Comparative thermal and thermo-mechanical properties of hot melt adhesives

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Thermal properties of hot melt adhesives as well as their bonds can reasonably be studied by thermogravimetric and thermomechanical methods. In addition to thermogravimetry, determination of thermo-oxidative stability is also suitable for assessing the thermal properties of hot melt adhesives. Effects of their components on the glass transition and melting temperatures (T_g and T_m respectively) and the viscoelastic behaviour of hot melt adhesives can be investigated by recording and evaluating of thermomechanical curves. Thermomechanical creep measurements used in the plastics industry are very useful for determining the thermal stability, that is the shear fail temperatures of adhesive bindings. In addition, these methods can be used for qualitative and quantitative investigations of the major ingredients of adhesive compounds.

In terms of quantities of material consumed, the book-binding industry is second only to packaging as a market for hot melt adhesives. Modern high performance book-binding machines, which combine assembly and binding operations, can operate at a capacity of 15 000 items per hour. Such machines make great demands on the quality and workability of the hot melt adhesives used for binding.

To date no satisfactory technique has been developed for characterizing these hot melt adhesives, something of extreme importance with regard to future developments of the materials. However, certain properties of these adhesives — thermal and thermo-oxidative stability, temperature range of operation (defined as the difference between T_m the softening, or melting, point and T_g the glass transition temperature of the adhesive) and the temperature at which the butt or lap shear tensile strength vanishes (tear fail or shear fail temperature respectively) — are of particular importance in terms of their potential applications and thus techniques for determining these properties will be of interest. This paper describes such methods in some detail and demonstrates their potential for characterizing hot melt adhesives.

Experimental details

Materials

Various ethylene-vinyl acetate (EVA) copolymer based adhesives (supplied by Henkel, Croda, Planatolwerk, Isar-Rakoll Chemie and a Hungarian-made Budacolor product) and an amorphous polypropylene (APP)-based adhesive (supplied by Paper-Making Enterprise of Budapest) were used.

Thermogravimetric and DTA analysis

Thermograms were recorded using a Derivatograph (manufactured by System Paulik-Paulik-Erdey, Hungarian Optical Works, Budapest) which is capable of recording TG, DTG and DTA curves simultaneously. 200 or 500 mg samples were weighed into ceramic crucibles and heated at 6°C/min in air. In an identical crucible, calcined Al_2O_3 was used as an inert reference material, heated in the same furnace chamber. In a linear heating regime the weight of the sample is continuously registered by a thermobalance (TG and its derived DTG) and the temperature difference between the sample and the inert material indicates the enthalpy changes recorded as a DTA curve.

Thermo-oxidative stability

The thermo-oxidative stabilities of the adhesives were measured using a Dynamoxmeter developed in the Research Institute for the Plastics Industry in Budapest. In a sample chamber pure oxygen is passed over the molten sample in a closed-loop system. 1 g of hot melt adhesive was studied isothermally at 180°C, this temperature being chosen as representing the usual operating temperature of the adhesives. The thermo-oxidative stability of a substance is in fact defined either dynamically by the temperature (using temperature programming) or statically by the period (isothermal measurement) at which the sample begins to take up oxygen or the oxygen consumption reaches 10 cm³/g.

Thermomechanical measurements

For the determination of T_g and T_m values of the adhesives, pulsed compression thermomechanical curves of the samples

were recorded using a Unirelax instrument (also developed by the Research Institute for the Plastics Industry, Budapest, and manufactured by the Tetrahedron Associates, Inc). A small specimen plate of about 4 mm in thickness is placed below a spherically tipped rod with radius of curvature of 10 mm. The system, which is thermostatically controlled, is initially cooled by liquid nitrogen to about −100°C and pneumatic pressure signals of 25 kPa are then periodically applied to the rod causing penetration of its spherical tip into the specimen. The period of the pressure signal is 12 s followed by an intermission of 178 s permitting the specimen to relax. During the measurement, temperature control is programmed at a heat rate of 1.5°C/min and deformation, ie the depth of penetration, is recorded as a function of temperature. The instrument is connected with an in-line microcomputer (Type EMG 666) programmed for calculation of plastic and elastic characteristics of the material from the penetration values obtained from the analogue curves (see below). The measurements thus permit separation of the plastic and elastic components of a viscoelastic hot melt adhesive by recording the penetration at three different moments of the pressure signal (after 1, 3.1, and 10 s) producing isochronous elastic moduli. A detailed description of the instrument has been published elsewhere[1].

Thermomechanical creep measurements

Plastics materials and products are extensively characterized in the plastics industry by means of tensile creep measurements. For recording the thermomechanical creep, the thermostated specimen is loaded with a given force: its temperature is programmed so that the strain can be measured as a function of temperature. This technique is very suitable for determining the temperature at which adhesive bonds between various substrates are reduced.

Thermomechanical creep measurements were also carried out by the Unirelax instrument. Test specimens were prepared using lap adhesion between aluminium foils. Experimental conditions of measurements were as follows:

Heating rate: 1.5°C/min
Substrates: aluminium foil, 0.05 mm thick
Area of adhesive bonding: 2 cm² (8 × 25 mm)
Loading mass: 41.6 g

Under these experimental conditions, the lap shear stress is 0.208 N/cm². Adhesive bonds were formed in an identical manner for all the samples: the construction of the Unirelax instrument permits changing the shear stress by variation of loading mass.

Results and discussion

Thermogravimetric analysis

The derivatogram shown in Fig. 1 gives simultaneously the temperature (T), weight loss (TG), derivative weight loss (DTG), and exothermic or endothermic (DTA) curves. It can be established by means of the TG and DTG curves that multistep decompositons of hot melt adhesives take place. The DTG curve in Fig. 1 shows 3 peaks, which corresponds with observations made with multicomponent composite systems where the decomposition steps correspond to the amounts of major ingredients having different thermal stabilities. Weight loss as a function of temperature relations for several samples is shown in Figs 2 and 3. Samples of adhesives supplied from outside Hungary undergo consider-
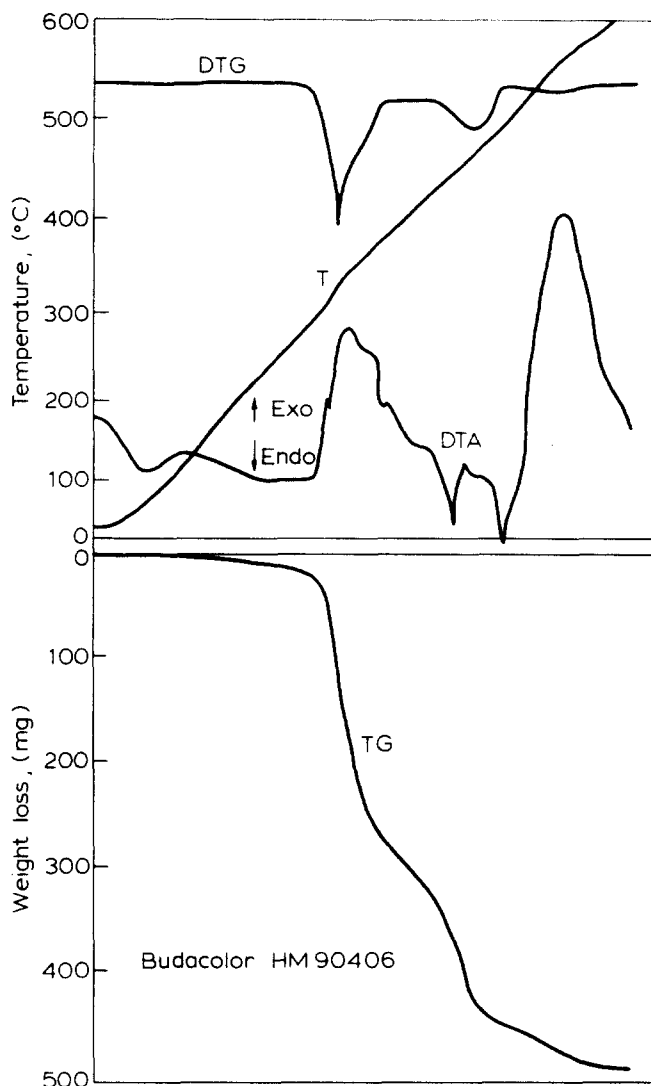

Fig. 1 Derivatogram of the hot melt adhesive HM 90406

able decompositions from about 300°C (Fig. 4). The TG curves are approximately identical, however, leading to the conclusion that the major ingredients of the hot melt adhesives (polymers, resins) are the same. This is supported by the informations from DTA curves (see below). TG curves of the Hungarian-produced hot melt adhesives indicate the presence of the same polymer and resin components as in the imported compositions. Thermal decomposition of APP-based hot melt adhesives starts at about 260°C which is lower than that of EVA based resins. The shape of the TG curves clearly indicates that some of the samples contain inorganic pigments since their weight losses do not reach 100% (Fig. 3).

The first endothermic DTA peak may be assigned to the melting of the adhesive. These T_m values are between 65° and 110°C for various samples, which is in good agreement with those determined by DSC and microscopic methods. The endothermal effect of melting is followed by a prolonged endothermic plateau (Fig. 1) accompanied by a moderate weight loss as shown by the TG curves. This effect can be related to the escape of plasticizer, and occurs from the melting point up to about 280°C.

The subsequent intensive exothermic peaks refer to the thermal decomposition of the material which is an extremely complex process, including 2 or 3 major peaks accompanied by several minor signals and 'shoulders'. The main peaks correspond to the thermal decompositions of the principal
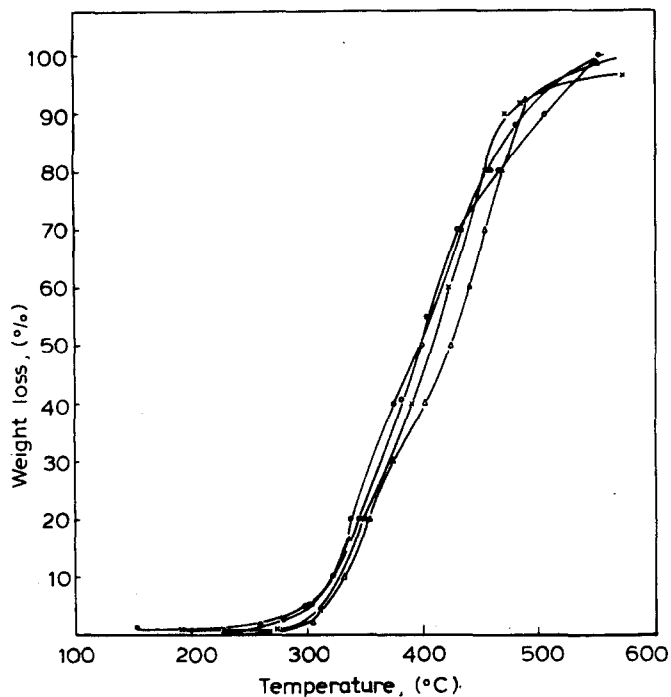
Fig. 2 Weight loss as a function of temperature for non-Hungarian adhesives: O Ipatherm S 22/160 ● Henkel Q3103 x Planatol HM 93/94 △ Crodamelt 36-38500
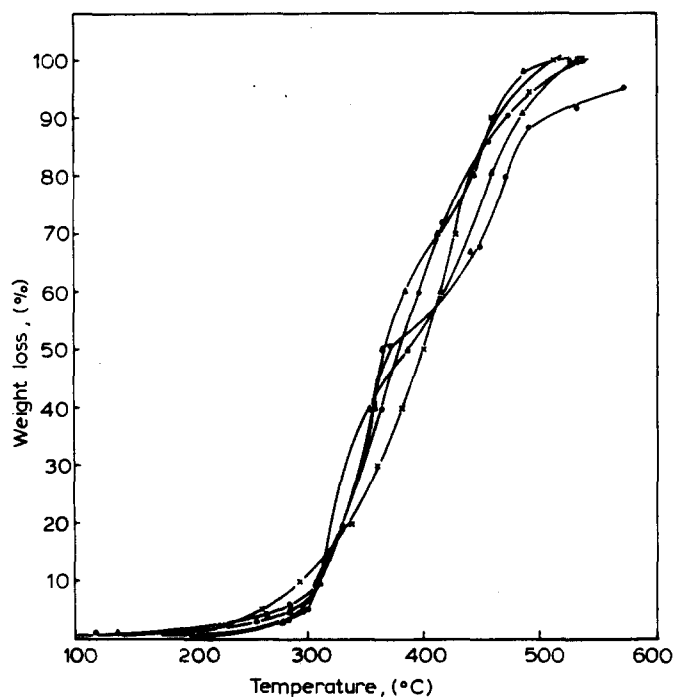

Fig. 4 DTA curves for various EVA-based adhesives: 1—HM 90411; 2—Henkel Q 3103; 3—HM 90405; 4—HM 2959; 5—Planatol HM93/94

Fig. 3 Weight loss as a function of temperature for Hungarian manufactured adhesives: ▲ HM 90405 O HM 90411 ● HM 90406 △ HM 2959 x HM PV 75/Va-III

Fig. 5 Oxygen uptake of adhesives as a function of time, measured with the Dynamoxmeter: 1—HM 2959; 2—Planatol HM 93/94; 3—HM 90411; 4—HM PVl75/Va-III; 5—Henkel Q3103; 6—HM90406; 7—HM 90405; 8—Ipatherm S22/160; 9—Crodamelt 36-38500

components. That these major peaks appear at similar temperatures for the various samples suggests a common formulation of the adhesive materials (Fig. 4). Definite assignations of peaks should, however, be based on thermogravimetric investigations of the individual ingredients.

It can be seen that qualitative and quantitative characterization of the components, kinetics of the thermal decompositions, volatility of possible plasticizers, destruction of the adhesive, etc, can be clearly determined by thermogravimetric methods[2].
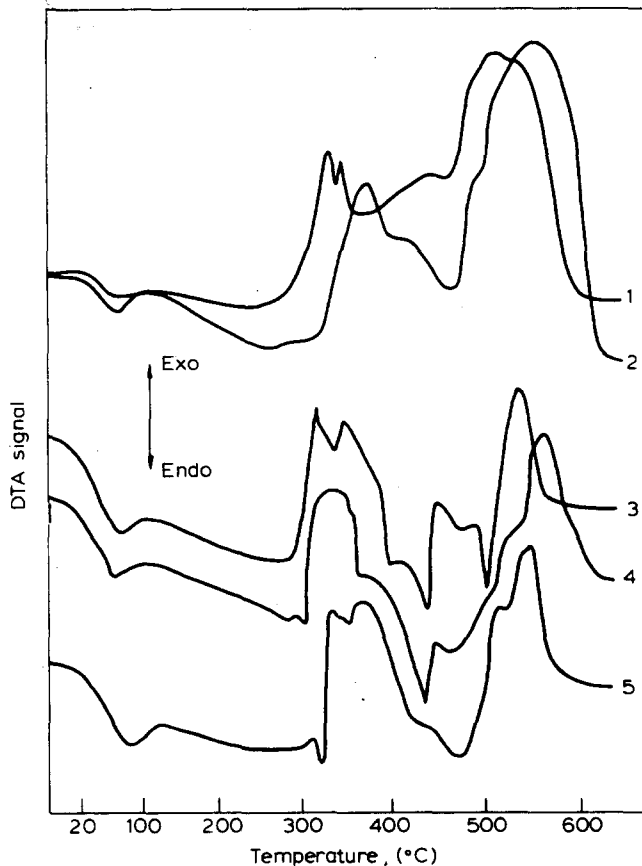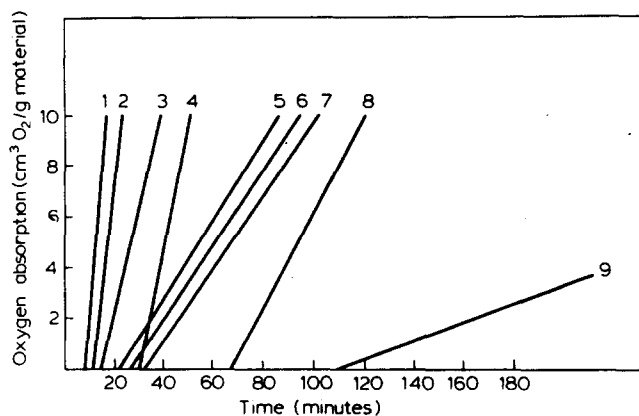
Thermo-oxidative stability

Oxygen uptake of the adhesives determined by the Dynamoxmeter is plotted as a function of time in Fig. 5: the order of numbering of the adhesives in the diagram corresponds to the increasing degree of their thermo-oxidative stabilities.

It should be noted from the curves in Fig. 5, which have slopes near to 90° after the induction period, that the adhesives contain thermal stabilizers having no secondary suppressing or retarding effect on the decomposition. The lower the slope of the straight line of oxygen absorption, the greater is the retarding effect of the stabilizer. Thus, this method is excellent for investigating the thermal stabilities of various adhesive compositions and for determining the operating mechanism of the stabilizers.

Pulsating thermomechanical measurements

The analogue pulsating thermomechanical curve represents the periodical penetration of the spherical tipped probe plotted against temperature (Fig. 6). These penetration versus temperature curves clearly demonstrate the viscoelastic properties of the hot melt adhesives: their shape is characteristic for viscoelastic substances.[3] The heights of 'spurs' on the analogue curves corresponding to the elastic recovery after penetration as a function of temperature represent the separated elastic behaviour; while the covering curve through the bisecting points between the spurs on the horizontal regions of the steps represents the viscous nature of the material.

Thermomechanical curves of EVA-based hot melt adhesives (Fig. 6) show two transitional points around 0° and 50° irrespective of their origin. Pulsating analogue thermomechanical curves of APP-based hot melt adhesives exhibit less sharp transitions at about -30 and $+20°C$. For both types, the lower-temperature transitions correspond to T_g (glass transition temperature) while the others at the higher temperature refer to the melting temperature T_m. More information can be obtained by converting these analogue curves into plots of plastic moduli, momentary elastic moduli and their derivatives as functions of temperature (Figs 7-10). The pulsating penetration method thus introduces new means for investigating hot melt adhesives: thermomechanical curves make studies on compatibility of the individual adhesive components possible.

The substance shown in Fig. 7 has a shoulder on the derivative curve of plastic modulus around 50°C and two peaks on that of elastic modulus at about 0° and 70°C. This indicates phase heterogeneity, ie, the components of the adhesives are, at least partially, incompatible (Figs 7 and 8). It is remarkable, with respect to Fig. 8, that isochronous moduli recorded at different moments of penetration enhance considerably the resolution of the measurement. On the 1s curve of the derivative elastic modulus, only two peaks appear; on the 3.1 s curve one of the peaks has a well separated shoulder while on the 10 s curve, this shoulder has grown into a definite new peak. This indicates that the resolution of the thermomechanical curves corresponding to longer loading times is higher than those for shorter times (Fig. 8).

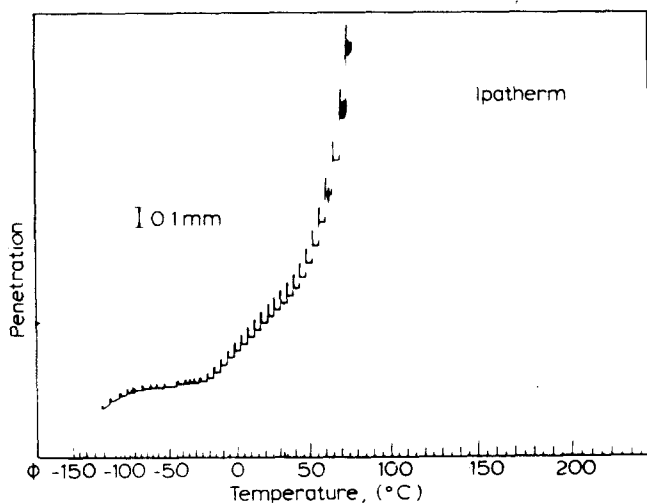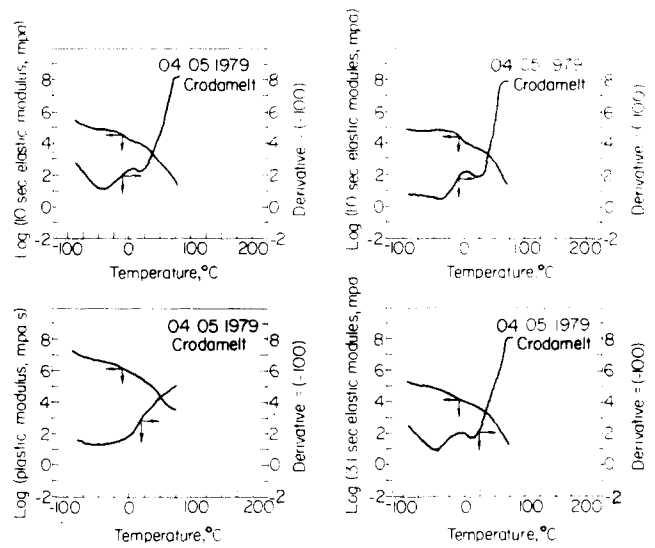This pulsating thermomechanical measurement is also

Fig. 7   Plastic and elastic moduli and derivatives as a function of temperature, as processed by computer from the analogue thermomechanical curve for Crodamelt 36-38500
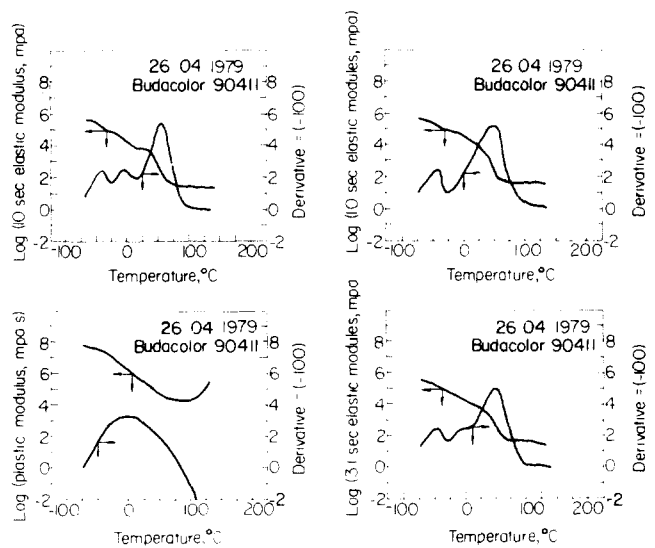
Fig. 8   Plastic and elastic moduli and derivatives as a function of temperature, as processed by computer from the analogue thermomechanical curve for HM 90411

useful for studying the changes in hot melt adhesives due to thermal ageing. Samples were aged in an oven at 180°C for 24 h and moduli and their derivatives obtained from pulsated thermomechanical curves by computer processing are plotted as functions of temperature in Figs 9 and 10 for the initial and aged hot melt adhesives respectively. The analogue pulsating thermomechanical curves showed that both T_g and T_m decreased by about 10°C, ie the entire thermomechanical curve was shifted toward lower temperatures. This may be explained by chain scission decomposition of the polymeric component (or possibly some other macromolecular ingredients) of the hot melt adhesive and the fact that the lower-molecular products yield more readily (lower T_m) and have higher chain mobility (lower T_g). This interpretation is supported by Figs 9 and 10. In can readily be observed in Fig. 9 that the derivative plastic modulus shows a single peak while the elastic modulus has 2 peaks. Because of thermal ageing (Fig. 10), the appearance of two peaks in the derivative plastic modulus curve can be attributed to the concept that the original components, compatible in terms of viscosity but

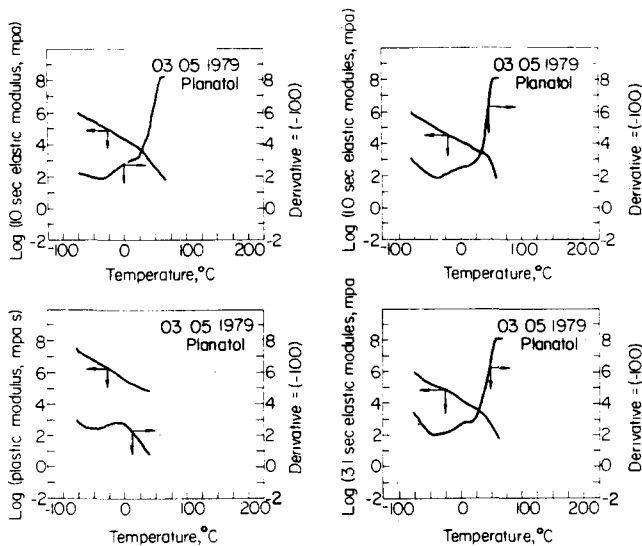Fig. 6   Pulsating analogue penetration thermomechanical curve of the adhesive Ipatherm S22/160

Fig. 9 Plastic and elastic moduli and derivatives as a function of temperature as processed by computer from the analogue thermo-mechanical curve for Planatol HM 93/94
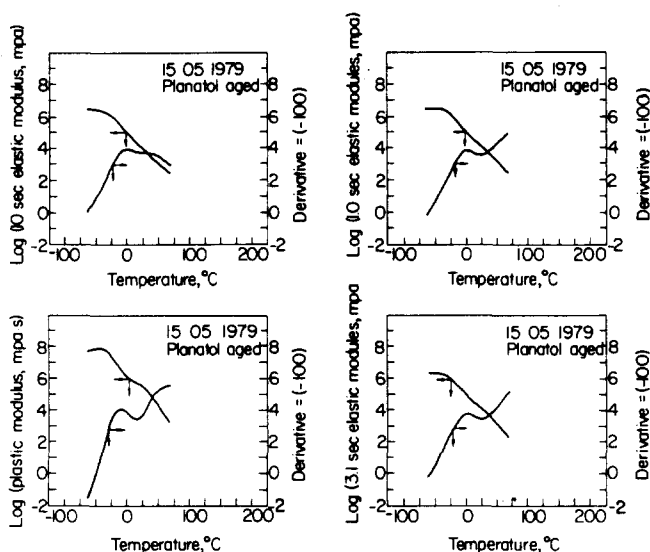

Fig. 10 Plastic and elastic moduli and derivatives as a function of temperature as processed by computer from the analogue thermo-mechanical curve for Planatol HM 93/94 after thermal aging

having different thermal stabilities, decompose unequally, thus reducing the compatibility. Thus the viscous characteristics are governed by two ingredients at least. Considering the course of the plastic modulus versus temperature plot shown in Figs 9 and 10, it can be established that its slope is much higher after thermal ageing reflecting the decrease in the activation energy of the viscous flow (resulting in lower melt viscosity values).

Thermomechanical creep measurements

The thermomechanical creep measurements carried out in this investigation can be considered as being equivalent to special lap shear tests conducted at programmed temperature. The characteristic creep curves, produced by a line recorder, are shown in Fig. 11, where the strain of the lap adhesion is plotted against temperature and the lap shear failure temperature can be read on the abscissa. At this temperature the lap adhesion ceases and thus the strain curve becomes vertical. The thermomechanical creep curves were produced using the line recorder specifically to study the mechanism of releasing and detachment of the adhesion. Adhesives
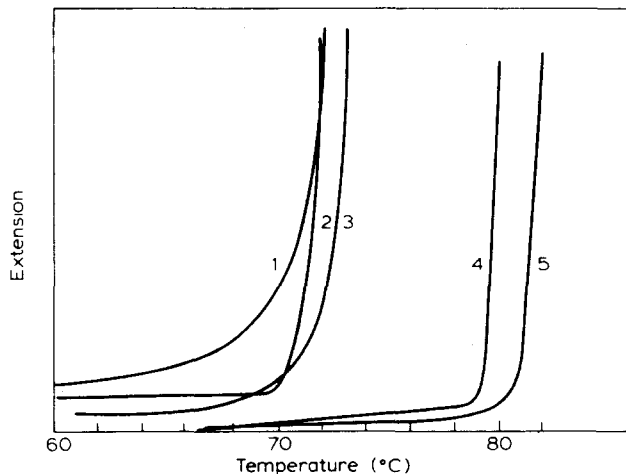

Fig. 11 Thermomechanical creep curves plotted by a line recorder for lap bonds of various adhesives between aluminium foil substrates: 1—HM 90406; 2—HM PU 75/Va-III; 3—HM 90405; 4—Planatol HM 93/94; 5—Crodamelt 36-38500

having higher adhesion strength than the cohesion strength can be readily distinguished since their thermomechanical creep curves can be approximated by two nearly perpendicular straight lines — ie their adhesive bonds release quasi-instantaneously at the appropriate temperature (curves 2, 4, and 5 in Fig. 11).

Alternatively, adhesives having higher cohesion than adhesion strength exhibit different thermomechanical creep curves (curves 1 and 3 in Fig. 11). The superiority of the adhesion or cohesion strength of the adhesive was determined by examination, after failure, of the substrates to assess whether the adhesive had wetted the substrated, forming a continuous layer. If so, adhesion strength was higher than the cohesion strength. If the adhesive had not wetted both substrates perfectly, cohesion strength was higher than adhesion.

Summary

Techniques such as thermogravimetry, determination of thermo-oxidative stability, and thermomechanical measurement, already widely used in the plastics industry, appear to be very suitable for testing and characterizing hot melt adhesives, which may be regarded as multicomponent thermoplastic systems.

Thermal stability and kinetics of decomposition can be studied by thermogravimetry. Using individual investigations of the components of hot melt adhesives, the most favourable additives can be selected in order to increase the thermal stability. This technique is very useful in comparisons of different adhesives.

Thermo-oxidation stability of hot melt adhesives measured by oxygen absorption is capable of ascertaining mechanisms of operation of thermostabilizers used in the formulation of the adhesives.

T_g and T_m values of the adhesives have been determined by pulsating thermomechanical measurements; and the chilling resistance of adhesives has been characterized by the brittleness temperature or by the low-temperature flexibility. Since a hot melt adhesive is principally a thermoplastics system, the conventional thermomechanical techniques are much more feasible for determination of T_g. The pulsating thermomechanical measurement described permits the separation of viscous and elastic characteristics of the thermoplastic hot melt adhesives so that they can be

studied separately as functions of the temperature and of the major components of the material. The pulsating thermomechanical technique is very suitable for investigating the compatibility of the components and the effect of thermal ageing on this compatibility.

Thermomechanical creep measurements are widely used in the plastics industry for characterization of materials and products. They can also be very useful for the practical determination of failure temperatures of adhesive bonds. The adhesion and/or cohesion characteristics of adhesives can also be assessed using the technique. A further use of this technique is that of determining creep of adhesive bonds in different pressure-sensitive adhesives, at any selected temperatures as a function of time.

References

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