Supporting Information

Isostructural Softening of Vulcanized Nanocomposites

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1. Neat SBR vulcanization probed with Dynamical Mechanical Analysis.

We present in Figure S1 below the non-normalized data corresponding to the Figure 2 in the article. Note that the ratio of the storage modulus E' between the softest and the stiffest nanocomposites (all containing 15 vol.% in silica) before and after the vulcanization process are close to 1.3. The evolution with the polypropylene glycol is hieratical, similarly as what we observed in our previous study on crude nanocomposites.[1] This result is explained by the "industrial" nature of these materials, in particular by their processing route consisting successively in internal mixing, two rolls milling and hot-pressing, necessarily implying small variations in terms of structure and properties.

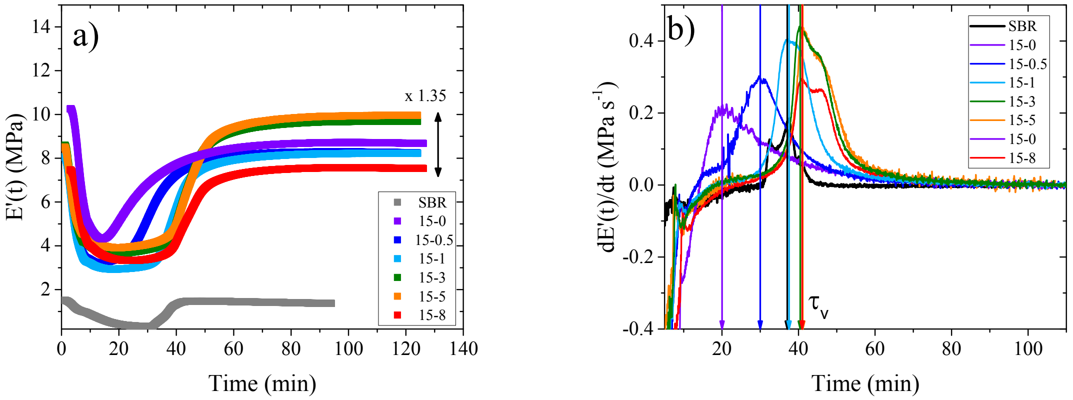

Figure S1. a) Storage modulus as a function of time during the vulcanization process for nanocomposites containing 15 vol.% in silica and their neat SBR counterpart. b) Derivative data, the vulcanization time τ_v (reported in Figure 2b) is extracted from the maximum position.

2. $I_n{}^{DQ}$ signal from all the composites and corresponding raw data (I_{ref}, I_{DQ})

We present the whole set of MQ-NMR measurements in Figure S2 below. Figure S2a is the analog of Figure 3b in the article to which we have added $I_n{}^{DQ}$ signals coming from nanocomposites containing a large fraction of PPG, namely 15-3, 15-5 and 15-8. Figure S2b presents on the other hand, the raw data I_{ref} and I_{DQ} required for the calculation of $I_n{}^{DQ}$. In the latter, the mobile PPG contribution (dashed line) is particularly well visible in 15-5 and 15-8 confirming once again the formation of a liquid PPG shell at the silica/SBR interface (already evidenced by DSC and suspected from TEM in ref.[1]).

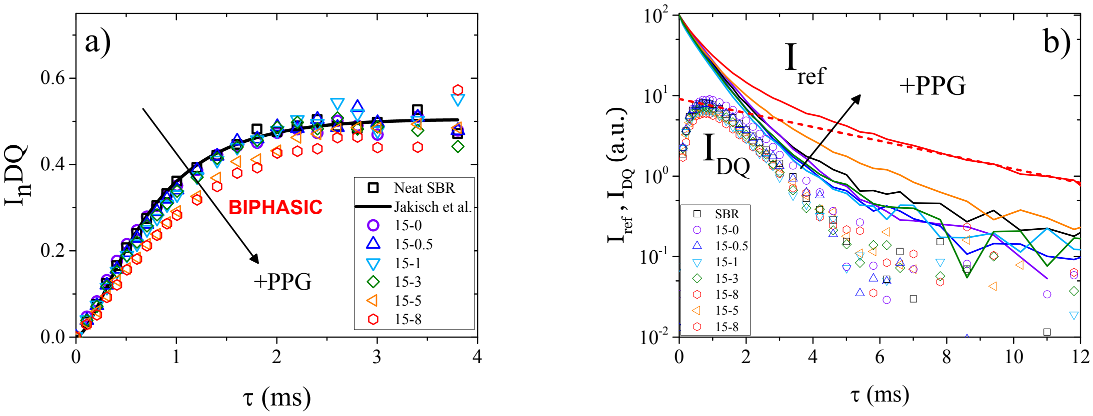

Figure S2. a) Multiple-quantum signal $I_n{}^{DQ}$ as a function of time for the whole set of composites and the neat SBR – (analog to Figure 3b in the article). b) Corresponding raw data I_{ref} (solid lines) and I_{DQ} (open symbols) enabling the calculation of $I_n{}^{DQ}$. Red dashed-line stands for the correction related to the presence of a significant fraction of mobile PPG chains in 15-8.

While it is easy to conclude on the structural similarity of the polymer network in neat SBR, 15-0, 15-0.5, and 15-1, (even in 15-3), the task is made more difficult in 15-5 and 15-8 because of the significant fraction of PPG within the materials. We remind the reader that the method we employ in the present work lies in measuring the dynamical heterogeneities of a polymer matrix made of a single type of chain. In fact, apart from the tail observed at long times, it is a priori difficult to know precisely how the PPG adsorption deforms the raw signals at shorter time, resulting in a significant error bar on ${I_n}^{DQ}$ between 0 and 3 ms in 15-5 and 15-8 data (Figure S2-a). A quantitative analysis of I_{ref} is proposed in Figure S3 revealing the following:

- Ca. 1 % of the SBR is seen to be very mobile in 15-0 samples, similarly as in Neat SBR, most likely due to the dangling ends of the network.
- Ca. 4 % of mobile phase is found in 15-5 meaning that roughly 4 % of the organic matrix is made of mobile species. (*Note that the Hudrogen mass fraction and the macroscopic densities are similar in SBR and PPG, being respectively 10% (+/- 1%) of the polymer mass and 0.97 g cm*^{3} *(+/- 0.03 g cm*^{3}*)*). One can then compare this result with the PPG mass fraction in the 15-5 sample, being close to 13%, suggesting that only 1/3 of the PPG is free to move. The remaining 2/3 are likely adsorbed at the silica interface, perturbing in consequence the measurement of I_{ref} and ${I_n}^{DQ}$ at short time scale.
- Ca. 11% of mobile phase is found in 15-8. Following the same logic as in the previous case, we thus obtain that roughly half (≈11/21) of the PPG is in the liquid state, i.e., relatively more than in 15-5. This is explained by the fact that PPG chains aggregate at the silica surface, making the shells progressively thicker when their content is raised. It is also confirmed by the absence of additional tail on samples containing lower amount of PPG (15-0.5, 15-1, and 15-3) in which the short chains are likely adsorbed onto the silica and becomes therefore rigid from a dynamic point of view. Interestingly, we remind the reader that the PPG shell was becoming visible in TEM from 15-5[1], i.e., when a significant amount of mobile chain is detected in NMR.

To sum up, because the vulcanization kinetics are very close in 15-1, 15-3, 15-5 and 15-8 (see Figure 2 in the manuscript), we thus believe that the network topology must be similar in all these samples in spite of the slightly different NMR measurements caused by the biphasic nature of the organic phase and the relaxation time distribution of the PPG chains.

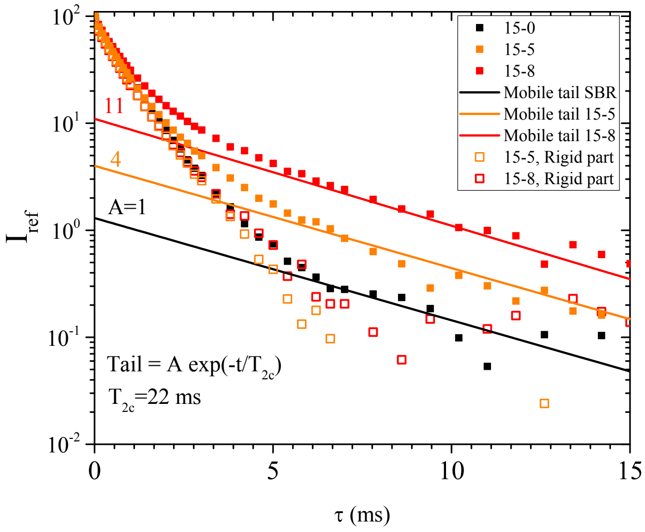

Figure S3. I_{ref} measured on 15-0, 15-5 and 15-8 samples. Solid lines stand for the mobile contribution in the corresponding samples (long relaxing time). Open symbols are calculated from I_{ref} – Tail for 15-5 and 15-8. The relaxation time of the mobile phase was fixed to 22 ms and the amplitude fitted to the data at τ longer than 6 ms.

References

1. Trinh, G. H.; Desloir, M.; Dutertre, F.; Majesté, J.-C.; Dalmas, F.; Baeza, G. P. Isostructural softening of the filler network in SBR/silica nanocomposites. *Soft Matter* **2019**