

THE BRITISH SOCIETY OF RHEOLOGY

BULLETIN



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EDITORIAL

The Bulletin does not usually deal with book reviews, but I will allow myself some editorial privilege to recommend to the members "*Rutherford - Simple Genius*" by David Wilson, recently published by Hodder & Stoughton. The story is unfolded of the often forgotten scientist who pioneered the modern research "school" and government sponsored research in universities. One interesting point to emerge is the fact that on the one hand Rutherford had great intuitive ability, believing he could "picture" the atom and predict the existence of the neutron for instance, while at the same time following up ideas that were basically wrong. The latter is excused by his biographer who points out that Rutherford's ideas were governed by the current state of knowledge. It doesn't take many years in rheology to recognise this in oneself or one's rheological colleagues, for every "head of gold" has "feet of iron and clay". So rheology as every other science when viewed microscopically moves two steps forward and one step backwards, whereas overall there is steady progress.

While we're on the subject of books - could I also recommend "*A Handbook of Public Speaking for Scientists & Engineers*" by Peter Kelly published by Adam Hilger Ltd., Bristol. John Benbow kindly passed on his copy for my perusal, and I found all aspects of the subject are well covered.

My copy of "*Rutherford - Simple Genius*" is now on its way back to the NLL and, you'll get your "Handbook" back soon, John!

Arriving at novel results and communicating these in an effective way will always remain the chief aim of the basic rheologist - of whom there are far too few among us.

Howard Farnell

PROF. A CHARLESBY - EX PRESIDENT B.S.R.

I would like to draw attention of members to some recent work arising from NMR measurements on a series of irradiated polymers above T_g in which the degree of cross-linking could be controlled quantitatively by the radiation dose. When examined by pulsed NMR they showed the usual T_1 and T_2 relaxation spectra, and T_2 could be related directly and simply to the degree of cross-linking.

For a partially cross-linked polymer, the T_2 relaxation curve consists of two exponentially decaying components, of initial amplitudes f and $1-f$, and with characteristic times T_{2L} and T_{2S} . $1-f$ is found to be the network fraction, f the non-network (sol) fraction. T_{2S} is related to M_c (or to the density of elastically deformable segments, i.e. the moduli) in the network, while T_{2L} appears to relate to the viscosity of the remaining (sol) molecules within the confines of the network. Insofar as this pulsed NMR technique can be applied to curable polymer networks, it provides a rapid, non-destructive method of measuring degree of cure etc. Previously it was often necessary to resort to tedious and lengthy extraction procedures to determine the non-network fraction or sol(s). The identity of f and s has been shown directly for appropriate polymers of lower molecular weight ($< 10^4$ about) and demonstrated in other ways, notably by the observation that if the number of cross-linked units per weight average molecule (δ) sinks below unity no network is formed and $s = f = 1$. No T_{2S} component is then observed. Above this number ($\delta > 1$), theory predicts a partial network, as is confirmed both by solubility determinations of s , and NMR of f .

This simple allocation ceases for higher MW polymer (typically $> 10^4$) when a two component relaxation curve is obtained in a non-cross-linked completely soluble polymer system. Pulsed NMR behaves as if a network is present, but this is not shown in the solubility behaviour. The explanation is that a dynamic network is being measured, formed not by permanent cross-links, but by temporary entanglements, of lifetime longer than the few ms involved in a pulse measurement, but far shorter than the many hours in extraction.

Pulsed NMR therefore represents an excellent method of determining the extent of this dynamic network in the specimen. Furthermore the usual theoretical relations apply between network fraction ($1-f$) and cross-link-coefficient δ , and if the molecular weight distribution is known δ can be deduced, and its variation with temperature derived by a series of simple NMR measurements. Expressed in the form $\delta = \delta_0 \exp E/kT$, the activation energy E is similar to that found in mechanical measurements in polystyrene.

We can now present a simple and remarkably accurate quantitative explanation of the variation of elastic moduli with temperature (above T_g or T_m) and with molecular weight. This depends on the well-established theoretical relationship that requires at least one cross-link (or entangled) unit per WA molecule for a network to form. If on melting this condition is not met ($\delta < 1$) no dynamic network is formed, and the polymer melts directly into a viscous liquid. If $\delta > 1$, the moduli of the network can be expressed as:

$$Y = (3 \rho RT/M_w) \delta c_1$$

where c_1 is a correction factor for chain ends (e.g. $1 - 2 M_c/M$ or similar). Since the temperature dependence is small Y shows an approximate plateau behaviour, with T rising and δ falling, until δ approaches the critical value of unity. Y then sinks rapidly and at $\delta = 1$ the polymer is a viscous liquid.

The entanglement density (number per unit mass) appears to be independent of molecular weight, so that δ is proportional to molecular weight, and a higher temperature is needed to reach the critical value of $\delta = 1$. There is good agreement between values of E determined by such mechanical measurement of Y in polystyrene and that deduced from network determination by pulsed NMR.

It is concluded that pulsed NMR offers a valuable new technique for characterising polymeric systems and studying their morphology. It has been used for example to determine the long-term memory of polymer configuration built into a polymer during its precious history, and can be applied to determination of crystallisation rate, degree of cure, the nature of the carbon-black-polymer mixture, the role of solvents and plasticizers (which increase free volume, reduce viscosity and lifetime and density of entanglements). The role which can be played by network theory in the effects of entanglements should also not be ignored. Fuller details of these uses of pulsed NMR are being published separately.

This brief exposition still leaves open some basic questions. What is the nature of an entanglement, and why does it depend on temperature? What is its average lifetime, and how does this vary with temperature, free volume etc? Numerous exciting hypothesis can be readily formulated, but must now be verified or rejected. Finally we must see how far these concepts are applicable to the changes in morphology of biomolecules, which might be as important as their chemical structure.

A CHARLESBY

Professor Emeritus
Silver Spring
Eagle Lane
Watchfield
Swindon
SN6 8TF

Modulus E calculated from entanglement density
(deduced from pulsed NMR)

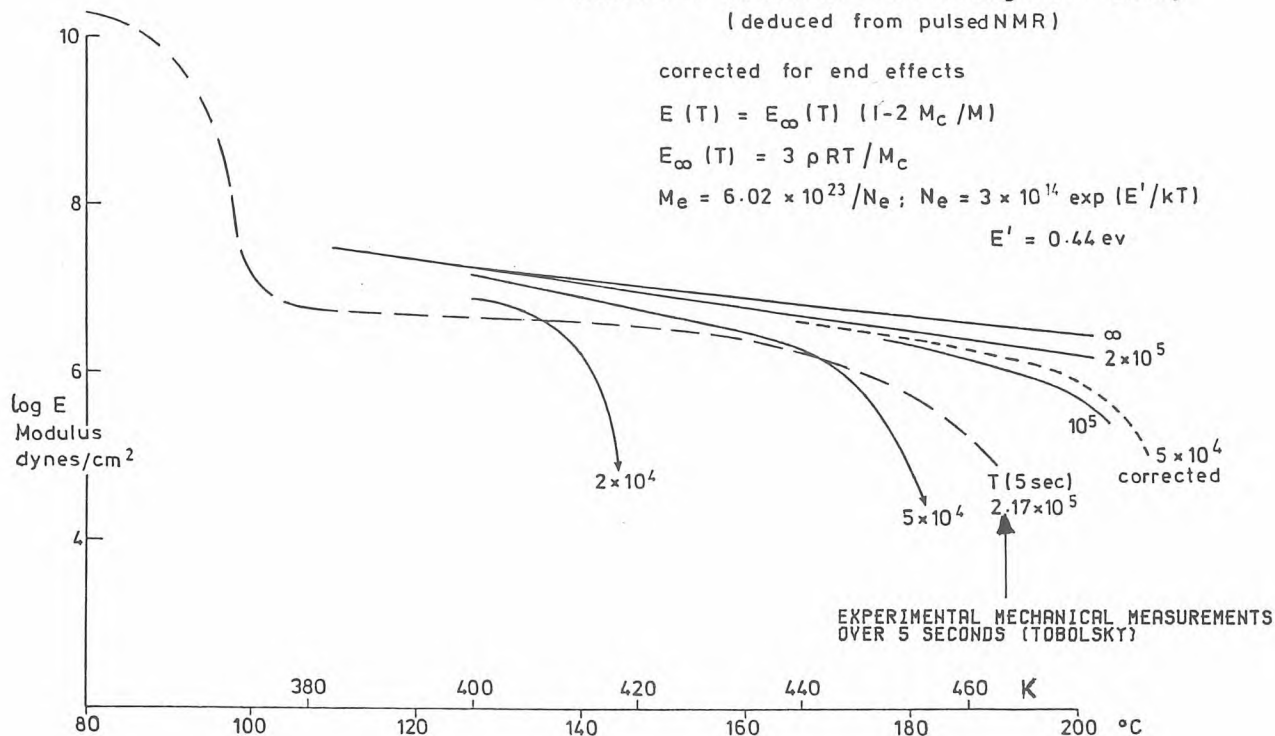
corrected for end effects

$$E(T) = E_{\infty}(T) (1 - 2 M_c / M)$$

$$E_{\infty}(T) = 3 \rho RT / M_c$$

$$M_e = 6.02 \times 10^{23} / N_e ; N_e = 3 \times 10^{14} \exp(E'/kT)$$

$$E' = 0.44 \text{ eV}$$



MEMBERSHIP NEWS

The following applications for Membership were approved at the Council Meeting on July 6th 1984

(KEY TO SYMBOLS - SEE LAST ISSUE)

Mr Peter APPLETON Cadbury Schweppes plc Bournville Birmingham, B30 2LU	BSc Hons (Chem Eng) peta L
Mr Peter A BERN BP Research Centre Chertsey Road Sunbury-on-Thames Middlesex, TW16 7LN	BSc fea DFGJ
Dr Martin P DARE-EDWARDS Shell Research Ltd Thornton Research Centre PO Box 1, Chester, CH1 3SH	MA (Oxon), D.Phil (Oxon) fetsa J
Dr David Michael HEYES Department of Chemistry Royal Holloway College Egham Hill, Egham Surrey, TW20 0EX	BSc, PhD fetsa BCDEFGHIJKLMN
Dr Nicolas Edward HUDSON Fibre & Textile Research Unit University of Strathclyde George St., Glasgow, G1 1XW	BSc, PhD fetsa DFN
Mr Torjecki JACEK Technical University of Lodz Polanol, Lodz POLAND	MSc (Chem Eng) feta DM
Dr Dilhan M KALYON Stevens Institute of Technology Dept. of Chemistry & Chemical Engineering Castle Point, Hoboken New Jersey 07030 U.S.A	B.Eng, M.Eng, Ph.D peta CD
Prof. Alvin William NIENOW Department of Chemical Engineering University of Birmingham PO Box 363, Birmingham, B15 2TT	BSc, PhD, DSc, F.I.Chem.E. fea DGHJL

Dr James Henry PRENTICE
16 Walden Ave., Arborfield
Reading
Berkshire

PhD, F.Inst.P.
fetsa FL

Mr Donald Peter STAIT
Contraves AG
Schaffhauserstrasse 580
CH-8052 Zurich
SWITZERLAND

HNC (Mech.Eng)
peta FGJLM

Dr A.R David THORLEY
The City University
Northampton Square
London, EC1V 0HB

BSc, M.Phil, PhD
pea EFGH

Mr Chun-nam (Sidney) TSANG
Department of Applied Physics
Sheffield City Polytechnic
Sheffield, S1 1WB

MSc
fea D

HONORARY MEMBERSHIP

Prof A.I LEONOV of the USSR has accepted Honorary Membership.

RESIGNATIONS

Dr A.E Hawkins, Unilever Research, Sharnbrook.
Joined in 1965.

Mr R.S Lenk, London School of Polymer Technology.
Joined in 1963.

Mr F Moore, British Ceramic Research Association, Stoke-on-Trent.
Joined in 1968.

Prof. A.M North, University of Strathclyde, Glasgow. Now President
of the Asian Institute of Technology, Bangkok, Thailand.
Joined in 1970.

Miss J.A Norris, Unilever Research, Port Sunlight.
Joined in 1980.

DEATH

We regret to announce having received notification of the death
of Prof. Bun-ichi Tamamushi, Japan in July 1982 aged 84. He joined
the Society in 1956.

MEMBERSHIP SUBSCRIPTION REMINDER

The annual membership subscription of £5 falls due on the 1st of October for the year 1984/85. May I please remind all members who have not paid in advance or who do not pay by Banker's Standing Order to send their payment now to

The Hon. Membership Sec.
Mr P.C.Anderson
32 Queensway
Feltham
MIDDLESEX
TW13 7NS

If you do not pay your subscriptions by Banker's Standing Order, I would urge you to do so for the convenience of the both of us. It would reduce the onerous task I have each year of sending out subscription reminders. The order should be made payable to the British Society of Rheology Membership Dues Account number 0180985 at Lloyds Bank, 20 North Street, Leatherhead, Surrey. (Branch Code number 30-94-94). In addition please also notify me at the above address that you have so instructed your bank.

Overseas Members: Please note that you may pay for several years' membership in advance, but please ensure that the amount remitted, if not already in Sterling, should include an extra £1.60 to defray our Bank charges. It is also perfectly acceptable for any number of members to send a single cheque covering their combined subscriptions, to save exchange expenses.

RHEOLOGY ABSTRACTS

Abstractors urgently required.
Would any member willing to take
on this useful task please contact
the Abs. Editor, Dr D R Oliver.
(see front inside cover for address)

ROYAL SOCIETY OF CHEMISTRY : INDUSTRIAL DIVISION
PROCESS TECHNOLOGY GROUP

and

THE BRITISH SOCIETY OF RHEOLOGY

*announce a
one-day Seminar on*

"RHEOLOGY IN THE PROCESS INDUSTRIES"

*to be held at
The Learned Societies Lecture Theatre
Saville Row
LONDON*

on

WEDNESDAY, 8TH MAY, 1985

Six leading figures in the field of rheology will review the latest ideas in this important and practical branch of science. The Seminar is aimed at the industrial chemist, process technologist and chemical engineer and those academics interested in process technology.

This meeting is a follow-up to the successful 1981 meeting when Dr H A Barnes presented the results of his Survey on Dispersion Rheology following his Industrial Fellowship.

The meeting will be moderately priced, with lunch provided. Full details will be announced in the next issue.



The Deutsche Kautschuk-Gesellschaft e.V. has pleasure in drawing the early attention of its friends and members to the

ikt '85

**International Rubber Conference
held in conjunction with a Trade Exhibition**

on 24–27 June 1985 in Stuttgart.

Researchers, specialists and industrial technologists from all over the world will present papers, and exchange ideas, on the most recent scientific and technical developments in the rubber sector.

We invite you to join in any of 9 symposia, which will cover the following subjects:

- Developments in the tyre sector
- Reinforcing agents for the 1990's
- Advances in the reinforcement sector
- Elastomers and rubber chemicals
- New developments in machinery
- Quality improvement and quality assurance of rubber articles
- Performance limits of rubber
- Modern analytical methods for vulcanised products
- General developments in the rubber sector

We shall be pleased to receive, any time from now, proposals for scientific contributions to the individual symposia. The Congress languages will be German and English, with simultaneous translation.

In order to extend the information on offer beyond the actual lectures, we intend to hold poster sessions, as was also the case at the dkt '83 in Wiesbaden.

Proposals for lectures and posters should be submitted by 30 September 1984.

The round-table discussion on "Research and Promotion of Research in the Rubber Industry" promises to be of particular interest.

OTHER MEETINGS

- 8-13 October Acapulco, Mexico: *IX International Congress on Rheology*
 Contact: Prof. B Mena, Instituto de Investigaciones
 en Materiales, Apdo. Post. 70-360,
 Ciudad Universitaria, Coyoacan 04510,
 Mexico D.F., Mexico.
- 16-18 October Madison, USA: *Symposium on Viscoelasticity & Rheology*
 Contact: Conference Sec., Mathematics Research Center,
 University of Wisconsin-Madison,
 610 Walnut St., WARF Bldg., Madison, WI 53705.
- 12-15 December Cambridge, England: *The Physics of Dispersion of Small
 Particles (Euromech 191)*
 Contact: Dr E J Hinch, Dept. of Applied Mathematics &
 Theoretical Physics, University of Cambridge,
 Silver Street, Cambridge CB3 9EW.
- 1985
- 24-26 February USA: *56th Annual Meeting Soc. of Rheology*
 Contact: Secretary (J R Collier)
- 5-7 March Birmingham: *POWTECH '85*
 Contact: Miss Fiona Dendy
 The Institution of Chemical Engineers
 165-171 Railway Terrace, Rugby CV21 3HQ, UK.
- 1-4 April Cambridge, England: *6th Churchill Conference on
 Deformation, Yield and Fracture
 of High Polymers (DFI, BSR)*
 Contact: Plastics & Rubber Institute,
 11 Hobart Place, London, SW1 OHL.
- 10-12 September Reading: *New Techniques in Experimental Rheology (BSR)*
 Contact: Mr H Schimanski, Contraves Industrial Products,
 Times House, Station Approach, RUISLIP,
 Middx. HA4 8LH.



DEPARTMENT OF MATHEMATICS, STATISTICS & COMPUTING
RESEARCH FELLOWSHIP IN CONTROLLED STRESS RHEOMETRY

Applications are invited for a research fellowship to undertake a theoretical and experimental study of a controlled stress rheometer particularly in its oscillatory mode.

This project is financed by an SERC cooperative research grant and will be carried out in close collaboration with Carri-Med Ltd. There will be an opportunity for the applicant to work in industry during the period of this research.

Applicants should possess or be about to obtain a Ph.D or have equivalent qualifications in Mathematics, Rheology or relevant engineering discipline. Additional experience in computing would be welcome.

Salary will be in the range £7251 - £8091 , according to age and experience.

The appointment will commence on 1st October 1984 or as soon as possible after and will last for a period of 2 years.

Application forms together with further particulars may be obtained from the Personnel Officer, Plymouth Polytechnic, Drake Circus, Plymouth, Devon, PL4 8AA.



Training Course in Fluid Rheology

at Warren Spring Laboratory, Stevenage, 19-23 November 1984

13th in a series. 5-day residential course

WHO SHOULD ATTEND

The course is aimed at the practising rheologists, physicists, chemists and engineers who have responsibility for product formulation, quality and process control, process plant design, selection and operation. But it should also be useful for the newly-appointed rheologist who wishes to be brought quickly up-to-date on information and know-how relevant to his/her job.

COURSE CONTENTS

Lectures - on material science aspects: (1) overall view of rheological properties, (2) physical and (3) chemical bases of dispersion rheology, (4) behaviour of pastes and high solids content materials and (5) molecular aspects of polymer rheology.

- on viscometry, covering basic principles, calibration, instrumental errors and commercial equipment. (6) Coaxial cylinder, (7) Cone and plate, (8) Parallel plate, (9) Rotating disc, (10) Falling sphere and (11) Tube viscometers. Measurement of (12) thixotropic and (13) viscoelastic properties: normal stresses, dynamic moduli and elongational viscosities.

- on applications in (14) product formulation, (15) quality and process control, (16) pipeline design and (17) mixing.

Practical Periods These will give hands-on experience on the wide range of viscometers and rheometers available commercially. Engineers from the major instrument manufacturers will be in attendance with their latest models. Samples brought to the Course by participants can be tested.

Seminars and Surgeries on Industrial Problems Ample opportunity will be available to discuss industrial problems with WSL staff and with other Course participants. Two Seminars will be organised: (i) Rheometry in the microprocessor age and (ii) How would you test this material? (A number of samples will be handed out for assessment.) In Surgeries, problems will be discussed with individual participants in confidence.

Syndicate Exercise The Course participants will be divided into teams and each team will consider the rheological specification of a novel product. The results will be judged by all and a prize will be awarded to the winning team.

Course Manual A comprehensive Course Manual will be supplied.

COURSE FEE

The Fee for the Course is £724.50 inclusive of VAT, which includes accommodation for five nights - bed and breakfast - from Sunday night (18 November) to Friday morning (23 November), lunches and refreshments at WSL and a Course Dinner during the Thursday evening.

FOR FURTHER INFORMATION

Contact Mrs L J Viney

WARREN SPRING LABORATORY
Department of Trade and Industry
Gunnels Wood Road
Stevenage
Hertfordshire SG1 2BX

Telephone: Stevenage (0438) 313388
Telex: 82250

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