Journal of Thermal Analysis, Vol. 13 (1978) 85—9

SOME APPLICATIONS OF THERMAL METHODS OF ANALYSIS TO POLYMERS

J. M. Barton, W. A. Lee and W. W. Wright

Materials Department, Royal Aircraft Establishment, Farnborough, Hants, U.K.

(Received April 17, 1977)

Some examples are given of the application of thermogravimetry, differential scanning calorimetry, thermomechanical analysis, torsional braid analysis, stress relaxometry and dynamic viscoelastometry to the study of cross-linked polymer systems. The information derived by the use of each technique is outlined and the advantages and disadvantages of the different methods are compared.

Thermal and thermomechanical methods of polymer characterization and evaluation have been developed and have achieved wide acceptance over the past 10—15 years. The various techniques are in many ways complementary and each has its own advantages and disadvantages. This paper gives examples of the application of thermogravimetry, differential scanning calorimetry, thermomechanical analysis, torsional braid analysis, stress relaxometry and dynamic viscoelastometry to the study of practical cross-linked polymer systems. In each case the approach has been to outline (a) the purpose for which the technique can be used, (b) some of the results obtained and (c) the relative advantages and disadvantages of the method.

Thermogravimety (TG)

The major use of thermogravimetry on polymers has been the assessment of thermal stability. Subsidiary uses have been the measurement of the relative efficiency of antioxidants and the monitoring of curing conditions for condensation polymers.

Thermal stability assessment may be directed towards comparison of the heat resistance of different polymer structures, or may serve as an accelerated test for life-time prediction. In the latter case, the method only has real quantitative significance if breakdown is by a single well-defined mechanism and if the retention of the properties of interest is directly related to weight loss. The test may nevertheless be used as a preliminary screening procedure to eliminate those materials, which will obviously not withstand the required conditions.

Much emphasis in this field has been placed upon dynamic methods of analysis, i. e. at different rates of temperature rise, and the reported ways of analyzing the test data are legion. We view dynamic data with considerable reservation as many instances have been observed, where orders of stability as determined by this method are not confirmed when isothermal tests are carried out.

The advantages of thermogravimetry are that it is a quick and easy test to make, instrumentation and data analysis can be fully automated and only small quantities of material in a non-specific form are required. The major disadvantage is that it only records phenomena which are associated with weight loss. This can be illustrated from polyimide chemistry. Polyimides are attacked by bases – a drawback for some applications, but analytically very useful as by treatment of a polyimide with hydrazine hydrate it is possible to recover quantitatively the diamine used in the preparation and the cyclohydrazide derivative of the dianhydride. Samples of poly-N,N'-(4,4'-diphenylether) pyromellitimide film (approximately 0.6 g) were oxidized in a muffle furnace at 400° for different periods of time. Weight loss was recorded and the film then broken down chemically to determine how much of the original structure remained. The results (Fig. 1) showed that at only 2–3% weight loss approximately 50% of the diphenyl ether and 30% of the pyromellitimide units in the original polymer chains had been chemically modified[1]. This raises the question of the extent of this sort of reaction in other high temperature polymer systems, which do not have such a convenient method of chemical analysis.

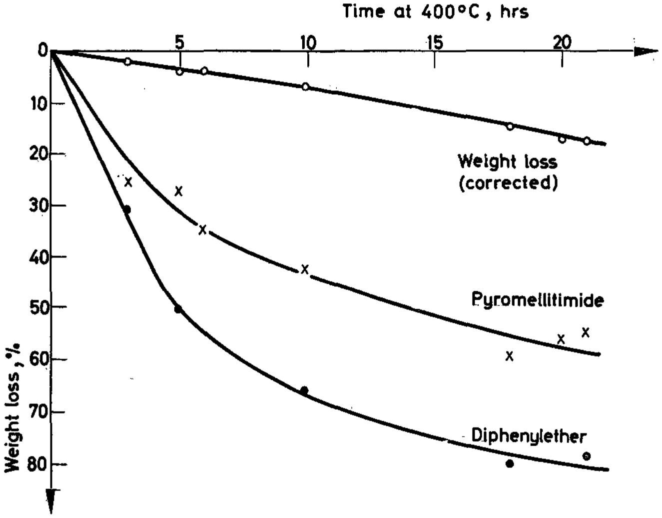

Fig. 1. Change in yield of pure components with time of ageing of polyimide film at 400°

Thermogravimetry has also proved very useful for monitoring the cure of condenzation type polyimides. Weight loss determinations were made for the time/temperature profiles used throughout the curing cycle (i. e. for precure, cure and postcure) using the Du Pont 900 thermal analyser and 950 TG attachment with a flow of dry nitrogen through the sample chamber. Significant differences were observed in the characteristics of different experimental batches of resin and as a result a simple quality control test based on a rising temperature experiment (Fig. 2) was developed [2]. For acceptance of the resin, the values of T_i, T_0, T_f and $W_f - W_i$ had to lie within prescribed limits.

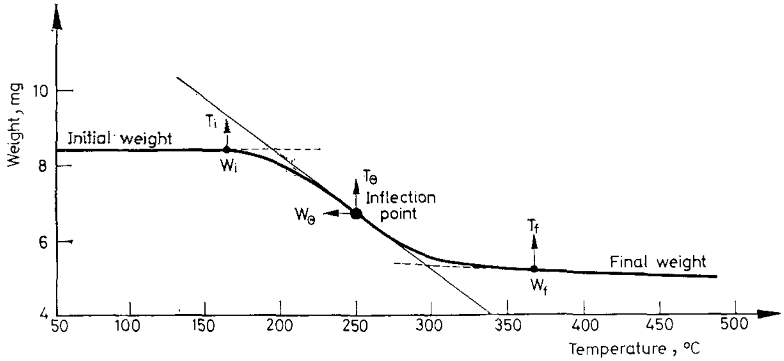

Fig. 2. Dynamic weight loss curve for polyimide resin at 10°/min heating rate

Quality control of prepreg was also possible, weight loss measurements being used to ascertain the amount of precure that had taken place and whether, as a consequence, changes were required in the subsequent moulding conditions. These techniques can be applied in principle to any curing reaction involving weight loss.

Differential scanning calorimetry (DSC)

The advantage of DSC over thermogravimetry is that it is sensitive to any reaction involving a change in heat content and this makes it especially useful for monitoring the curing reactions of resins used in composites and adhesives. It also detects transitions such as T_g (glass transition temperature), when a specific heat change is involved, and T_m (melting).

Points in favour of the technique are that it measures a parameter directly related to a curing reaction, the estimation is relatively rapid and only small amounts of material of non-specific form are required. Disadvantages are that it gives no indication of changes, which may be occurring in mechanical properties. The transition temperatures recorded are very dependent upon the heating rate and the thermal history of the sample and hence care is needed in the interpretation of the results. Transition temperatures below T_g are hardly detectable, but these can be very important in relation to energy absorption processes, e. g. impact strength and ductility.

In fibre reinforced composites, the mechanical and physical properties are dependent upon the state of cure of the resin. The production of components with consistent and reproducible properties therefore requires the resin to be cross-linked to the same degree when ever fabricated. If the resin is slightly undercured, this may not be apparent from the initial property levels, but may well be reflected in a reduced life-time of the component when stressed under adverse environmental conditions.

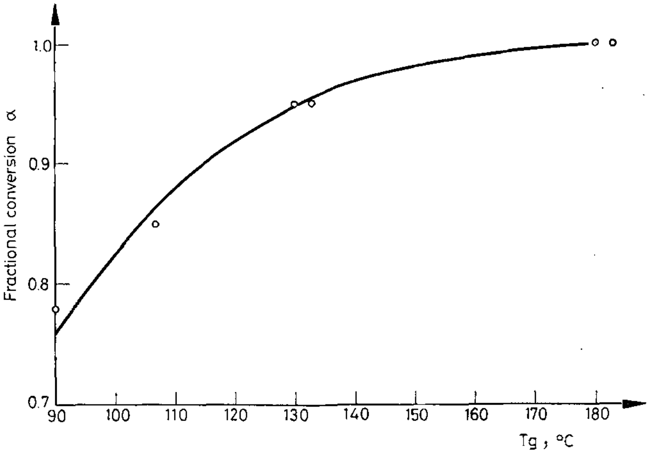

Fig. 3. Dependence of T_g of an epoxy resin upon fractional conversion; from isothermal experiments

The curing reaction of a bisphenol A type epoxide resin with diaminodiphenylmethane was investigated using the Du Pont 900 thermal analyser and DSC cell [3, 4]. It was shown that measurement of the heat of reaction was a quite sensitive method for following cure up to about 90% conversion, but that beyond this point determination of T_g was a more precise method (Fig. 3). Scans at 20°/min produced definite inflections in the curves of differential temperature against programme temperature, and the inflection temperatures were used as a measure of T_g.

Isothermal DSC data were obtained in the form of rate of exothermic heat flow versus time, and these plots were converted to curves of fractional conversion versus time. These curves when plotted on a log scale could be approximately superimposed to give a master curve by horizontal shifts along the log time axis (Fig. 4). The shifts were related to the overall activation energy for the curing process and this allowed the prediction of isothermal cure curves at various temperatures from experimental data obtained at a single temperature. It was also shown that isothermal cure curves can be predicted to a fair approximation from the results of dynamic DSC experiments. This enabled a profile of the cure characteristics of the system to be built up from only two experiments.

Three commercially available addition-type polyimides were also studied using DSC, as well as thermogravimetry and thermomechanical analysis tests [5]. Differences in curing characteristics are illustrated in Fig. 5. The overall results showed that

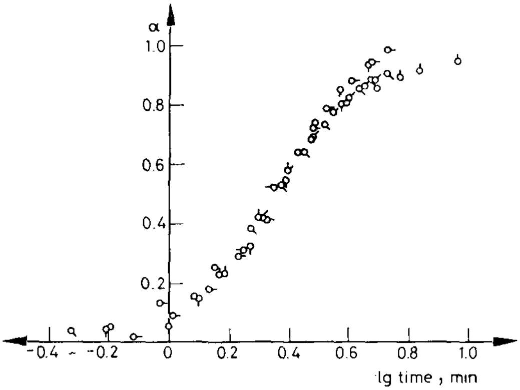

Fig. 4. Master cure curve at 179° for an epoxy resin from superposition of isothermal curves

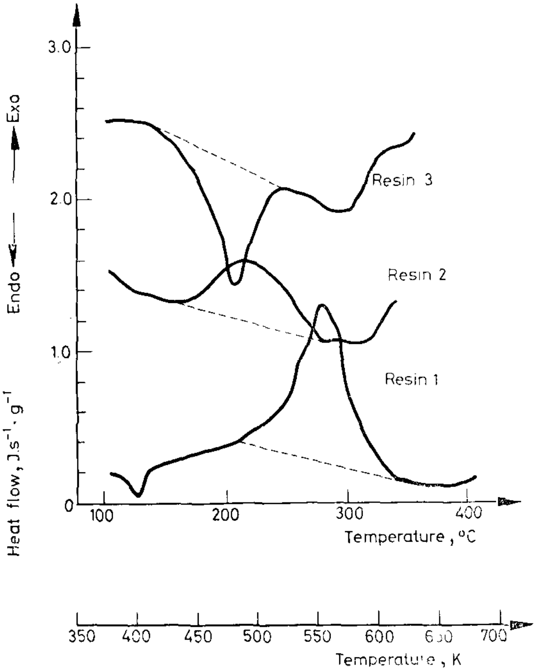

Fig. 5. DSC scans on uncured addition-type polyimide resins. For clarity Y-axis shifts have been applied to the curves as follows: resins 1 and 2, $+0.6$ J $s^{-1}g^{-1}$; resin 3, $+$ 1.2 J $s^{-1}g^{-1}$

a. Resin 1 followed first order kinetics up to about 60% conversion. It was possible to lose a component of this material by volatilization.

b. Resin 2 followed second order kinetics up to 30% conversion. It began to cure in a lower temperature range than Resin 1, but was not fully cured on heating to 350°, a temperature well above the recommended cure cycle.

c. Resin 3 was in the amic acid form as supplied and cure was accompanied by significant weight loss due to the cyclization process.

Differences such as these have a marked influence upon the fabrication procedures necessary and hence on properties and subsequent behaviour.

Thermomechanical analysis (TMA)

Besides measurement of transition temperatures, thermomechanical analysis may also be used for determination of modulus, of reversible compression characteristics, of creep under load at various temperatures and of solvent swelling characteristics of rubbers. The last determination leads to the derivation of the length of chain between cross-links in an elastomer.

Our main uses of the technique have been for transition temperature measurement – as a complement to DSC, measurement of thermal expansion coefficients and assessment of the properties of elastomers. For T_g measurement TMA gives lower values (up to 20° for highly cross-linked materials) than DSC because of stress activation of relaxation processes. The method is, however, very good for detection of transitions below T_g and is more sensitive in this respect than either DSC or torsional braid analysis. Small samples only are needed for test, but these must be carefully prepared if the mechanical data obtained are to be reproducible.

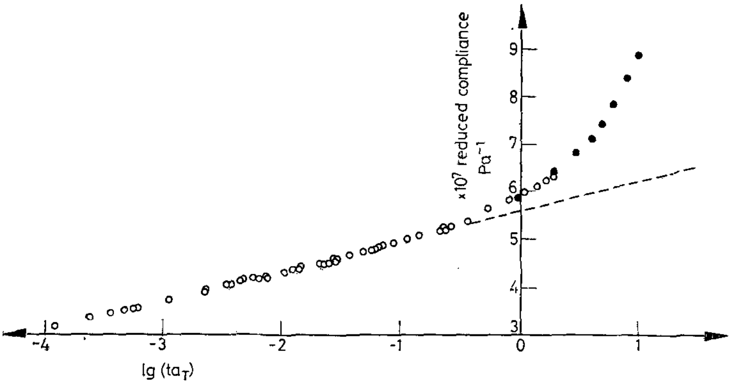

Fig. 6. Master creep curve at 250° for a compounded hydrofluoro-elastomer from superposition of reduced data at 75°, 98°, 147°, 172° and 198° in nitrogen on data at 250°C in oxygen. ○ 75 – 198 °C data; ● 250 °C data

Cure can be monitored by following changes in T_g exactly as with DSC. Both techniques were used for the addition-type polyimides and the results paralleled each other. The TMA data also showed that one of the resins should offer superior performance under load at elevated temperatures for short times.

The technique has proved its worth as a rapid and simple method for characterizing elastomers using small samples of material. The Du Pont 900 thermal analyser and the 941 thermomechanical analyser attachment were used with the hemispherical probe. These penetrometer tests gave the Young's modulus of the rubber in good agreement with the Young's modulus determined by tensile loading at low strains. The same penetrometer test was used to measure creep at elevated temperatures of a compounded Viton B elastomer and from the results a master creep curve could be constructed (Fig. 6.). This showed that degradation of the elastomer was detectable at 200° and occurred rapidly at 250°. The method was also applied to fluoroelastomer samples containing various inorganic compounds as hydrogen fluoride (HF) acceptors and it was shown, which additives were best for a combination of high resistance to creep and high efficiency as HF acceptor [6]. By operating in the expansion mode the solvent swelling characteristics of the same rubber samples were determined and it was confirmed that an acceptable cross-link density was developed during cure of the fluoroelastomer in the presence of the preferred additives. Because very small samples are used, swelling equilibrium is reached quickly (in less than two hours).

Torsional braid analysis (TBA)

TBA is another technique which can be used for determination of transition temperatures, although it does not distinguish between T_g and T_m as say DSC does. Measurement is made of the complex modulus of a fibre/resin combination and only relative not absolute values can be obtained. The measurement is, however, much more directly related to the composite situation than any of the other techniques so far considered, as the actual resins and fibres of interest may be used in making up the braid. Because of the fibre support, polymers can be studied in the liquid state above T_g and T_m.

Our major use of TBA has been for the study of the cure of epoxy and polyimide resins and for assessing the effect of heat, or water uptake, upon mechanical properties. A drawback of the technique is that a sample must either melt, or dissolve in a solvent for braid impregnation and hence the method cannot be applied to already cured components. The effect of heat upon the mechanical properties of some aromatic fluoropolyimides was studied [7]. Glass fibre woven braids were impregnated with the polymer solution and then dried. The torsional braid analyser was used to measure relative changes in the modulus and mechanical loss of the braids as a function of temperature and time. The loss peak heights were observed to diminish and the temperatures at which the peaks occurred to increase with increase in temperature (Fig. 7). The heights also diminished initially with time of heating at constant temperature, but then stabilized, further

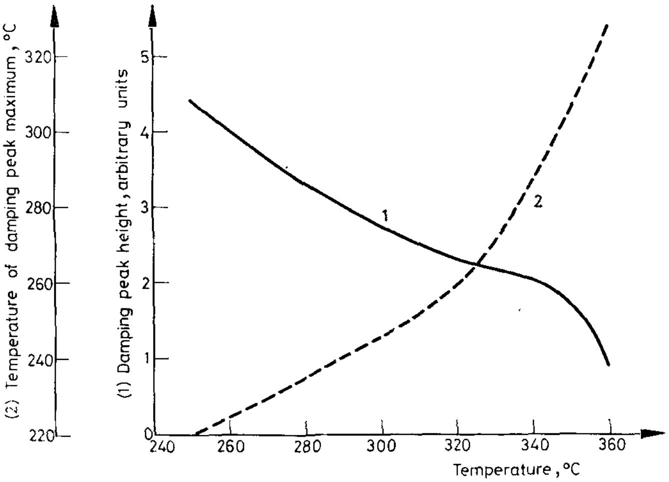

Fig. 7. Change in height and temperature of damping peak with temperature for a fluoro-polyimide adhesive film. Peak height ———. Temp. of peak maximum — — —

decreases only resulting if the temperature was raised. By 360° the loss peaks were virtually non-existent. These changes must be associated with chain stiffening brought about either by cross-linking, or cyclization reactions. The deliberate introduction into some of the polyimides of functional groups capable of cross-linking did not, however, increase the rate of diminution of the peaks.

Stress relaxation measurements

Stress relaxation measurements are widely used for assessing the stability of rubber vulcanisates at elevated temperatures. The stressing may either be continuous, when the rate of network scission reactions is measured, or intermittent when the overall change in network structure resulting from both scission and cross-linking reactions is recorded. By such measurements it is possible to ascertain whether scission occurs primarily in the polymer chain, or in the cross-links. The technique is effectively limited to elastomeric systems and requires that a sheet of material can be made from which test-pieces can be cut. A study can be fairly laborious as behaviour must be studied over a range of temperatures and times.

Materials Department has used the technique most extensively for assessment of the thermal stability of different rubbers and for determining the relative efficiencies of antioxidants; for these purposes it has proved very successful. Attempts have also been made to utilize the results for prediction of the long term stability of a rubber over a range of temperatures in either an unstrained or strained condition. This is not easy because of the difficulty of fitting kinetic equations to relaxation curves obtained at elevated temperatures in a form suitable for extrapolation to longer times at lower temperatures. In addition, rubbers differ widely in their relaxation behaviour and a standardized approach to the analysis of stress-relaxation curves has not yet been evolved. Initial experiments were made with polychloroprene and a copolymer of butadiene and acrylonitrile [8]. It was possible to extrapolate the results of intermittent stress-relaxation experiments at elevated temperatures to room temperatures and, in so doing, to describe the rate of change of modulus with time at that temperature. Good correlations were found between changes predicted in this way and those observed in shelf-storage experiments (Fig. 8). This in itself is inadequate as an indication of storage life of rubbers as it is possible for the modulus to remain relatively constant, whilst properties are changing markedly.

More success has been achieved with butyl rubbers [9]. For a sulphur accelerator cured system it was shown that the reactions leading to changes in network structure at or near room temperature were predominantly non-oxidative in nature. Hence oxygen bomb, or conventional oven ageing tests are inappropriate

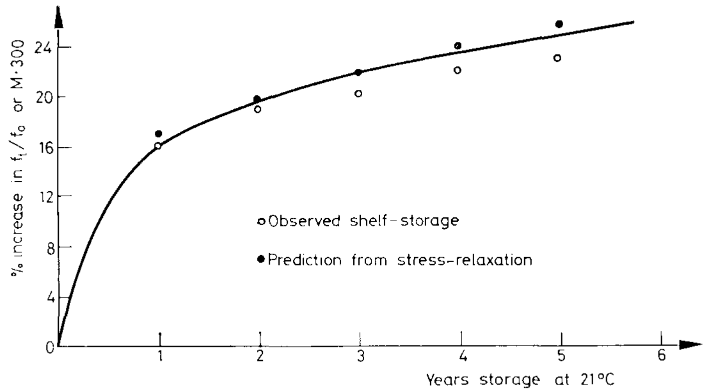

Fig. 8. Comparison of modulus changes for a neoprene rubber predicted from stress-relaxation experiments and those observed during shelf-storage

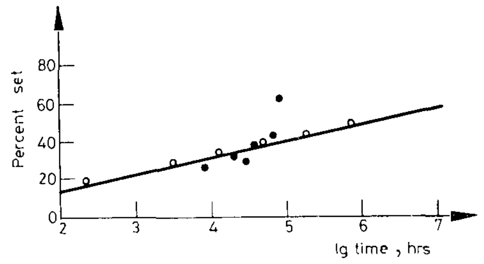

Fig. 9. Long term permanent set in butyl rubber at room temperature. Comparison of values calculated from stress relaxation data with observed values. ● Rapra observed values; ○ calculated values

for assessing suitability of this formulation for use, or storage, under these temperature conditions. Results of intermittent stress-relaxation tests in nitrogen, however, give useful indications of the long term stability of the vulcanisate when stored in the unstrained condition. More interesting was the finding that by using a two network model for the ageing rubber under 20% strain, it was possible to calculate from the relaxation results "permanent set" values, which agreed well with compression set values obtained during long term storage under ambient conditions (Fig. 9). This agreement encourages the hope that accelerated ageing techniques, when carried out under the right conditions can be of value in the difficult area of assessing life in storage or in use of a continuously strained rubber.

Dynamic viscoelastic measurements

With the Rheovibron direct-reading viscoelastomer absolute measurements can be made of the complex dynamic tensile modulus and of the mechanical loss factor at different frequencies over the temperature range −150 to +250°. With suitable modifications the tensile shear modulus and the corresponding loss factor can also be obtained.

The apparatus has been used to examine the effects of exposure to high humidity upon the dynamic mechanical properties of epoxy-polyamide and fluoropolyimide adhesives. Only small test-pieces are required, but measurements have to be made over a range of test lengths of the specimens to obtain a correction factor, which is applied to the measured values of the dynamic forces. This has to be done to allow for the error imposed on the measurements by the modulus of elasticity and displacement of the Rheovibron stress gauge and its chuck during passage of sinusoidal wave. Accurate measurements of the dimensions of test-pieces are required. The apparatus is not easy to set up and some determinations are tedious to make. Automation of the instrument would overcome this.

Exposure of an epoxy-polyamide adhesive in film form to high humidity resulted in a large water pick-up (11−14%) and a substantial decrease in the complex dynamic tensile modulus [10]. Figure 10 shows the effect of exposure to a laboratory environment; at 43° and 97% RH the modulus fell to approximately 0.33 GN/m^2. If the water were then removed, the original value of the modulus was restored. No corresponding effects of moisture were observed for fluoropolyimide adhesives. DSC measurements on the same epoxy-polyamide samples showed that the T_g was lowered by a maximum of approximately 40° on exposure and that the original value was regained on drying out. In contrast to these reversible changes observed in the adhesive film, bonded joints made with the adhesive suffered losses in strength, when aged in humid conditions, which could not be restored by removal of water. The mode of failure of the joints changed progressively from wholly cohesive to predominantly adhesive with moisture absorption. The results, therefore, indicate that the primary role of water in joint degradation was to displace adhesive from the metal substrate and not to induce cohesive failure of the adhesive itself. Attempts to improve durability with this adhesive

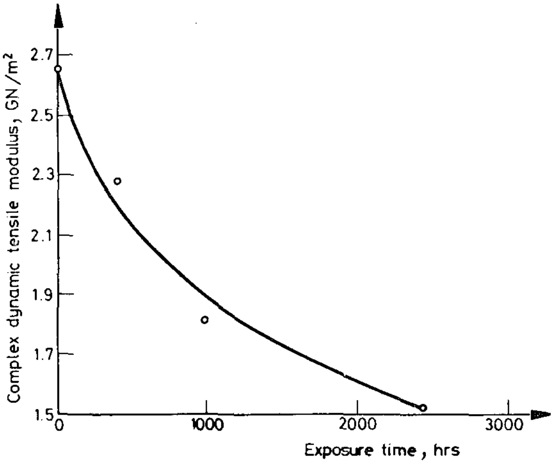

Fig. 10. Effect of laboratory environment (20°, 34% RH) on the complex dynamic tensile modulus of an epoxy-polyamide adhesive

must therefore be directed to increasing the moisture resistance of the interface by the use of surface pretreatments and primers capable of rendering the metal surface less susceptible to attack by moisture, or by the use of adhesion promoters whose primary role would be to increase the extent of covalent bonding between the adhesive and the metal substrate.

Conclusions

In Table 1 an attempt has been made to summarize the salient features of the six techniques discussed. The table shows where the techniques complement one another and what are some of the advantages and disadvantages of the individual methods. Obviously the application of a number of tests rather than just one to a polymer results in a much fuller and more definite characterization. The particular features of a polymer defined by these thermoanalytical techniques are:

1. Transition temperatures and effects of environment upon these. It should be noted that T_g is related to the maximum temperature of use of a thermoplastic and the minimum temperature of use of an elastomer. For a thermoset large changes in mechanical properties may also occur at T_g and this would then represent a limiting temperature for use. Sub-T_g transitions may be of importance for dielectric, impact and toughness properties.
2. Curing cycle and degree of cure of a cross-linked system. The degree of cure affects mechanical properties and the retention of these under various environmental conditions.
3. Thermal stability.

Table 1

Comparison of thermoanalytical methods

	TG	DSC	TMA
Parameters measured	Weight loss	Differential heat flow	Penetration under load; thermal expansion; elasticity
Main uses	Measurement of (a) Thermal stability (b) Efficiency of antioxidants (c) Cure (of some resins)	Measurement of (a) Transitions (b) Cure (c) Efficiency of antioxidants (d) Purity	Measurement of (a) Transitions (b) Cure (c) Modulus (d) Creep (e) Thermal expansion (f) Swelling behaviour
Advantages	Quick Easy Small samples, no specific form	Quick Small samples, no specific form Sensitive to any thermal reaction Parameter measured directly related to cure	Quick Small samples Measured transitions below T_g
Disadvantages	Weight loss only recorded	Results depend on thermal history of sample Transitions below T_g not detected Thermal changes only recorded	Transitions measured affected by stress applied Samples need careful preparation

4. Certain physical and mechanical properties, e.g. modulus, creep, thermal expansion.

All of the methods cited can normally be applied to a pure polymer, or a particular formulation of it. They are not strictly non-destructive tests, but the quantity of material needed in many cases is so small that it could be taken from a component without detriment. For monitoring of service life it would be necessary first of all to ascertain precisely what are the relationships between the properties of crucial interest and the change of these in use, and the parameters measured by the thermoanalytical techniques.

Table 1 (continued)

	Torsional braid analysis	Stiess relaxation	Dynamic viscoelastometry
Parameters measured	Modulus of braid; mechanical loss	Change in stress for fixed strain	Dynamic tensile modulus; mechanical loss
Main uses	Measurement of (a) Transitions (b) Cure (c) Modulus (d) Effect of environment on mechanical properties	Measurement of (a) Thermal stability of rubbers (b) Efficiency of antioxidants	Measurement of (a) Modulus (b) Effect of environment on mechanical properties
Advantages	Directly related to composites Polymers can be studied in liquid state above T_g. Modulus can be followed through cure to degradation	Indicates where chain scission occurs	Gives absolute values of modulus
Disadvantages	Samples must melt, or dissolve, for braid to be made Gives only relative moduli Does not distinguish between T_g and T_m	Limited to elastomers Laborious Needs sheet for specimens	Laborious Needs sheet, or film for specimens Accurate test-piece dimensions required Tests must be made over range of lengths

References

1. R. A. Dine-Hart, D. B. V. Parker and W. W. Wright, British Polymer J., 3 (1971) 235.
2. J. M. Barton, RAE Technical Report, 72113 (1972).
3. J. M. Barton, Makromol. Chem., 171 (1973) 247.
4. J. M. Barton, J. Macromol. Sci., A8 (1974) 25.
5. J. M. Barton and G. J. Knight, Proceedings 1st ESTA, 1976, p. 171.
6. J. M. Barton, RAE Technical Report, 73125 (1973).
7. J. H. Sewell, Unpublished RAE Report.
8. D. K. Thomas and B. B. Moore, RAE Technical Report, 68016 (1968).
9. D. K. Thomas, RAE Technical Report, 74108 (1974).
10. R. I. Butt and J. L. Cotter, J. Adhesion, 8 (1976) 11.

RÉSUMÉ — On donne quelques exemples de l'application de la thermogravimétrie, de l'analyse calorimétrique différentielle (DSC), de l'analyse thermomécanique, de l'analyse au fil de torsion, de la mesure de la relaxation des tensions, de la viscoélastométrie dynamiques, à l'étude des polymères à réseau tri-dimensionnel. On souligne les renseignements obtenus en utilisant chacune de ces techniques et on compare les avantages et les inconvénients de ces différentes méthodes.

ZUSAMMENFASSUNG — Einige Beispiele der Anwendung der Thermogravimetrie, Differential Scanning Kalorimetrie, thermomechanischen Analyse, Torsionsfadenanalyse, Streßrelaxometrie und dynamischen Viscoelastometrie zur Untersuchung quervernetzter Polymersysteme werden gegeben. Die an Hand des Einsatzes der einzelnen Techniken erhaltenen Informationen werden beschrieben und die Vor- und Nachteile der verschiedenen Methoden miteinander verglichen.

Резюме — Приведены некоторые примеры применения термогравиметрии, дифференциальной сканирующей калориметрии, термомеханического анализа, крутильно-шнурового анализа, напряженной релаксометрии и вязко-эластометрии к изучению поперечно связанных полимерных систем. Приведена информация, полученная при использовании каждого метода, а также сопоставлены преимущества и недостатки каждого метода в отдельности.