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Short communication:

Interfacial interactions-controlled thermoelastic behaviour of synthetic rubber/organoclay nanocomposites

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Abstract: Thermoelastic measurements of synthetic rubber/organoclay nanocomposites provided the first experimental evidence for the dramatic dependence on interfacial interactions of the scale of nanoparticle displacements within filler aggregates of synthetic rubber/organoclay nanocomposites at high uniaxial extensions.

Introduction

Pronounced stress-softening (the so called Mullins-Patrikeev (MP) effect [1,2]) is one of the most salient manifestations of irreversible structural changes during quasi-static, successive uniaxial loadings of filler-reinforced rubbers. Among many possible interpretations of the MP effect (e.g., refs. [1-8]), the approach assuming hydrodynamic strain amplification by strain-dependent filler aggregates [7,8] seems physically most realistic. In fact, this approach proved to be in fair agreement with the exponential decrease of the strain amplification factor [8], as well as with the characteristic power law increase of electrical conductivity [9] of carbon black-filled rubbers during repeated uniaxial stretching to higher elongations.

It is pertinent to remark at this point that the experimental evidence for a strain dependence of the size of filler aggregates was obtained for systems with relatively weak (non-chemical) interactions at the rubber/filler interface [8,9]. It can be expected, therefore, that such an effect would be minimized for similar systems with much stronger (chemical) interfacial interactions. Thus, it is the purpose of the present communication to check this suggestion by careful thermoelastic measurements of synthetic rubber/organoclay nanocomposites in the range of relative extensions where the strain-dependent strain amplification factor becomes operative.

Experimental part

The pristine rubber matrix (BUNA-SL18, Bayer AG) was a synthetic styrene-*co*-butadiene rubber (styrene content: 18%; M_w = 4·10^5 g/mol). The rubber/organoclay

composites were prepared by melt compounding at 80 - 90°C for 10 min using an internal mixer (Haake Rheocord 90, Banbury rotors) followed by a treatment on a 3-roll mill (Exakt, 80S) at 80°C for 10 min. Then sulfur vulcanization of the matrix was performed in a hot stage press (Collin) at 160°C for 50 min under a pressure of 20 bar [10]. The reference sample with weak interfacial interactions (RS) contained 30 phr (parts per hundred rubber) of clay modified with dioctadecyldimethylammonium salt (Nanomer I.42 E, Nanocor). The test sample with strong interfacial interactions (TS) contained the same amount of the same clay nanoparticles (average thickness and length in the composite as measured by transmission electron microscopy: 60 and 500 nm, respectively), which were, however, chemically bonded to the rubber matrix with the silane coupling agent bis(triethoxysilylpropyl)tetrasulfan (TESPT) (10 wt.-% of filler, Si69, Degussa AG). For silica/TESPT/rubber systems analytical proofs have been given for the existence of Si-O-Si bonds and sulfur bridges coupling the filler to the rubber matrix [11,12]. We assume the presence of similar interfacial coupling in the present organoclay/TESPT/rubber compound on the basis of previous small-angle X-ray scattering measurements under cyclic strain [13]. The experiments have demonstrated a reversible reorientation of aggregates in the system with coupling reagent in contrast to an irreversible orientation in the vulcanizate without coupling agent.

The mechanical work (W) and concomitant heat effects (Q) in the step-wise loading (stretching) / unloading (contraction) cycles were measured at room temperature with the stretching calorimeter described in detail elsewhere [14,15]. Repeated calibrations of the stretching force (using different static loads), and of the heat effects (using a calibrated electrical heater) proved that the mean measurement errors of both W and Q were below 2%. In the range of small relative extensions λ (< 1.10 - 1.20), each specimen was stretched at a constant velocity q^+ (10% of the total specimen length per minute) to a predetermined λ_i, stored at fixed λ_i to the full completion of mechanical and thermal relaxations, and thereafter allowed to contract at the same velocity q^- to zero force. The typical difference between fixed extensions in two successive steps, $\Delta\lambda = \lambda_{i+1} - \lambda_i$, varied from several digits in the fourth place to a few digits in the third place. At higher elongations, the mechanical work and heat effects were measured only in the regime of successive step-wise stretching at larger $\Delta\lambda$ (a few digits in the second place).

Results and discussion

As expected, both the mechanical work and the heat effects in the stretching/ contraction cycles for the pristine rubber were completely reversible (regrettably, mechanical failure of the sample made the measurements impossible at $\lambda > 1.3$ [16]). The experimental values of specific (per unit of mass m) mechanical work W/m, specific heat effects Q/m and of the ratio Q/W (Fig. 1) could be quantitatively fitted to the standard equations of elasticity of real rubbers [17].

$$W/m = A\,(E/6\rho)\,f_1(\lambda) \qquad (1a)$$

$$Q/m = -\,(W/m)\,[1 - T\beta - 2\alpha T / f_2(\lambda)] \qquad (1b)$$

$$Q/W = -1 + T\beta + 2\alpha T / f_2(\lambda) \qquad (1c)$$

The best fit parameters are E = 0.515 MPa, $\beta \approx -5\cdot10^{-3}$ K^{-1} and $\alpha \approx 2.4\cdot10^{-3}$ K^{-1}. Here $A = \langle h^2_0\rangle/\langle h^2\rangle$ is the front factor (A is assumed to be 1 as usually); $\langle h^2_0\rangle$ and $\langle h^2\rangle$ are the mean-square end-to-end distances of an isolated, unperturbed chain and of an identical chain in the network, respectively; E is the elasticity modulus in the

simple stretch regime; ρ = 0.929 g/cm^3 is the density (assumed to be strain-invariant); $\beta = d \ln \langle h^2_0 \rangle / dT$ is the temperature coefficient of unperturbed chain dimensions; $\alpha = - d \ln \rho / dT$ is the thermal expansion coefficient of bulk rubber; $f_1(\lambda) = \lambda^2 + 2/\lambda - 3$ and $f_2(\lambda) = \lambda^2 + \lambda - 2$.

As judged by the best-fit value of the apparent modulus E = 2.9 MPa for the RS, which was derived by Eq. (1a) for the range of reversible deformations, $\lambda < 1.15$, the organoclay nanoparticles provide a significant mechanical reinforcement effect to the pristine rubber. However, the glaring deviations between the experimental values of W/m for the RS and the theoretical curve, which was calculated by Eq. (1a) assuming reversibility (curve 1 in Fig. 2a), steadily increased, with increasing λ. As mentioned in the introductory paragraph, it is the violation of this latter assumption that is believed to be at the root of the observed discrepancies. Formally, such effects can be accounted for through the strain amplification factor $X = \varepsilon_{int} / \varepsilon$ which relates the microscopic intrinsic strain of the rubber ε_{int} to the macroscopic extension, $\lambda = 1 + \varepsilon$ [8].

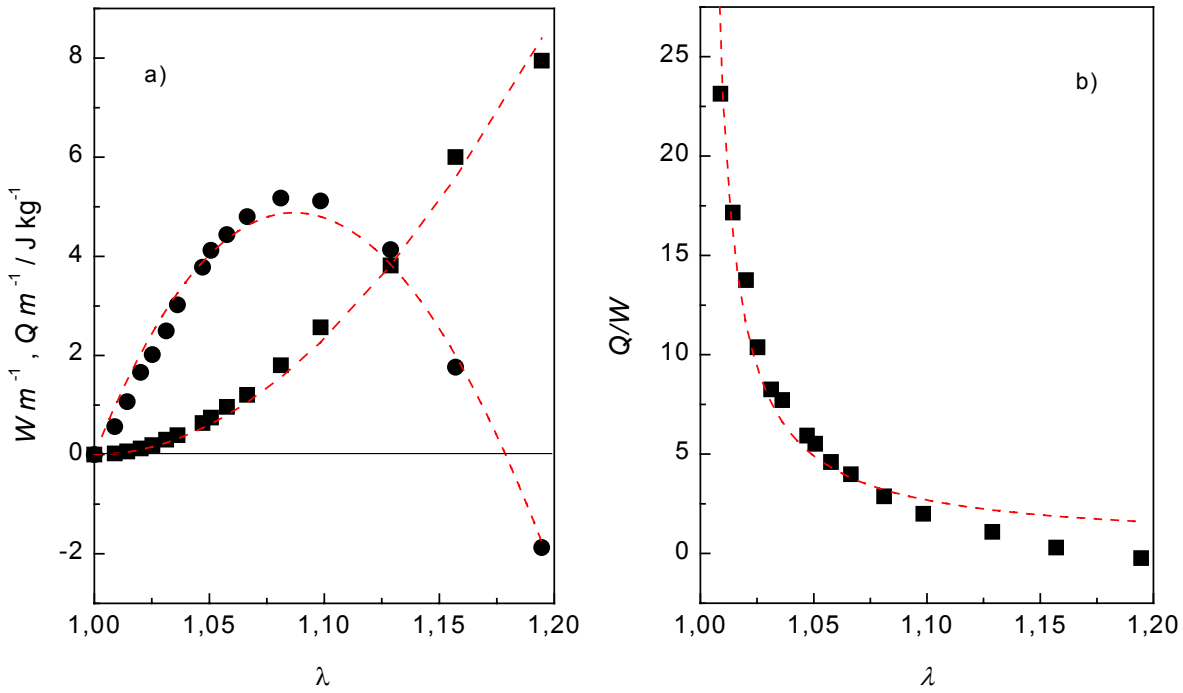

Fig. 1. Dependencies on relative elongation λ of specific mechanical work (squares) and specific heat effects (circles) (a), and of the Q/W ratio (b) for the pristine rubber. Dashed lines are the best non-linear fits to Eqs. (1)

In this context, for filled rubbers Eq. (1a) should be rewritten as

$$W/m = A\,(E/6\rho)(\lambda_{int}^2 + 2/\lambda_{int} - 3) \qquad (2)$$

where $\lambda_{int} = 1 + \varepsilon X$ is the normalized relative extension.

The relevant experimental data for nanocomposites were fitted to Eq. (2) assuming either of the following two cases [8]:

$$X \neq f(\varepsilon_{max}) = \text{const} \qquad (3a)$$

$$X = f(\varepsilon_{max}) \approx X_\infty + (X_0 - X_\infty) \exp(-z\varepsilon_{max}) \qquad (3b)$$

where X_0, X_∞ and z are the fitting parameters, and ε_{max} is the maximum strain at each successive loading step.

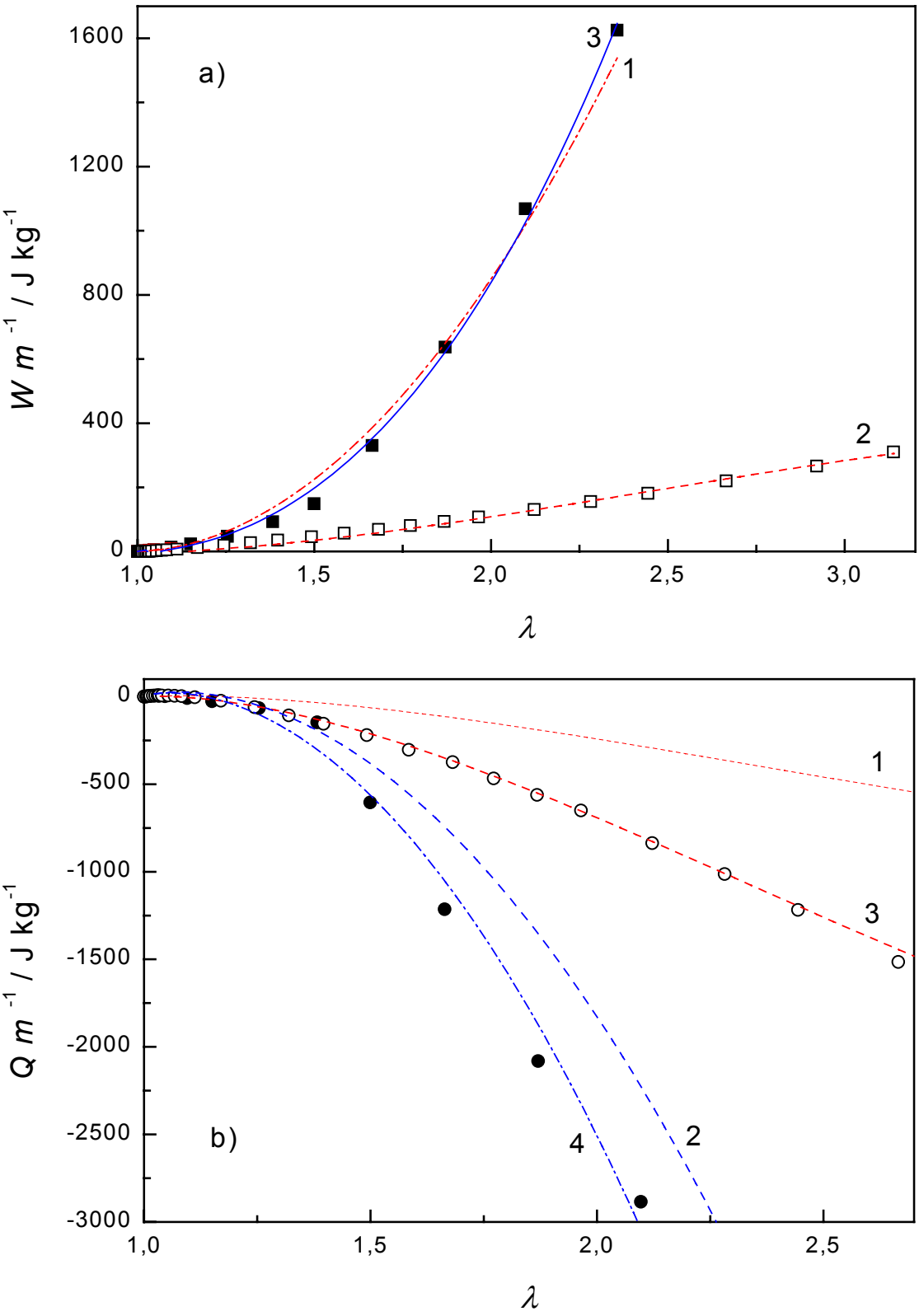

Fig. 2. Dependencies on relative elongation of specific mechanical work (a) and specific heat effects (b) for the reference sample (RS, open symbols) and the test sample (TS, filled symbols). For explanations see the text

It could be easily verified that the values of *W/m* for the RS did not quantitatively fit to Eqs. (2) and (3a), whereas the quality of the data fit to Eqs. (2) and (3b) was reasonably good (dash-dotted line 2 in Fig. 2a calculated assuming the same value E = 0.515 MPa as for the pristine rubber, and X_0 = 11.5, X_∞ = 8.5, z = 0.6). This result supports the concept of a strain-dependent strain amplification factor as the major parameter controlling the stress-strain behaviour of nanocomposites with weak interfacial interactions [8].

Incidentally, the theoretical curve 1 calculated by Eq. (1a) assuming E = 2.9 MPa for the RS roughly fitted to the experimental values of *W/m* for the TS (Fig. 2a). Moreover, a nearly identical curve proved to be the best fit of these latter data to Eqs. (2) and (3a) (assuming E = 0.515 MPa and X = 28.2). A slightly fit (curve 3 in Fig. 2a) could be achieved by the use of Eqs. (2) and (3b) (assuming E = 0.515 MPa, X_0 = 26.7, X_∞ = 30.2, z = 0.6); however, this fit should be discarded in view of its physically unreasonable result ($X_\infty > X_0$). Thus, these data can be regarded as evidence for the strain amplification-induced mechanical reinforcement of the rubber matrix by filler aggregates, and for the negligible (if any) decay of the latter with increasing extension (i.e., for the vanishingly small MP effect) in a nanocomposite with strong interfacial interactions.

In view of the above results, it could be expected that the original Eq. (1b) would also apply to the specific heat effects in stretching of nanocomposites, provided the strain-dependent strain amplification factor would be properly accounted for, i.e.,

$$Q/m = -(W/m)\,[1 - T\beta - 2\alpha T/(\lambda_{int}^{\,2} + \lambda_{int} - 2)] \qquad (4a)$$

It turned out, however, that Eq. (4a) badly underestimated (dashed lines 1 and 2 in Fig. 2b) the experimental values of *Q/m* for both nanocomposites, whereas reasonably good fits (dash-dotted lines 3 and 4 in Fig. 2b calculated by Eq. (4b) assuming C = 4.0 and 0.8, respectively) could be achieved through the introduction of an additional, dimensionless fitting parameter C into Eq. (4a), as

$$Q/m = -(W/m)\,[1 - T\beta - 2\alpha T/(\lambda_{int}^{\,2} + \lambda_{int} - 2) + C] \qquad (4b)$$

This important result is considered as experimental evidence for additional, intrinsically similar exothermal effects setting on at the uniaxial stretching of nanocomposites in the range of relative extensions where the strain amplification factor becomes operative. As argued elsewhere [18], the fitting parameter C in Eq. (4b) can be regarded as a dimensionless measure of external frictional forces between nanoparticles during their successive rearrangements in a viscoelastic matrix after stepwise loadings to higher uniaxial extensions. In fact, a continuous change of the shape and/or size of the initial infinite cluster of nanoparticles in nanocomposites, as consistent with the quantitative fit of the experimental *W/m* data to the modified Eq. (2), implies the generation of exothermal effects by the mechanism of interparticle slip, as reflected by non-zero values of the fitting parameter C in the modified Eq. (4b). In this context, the rather high value of the fitting parameter C for the RS suggests a significant contribution of large-scale interparticle motions during the successive breakdown of the initial infinite clusters of nanoparticles into small, isolated clusters [7,8], while the five-fold lower value of C for the TS implies small-scale (presumably reversible) displacements of nanoparticles within the infinite filler clusters, which leave the latter essentially undestroyed. Thus, these conclusions are totally consistent with those derived from the preceding analysis of specific mechanical work.

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