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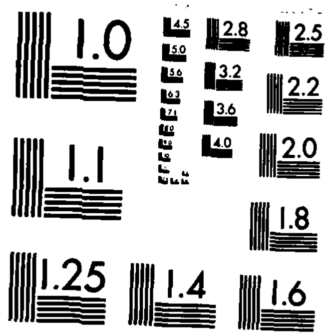

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IMPORTANCE AND SIGNIFICANCE OF TRANSITION TEMPERATURES

by

W. A. Lee

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IMPORTANCE AND SIGNIFICANCE OF TRANSITION TEMPERATURES

by

W. A. Lee

SUMMARY

The importance of the transition temperatures of polymers is described with particular emphasis on their practical significance. An outline of the RAE Transition Temperature Data Bank is provided and RAE publications in the transition temperature field are tabulated.

LIST OF CONTENTS

1 INTRODUCTION

This Memorandum is one of a series of reports and memoranda relating to the transition temperature (TTs) of polymers and explains briefly the motivation for studies in this area. The important part played by TTs in determining the properties of polymers is described with many examples of their practical significances. A keen academic and commercial interest in TTs is illustrated by reference to the RAE Transition Temperature Data Bank; RAE publications in the TTs field are listed.

2 IMPORTANCE AND SIGNIFICANCE OF TRANSITION TEMPERATURES

Over the last decade, a large number of polymers have been synthesised yet only a small proportion has achieved commercial success. Leaving aside those polymers synthesised solely for academic reasons, the origins of this failure are at least twofold. Firstly, there are many commercial polymers already available and between them they provide a wide spectrum of useful properties which makes it increasingly difficult to bring about a significant improvement on a cost effective basis. Secondly, the designing of new polymers for specific properties, 'molecular engineering', has sometimes been more hit and miss than it might have been. Nevertheless, there are important gaps at the top and bottom of the temperature scale and for special applications, and it becomes increasingly compelling to make more effective use of the vast amount of data currently available and direct new research into more profitable channels. To this end, many investigations are concerned with the relationships between structure and properties in order to make the best possible estimate of properties in advance of synthesis. In pursuit of this aim, an understanding is required of the main factors which govern polymer properties. A totally crystalline polymer, if such could be obtained, would be very brittle and not very useful. It follows therefore, that the state of the amorphous (non-crystalline) regions is one of the dominant factors insofar as physical, particularly mechanical, properties are concerned which determine, the degree of usefulness of a material. Differences in the physical properties of linear polymers are determined by variations in the types and rates of segmental motion of the polymer chains and the types and degrees of molecular ordering. Changes in the characteristics of the amorphous or crystalline regions occur at the TTs and it follows therefore that they are all important in determining the properties of a polymer. For example, transitions associated with the amorphous region determine the low temperature limit of the high reversible strain characteristic of elastomers, the moulding and the upper and lower service temperatures and to some degree the toughness of plastics, and the drawing temperature of fibres. In general terms, all physical properties of amorphous polymers which depend on the segmental relaxation rate undergo a major change on heating through the glass transition temperature (T_g) region. A plastic material which is largely amorphous may show a large drop in Young's modulus (perhaps 3 orders of magnitude) and, at the same time, a discontinuity in the temperature dependence of, or a marked change in, such properties as diffusivity, expansivity, refractive index, gas solubility, crazing, creep, damping, adhesion and chemical reactivity. For satisfactory strength and stiffness, many thermoplastic commercial polymers, particularly fibres, must have both the type and degree of crystallinity controlled within appropriate limits. At the temperatures of crystal-crystal transitions (T_{ccs}), changes in density and mechanical properties can occur and at the melting point (T_m) there is a catastrophic fall in strength and stiffness in crystalline polymers. T_{ms}, T_{ccs}, and crystallisation temperatures assume considerable importance in governing the temperatures of processing.

It is evident that before embarking on any programme of polymer development or synthesis, close attention must be given to both amorphous and crystalline region TTs. The amassing of reliable and comparable information on TTs is the first step in the attempt to resolve what sort of polymer will have the properties desired. It also yields much of the data needed to be able to decide whether an existing polymer has the required properties or may be further developed to do so.

In practical terms, the number of fields and applications in which a necessary interest in TTs has been shown is illustrated by the example index terms drawn from the RAE Transition Temperature Data Bank (see Appendix A) which was formed in co-operation with RAPRA and covers data up to 1979. Since that date, references to TTs have been recorded as a result of computer searches, but the references have mostly not been processed. An enormously diverse field of applications and interests is shown by the 1800 titles in the actual index. Appendix B briefly describes the RAE Data Bank the size of which is a measure of external interest in TTs and therefore of their significance to workers in the polymer field.

RAE papers and publications on transition temperatures have attracted much interest[1-20] as can be judged from over 100 citations in the Science Literature Index and correspondence on the subject from over 140 different persons.

3 CONCLUSIONS

Transition temperatures determine what sort of material (elastomer, plastic or fibre) a polymer may be, its temperature limitations, or advantages, in processing and in use, whether or not it will be in the glassy or rubbery state at its use temperature, and the temperatures at which some of the more significant changes in physical properties occur. They are of the greatest importance to the engineer as well as to the scientist trying to make new polymers with improved properties and to correlate properties with structure, indeed it has been said that "it is impossible to understand the properties of polymers without a knowledge of the types of transitions that occur in such materials. Nearly all the properties of polymers are determined primarily by these transitions and the temperatures at which they occur"[21].

Appendix A

EXAMPLES OF INDEX TERMS USED IN THE RAE TRANSITION TEMPERATURE DATA BANK

Abrasion
Activation energy
Adhesion, adhesive
Adhesive sheet
Adhesive tape
Ageing see also/Degradation
Aircraft window
Allotropy
Annealing
Antioxidant
Antiplasticiser
Artificial leather
Bearings
Binding power index
Biomedical
Birefringence
Bond interchange
Bottle
Brillouin scattering
Carbohydrate
Car interior
Casting solvent
CED see/Cohesive energy density
Chemiluminescence
Clathrate
Coating compositions
Cohesive energy density (CED)
Cold forming
Cold rolling
Compressibility
Conduction/elect. Conductivity/elect.
Cracking
Crease recovery
Creep
Critical surface tension
Crystallinity
Crystallisation
Crystallisation (Rate)
Crystallisation Temp
Current regulating
Damping /Vibration damping
Deformation
Deformation energy
Degradation
Densified vol.
Density
Dental crowns
Depolarisation current
Dielectric properties
Dielectric relaxation
Diffusion
Dimensional stability
Drape stiffness
Drawing, /Drawn
Drawing temperature
Dyeing
Dynamic mechanical
Elasticity
Elasticity minimum temperature
Elastomers
Electrets
Electrical conductivity
Electrical insulation
Electrical resistance
Electric discharge
Elongation
Elongation ratio
Emulsion freeze-thaw stability
Encapsulation
Energy of rotational isomerisation
Etching
Excluded volume
Expansion coefficient
Explosives
Fabrication
Fabric production
Failure envelopes see Ultimate properties
Fatigue
Fibres
6T Fibre

Fibrillation
Filler
Films
Fire retardant
Flatspot index
Flex abrasion
Flexibility
Flow temp.
Fluids
Footwear
Fracture
Free volume
Freezing point
Friction
Gas chromatography
GEM disubstitution
Glass reinforced plastics
Golf balls
Grafting
Granulating
Grease
Hardener see/Crosslinking (Structure)
Hardness
Heat capacity
Heat conductivity
Heat distortion
Hot pressing
Impact (Resilience) (Resistance) (Strength)
Internal friction
Internal pressure
Interpenetrating polymer network
Interplanar slippage
Ionic charge
Irradiation
Ladder polymers
Lamella thickness
Lamination
Laser-induced damage
Latex manufacture
Leather coating
Leather substitutes
Liquids
Load
Lubricant

Luminescence
Magnetic field
Magnetic tape
Mechanical behaviour
Medical implant
Membrane
Minimum film fusion temperature
Modulus
Molar Ht.
Molar volume
Molec motion
Mooney viscosity
Moulding
Natural leather
Necking
Nucleation
Oil
Optical activity
Ozone cracking
Packaging
Paint
Paper coating
Peeling strength
Penetrant
Permeation, /Permeability
Phase equilibria
Phosphorescence
Photodegradation
Pipe couplings
Plastic yield
Poisson's ratio
Polishes
Polymer characterisation
Polymer design
Polymer networks
Polymerisation conditions
Powder preparation
Processability
Product design
Propellants
Propellant binders
Puhl Coef
Radiation see Irradiation
Radical concentration

Reactivity
Reduced electrical resistivity
Refractive index
Relaxation time
Rigidity
Rolling
Safety glass
Scintillation intensity
Sealant
Seals
Sheet formation
Shrinkage
Surface tension
Surgical
Swelling
Tearing
Tear Strength
Temperature conductivity
Tensile properties
Theory
Thermal conductivity
Thermal expansion
Thermal history
Solubility
Solubility parameter
Solution properties
Sound velocity
Specific heat
Specific retention Volume
Specific Volume
Spherulitic growth rate
Strain
Stress-optical coef.
Stress relaxation
Stretching
Thermal stability
Transport
Tyres
Varnish see/Paint
Vibration dampers
Viscoelasticity
Void formation
Volume expansion
Vulcanisation

Water absorption
Wear
Welding strength
Wetting
Wrinkle recovery (resistance)
(see /Crease recovery (resistance)
Yarn production see also /Fibrillation
Yielding behaviour

Appendix B

THE RAE DATA BANK ON TRANSITION TEMPERATURES

As part of a programme on polymer development at RAE a data bank on transition temperatures of polymers was compiled. The majority of data related to transitions of the non crystalline phase of undiluted linear homopolymers, but a wider field of interest had been indexed to a limited extent. The data bank comprised:

(a) Index of 10700 data cards showing transition temperatures of individual polymers.

(b) Author index comprising 11000 entries (based on first-named authors).

(c) Subject index with 1800 subject headings and 14500 referenced information cards.

(d) Computer based index of 1200 critically assessed glass transition temperatures of undiluted linear homopolymers in a chemical hierarchy and Tg value order together with a suite of over 100 computer programs to manipulate the data. Data up to 1972 was published in the second edition of the Polymer Handbook[1].

(e) Handbook of Data Sheets on 90 carbon-chain fluoropolymers[2]

(f) Handbook of Data Sheets on 197 fluoropolymers containing main-chain nitrogen[3].

(g) A Handbook of Data Sheets on fluoropolymers containing main-chain oxygen[4].

REFERENCES

No.	Author	Title, etc
1	W.A. Lee R.A. Rutherford	Glass transition temperatures. In Polymer Handbook, edited by J Brandrup, second edition, Section III, pp 139-192 J Wiley and Sons, Inc, New York, (1975)
2	W.A. Lee R.A. Rutherford	RAPRA Data Handbook. Polymer transition temperature data sheets, carbon chain fluoropolymers, Vol I. RAPRA, Shawbury, (1973)
3	W.A. Lee R.A. Rutherford	RAPRA Data Handbook. Polymer transition temperature data sheets, fluoropolymers containing main-chain nitrogen, Vol II, Parts 1 and 2. RAPRA, Shawbury, (1974)
4	W.A. Lee R.A. Rutherford	RAPRA Data Handbook. Polymer transition temperature data sheets, fluoropolymers containing main-chain oxygen or sulphur, Vol II, Parts 1 and 2 RAPRA, Shawbury, (1976)
5	W.A. Lee	An analysis of factors governing the glass transition temperatures of polymers based on a review of available measurements. RAE Report No.CPM 8 (1964)
6	W.A. Lee	Glass transition temperature of homopolymers: a bibliography and assessment of available data. RAE Technical Report 65151 (1965) Also published as Chapter III or Polymer Handbook, edited by J. Brandrup and E.H. Immergut, Interscience, NY, (1966)
7	W.A. Lee J.H. Sewell	The influence of cohesive forces on the glass transition temperatures of polymers. RAE Technical Report 65112 (1965) Also published in J. Applied Polymer Science, 12(6), 1397 (1968)

REFERENCES (continued)

No.	Author	Title, etc
8	W.A. Lee G.J. Knight	The ratio of the glass transition temperature to the melting point in polymers. RAE Technical Report 66005 (1966) Also published in British Polymer J., 2, 73 (1970)
9	G. Allen W.A. Lee	A critical survey of current views of the glass transition phenomena. RAE Technical Report 66090 (1966)
10	W.A. Lee D. O'Mahony	Calculation of the glass temperatures of polymers having alkyl side chains. RAE Technical Report 66292 (1966) Also published in J. Polymer Sci., Pt A-2, 8, 555 (1970)
11	W.A. Lee G.J. Knight	The glass transition temperatures of polymers. In Polymer Handbook, first edition, Edited by J. Brandrup and E.H. Immergut, (Section III, pages 61-91), published by J. Wiley and Sons, Inc, New York, (1966)
12	W.A. Lee	Some aspects of the problem of designing new heat-resistant fluids and elastomers; structures containing phenyleneperfluoroalkylene units. RAE Technical Report 66409 (1966)
13	J.M. Barton W.A. Lee	Definition of structural groups in the calculation of glass temperatures of homopolymers. RAE Technical Report 67119 (1967)
14	J.M. Barton W.A. Lee D. O'Mahony	Correlation of the glass transition temperatures of polyacrylates, polymethacrylates and polychloroacrylates with their chemical structures. RAE Technical Report 67298 (1967)
15	J.M. Barton W.A. Lee	Contribution of the methylene group to the glass transition temperatures of polymers. Polymer, 9, 603 (1968)
16	W.A. Lee	Proposal for the evaluation of potentially flexible and heat resistant units in polymers. RAE Technical Memorandum Mat 67 (1969)

REFERENCES (concluded)

No.	Author	Title, etc
17	W.A. Lee B. Stagg	The internal plasticisation of aromatic polyesters by alkyl side chains. RAE Technical Report 71223 (1971)
18	W.A. Lee Shirley A. Watts	Correlation of the glass transition temperatures of carbon-chain fluoropolymers with their chemical structures. RAE Technical Report 74060 (1974)
19	W.A. Lee	Correlation of the properties of fluoropolymers with chemical structure. RAE Technical Memorandum Mat 195 (1974) (Invited paper presented at the 5th European Symposium on Fluorine Chemistry, Aviemore, Scotland, September 1974)
20	W.A. Lee Shirley A. Fowler	Correlation of the glass transition temperatures of heteroatom-chain fluoropolymers with their chemical structures. RAE Technical Report 75043 (1975) (Commerical-in Confidence)
21	D.W. van Krevelen	Properties of polymers. Correlations with chemical structure. Elsevier Scientific Publishing Company, Amsterdam, second edition, page 20 (1976)

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17. Abstract

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