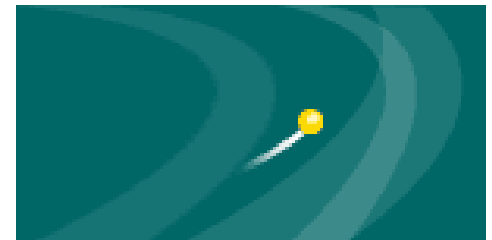


Jessica Gwyther

Characterisation of Plasticised Nitrocellulose using NMR and Rheology



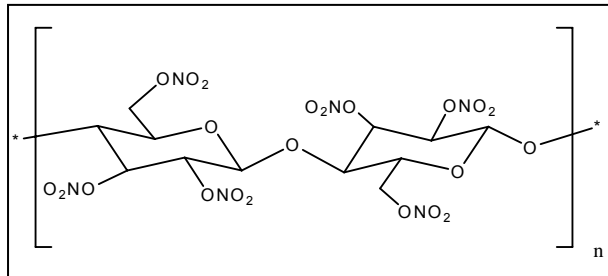
Project Aims

- Prepare 5 inert PBX binder formulations using nitrocellulose polymer and a series of nitroaromatic plasticiser
- Characterisation of formulations that form gels
- Investigation of the molecular dynamics of the small plasticiser molecules in the NC matrix using NMR
- Characterisation of bulk physical properties of the binders using rheological measurements.

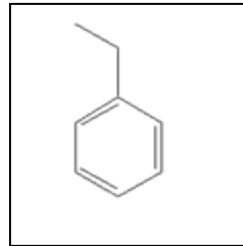
Binder Formulations

- NC +
- ethylbenzene (EB)
 - mononitroethylbenzene (MNEB)
 - dinitroethylbenzene (DNEB)
 - trinitroethylbenzene (TNEB)
 - K10 (DNEB (65%) TNEB (35%))

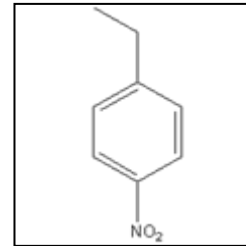
Film
Gel
Gel
Solid
Gel



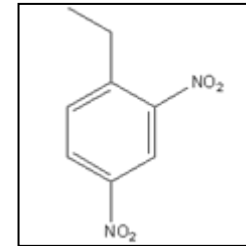
NC



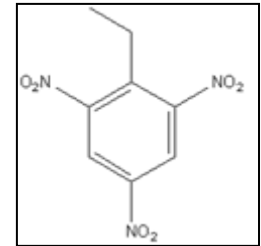
EB



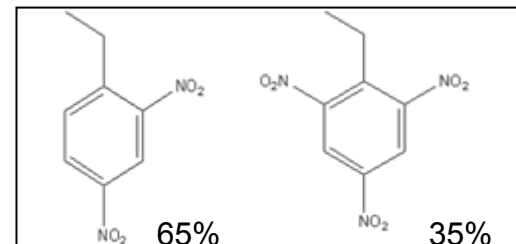
MNEB



DNEB

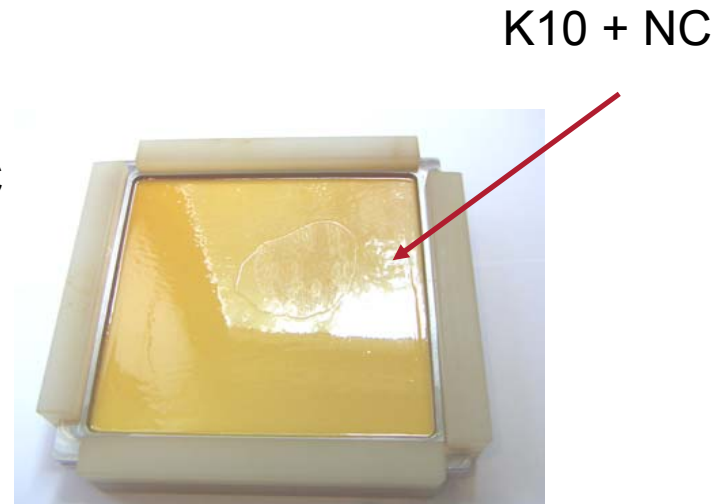
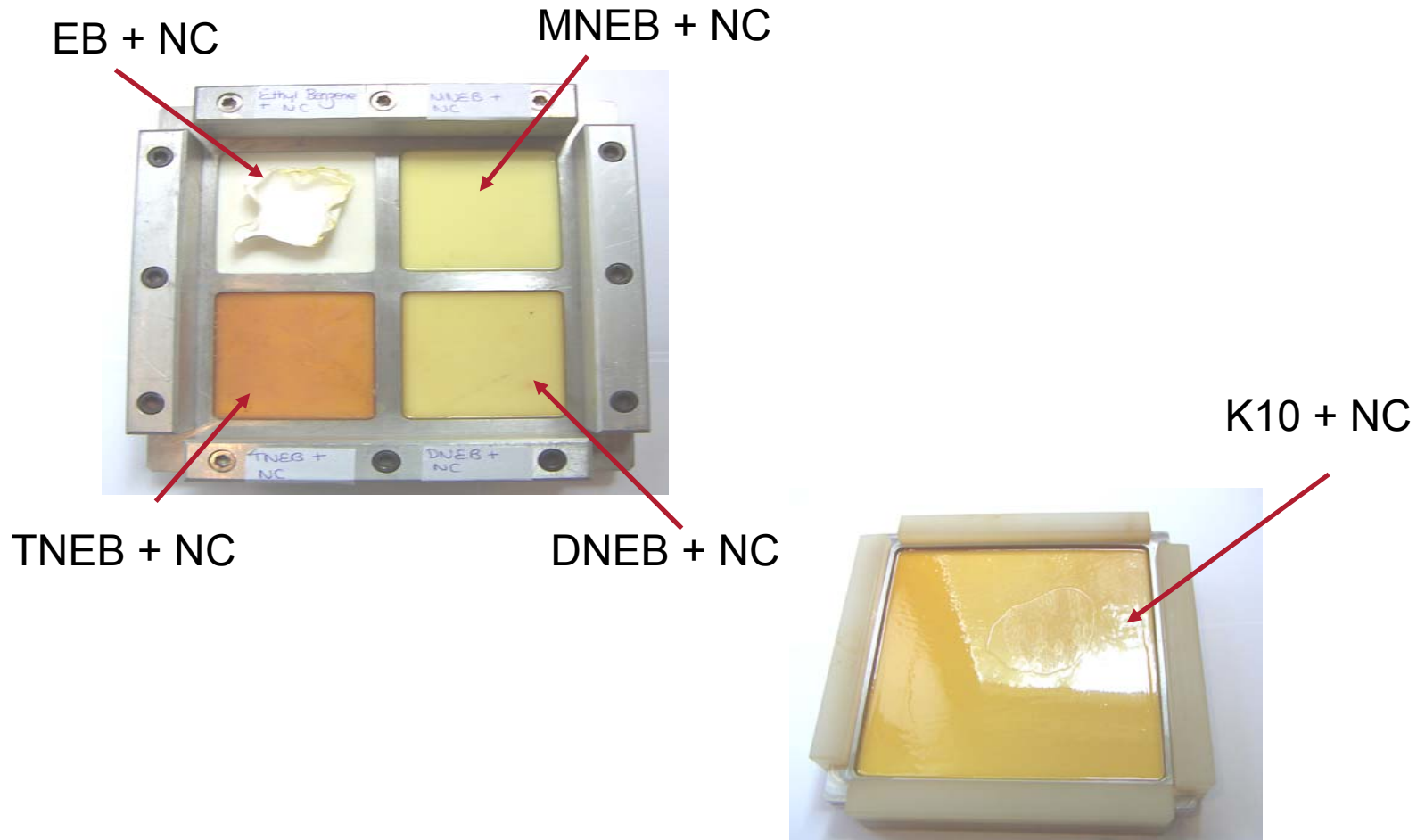


TNEB



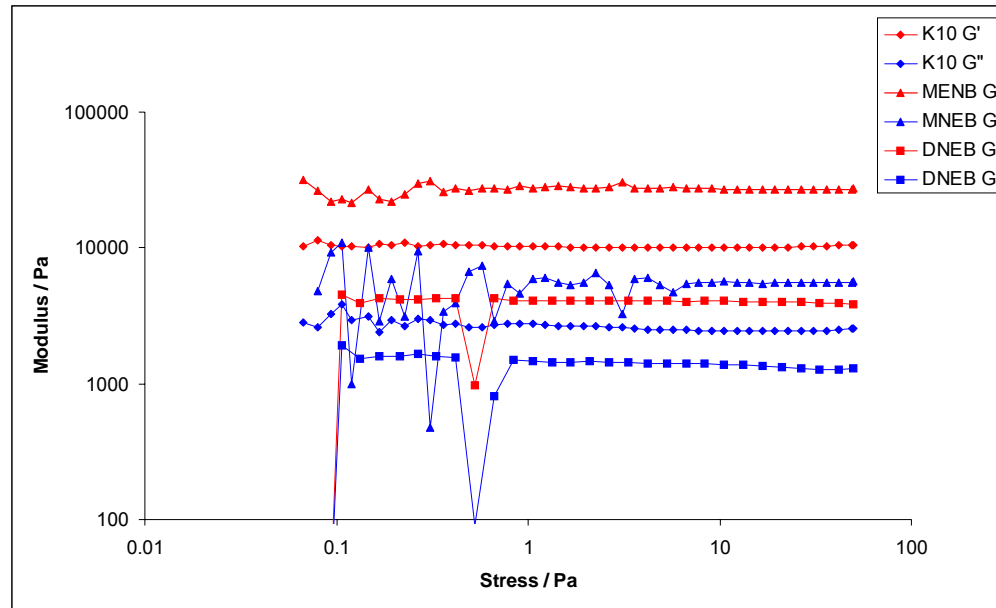
K10

Binder Formulations



Rheology – Amplitude Sweep

- Oscillation expt. Stress sweep at constant frequency to find linear viscoelastic region and good signal.

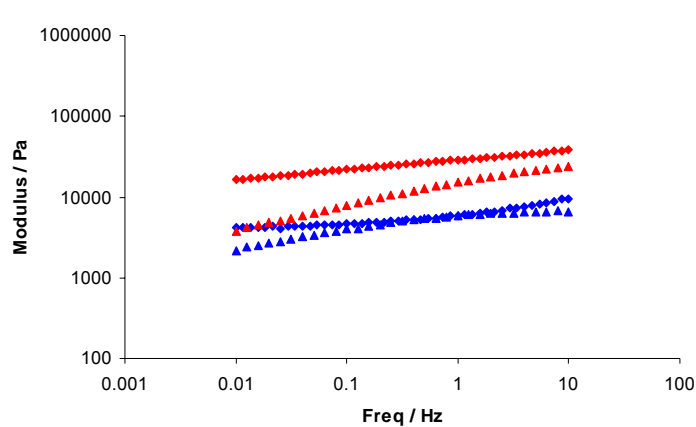


- G' greater than G'' for each gel – more **Elastic** than viscous.
- Relative 'rigidity' of gels:

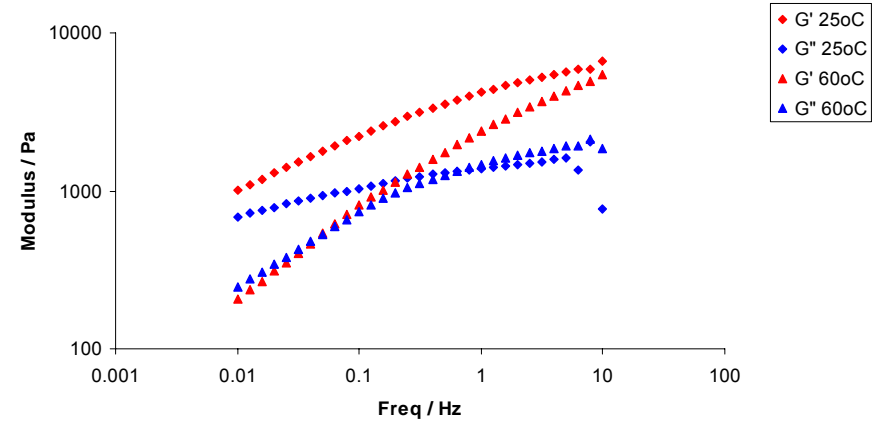
DNEB + NC < K10 + NC < MENB + NC

rigidity →

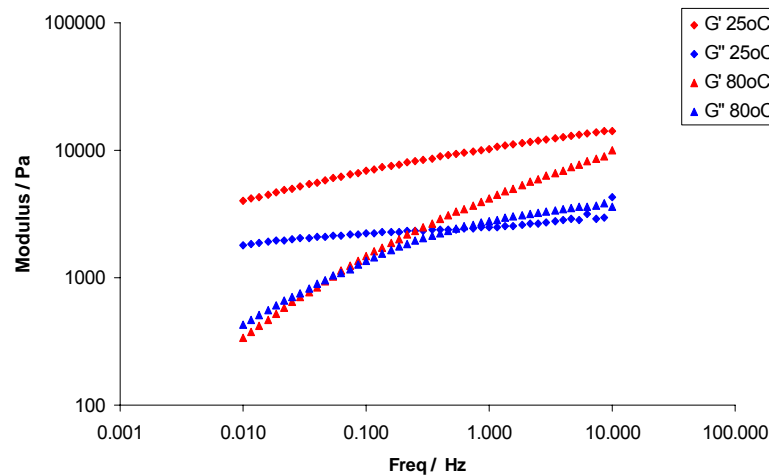
Rheology – Oscillation at Elevated Temperatures



MNEB + NC binder

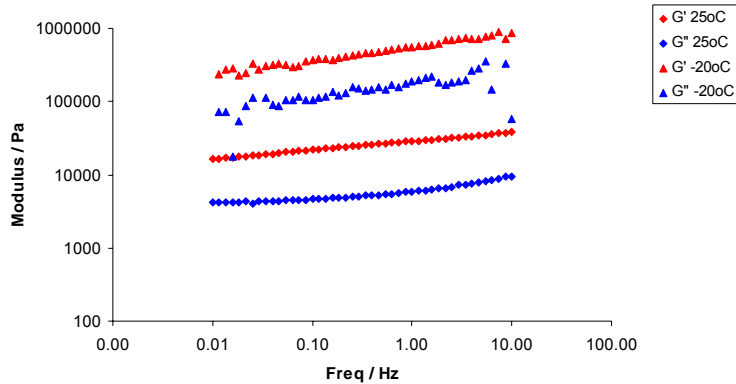


DNEB + NC binder

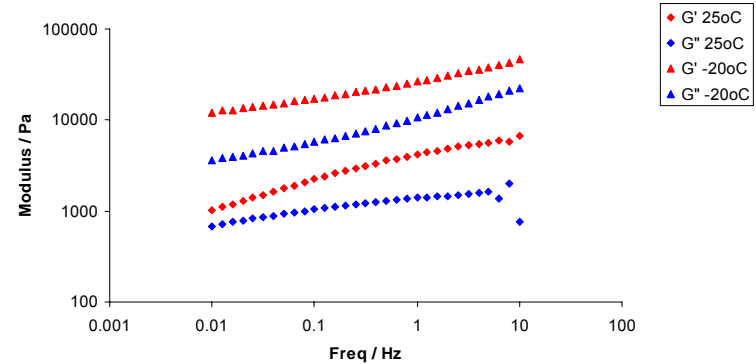


K10 + NC binder

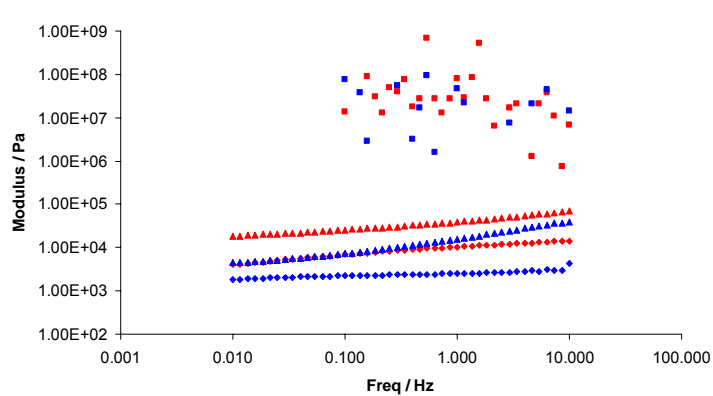
Rheology – Oscillation at Sub-ambient Temperatures



MNEB binder

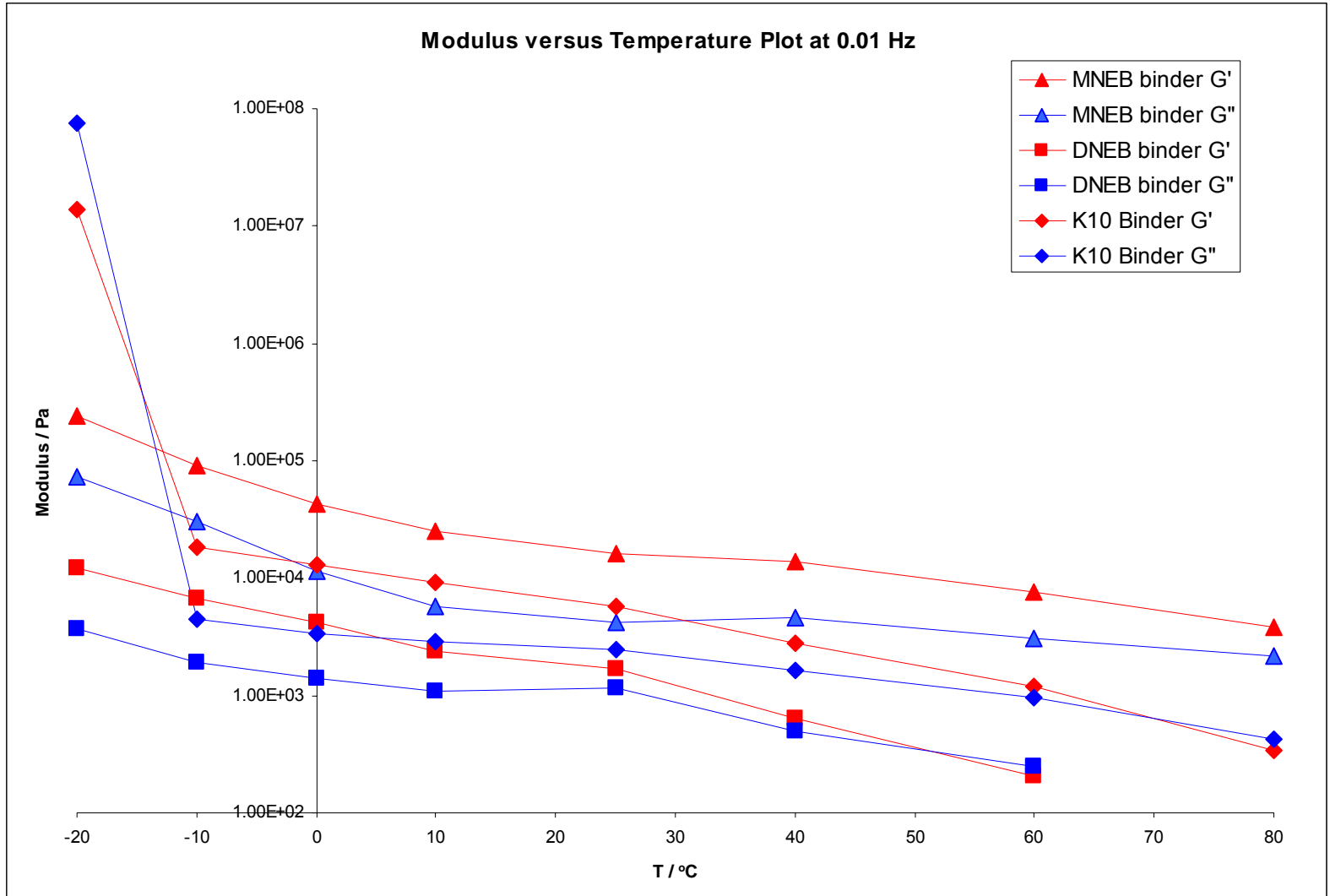


DNEB binder

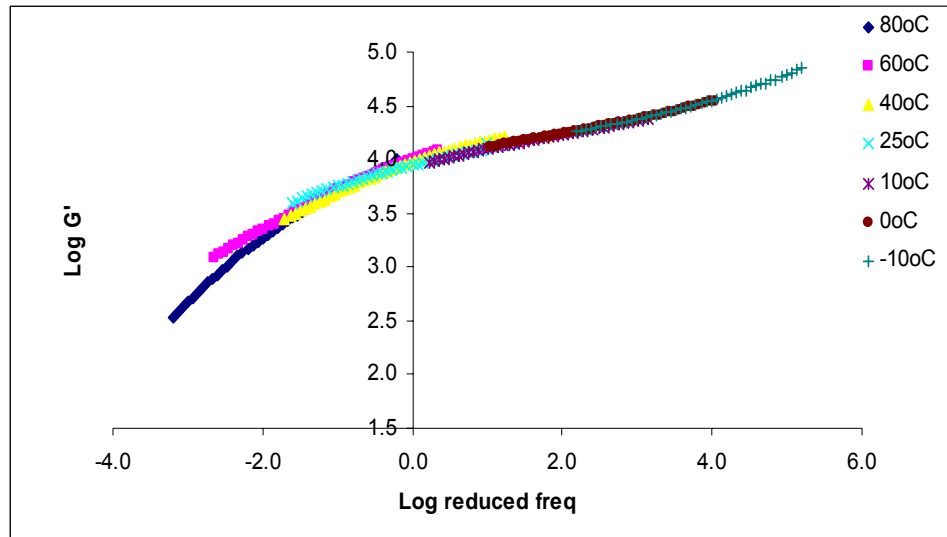


K10 binder

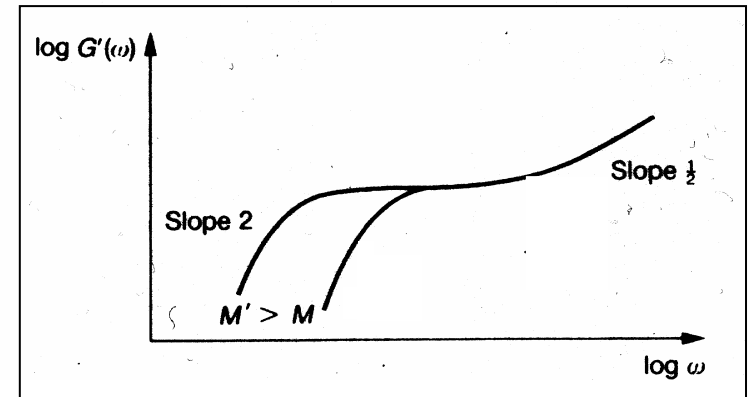
- Large G' and G'' at -20°C for K10 binder.
- Possible phase transition.



Time-temperature Superposition



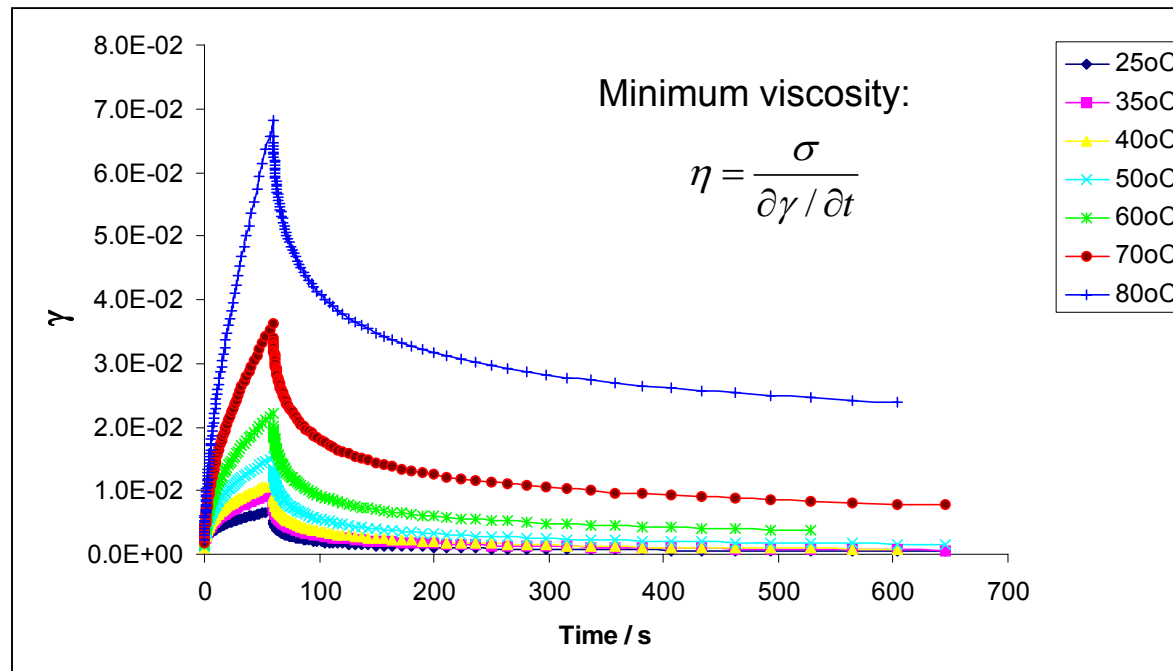
- Good overlay of oscillation data for all gels
- Rheology dominated by NC not small molecule plasticiser
- Evidence of highly concentrated solution of entangled polymer, not cross linked gel



M Doi and S. F. Edwards, The Theory of Polymer Dynamics

Creep Recovery

- Stress applied to sample and strain measured.
- Stress is removed after being applied for a time.
- If **no flow** has occurred = strain gradually **recovers to zero**.
- If some **flow has occurred** = strain **does not recover to zero**.



$T / ^\circ\text{C}$	$\text{Min. } \eta \times 10^5 / \text{Pas}$
25	13.1
35	9.57
40	7.37
50	3.93
60	1.63
70	0.78
80	0.25

NMR – T₂ of Gels

T₂ is a time constant which is related to molecular dynamics by:

$$\frac{1}{T_2} = A \frac{\tau_c}{1 + \omega^2 \tau_c^2} + B \tau_c$$

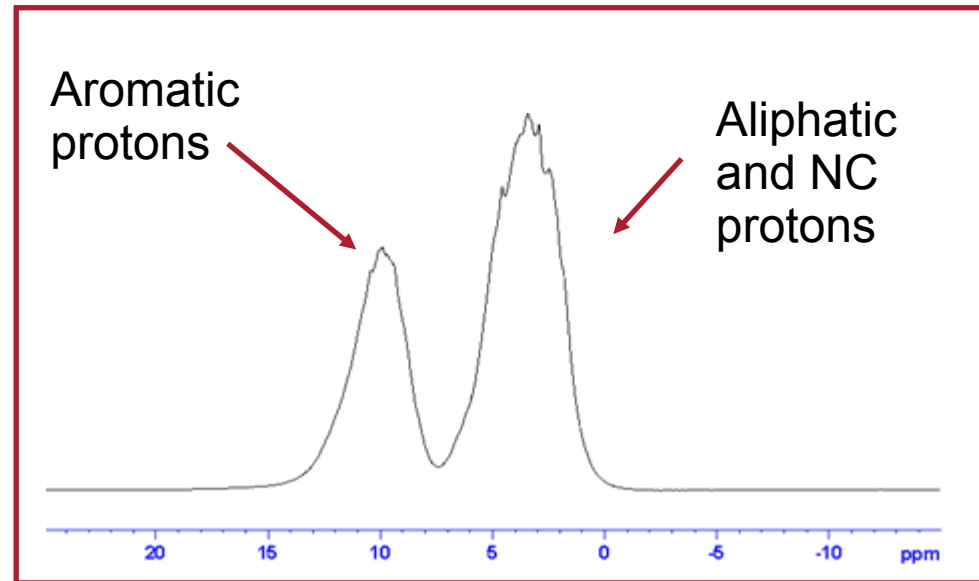
τ_c = Molecular Correlation Time
 ω is the Larmor frequency and
 A and B are constants.

Liquids $\omega^2 \tau_c^2 \ll 1$

$$\frac{1}{T_2} = (A + B) \tau_c$$

Solids $\omega^2 \tau_c^2 \gg 1$

$$\frac{1}{T_2} = B \tau_c$$



Spectrum K10 + NC gel

K10 (DNEB + TNEB) < DNEB ≤ MNEB

Molecular Mobility

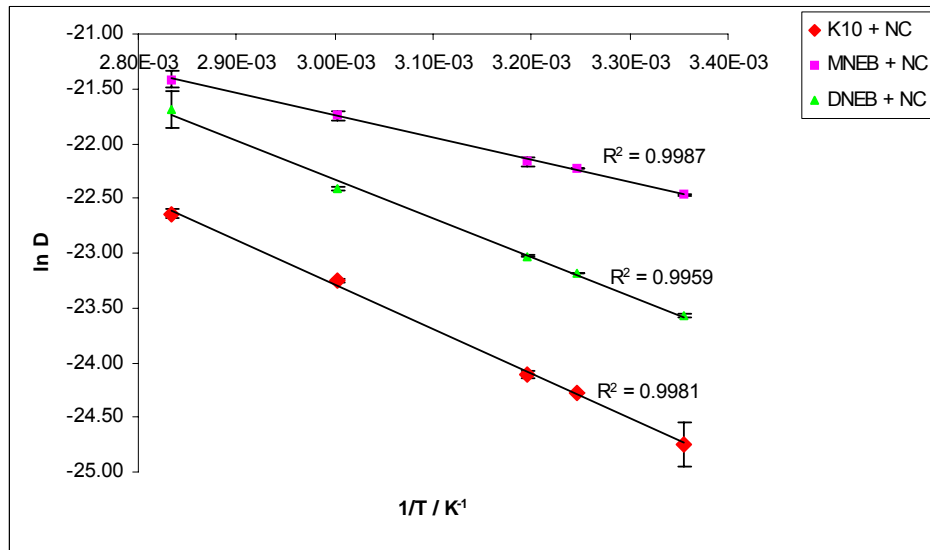
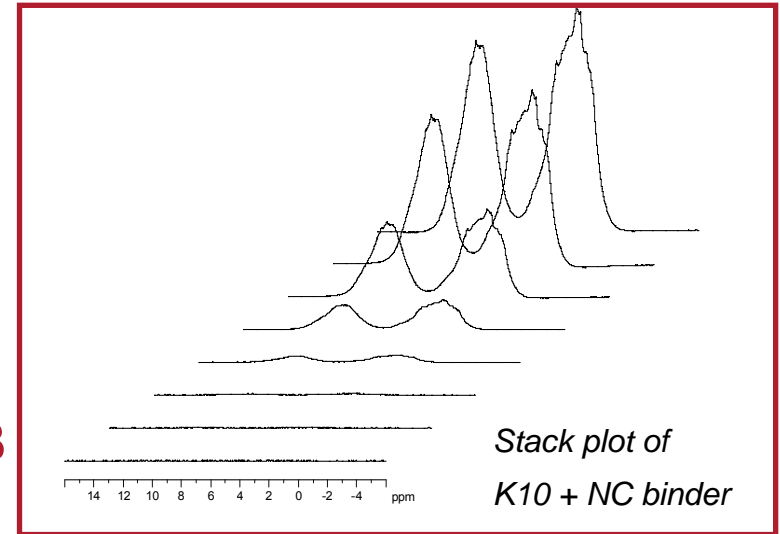
NMR – Diffusion of Gels

- Pulse Field Gradient (PFG) NMR used to find **translational diffusion co-efficient**
- Larmor equation: $\omega = \gamma B_0$
- B_0 spatially homogeneous, ω same throughout sample
- However, if in addition to B_0 magnetic field gradient applied...
...Larmor frequency varies with position and becomes a **spatial label**.

NMR – Diffusion Gels

- Whole molecule has same diffusion coefficient
- Relative ordering of gels according to D :

K10 (DNEB + TNEB) < DNEB < MNEB
(consistent with T_2)



- Diffusion expt's repeated between 25°C – 80°C
- Arrhenius plots

Conclusions

- Three formulations formed gels.
- Bulk Properties:
 - Rheological properties of the gels dominated by NC polymer
- Molecular Dynamics:
 - T_2 and diffusion coefficients of small molecules within gels.
 - Increasing molecular mobility with decreasing molecular size.
 - Molecular dynamics dominated by small molecule plasticisers.
- Evidence that gels are concentrated solutions of entangled polymer, not cross linked gels.

Acknowledgements

- AWE – Dr. Paul Deacon
- Prof. Terence Cosgrove and Dr. Roy Hughes
- Polymers at Interfaces Group – Dr. Youssef Espidel
- Bristol Colloid Centre – Dr. Cheryl Flynn