Tuning structure and rheology of silica-latex nanocomposites with the molecular weight of matrix chains: a coupled SAXS-TEM-simulation approach

SUPPORTING INFORMATION

Amélie Banc[1,2], Anne-Caroline Genix[1,2], Mathieu Chirat[1,2], Christelle Dupas[1,2], Sylvain Caillol[3], Michael Sztucki[4], Julian Oberdisse[1,2]

[1] *Université Montpellier 2, Laboratoire Charles Coulomb UMR 5221, F-34 095, Montpellier, France*

[2] *CNRS, Laboratoire Charles Coulomb UMR 5221, F-34 095, Montpellier, France*

[3] *Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-UM2-ENSCM-UM1, Equipe I.A.M., 8 rue de l'Ecole Normale, F-34 296 Montpellier Cedex 5, France*

[4] *European Synchrotron Radiation Facility, ESRF, 6 rue Jules Horowitz, BP 220, F-38 043, Grenoble, Cedex 9, France*

This document gives additional information on the structural characterization of the silica beads (section 1), the matrix glass-transition temperature (T_g) evolution (section 2), the impact of annealing on the matrix molar mass (section 3) and the shift factors as obtained by rheology (section 4) for the different nanocomposites investigated in this work.

1. Silica nanoparticles (NPs)

1.1 SAXS results

The aqueous solution of Ludox TM40 was first characterized by SAXS at high dilution. The scattered intensity shown in Figure S1 can be well described by the form factor of a sphere including polydispersity with a log-normal size distribution leading to R_{si} =14 nm and σ = 11%.

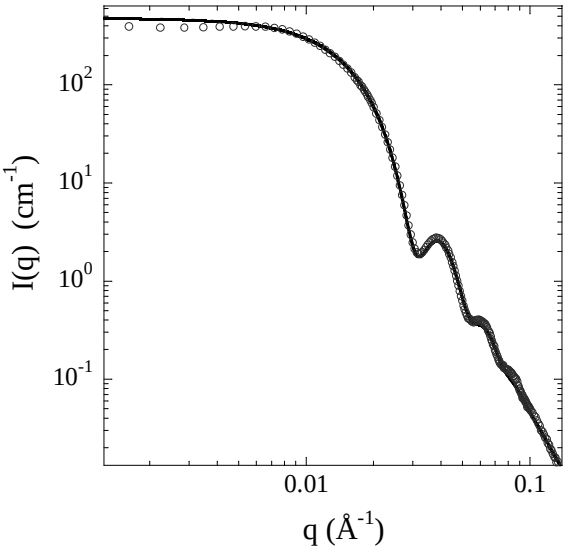

Figure S1: Scattered intensity I(q) of colloidal silica at 0.4%v in deionized water. Line is the description by the form factor of sphere taking into account polydispersity.

1.2 TEM results

The silica NPs distribution in size was also determined by image analysis of TEM pictures. This was done on a nanocomposite with 1%v silica at the highest polymer mass (PEMA160) where dispersion is best. The distribution shown in Figure S2 was obtained using a picture with a 3000 magnification. Note that 5 different pictures were analyzed leading to similar distributions. Fitting with a log-normal distribution gives R_{si} = 13.1 nm and σ = 12%.

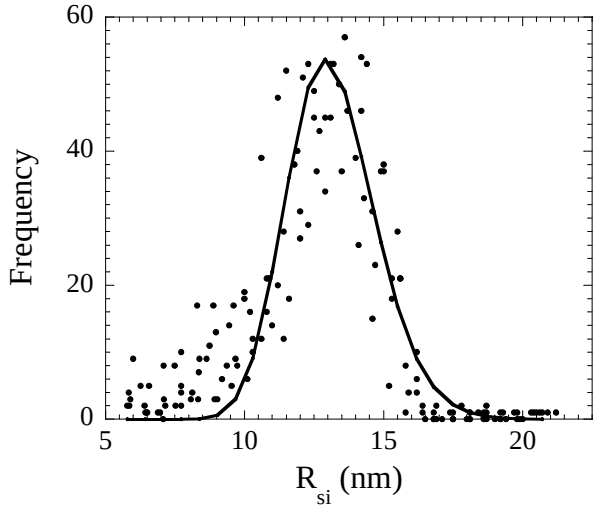

Figure S2: Distribution in size for the individual silica NPs. Data are described by a log-normal function (line).

2. T_g versus molecular weight

The glass-transition temperatures obtained by DSC at 20 K/min for the 3 different matrices are shown in Figure S3.

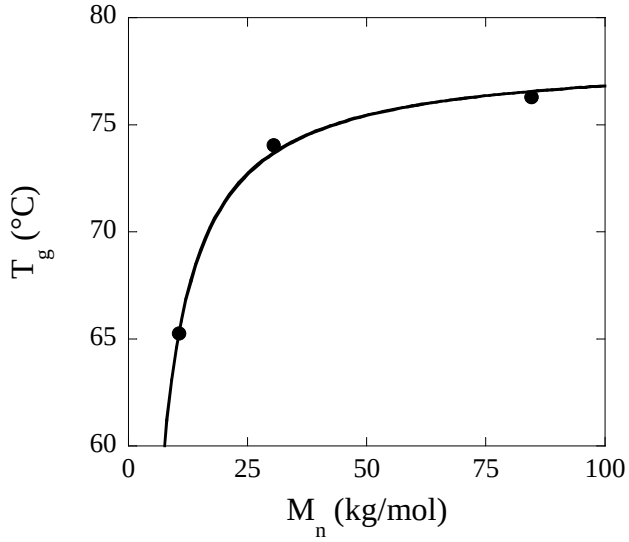

Figure S3: T_g of PEMA matrices as a function of molecular weight M_n. Data are fitted with the Flory-Fox equation: $T_g = T_g^{\infty} - {}^{C}/_{M_n}$ leading to T_g^{∞} = 351 K and C = 1.4 10^5 K.g/mol.

3. Impact of annealing on the molar mass

One representative PEMA latex sample with M_w = 102 kg/mol (polydispersity index = 2.1) was measured by GPC after drying (NA) and after 1 week of annealing at 180°C. As one can see from the distributions shown in Figure S4, annealing has no impact on the polymer molecular weight.

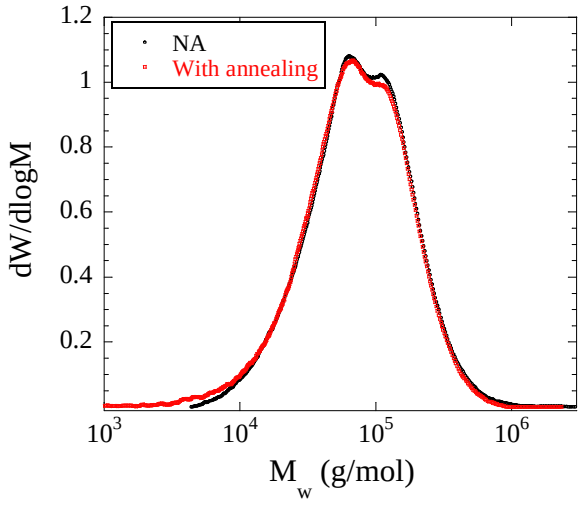

Figure S4: Molecular weight characterization of PEMA chains without (NA) and with annealing.

4. Rheology shift factors

The shift factors obtained from the master-curve construction (T_{ref} = 180°C) are shown in Figure S5 for the three molar masses. Up to Φ_{si} = 10%v, there is no significant impact of the silica fraction. The shift factors temperature dependence is well described using the Williams−Landel−Ferry (WLF) equation [1]

$$\log a_T = \frac{-C_1(T - T_{ref})}{C_2 + T - T_{ref}} \quad (1)$$

Free fits performed over the whole data points (all silica concentrations) gives (C_1, C_2) = (8.7, 245 K), (8.5, 229 K) and (11.3, 256 K) for PEMA20, PEMA50, and PEMA160, respectively. For comparison the WLF equation calculated with the coefficients from ref. [2] (C_1 = 6.3 and C_2 = 184 K at our reference temperature) is given in Figure S5 (b).

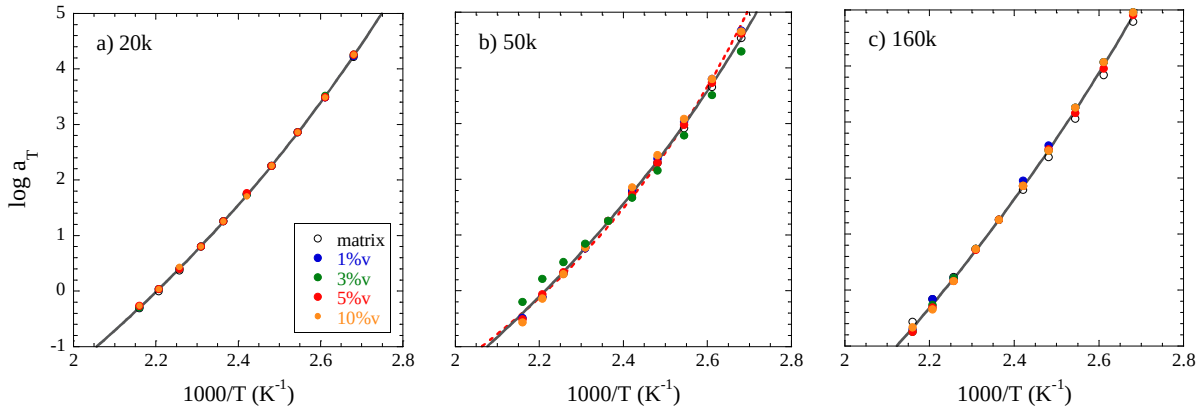

Figure S5: Shift factors versus 1000/T at a reference temperature of 180°C for a) PEMA20, b) PEMA50 and c) PEMA160 at different silica fractions. Lines are free fits using the WLF equation (see text for details). Dotted line in (b) is the calculated curve using the WLF coefficients from Ref [2].

References

(1) Williams, M. L.; Landel, R. F.; Ferry, J. D. *Journal of the American Chemical Society* **1955,** *77* (14), 3701-3707.

(2) Ferry, J. D.; Child, W. C.; Zand, R.; Stern, D. M.; Williams, M. L.; Landel, R. F. *Journal of Colloid Science* **1957,** *12*, 53-67.