nitrogen atmosphere

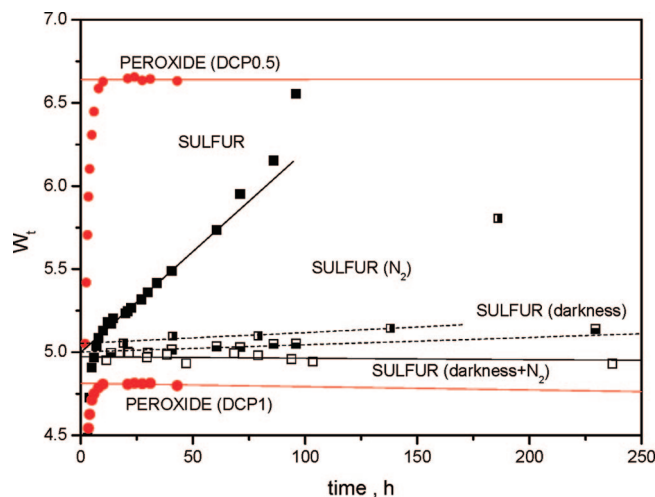


Figure 4. Degree of swelling vs immersion time for the sample C-1 (squares) under different storage conditions: stored in air and exposed to light (solid squares), under inert atmosphere of N₂ but exposed to light (N₂), protecting the sample against light but in air atmosphere (darkness), and stored under nitrogen atmosphere in the darkness (darkness + N₂). The degree of swelling for the samples DCP0.5 and DCP1 (NR vulcanized with 0.5 and 1 phr of DCP, circles) was determined after storage in air and exposed to the light. Lines are linear fits of the experimental data after the step controlled by diffusion.

and complete darkness conditions it is possible to reach the equilibrium swelling in this type of network. The good news is, however, that an extrapolation to zero time gives a swelling degree that is very close to the equilibrium value in all the cases.

In conclusion, to obtain a good equilibrium weight of liquid, w_0^{sol} , from which ϕ_r could be calculated, the excess of solvent produced by the network degradation has to be corrected. The best approach is as follows

$$w_0^{sol} = w_{3d}^{sol}(1 - d_{3d}) \quad (16)$$

where d_{3d} is the increment of swelling degree caused by the degradation processes estimated as $d_{3d} = (w_{3d} - w_0)/w_0$. In this expression, w_0 is the swelling degree at $t = 0$, obtained by extrapolation in Figure 2. It is important to emphasize that, in contrast to the method proposed by Ellis and Welding, w_0 was estimated by using time rather than its square root for the X-axis. In this way, the slope more correctly and intuitively reflects the decomposition kinetics (where a linear fit is just an approximation to a first-order growth law), rather than a diffusive process.

2. Determination of the Volumetric Fraction of Rubber, ϕ_r . The definition of volumetric fraction of rubber in swelling experiments is simple and unequivocal, $\phi_r = (\text{rubber volume})/(\text{rubber volume} + \text{solvent volume})$. However, some different approaches have been used in the literature according to the studied system. In rubber compounds that contain insoluble components, it is necessary to properly eliminate this fraction in order to obtain a ϕ_r with a real meaning. The most useful and general method was again described by Ellis and Welding.^{63,64}

In a first approximation, the authors suggested to take into account only the polymer in order to calculate ϕ_r . The influence of insoluble components such as sulfur, zinc oxide, or accelerants is corrected according to the following expression

$$\phi_r = \frac{\frac{w_d - f_{\text{ins}} w_i}{\rho_r}}{\frac{w_d - f_{\text{ins}} w_i}{\rho_r} + \frac{w_0^{\text{sol}}}{\rho_s}} \quad (17)$$

where f_{ins} is the weight fraction of insoluble components, defined as $f_{\text{ins}} = (\text{insoluble components weight})/(\text{recipe weight})$ (in our case it should be $f_{\text{ins}} = f_{\text{ZnO}} + f_{\text{sulfur}}$). It is the most useful method in rubber science and technology, but in our opinion it could be improved since the substances that are able to create cross-links are not included in the fraction of the actual rubber network.

We favor another approach, also alluded to in the original work⁶⁴ of Ellis and Welding, in which ϕ_r is calculated taking into account the rubber network. Consequently, only the zinc oxide is considered insoluble ($f_{\text{ins}} = f_{\text{ZnO}}$). Conceptually, the latter approach seems to be more correct, and the noninclusion of the sulfur in the network leads to a deviation in the final cross-link densities between 1.5% and 6.3%, depending on the amount of sulfur. In addition, not only the volume of the insoluble particles but also an excess of solvent that arises in the case of noninteracting filler particles (ZnO) should be corrected for. In swollen samples, some amount of solvent is inside a vacuole that is formed at the rubber/ZnO interface and therefore is measured but actually does not take part in the swelling process of the rubber (see inset in Figure 5). This means that the volumetric fraction of rubber measured by eq 17 (here it is defined as ϕ_r^* to distinguish it from the *corrected* value ϕ_r which will be defined below) is underestimated because it takes into account the excess of solvent as follows:

$$\phi_r^* = \frac{V_r}{V_r + V_s^* + V_s^v} \quad (18)$$

Here, V_r is the volume of rubber, V_s^* is the volume of solvent that swells the rubber network, and V_s^v is the volume of solvent imbibed in the vacuole formed at the ZnO/rubber interface. The

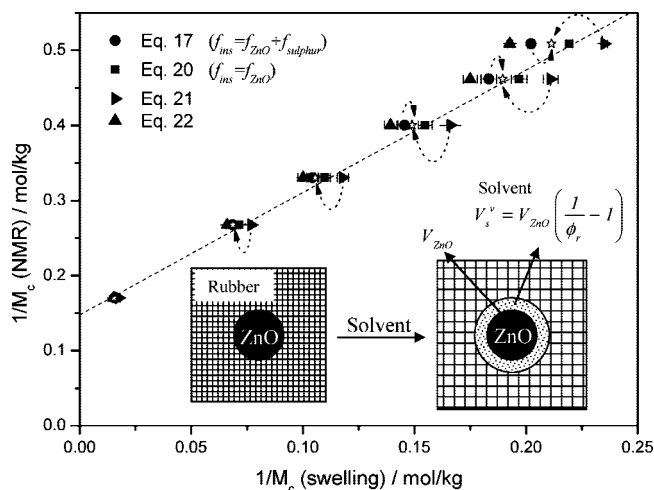


Figure 5. Comparison of swelling-determined reciprocal inter-cross-link molecular weights with corresponding results from NMR experiments. Variations of the estimated cross-link density via equilibrium swelling according to the different approaches used to take account the insoluble substances in the calculation of ϕ_r (see text). In addition, $\chi = 0.393$ and an affine model were assumed. Arrows indicate the variation of the data (from eqs 17 and 21) when the correct density value in relation to the definition of the approach is applied (stars indicate the value). The line connects the corrected values. The inset shows the excess of solvent (assuming an affine deformation) imbibed in the ZnO/rubber interface caused by the noninteraction between the solid particles and rubber.

volumetric fraction of rubber properly defined should be written as

$$\phi_r = \frac{V_r}{V_r + V_s^*} \quad (19)$$

Assuming an affine deformation, the excess volume should be a function of the volume of ZnO (V_{ZnO}) as well as the volumetric fraction of rubber ϕ_r via $V_s^* = V_{\text{ZnO}}(1/\phi_r - 1)$. Therefore, it is possible to define the corrected volumetric fraction of rubber as a function of experimentally accessible parameters:

$$\phi_r = \frac{1 + \frac{V_{\text{ZnO}}}{V_r}}{\frac{1}{\phi_r^*} + \frac{V_{\text{ZnO}}}{V_r}} = \frac{1 + \frac{(f_{\text{ZnO}} w_i)/\rho_{\text{ZnO}}}{(w_d - (f_{\text{ZnO}} w_i))/\rho_r}}{\frac{\frac{w_d - f_{\text{ZnO}} w_i}{\rho_r} + \frac{w_0^{\text{sol}}}{\rho_s}}{\frac{w_d - f_{\text{ZnO}} w_i}{\rho_r}} + \frac{(f_{\text{ZnO}} w_i)/\rho_{\text{ZnO}}}{(w_d - (f_{\text{ZnO}} w_i))/\rho_r}} \quad (20)$$

The last correction (only valid for particles that do not interact with the rubber) only leads to differences around 2% in these samples with 5 phr of ZnO. However, at higher content of an insoluble fraction, such as actual fillers, it will play a major role in the determination of cross-link density by swelling measurements. This will be reported in future work. The results are shown in Figure 5, where for the first time now the different swelling approaches are represented in relation to the NMR results (in order to avoid interferences with the discussion in the following section, M_c values presented here were calculated using a standard value of $\chi = 0.393$ for the NR/toluene pair^{39,95}).

However, if we are consistent with the main idea of the more common approach, i.e., sulfur is not included in the network, ρ_r should be taken as 0.92 g/cm³. In this case, the error is reduced (around 2.4% in average), as it is indicated in Figure 5 by the arrows. In order to delineate the importance of the insoluble component correction, two other approaches are represented in Figure 5. In the first one, all the sample volume is considered as rubber volume

$$\phi_r = \frac{\frac{w_d}{\rho_r}}{\frac{w_d}{\rho_r} + \frac{w_0^{\text{sol}}}{\rho_s}} \quad (21)$$

In the other extreme, all the ingredients, with exception of rubber, can be considered insoluble

$$\phi_r = \frac{\frac{w_f f_r (1 - \alpha)}{\rho_r}}{\frac{w_f f_r (1 - \alpha)}{\rho_r} + \frac{w_0^{\text{sol}}}{\rho_s}} \quad (22)$$

where f_r is the weight fraction of rubber, expressed as $f_r = (\text{rubber weight})/(\text{recipe weight})$ and α is the mass fraction lost during the swelling ($\alpha = (w_i - w_d)/w_i$).

Obviously, the application of both methods to our system is a complete mistake. The M_c values not only are conceptually false but also show deviations up to 10%. In the first case, the overestimation of the cross-link density is lessened by the use of the compound density, which is more appropriate according to the definition of this method, obtaining similar values with respect to the approach of Ellis and Welding. This fact is easily explained since, as is shown in Figure 6, the deviation produced

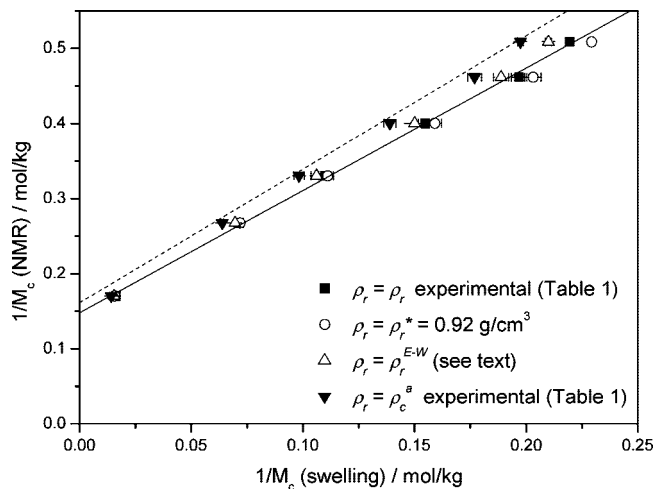


Figure 6. Variation of the reciprocal inter-cross-link molecular weights from equilibrium swelling data with the value of rubber density. The dashed line connects the results if the excess of imbibed solvent during 3 days of immersion time is not suppressed to calculate ϕ_r . The solid line is a linear fit of the values obtained by use of the most correct approach to calculate ϕ_r . In all the cases, eq 20 was used to calculate ϕ_r , and the affine model and $\chi = 0.393$ were assumed.

by using the compound density is partially canceled by the conceptual error of the method. Nevertheless, it is important to remember that even when the values are close to those obtained by the better approach, these values arise from a cancelation of errors in a conceptually false definition (at least within our interpretation). In addition, this “trick” is not recommendable since, for higher insoluble fractions, the deviation respect to the correct approach always increases.

In conclusion, it could be shown that the method described by eq 20 is the most general and correct approach in the estimation of ϕ_r when there are insoluble particles that do not interact with the rubber molecules. The use of any other approach inevitably leads to inconsistencies.

In order to close the discussion about the measurement of the volumetric fraction of rubber, it is important to stress the importance of using the corrected equilibrium weight of liquid in order to eliminate the excess of imbibed solvent caused by the photo-oxidative degradation of the network. As is also shown in Figure 6, the neglect of this correction leads to an underestimation of the cross-link density of about 15% on average. Here, we would like to point out that the use of the solvent weighted after 20 h, or 3 days of immersion gives the same results (discrepancies are inside the experimental error, around 1%) when the above-mentioned correction is taken into account (obviously, the factor of correction is different and it is necessary to calculate it).

3. Influence of the χ Parameter. The Flory–Huggins polymer–solvent interaction parameter χ introduced in eq 3 describes the change in the chemical potential of the solvent accompanying the formation of a real solution, minus the corresponding quantity of solvent in the formation of the reference solution.⁴³ The parameter χ is a complex parameter influenced by both entropic and heat of mixing terms.²⁴ It has been used as a measure of the “goodness” of a solvent in a given polymer–solvent pair. Therefore, it is the key parameter to describe solution properties of linear polymer molecules (non-cross-linked polymers) and swelling behavior of networks.

The parameter χ was originally introduced by Flory and Huggins as a measure of the intermolecular potential energy in polymer solutions. Initially, it was defined as being inversely proportional to temperature, $\chi = f(1/T)$, but independent of the polymer concentration.^{24,96} However, subsequent experimental

and theoretical results demonstrated the necessity of treating χ as a function of ϕ_r .^{37–45}

Later on, Flory et al.^{36,37} suggested that the χ parameter, originally expressed as a constant, should be replaced by power series:

$$\chi = \chi_0 + \chi_1\phi_r + \chi_2\phi_r^2 + \dots \quad (23)$$

The concentration dependence of χ was included in other thermodynamics of polymer solutions theories, as it was reviewed by Orwoll.⁴³ However, the most important of them was the equation of state theory described by Flory.^{40,97–99} In this theory, the thermodynamics of polymer solutions are deduced from the equation of state of the pure components of the system. Nevertheless, the most significant conclusion concerning our discussion is that the dependence of χ with the temperature and polymer concentration in solution is justified. This new statistical theory of Flory represents a significant improvement over the early approach, which has been a comprehensive model to obtain qualitative information about the properties of polymer solutions.

Gee et al.⁴⁶ showed that, for cross-linked natural rubber in benzene, the swelling activity parameter, S , went through a maximum near to the maximum swelling and did not go toward zero in the unswollen state. These findings were later related by McKenna and co-workers with the possibility that the Flory–Huggins χ parameter for the cross-linked and un-cross-linked rubbers could be different. This possibility was intensely studied,^{46,58–60} in particular by McKenna^{47–51} and Horkay^{52–57} in diverse polymer systems. These authors showed that, in all studied systems, χ_c of the cross-linked polymer is always higher than the parameter for the un-cross-linked system in solution, χ_u , at identical polymer concentration (i.e., identical volumetric fraction of polymer).

McKenna et al.^{47–49} (and some other groups^{58,59}), being based upon the works of Freed et al.,^{100,101} suggested a linear dependence of the effective value of χ_c with the cross-link density, ν

$$(\chi_c - \chi_u)/\chi_u = \alpha\nu \quad (24)$$

Along these lines, Tan et al.⁵⁸ even claims a dependence of this parameter on the structure of the formed network.

However, some years later, McKenna and Horkay⁵¹ demonstrated that the Flory–Huggins χ_c parameter for cross-linked polymers is dependent on the volumetric fraction of polymer ϕ_r but totally independent of the detailed network structure, i.e., mainly the actual cross-link density. In all cases, the expression $\chi_c > \chi_u$ was demonstrated to be correct. This suggests that the total loss in the degree of translational freedom, caused by the introduction of cross-links, could be the reason for the conceptually different concentration dependence exhibited by χ in polymer gels and solutions. It simply points to an entropic origin of the large value of χ for both cross-linked and star polymers¹⁰² as compared to the linear systems. For more details on this topic, we recommend the original articles of McKenna and Horkay and the recent review of Horta and Pastoriza.⁶¹

Figure 7 shows the variation of χ with polymer concentration for both un-cross-linked and cross-linked natural rubber, using toluene and methyl ethyl ketone (MEK) as solvents. Note that, in the case of the NR–toluene pair, the original data for the cross-linked system were obtained from poly(*cis*-isoprene) and deuterated toluene.⁵⁵ In addition, these values represent a system at 25 °C, therefore, and according to the temperature dependence of natural rubber–toluene system,¹⁰³ a deviation of about 3% is expected since we use these values for experiments at 22 °C. It should be emphasized that there is an obvious disproportion between the importance of the χ parameter to describe the

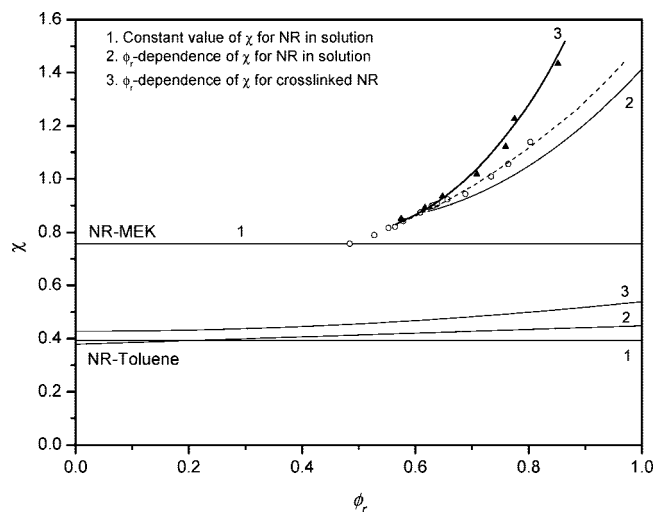


Figure 7. Dependence of the Flory–Huggins parameter on the polymer concentration. For the natural rubber–toluene pair (at 25 °C), χ was taken as 0.393 when it is considered constant,^{39,95} $0.378 + 0.07\phi_r$ for in NR solution,³⁹ and $0.427 + 0.112\phi_r^2$ for cross-linked poly(*cis*-isoprene) swollen with deuterated toluene at 25 °C.⁵⁵ In the case of natural rubber swollen with methyl ethyl ketone (MEK), triangles show the dependence of χ on polymer concentration in natural rubber networks according to ref 49 (line is only a guide to the eye). The concentration dependence of χ in solutions of NR in MEK was obtained from ref 96. Circles represent the “experimental” values of χ for the NR samples swollen with MEK that are needed to obtain the same cross-link density as obtained from swelling experiments with toluene. The lowest value ($\chi = 0.757$) was used as a constant χ . Finally, the dashed line represents the χ behavior described in ref 41 for NR dissolved in MEK.

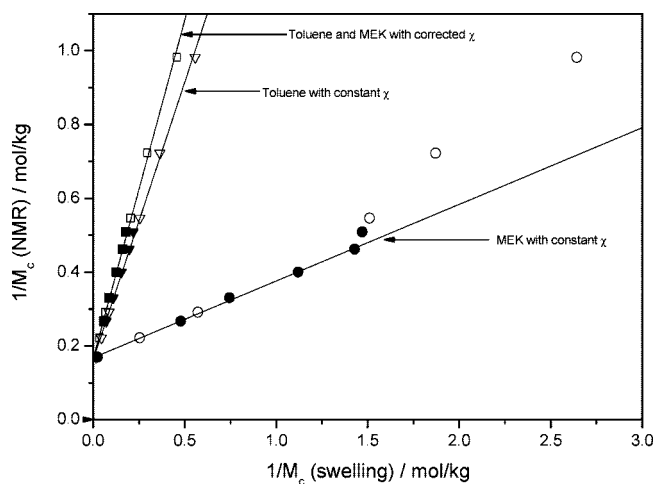


Figure 8. Variation of the reciprocal inter-cross-link molecular weights measured by swelling experiments (affine model) with respect to the value of the Flory–Huggins parameter for natural rubber swollen by toluene and MEK. Filled symbols correspond to sulfur-cured samples, whereas empty ones are for NR vulcanized with different contents of DCP.

swelling properties of cross-linked polymers and the scarce experimental results on its temperature and polymer concentration dependence for many important polymer–solvent pairs. It is even possible to find exactly opposing behaviors for the same polymer–solvent system.^{39,104}

From the prior arguments, it is obvious that the use of the Flory–Huggins parameter obtained for polymer solutions (even when the dependence with the polymer concentration is assumed) will lead to overestimated cross-link densities (around 25–30%), as is shown in Figure 8. The central conclusion is that, taking into account the widespread use of the solution-

based χ parameter to characterize natural rubber networks, most of the previously reported data for its cross-link density are overestimated.

On the other hand, the deviations between the cross-link densities from constant and concentration-dependent solution values of χ are relatively minor (not shown). Unfortunately, for toluene as solvent, no deviation from linearity is observed in our NMR-correlation plots for any of the adopted Flory–Huggins polymer–solvent interaction parameter models (Figure 8). This is mainly due to the fact that the volumetric fraction of rubber at swelling equilibrium over the typical cross-link density range used for practical purposes coincides with the range of ϕ_r where the crossover between both behaviours occurs (roughly from 0.1 to 0.3; see Figure 7). In addition, the values for the cross-linked systems have a tendency almost parallel to the linear-polymer values in the typical polymer concentration range. Obviously, more significant differences and possible deviations from linearity should be expected for very highly cross-linked NR samples which correspond with higher polymer fractions at swelling equilibrium.

In order to check the feasibility of the NMR correlation approach, another alternative is the use of a poorer solvent, in this case MEK. Significant differences in χ concentration dependence between un-cross-linked NR in solution or swollen NR networks in MEK are reported in the literature.^{49,96} However, $1/M_c$ is very sensitive to small variations in the value of χ in this system. It causes large deviations as compared to the results obtained with toluene as swelling agent. In addition, we have not found any value of χ in the literature that covers the lower polymer concentration range of our samples. Therefore, a workaround the problem is to use the cross-link density obtained from the swelling experiments in toluene (assuming those results as being correct) and calculate the corresponding Flory–Huggins parameter for the NR–MEK pair. Of course, in order to obtain the experimental values of ϕ_r in MEK, all the previously mentioned considerations and corrections were taken into account.

For this reason, we used the lower value of χ obtained in this way as constant value for this system instead of the traditional value of 0.835 given by Bristow and Watson³⁹ (this value was obtained from a system with $\phi_r = 0.5794$, and as a consequence, all our samples, having lower values of ϕ_r at equilibrium, would show a negative and thus meaningless $1/M_c$).

Figure 7 shows that, at lower polymer concentration, our experimental points are superimposed with the χ values obtained for NR networks (ref 49). However, at higher polymer concentration, an inflection point becomes apparent where both tendencies start to differ. In any case, the so-obtained χ values are notably higher than those described in ref 96 for NR solutions in MEK. This again confirms the different concentration dependence of the Flory–Huggins polymer–solvent interaction parameter for linear and cross-linked polymers.

This conclusion is in contradiction to the behavior of χ for this system obtained by Brostow.⁴¹ He corrected the data of Gee et al.⁹⁶ in order to obtain χ as a function of segment fractions instead of volume fractions (according to the equation of state of the pure components of the systems proposed by Flory). As is illustrated in Figure 7, the dependence for NR in solution (un-cross-linked NR) perfectly fits our data for swollen NR networks, in clear disagreement with the main idea. However, when Brostow’s data are examined in detail, it appears that he calculated the values of χ mixing experimental data obtained from un-cross-linked NR in MEK and cross-linked samples, as Gee et al.⁹⁶ explained in their original work. Consequently, he obtained some parameters without physical meaning. The cancelation of errors seems to be the reason for the unexpected coincidence of both results.

Coming back to the main goal at this point, the χ behavior for a NR network swollen in MEK is far away from constant (as traditionally assumed in rubber science). Therefore, it is a perfect system to check the importance of the Flory–Huggins polymer–solvent interaction parameter on the average molecular weight between cross-links calculated by swelling experiments. According to the comparison between the average molecular weight between cross-links calculated by swelling experiments or by NMR (Figure 8), the use of an underestimated and polymer concentration-independent χ parameter (an unrealistic value for the NR–MEK pair) does not only lead to a gross overestimation of $1/M_c$, like in the case of toluene, but now also to very significant deviations from the linearity predicted by a concentration-dependent χ . It is thus demonstrated that, indeed, the comparison of independent experimental methods, in this case NMR, with swelling results is a viable strategy to evaluate models that describe the thermodynamics of swollen rubbers.

Summarizing all results, it can be concluded that the Flory–Huggins polymer–solvent interaction parameter is the key to a better understanding of the thermodynamics of swelling in rubber networks. However, the literature on this topic is not sufficient to completely clarify the meaning of this parameter. In some cases, results are contradictory, and of course only a few polymer–solvent systems have been studied. For this reason, uncertainties in χ are among the most important contribution to the uncertainty in the determination of cross-link density by equilibrium swelling experiments.

4. Dependence on the Theory of Rubber Elasticity. The elastic behavior of a rubber network is usually assumed to be in between the two extreme suppositions of the affine theory³² and the phantom network model.^{33,34} In the first case, the macroscopic deformation is assumed to be essentially the same as the microscopic deformation, and consequently, the cross-links are supposed to be fixed in space. Contrarily, the phantom model implies the free movement of the cross-links around a mean position. The later theory of Flory and Erman^{35,36} to explain the thermodynamics of swollen networks assumes that, in the real behavior of rubber networks, the fluctuations of the cross-links are reduced by topological restrictions, i.e., entanglements. These restrictions are considered in the theory by the definition of a K parameter, which varies from 0 (implying an affine network) to ∞ (for phantom behavior).

Traditionally, the most widely used equation to determine the cross-link density in swollen rubbers has been eq 5, which is based on the affine model.^{24–26} Nevertheless, several works suggest that the phantom network behavior provides a better approximation to the elastic behavior of swollen networks^{55,58,105} (based on the supposition that the topological restrictions are relaxed because of the swelling process). If the latter hypothesis is accepted, a considerable increase of $1/M_c$ is observed (Figure 9).

Obviously, as a consequence of the impossibility to quantify the real behavior of the network, the *true* cross-link density of the system should be in the range delimited by both extremes (accepting of course the validity of such chain-based theories in general). This results in an overall uncertainty of around 40% (taking the phantom model as reference) and is probably the most important problem to be resolved.

Relationship between NMR and Swelling Results. Probably, the most important observation is, again, the linear relationship between $1/M_c$ obtained from equilibrium swelling and NMR, as seen, for instance, in Figure 9 (the obtained R value, using the phantom model, is 0.9999). This means that the relationship $S_b \sim 1/N$ assumed for the NMR analysis is qualitatively correct. If both swelling and NMR gave correct results, the slope in our correlation plots would be the unity.

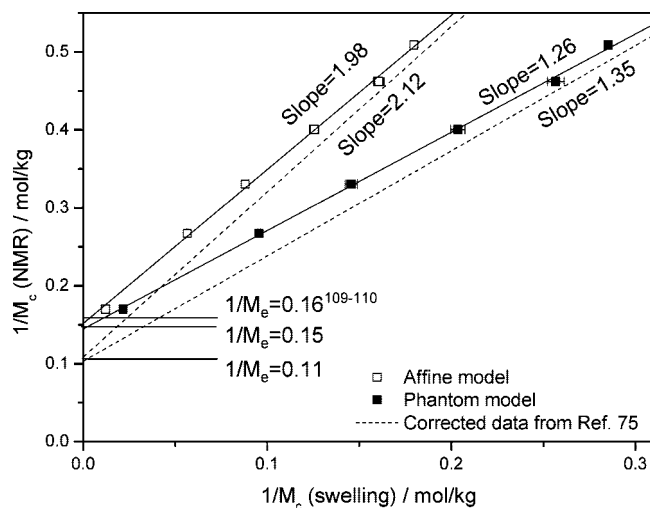


Figure 9. Comparison of swelling-determined reciprocal inter-cross-link molecular weights (using toluene as solvent) with corresponding results from NMR experiments. Variation of the estimated cross-link density via equilibrium swelling assuming the affine model (empty squares) or the phantom network (full squares) to define the elasticity of the swollen network. All other corrections were taken account to calculate the most accurate $1/M_c$ values. Dashed lines represent regressions of the data published in ref 75 (which are from different samples), but taking account all the corrections and the affine or phantom model.

As we have seen, swelling results based on the phantom model are most probably upper limits, with an uncertainty of about 40%. On the other hand, the many assumptions employed to relate the apparent D_{res} with M_c clearly indicate that the NMR value is also subject to an uncertainty, which we estimate to be in the 50% range (see Experimental Section and refs 75 and 94 for an in-depth discussion). An important factor that deserves more discussion is the influence of polydispersity and the type of average obtained by the method. The network chain length distribution is exponential in randomly cross-linked systems; thus $M_{w,c} \approx 2M_{n,c}$. To a first approximation, the swelling experiments “counts” the number of network chains; thus, the cross-link density $\sim 1/M_c$ should be a number-average. NMR measures every monomer unit; thus $D_{res} \sim 1/M_c$ should be a weight-average. NMR should thus be biased toward lower cross-link densities (higher M_c). Yet again, it should be stressed that NMR, even though measured at every monomer unit, gives only a single D_{res} rather than the expected wide distribution.⁹⁰ The cooperative reorientation dynamics that extends over a length scale of a few network chains somehow masks the chain-length polydispersity (and also the fact that different end-to-end separations should correspond to different order parameters), and the implications of this phenomenon with respect to the proportionality factor in $S_b \sim 1/N$ are as yet not fully understood.^{90,94}

Thus, for truly quantitative results, a proper calibration is desirable, but would only be possible if M_c were directly accessible. This is, for instance, possible for networks based on vinyl-functionalized poly(dimethylsiloxane), cross-linked by a silane and a Pt catalyst, where the cross-link points are chemically distinct and can be “counted” by high-resolution NMR methods. These results will be reported in a future publication.

Apart from these uncertainties, the combination of NMR and swelling measurements carries further complementary information on the network structure^{69,71,75} and allows us to draw some further conclusions on the range of uncertainty for both methods. In some previous works^{20,75,86,106–108} as well as in this article, a linear relationship between the network parameters determined

by both methods was found. The existence of a finite y-intercept (see Figure 9) is usually explained by the following relation:

$$\frac{1}{M_c(\text{NMR})} + \frac{1}{M_c} \approx \frac{1}{M_c(\text{swelling})} + \frac{1}{M_{te}} \quad (25)$$

It is attributed to the fact that additional restrictions caused by lateral chain packing or entanglements (tube constraint) sensed by NMR in bulk samples are at least partially relaxed at swelling equilibrium, i.e., $M_{te} \leq M_c$.^{75,109,110} As stated by Flory,¹² the total suppression of entanglement restrictions could only be obtained by preparation under high-dilution conditions. As this is not the case here, the retention of some topological restrictions, i.e. trapped entanglements, is realistic. Consequently, as implied by eq 25, the y-intercept cannot simply be equated with the inverse entanglement length. If this is however done, the obtained value for M_c should certainly be overestimated (as the experimental intercept is always lowered due to a noninfinite value of M_{te}). In conclusion, the NMR results are sensitive to all types of restrictions (cross-links, entanglements, and trapped entanglements), whereas the elastic response in swelling experiments is determined only by cross-links, and those entanglements that could not be relaxed under the swollen conditions (= trapped entanglements). Therefore, the y-intercept could be related to the number of entanglements which effectively disappear in swollen state.

In Figure 9, the intercept expected for the literature value of the entanglement length (6.2 kg/mol) is indicated. It is seen to be somewhat higher than the experimental intercepts. We therefore conclude that the NMR result (in terms of M_c) is not too far from the "true" value (with respect to the rheological determination of M_c), and is, if at all, underestimated (cross-link density is somewhat overestimated). This yet again suggests that the phantom model with variable χ gives values that are close to the true ones, as the slope of 1.26 also suggests that the NMR values is overestimated, but not too much (the higher slope from the affine model would imply an even larger overestimation by NMR). However, this fact may only be accidental, and we do not want to imply that swollen rubber chains actually behave phantom-like.

This discussion is also in accord with our previously published data for the NR–toluene pair⁷⁵ (the samples are different in both works), which have here been revised with regards to the multiple corrections for the swelling data mentioned in the first part of this article (which in most of the cases were not taken into account in the original work). The corrected results, shown as a regression line in Figure 9, compare well with the new results as far as the slope is concerned. A small but significant difference is exhibited by the y-intercept, which could be associated with a different amount of trapped entanglements present in the different natural rubber raw materials. Differences in the chain characteristics (molecular weight, polydispersity, etc.) or in their processing could be the responsible. The control of the entanglements in the formed network thus appears to be the key to improve our understanding of rubber elasticity. In this sense, polymer melts that are free of entanglements, recently published by Lippits et al.,¹¹¹ may provide a very worthwhile starting point for future work.

Finally, we stress that all the natural rubber networks (independently of the cure system) swollen with toluene show the same linear relationship (Figure 10), at least over the typical cross-link density range used for practical proposes. This result further supports the correctness of the presented, improved approach to the analysis of swelling experiments, as well as it proves the independence of both methods from differences in the very local structure of these networks. Note that peroxide-cured systems can be assumed to have a certain fraction of highly functional cross-links or clusters due to radical chain reactions.¹¹²

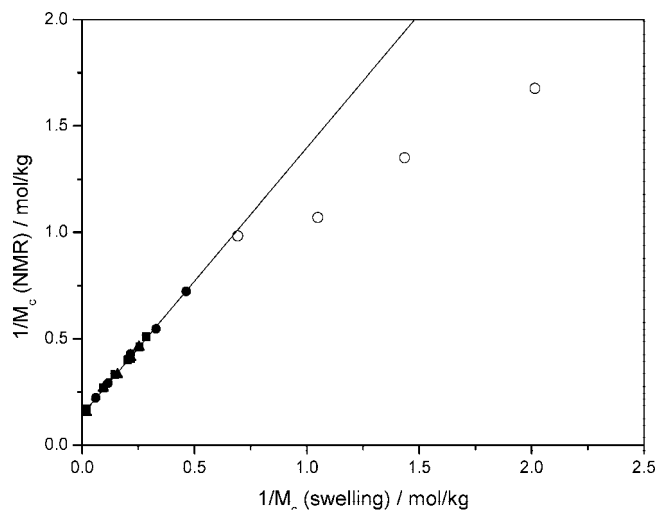


Figure 10. Comparison of swelling-determined reciprocal inter-cross-link molecular weights (using toluene as solvent, all discussed corrections, and the phantom model) with corresponding results from NMR experiments. Natural rubber networks vulcanized with different cure systems are compared: squares correspond to the conventional cure system defined in Table 1, triangles to samples vulcanized with an efficient system based on the same recipe as the conventional one but with different accelerant/sulfur ratio (12 instead of 0.2), and circles are from samples vulcanized with different contents of DCP. Full and empty symbols represent points that were taken into account for the linear fitting and those that do not follow the initial linear relationship, respectively.

Nevertheless, we also observe some deviation from linearity at very high cross-link density. One reason could of course be that very short network may show deviations from the assumed Gaussian deformation behavior (note that such rubbers are in fact technologically unimportant). Another obvious reason is certainly the increasing importance of higher-order corrections for the concentration dependence of χ , which is apparent from Figure 7. Also, the microstructure of very highly cross-linked elastomers might be different; e.g., higher network chain polydispersity or more pronounced spatial heterogeneities may arise, maybe as a consequence of the mentioned peculiarities of radical cross-linking.¹¹² The chain order distribution in these systems is in fact not as narrow as in sulfur-cured samples, sometimes with a clear bimodality, i.e., a small fraction with higher local cross-link density. Details on this topic will be the subject of a separate publication. Here, we can just conclude that a small number of such heterogeneities may well affect the swelling behavior much more than the bulk NMR response, in which they may lead to a more inhomogeneous local stress distribution in the swollen system. The fact that such effects may play a role also leads us to conclude that networks used to study the concentration dependence of χ should be carefully selected. For instance, McKenna et al.⁴⁹ used highly cross-linked samples, also vulcanized with DCP, to determine the behavior of χ in a large range of polymer concentrations. Their samples contained even more DCP than ours (up to 15 phr); therefore, their results could also be affected by the possible change in the swelling behavior.

Conclusions

In this work we have demonstrated the strong dependence of the cross-link density obtained from equilibrium swelling experiments on the model used to describe the thermodynamics of the swollen networks. This makes an accurate determination of this important parameter difficult if not impossible. On the basis of the Flory–Rehner theory, three possible sources of error/uncertainty have been identified and quantified: determi-

nation of the volumetric fraction of rubber, the Flory–Huggins polymer–solvent interaction parameter, and the applied model of rubber elasticity.

In the first part, the most important sources of error in the calculation of the volumetric fraction of rubber found in the literature were reviewed. The most general and correct method to calculate the concentration of polymer via gravimetric measurements was described by eq 20, where corrections in the solvent weight and rubber density must be made in order to obtain meaningful results. It was found to be particularly important to consider the kinetics of the swelling process and the degradation of the polymer. In addition, the inclusion of noninteracting solid particles leads to an excess of solvent that is imbibed in vacuoles formed at the particle/rubber interface, which should be corrected for. These problems are easily solved by proper experimental care and accuracy.

Although deviations caused by the calculation of ϕ_r are important, the largest dependences are due to the parameters that describe the thermodynamics of the swollen systems. A large uncertainty (around 50–60%) is associated with the interaction parameter χ . The correct value and concentration dependence of this parameter in cross-linked polymers is still an open challenge, mainly due to the small number of references on the topic. However, one can always define empirical procedures to determine this parameter experimentally; therefore, this issue should be not the main problem for accurate determination and comparison of cross-link densities via swelling experiments.

Finally, it is by far not clear which model should be used to describe the elastic behavior of swollen networks. Although most of our results indicate that the phantom model is the most appropriate, we believe that the better agreement is fortuitous. The elastic answer of swollen samples should be between the two extremes marked by the affine and phantom models, and the correct choice of the model is in fact one of the central problems. Currently, the dependence of the transformation of chain dimensions during swelling is not completely understood.

At this point, we would like to take up a very insightful comment of one of the reviewers, concerning the heuristic value of the Flory–Rehner approach and its relation to physically intuitive (but certainly not fully quantitative and thus here not considered) scaling approaches.³ Using the series ansatz (eq 23) for χ in combination with the Flory–Rehner or phantom model equations, for lower volume fractions ϕ_r it is in fact possible to reproduce any realistic power law $1/M_c \sim \phi_r^a$ (e.g., $a = 5/3$ for the Flory–Rehner model in good solvent²⁵) predicted by different scaling theories. Therefore, clearly, there are no a priori reasons to favor either scaling theories or empirical determinations/modifications of $\chi = f(\phi_r)$. The way in which the different model assumptions made in scaling approaches are related to an empirically nonconstant and network-specific χ parameter (which may be of thermodynamic origin, but also be due to nonaffine chain deformation, etc.) must be subject of independent interrogations of the swollen system (e.g., by light scattering, NMR).

In conclusion, the cross-link density of a network, which is one of the most important parameters defining the network structure and therefore the macroscopic properties, is a rather ill-defined parameter. Swelling experiments only yield a qualitative approximation to the real cross-link density of the sample, in particular when highly cross-linked samples are considered. The most important conclusion of this paper is therefore as follows: if swelling experiments should be used, as they are a rather simple and easy method, the only way to obtain a posteriori comparable data is to give a detailed description of the experimental procedure.

In contrast, MQ NMR experiments, possibly performed on a low-field instrument, have been proven to be an easy and direct alternative method to measure the total amount of cross-links and topological constraints in the system, and it has two important advantages; i.e., it does not depend of any thermodynamic arguments (although it is also model-dependent), and the NMR signal is more sensitive to the entanglement contributions that ultimately have an impact on the mechanical properties. On the basis of the in-depth comparison with swelling data presented herein, our calibration for the conversion of the measured residual coupling to cross-link density seems to give results that are close to the true value. Further work on independent calibrations is certainly necessary and will shortly be reported for the case of poly(dimethylsiloxane) networks.

Finally, we again stress that the linear dependence of the NMR observable on $1/M_c$ can be used to check the validity of thermodynamic models used to evaluate swelling experiments, which we have here demonstrated for the case of swelling experiments of natural rubber in MEK.

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