Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for:

Towards realistic simulations of polymer networks: tuning vulcanisation and mechanical properties

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1 Initial equilibration

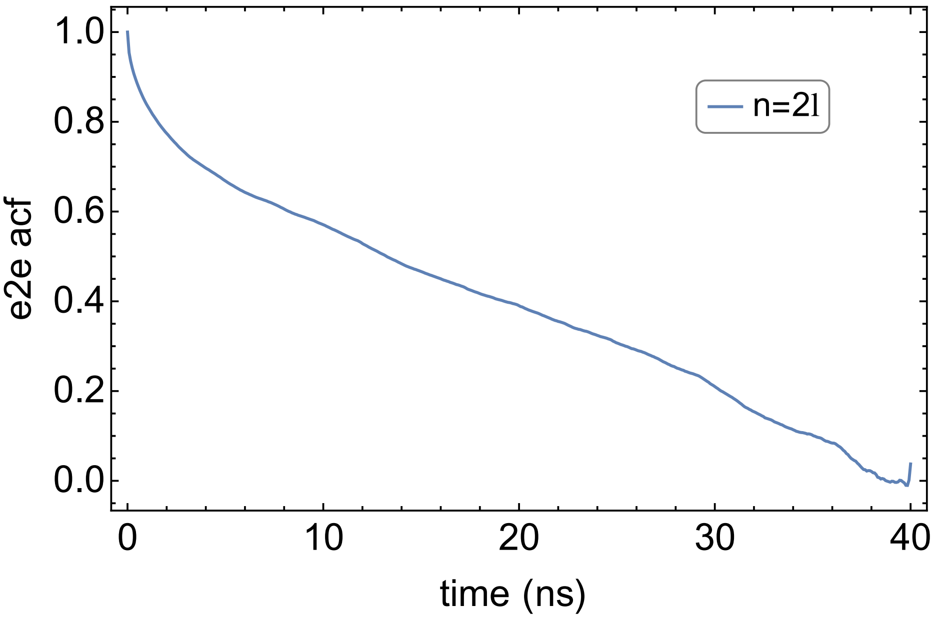

Figure ESI.1: Autocorrelation function of the end-to-end vector during the first equilibration using the soft potential. The chains completely loose memory of their initial orientation after 40 ns.

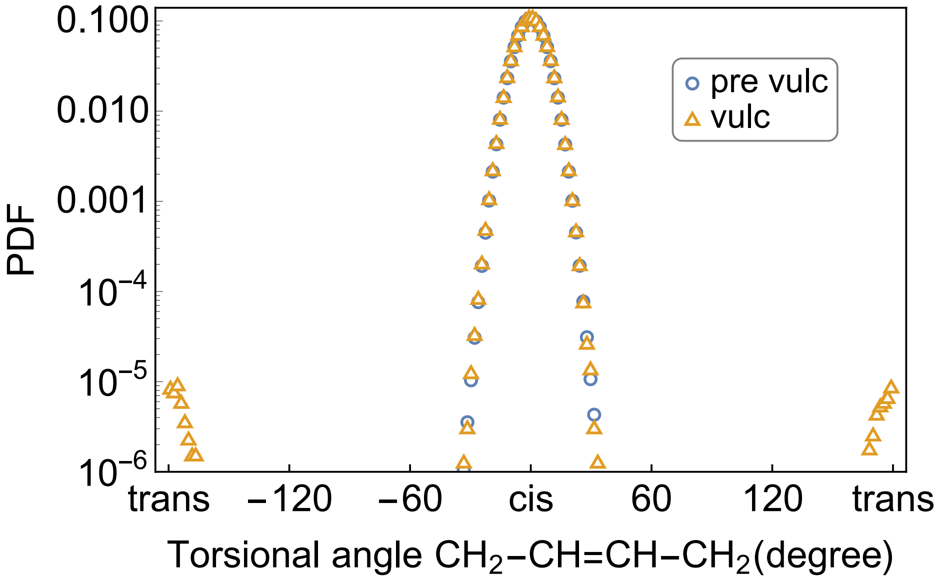

Figure ESI.2: Histograms of the torsion angles around the C=C bonds, before and after vulcanization. Note the logarithmic scale on the vertical axis.

2 LAMMPS implementation

For LAMMPS users, we present a more detailed flowchart of the vulcanisation, accounting for some technicalities of the input script [Figure ESI.3(a)]. The vulcanisation process is based on the command 'fix bond/create' which offers vast possibilities but also comes with some limitations.

With a naive implementation of the bond creation, the sulphur dimer would sometimes bridge onto the same chain, as pictured in Figure ESI.3(b). We solved this problem by introducing two types of chains: one having CH_2 beads of atom type '1' and the other with atom type '2'. Also the sulphur dimers are internally made of two atom types, each able to bond exclusively with one of the two types of CH_2 groups. Although the system is formally the same, the type differentiation guides the vulcanisation to a well constructed network in which dimers bridge different chains.

Prior to vulcanisation, a number of new bond types equal to the number of vulcanisation cycles has to be defined, in order to selectively stiff just the newly formed bonds. The bond creation command imposes a limitation on the atoms able to form bonds and on the number of bonds of given bond type. Since a new bond type is created at every cycle, previously bonded atoms are connected by different bond types, therefore they are still able to form new bonds. To avoid this, it is important to update the 'groups' of reacted (not able to form new bonds) and unreacted atoms.

The bond creation command allows to apply one type of angle constants to all newly formed angles. In our case, this has to be fixed afterwards to take into account all the different angles formed, and equilibrate the network again. The process of topology rebuilding is performed using Topotools[1] package distributed with VMD[2].

See Section 3 for a commented sample of the input.

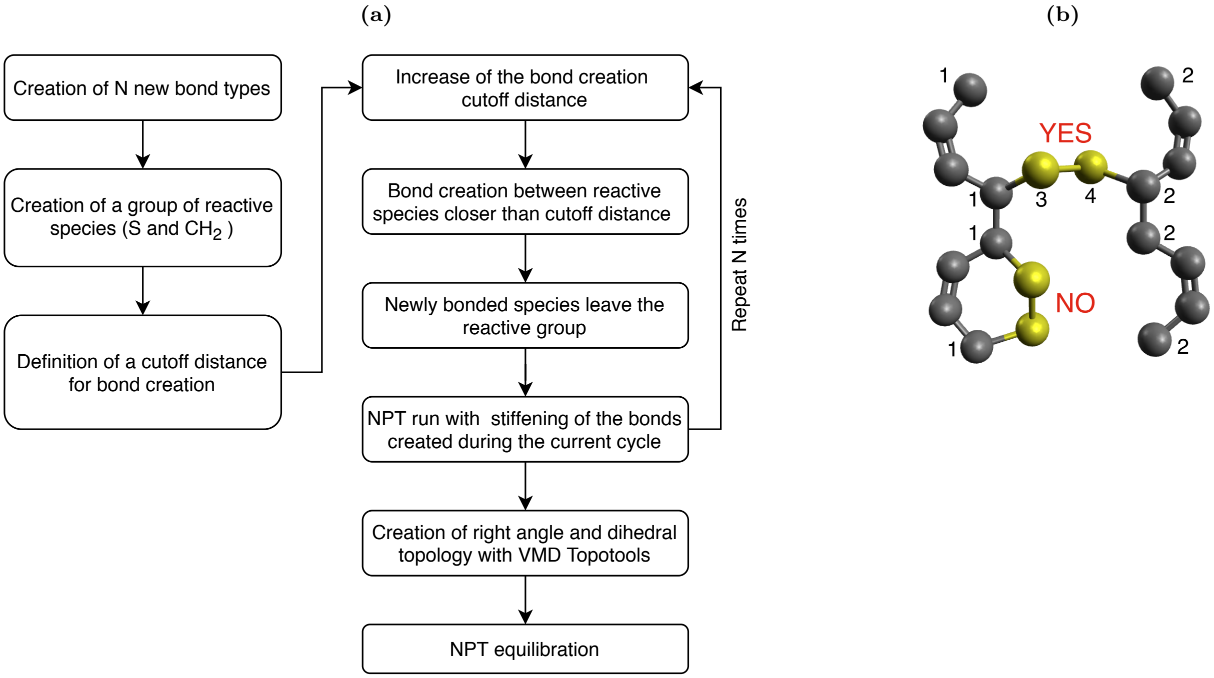

Figure ESI.3: (a) Detailed flowchart of the vulcanisation process implemented in LAMMPS. (b) Vulcanisation issues arising from dimers anchoring to the same chain and solution based on atom type differentiation. Type-1 CH_2 can bond to type-3 sulphur, while type-2 CH_2 can bond to type-4 sulphur.

3 Force field and LAMMPS input for vulcanisation

Extract of the code used to vulcanise the polymeric liquid.

```
variable nCL equal 200 # number of sulphur dimers
variable vulctry equal 40 # number of vulcanisation cycles
#### sulphur dimers insertion
molecule cl CL2.lammps offset 3 3 0 0 0
create_atoms 0 random $nCL 997 NULL mol cl 999
group totcl type 4 5
velocity totcl create 298 999
#### short minimisation and equilibration
minimize 0 0 100 10000
fix ensemble all npt temp 298 298 200 aniso 1 1 2000
run 50
unfix ensemble
#### parameters for new bonds and angles
variable finalbond equal 222 # bond stretching constant
variable finalangle equal 59 # bond bending constant
variable cutoffstart equal 4 # first loop vulcanisation cutoff
variable cutoffend equal 8 # last loop vulcanisation cutoff
#### to convert all created bonds and angles to one final C1-S bond type
variable lastbond equal 4+$vulctry+1 # prior to vulcanisation there are 4 bond types
variable lastangle equal 2+$vulctry+1 # prior to vulcanisation there are 2 angle types
bond_coeff $lastbond $finalbond 1.81
angle_coeff $lastangle $finalangle 109.2
#### printed information
variable totcl equal count(totcl)
variable totclstep equal 0
#### vulcanisation
label loopvulc
variable loopvulc loop $vulctry
fix ensemble all npt temp 298 298 200 aniso 1 1 2000
                    bondtype equal 4+$loopvulc # current created bond type
                    variable angletype equal 2+$loopvulc # current created angle type
                    variable cutoff equal $cutoffstart+($cutoffend-$cutoffstart)/($vulctry-1)*($loopvulc-1) # current cutoff used
                    group reactive type 1 3 4 5 # beads able to react
                    fix CL1 reactive bond/create 1 1 4 $cutoff $bondtype iparam 1 6 jparam 1 7 atype $angletype
                    fix CL2 reactive bond/create 1 3 5 $cutoff $bondtype iparam 1 6 jparam 1 7 atype $angletype
                    variable thermocl equal $totclstep+f_CL1[2]+f_CL2[2]
                    variable thermoclstep equal f_CL1[1]+f_CL2[1]
                    thermo_style custom step temp press density pe ke evdwl ebond eangle edihed v_thermoclstep v_thermocl v_totcl
                    thermo 1
                    run 5 # more than 1 step allows a complete vulcanisation of the beads that are eligible to bond according to bond distance
                    variable totclstep equal $thermocl
                    unfix CL1
                    unfix CL2
                    group reactive delete
                    #### bond stiffening
                    variable steps equal 20
                    label harden
                    variable harden loop $steps
                                        variable factor equal (1-.001)/($steps-1)^2*($harden-1)^2+.001
                                        variable bond equal $finalbond*$factor
                                        variable angle equal $finalangle*$factor
                                        print ‘vulcanisation cycle $loopvulc/$vulctry, hardening step $harden/$steps, k_bond=$bond, k_angle=$angle’
                                        bond_coeff $bondtype $bond 1.81
                                        angle_coeff $angletype $angle 109.2
                                        run 100
                                        next harden
                    jump SELF harden
                    unfix ensemble
                    group reacted type 6 7
                    #### trick to convert all created bonds to a unique final bond type
                    fix break reacted bond/break 1 $bondtype 0
                    thermo 1
                    thermo_style custom step f_break[1]
                    run 1
                    unfix break
                    fix create reacted bond/create 1 6 7 $cutoffend $lastbond iparam 1 6 jparam 1 7 atype $lastangle
                    thermo_style custom step f_create[1]
                    run 1
                    unfix create
                    group reacted delete
                    next loopvulc
jump SELF loopvulc
```

The force field parameters used in our simulation are given in Table ESI.1. The parameters are given also within the LAMMPS data files for each system, included separately with the ESI.

Table ESI.1: Force field parameters. CH_2 groups are referred as C1, CH groups are referred as C2. Parameters deduced by analogy are marked (*)

Stretching $V(r) = \frac{1}{2}k_s(r - r_0)^2$	k_s (kcal mol^{-1} Å^{-2})	r_0 (Å)				
C1-1	663	1.54				
C2-C2	1033	1.34				
C1-C2	769	1.5				
S-S	332	2.038				
C1-S	444	1.51				
Bending $V(\phi) = \frac{1}{2}k_b(\phi - \phi_0)^2$	k_b (kcal mol^{-1} rad^{-2})	ϕ_0 (°)				
C1-C1-C2	115	125.89				
C1-C2-C2	89.4	111.65				
C1-C1-S	100	114.7				
C1-S-S	136	103.7				
C2-C1-S (*)	100	114.7				
Torsion $V(\theta) = \sum_{n=1}^{6} \frac{k_n}{2}(1 - \cos(n\theta))$	k_1(kcal mol^{-1})	k_2(kcal mol^{-1})	k_3(kcal mol^{-1})	k_4(kcal mol^{-1})	k_5(kcal mol^{-1})	k_6(kcal mol^{-1})
C1-C2-C2-C1	0.000	24.200	0.000	0.000	0.000	0.000
C1-C1-C2-C2 (cis)	1.033	-0.472	0.554	0.263	0.346	0.164
C2-C1-C1-C2	-0.888	-0.619	-3.639	-0.066	-0.247	-0.190
C2-C1-C1-S (*)	-0.888	-0.619	-3.639	-0.066	-0.247	-0.190
S-C1-C1-S (*)	-0.888	-0.619	-3.639	-0.066	-0.247	-0.190
S-C1-C2-C2 (*)	1.033	-0.472	0.554	0.263	0.346	0.164
C1-C1-S-S	-1.941	-0.836	-0.935	0.000	0.000	0.000
C1-S-S-C1	0.000	-7.414	-1.705	0.000	0.000	0.000
C2-C1-S-S (*)	-1.941	-0.836	-0.935	0.000	0.000	0.000
Non-bonded $V(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$	ϵ (kcal mol^{-1})	σ (Å)				
C1,C1	0.0936	4.009				
C2,C2	0.1	3.385				
C1,C2	0.1015	3.792				
S,S	0.25	3.55				
non-listed mixed interactions	$\sqrt{\epsilon_1\epsilon_2}$	$\sqrt{\sigma_1\sigma_2}$				

4 Anisotropic barostatting

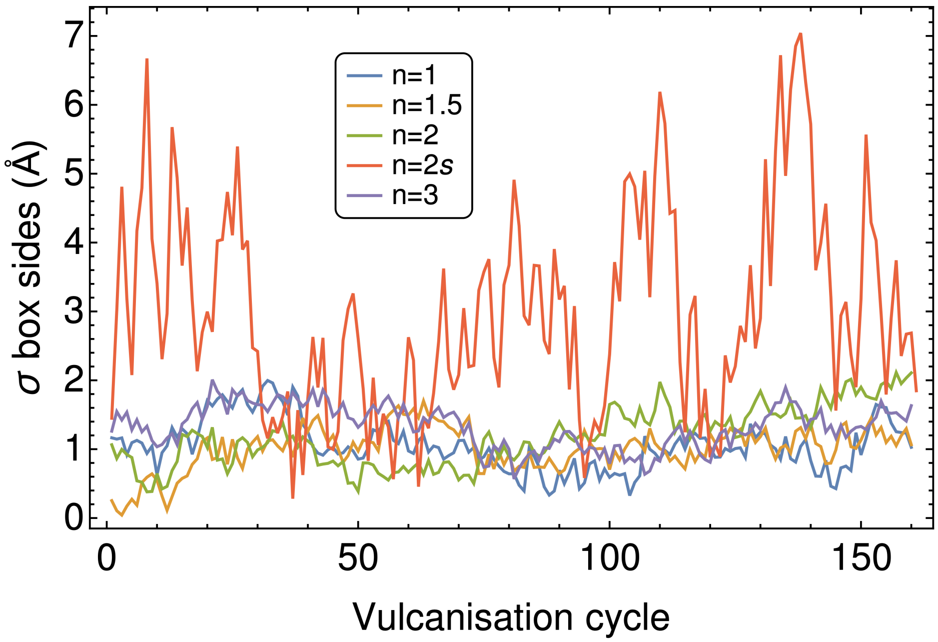

Figure ESI.4: Standard deviation over the three box sides through the vulcanisation

5 Network graph

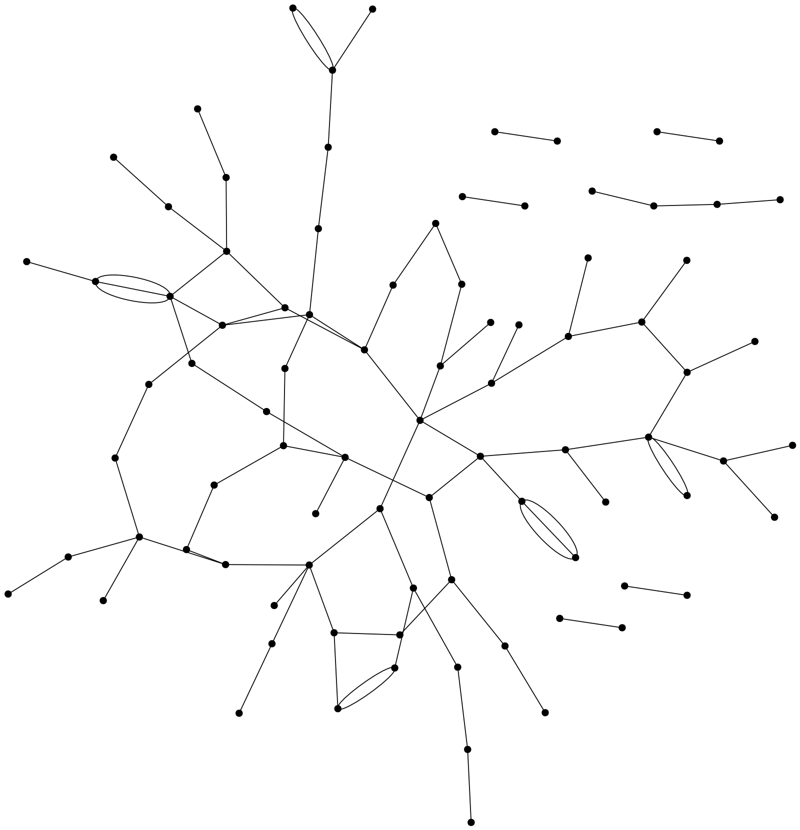

Figure ESI.5: Graph of the system $n = 1$. Each dot represents a chain, each line a sulfur bridge. Diagram generated with Graphviz (https://graphviz.org).

6 Mooney Rivlin fit

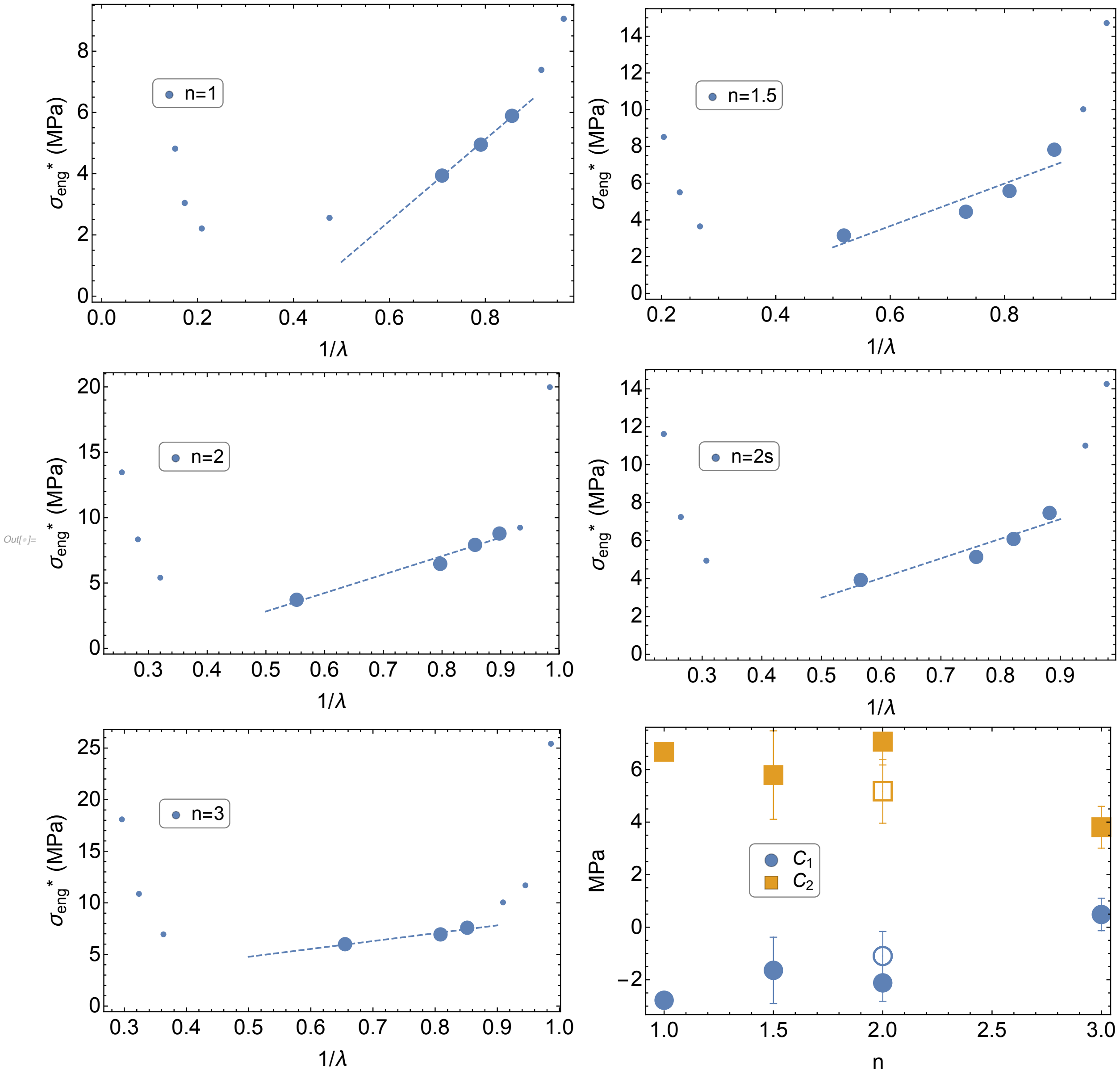

Figure ESI.6: Mooney Rivlin plots and fit in the range $\lambda = 1.1 - 2$. $C1$ and $C2$ parameters extracted from the fit.

7 Conversion of sulphur concentration to *phr* units

In order to allow comparison with experimental data, the sulphur concentration has to be converted to parts by weight, with respect to 100 g of rubber (*phr*, "per hundred rubber").[3] Let us consider for example a system with $n = 2$. This contains two S_2 dimers per PB chain. In turn, each chain contains 100 butadiene monomers, therefore its chemical formula would be $C_{400}H_{602}$. Therefore:

$$phr = \frac{m(S)}{m(PB)} \times 100 = \frac{2 \times 64.13(g/mol)}{5411(g/mol)} \times 100 = 2.37. \quad (1)$$

Table ESI.2 provides the conversion between the different measures of sulphur concentration.

n	phr
1.0	1.18
1.5	1.78
2.0	2.37
3.0	3.56

Table ESI.2: Conversion between sulphur concentrations.

8 Stress per strand

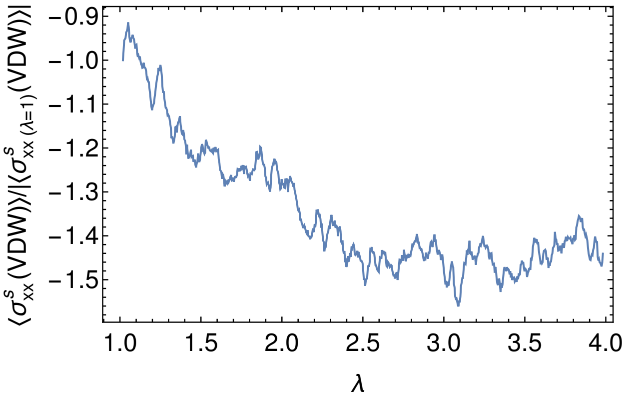

Figure ESI.7: Evolution of the pair contribution (Van der Waals VDW) to the stress per strand. Every point is calculated as an average over the strands, normalised by the absolute value of the stress in the undeformed state. The contribution to the stress coming from the pair interactions is always negative, while the total stress is always positive. The VDW contribution is linear with negative slope and reaches a plateau at about $\lambda = 2.5$

References

[1] Axel Kohlmeyer. Topotools. https://sites.google.com/site/akohlmey/software/topotools.

[2] University of Illinois. Vmd, visual molecular dynamics. https://www.ks.uiuc.edu/Research/vmd.

[3] Alan N. Gent. *Engineering with Rubber. How to Design Rubber Components.* Hanser, 2012.