

Correction to Cross-Link Density Estimation of PDMS Networks with Precise Consideration of Networks Defects

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In our previous paper,¹ the arguments above eq 12 concerning the correction of the Flory–Rehner equation for a fraction of elastically inactive defects $\omega_{\text{def,sw}}$ as determined by NMR experiments in the swollen state, were incorrect. Correcting only the elastic term, eq 10, by use of eq 12 is not correct, since its $\phi_p^{1/3}$ dependence on the polymer volume fraction at swelling equilibrium merely relates to the geometric deformation of the sample as a whole, not to the fact that a part of the material is inactive. Rather, the fraction of elastically active material $\omega_{\text{el}} = 1 - \omega_{\text{def,sw}}$ is to be used to correct the resulting overall density of active network chains $1/M_c$. In terms of M_c , a corrected version of the relevant eq 13 reads

$$M_c = -\frac{\rho_p V_s (1 - 2/f) \omega_{\text{el}} \phi_p^{1/3}}{\ln(1 - \phi_p) + \phi_p + \chi \phi_p^2} \quad (1)$$

Using the same χ parameter for PDMS/toluene of Horkay et al.² as used previously

$$\chi = 0.459 + 0.134\phi_p + 0.59\phi_p^2 \quad (2)$$

we obtain a corrected version of our previous Figure 9a (see Figure 1a). The best near-linear correlation (see the inset for a log–log representation) is still observed when all defect-related corrections to the network functionality f (from Miller–Macosko calculations) and the elastic fraction ω_{el} are taken into account. However, the best-fit relation is somewhat less linear, with a best-fit power-law exponent of 0.76 rather than the previous 1.04. This prompted us to check the literature for different sources of the χ parameter,

$$\chi = 0.495 + 0.160\phi_p \quad (3)$$

$$\chi = 0.487 + 0.192\phi_p \quad (4)$$

$$\chi = 0.445 + 0.297\phi_p \quad (5)$$

published by Mallam et al.,³ Soni and Stein,⁴ and Kuwahara et al.,⁵ respectively. It is noted that the network-specific values given by Horkay et al. and Mallam et al. rely on separately determined values for the elasticity modulus of swollen networks, which adds some model uncertainty, while the value of Kuwahara et al. has been determined for solutions of linear PDMS.

Figure 1b presents correlations of M_c values from swelling vs those based upon Miller–Macosko calculations and demonstrates that the best, near-linear correlation is provided by the χ parameter given by Kuwahara et al. Using the latter for a corrected version of Figure 9c, which relates swelling- and DQ NMR-based values, we confirm the same qualitative comparison between uncorrected (open symbols) and defect-corrected (solid symbols) values for the network chain density. However,

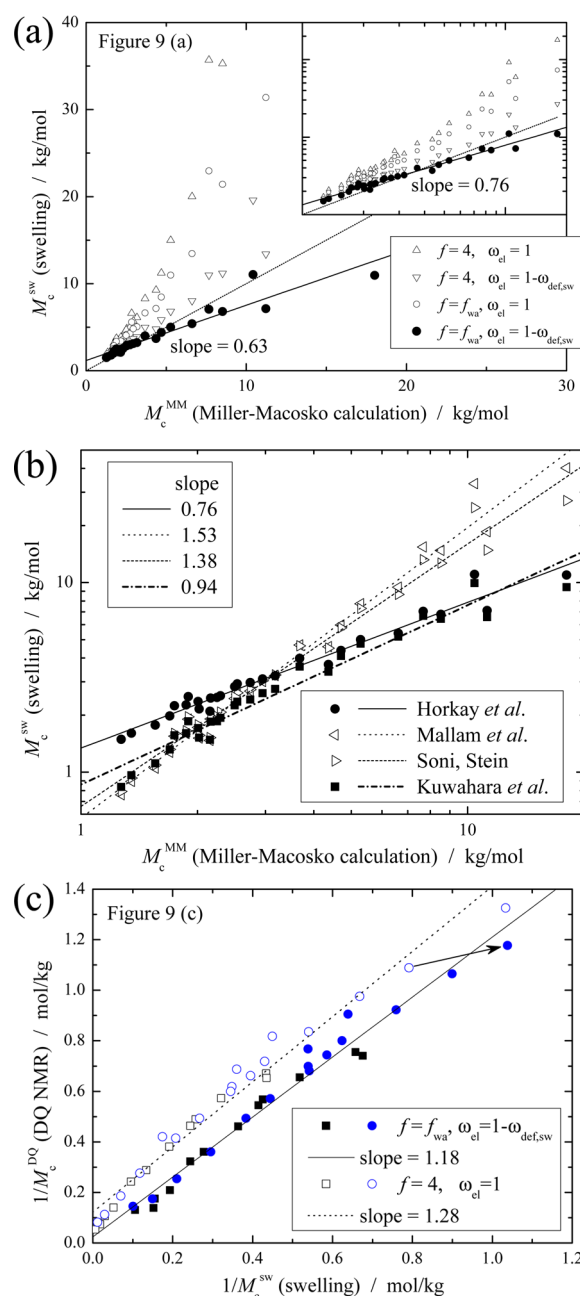


Figure 1. (a) Corrected version of Figure 9a of ref 1. (b) A log–log representation of the $\{f=f_{\text{wa}}, \omega_{\text{el}}=1-\omega_{\text{def,sw}}\}$ data set from (a) using different literature values for the χ parameter. (c) Corrected version of Figure 9c of ref 1 using the χ parameter of Kuwahara et al.⁵

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we now find a much better, near-quantitative correlation with a proportionality factor near unity (1.18) rather than 2.06. We finally stress that the variation of the $1/M_c$ results shown in Figure 1b once again sheds a critical light on the fact that the apparent ϕ_p dependence of χ represents an ad-hoc adjustment which, ultimately, arises from the apparent limitations of the Flory–Rehner model.⁶ The choice of a certain $\chi(\phi_p)$, related to a specific model-dependent determination procedure, is thus to a degree arbitrary.

■ REFERENCES

- (1) Chassé, W.; Lang, M.; Sommer, J.-U.; Saalwächter, K. Cross-Link Density Estimation of PDMS Networks with Precise Consideration of Networks Defects. *Macromolecules* **2012**, *45*, 899–912.
- (2) Horkay, F.; Hecht, A.-M.; Geissler, E. Thermodynamic Interaction Parameters in Polymer Solutions and Gels. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 1641–1646.
- (3) Mallam, S.; Horkay, F.; Hecht, A.-M.; Rennie, A. R.; Geissler, E. Microscopic and Macroscopic Thermodynamic Observations in Swollen Poly(dimethylsiloxane) Networks. *Macromolecules* **1991**, *24*, 543–548.
- (4) Soni, V. K.; Stein, R. S. Light Scattering Studies of Poly-(dimethylsiloxane) Solutions and Swollen Networks. *Macromolecules* **1990**, *23*, 5257–5265.
- (5) Kuwahara, N.; Okazawa, T.; Kaneko, M. Osmotic Pressures of Moderately Concentrated Polydimethylsiloxane Solutions. *J. Polym. Sci., Part C: Polym. Symp.* **1968**, *23*, 543–553.
- (6) Chassé, W.; Saalwächter, K.; Sommer, J.-U. Thermodynamics of Swollen Networks As Reflected in Segmental Orientation Correlations. *Macromolecules* **2012**, *45*, 5513–5523.