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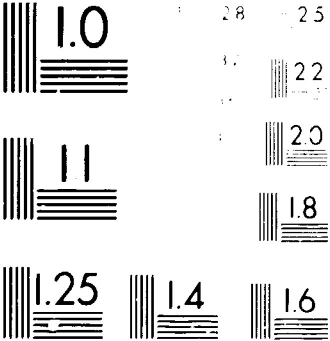

MICROCOPY RESOLUTION TEST CHART

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POLYMER MATRICES FOR CARBON FIBRE AND HYBRIDE FIBRE REINFORCED COMPOSITES*

by

H.D. Stenzenberger*

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DEVELOPMENT OF THERMOSETTING POLYIMIDE RESINS

(New and improved composite matrix resins)

Since the beginning of the space age in the late 1950s,research and development of polymers consisting of aromatic and/or heterocyclic ring structures of high thermal stability proceeded at an amazing rate.Those familiar with the early literature in this area are still fascinated by the many elegant synthetic routes to high temperature high polymers,examples of which are the polybenzimidazoles,polyoxadiazoles,polybenzothiazoles and polyquinoxalines.In most cases polymer synthesis was successful only because of the ability of the chemist involved to prepare high-purity starting materials.The heterocycle was constructed essentially in one condensation reaction by using the appropriate monomers leading in most cases to intractable low molecular weight materials.A real breakthrough was the introduction of the "precursor polymer" technique for assembling heteroaromatic units into a polymer chain.An intermediate soluble precursor polymer is synthesized in which functional groups pendant to the main chain are arranged so that on thermal or chemical treatment they cyclize to a desired heteroaromatic ring.This technique was employed successfully by E.I. du Pont de Nemours Company chemists for the synthesis of aromatic polyimides (Figure 1).An aromatic dianhydride is reacted with an aromatic diamine at room temperature in solvents suitable to yield a soluble polyamide,the polyamido-carboxylic acid,containing carboxylic groups ortho,to the amide linkages which propagate the polymer chain. Ring closure is effected either by thermal or chemical treatment.The polyimides thus obtained exhibit unusual chemical,thermal and oxidative stability.Processing to films,foams and mouldings includes a 350°C temperature cure to develop all advantageous properties fully.

Because of their attractive properties,aromatic polyimides have also been tried extensively as matrix resins for fibre composites.Usually the polyamido-carboxylic acid is used in polar solvents like N-methylpyrrolidone,dimethylformamide or dimethyl acetic acid amide as an impregnation varnish for fibrous materials.Unfortunately these solvents show an extremely good affinity to the resin and are therefore difficult to remove from the prepreg and the moulded composite.Residual solvent in a laminate acts as a plasticizer and when present in a laminate prevents the development of good high temperature physical properties.In addition, the condensation type cure reaction of the soluble intermediate prevents the formation of void-free laminates.Also,real thermoplastic totally aromatic polyimides were synthesized via the very attractive one step "isocyanate" route (Figure 2) but did not really overcome the processing problems associated with fibre composite preparation.Because aromatic polyimides failed as matrix resins for advanced composites,a wide variety of thermosetting polyimides was developed with the aim of improving the processing properties.

In general the idea behind all the synthetic routes is the preparation of an imide ring containing backbone that carries terminating polymerizable endgroups providing an imide prepolymer that shows real meltability and therefore advantageous flow properties during composite moulding.Some of the chemical concepts are discussed in this paper.

Norbornene endcapped polyimides.

H.R.Lubowitz,working with TRW,discovered polyimide systems that were endcapped with endomethylene tetrahydrophthalic anhydride (ETPA) groups. The synthetic route used again was the classical "amic acid precursor" route.A tetracarboxylic acid dianhydride,an aromatic diamine and ETPA are reacted to form a soluble prepolymer whose molecular weight could easily be adjusted by varying the molar proportions between the reactants.The prepolymer,commercially available (P13N - Ciba Geigy)[6] after cyclocondensation,showed a real melt transition at around 270°C and could therefore within limitations be processed to laminates.

The norbornene concept was further developed by NASA Lewis Research Center and culminated in the so-called PMR-concept,a novel class of addition type polyimides formed by in situ Polymerization of Monomer Reactants.In this approach a dialkylester of an aromatic tetracarboxylic acid,an aromatic diamine,and a monalkylester of norbornene 2,3-dicarboxylic acid (Figure 3) are dissolved in a low boiling alkyl alcohol.This solution is then used to impregnate the reinforcing fibres.After removal of the solvent and subsequent heating in the temperature range of 150-220°C,the monomers undergo in situ cyclodehydration to form a norbornenyl-endcapped low molecular weight imide prepolymer.The cure of the PMRs is generally accepted to proceed via the reverse Diels-Alder reaction of the norbornenyl endgroups to generate maleimide endgroups and cyclopentadiene in the temperature range of 270-310°C.The highly activated maleimide unsaturation immediately proceeds to copolymerize with cyclopentadiene and unrearranged norbornenyl groups to produce a crosslinked structure without the evolution of void forming volatiles.It is interesting to note that despite the fact that the prepolymer is formed by a classical condensation reaction,cure proceeds in a completely separate step thus providing void-free laminates.The best overall balance of processing characteristics,composite thermomechanical and physical properties,and 300°C thermooxidative stability was found to be provided by a monomer composition of benzophenonetetracarboxylic acid dianhydride,methylene dianiline and norbornene dianhydride adjusted to an average molecular weight of 1500.

The PMR-concept was developed further by NASA Langley Research Center to provide LARC 160 a melt processable resin,and the replacement of benzophenonetetracarboxylic diester with the diester of 4,4'-(hexafluorisopropylidene) bisphthalic acid leads to improvements in thermal oxidative stability.Both developments could nevertheless not overcome all processing difficulties because moulding of laminates still requires high temperature (285°C) and high pressure (14 hours).

Acetylene terminated polyimides.

The cyclotrimerization of ethynylbenzene leads to 1,3,5 triphenylbenzene, and consequently polycyclotrimerization of bis-ethynylbenzene yields a high temperature resistant polyphenylene resin.Using this chemical approach as a model for an addition type cure,it was only a question of time for the first ethynyl-terminated polyimide to appear in the literature.Figure 4 outlines the synthetic route characterized by simply condensing an aromatic tetracarboxylic acid dianhydride with an aromatic diamine in the presence of an ethynyl-substituted aromatic monoamine providing a fully imidized ethynyl-terminated thermosetting polyimide resin.One resin based on this chemistry became commercially available under the trade mark Thermide 600 (Gulf Oil Chemicals) but has unfortunately to be processed from N-methylpyrrolidone as a solvent to prepregs,leading back to all the problems associated with this high boiling high polar solvent.Nevertheless,the molecular weight of the prepolymer can be tailored to provide a resin that melts at around 190-200°C and polymerizes when molten immediately as is indicated by its differential scanning calorigramme (Figure 4).

Maleimide type resins.

Very attractive high temperature thermosets are based on bismaleimides. First Grundschober reported their homo- and copolymerization which can be achieved by simply heating the monomers to temperatures between 150 and 400°C resulting in the formation of highly crosslinked polymers.The usual synthesis of the monomers starts from maleic acid anhydride and aromatic diamines (Figure 5) forming a bismaleiamic acid as an intermediate which undergoes cyclodehydration at a temperature of 40-50°C in the presence of acetic acid anhydride and sodium acetate to form the bismaleimide in high yield.It is easily imaginable that a great variety of bismaleimides are possible by simply changing the structure and molecular weight of the diamine used.In particular resin formulators should pay attention to those bridging units that either provide low melting transitions or improve solubility in low boiling solvents.

The double bond of the maleimide is very reactive and can,for example, undergo a chain extension reaction with primary and secondary amino compounds.This reaction,known as Michael addition,is used to synthesize a well-known commercially available resin,Kerimide 601 of Rhone Poulenc, which is synthesized by reacting 4,4'bismaleimidodiphenylmethane with methylene dianiline either in the melt or in solution to form a polyamino-bismaleimide (Figure 6).The material is available as injection and transfer moulding compound and as a laminating resin.Unfortunately,like all the other polyimides discussed so far,the processing solvent is N-methylpyrrolidone but the moulding temperature of 170°C is fairly low and good high temperature property retention up to 200°C is achievable when postcured at 250°C,provided the prepreg used contained only 2 % of the residual solvent.

The M751 - Poly(amide-maleimide) resin concept.

The major disadvantage of all bismaleimide resins detected so far is their brittleness.Speaking in terms of mechanical properties,they are high modulus low strength materials accompanied by a very low elongation at break.This is all a consequence of their high crosslink density and the aromatic nature of the starting materials employed for their synthesis. Having been confronted with these problems the authors tried to achieve both a low temperature melt transition and a prepolymer molecular weight high enough to provide a substantially increased elongation at break.

The chemical approach towards these technical goals within a bismaleimide type resin is outlined in Figure 7.Meta-maleimidobenzoic acid chloride is reacted with 4,4'-diaminodiphenylmethane preferably in methylene chloride as a solvent in the presence of a hydrogen chloride acceptor in such a way that the molar proportions of the difunctional aromatic amine and the acid halide are between 1:2 and 1:1.The resulting polymaleimide prepolymer consists,depending on the molar proportions of the reactants, of a mixture of the bismaleimide IV and the amino-terminated monomaleimide IV.The polymerization of the resin can be accomplished simply by heating the resin to temperatures between 180-260°C.The polymerization proceeds controlled in such a way that firstly the free amino groups of the monoimide (III) react via the Michael addition with the double bonds of the bismaleimide IV forming a high molecular weight linear prepolymer which secondly crosslinks by a free radical polyaddition mechanism.The advantage of this chemical approach is that resins with controlled prepolymer molecular weight can be obtained reproducibly by simply selecting the molar composition of m-MIC(I) and 4,4'diaminodiphenylmethane.The formulated molecular weight of the commercially available material,TECHNOCHEMIE M751,is 1140,providing,when cured,high mechanical strength properties and good extensibility (flexural elongation = 4.81 %). For comparison two resins with lower formulated molecular weights have been prepared and cured under the same conditions and,as was to be expected,they show lower strength properties and lower elongations at break.Interestingly all the three resins show almost the same value for the elastic modulus,leading to the conclusion that the backbone chemistry defines the elastic modulus while the crosslink density influences both the strength and elongation properties.

Figure 8 summarizes the properties of TECHNOCHEMIE M751 resin.A real melt transition is present as can be seen from the differential scanning calorigramme.The torsional modulus curve indicates a Tg for the cured resin of 240°C after a standard postcure at 250°C for 15 hours.The TGA-thermogramme is typical for cured bismaleimides.

The extensive investigation of the bismaleimide resins from this concept allowed the elucidation of many structure property correlations but because of the starting materials used TECHNOCHEMIE M751 has to be processed from N-methylpyrrolidone to fibre laminates.To overcome this disadvantage,work is in progress with the aim of obtaining modified types which are soluble in low boiling solvents like acetone.methyl-ethyl ketone or methylene chloride.

TECHNOCHEMIE H 795-bismaleimide resin concept.

The aerospace industry requires resin systems that do not emit volatile by-products during cure to allow the production of void-free laminates by using standard 350°F epoxy-like cure.Tooling,bagging materials,curing procedures and production facilities established for epoxies need to be met by the processing properties of new resin candidates to find acceptance by the industry.Processing of a resin with respect to its use as a matrix in fibre laminates is represented by its prepregging properties and overall moulding characteristics.

Prepregging from solvent is usual for fabrics in order to obtain uniform impregnation of the reinforcement.Low boiling solvents like acetone, methyl-ethyl ketone and methylene chloride are preferred because they can be stripped off easily in circulating air at moderate temperatures. Unidirectional tape material can either be produced by a hot melt technique or by a solution dip-coating technology.

Recently TECHNOCHEMIE GMBH-Verfahrenstechnik developed and patented a bismaleimide type resin formulation which shows outstanding prepregging properties.A bismaleimide is prereacted with m-aminobenzoic acid hydrazide either in the molten phase or in solution to provide a prepolymer (see formula III,Figure 9) which shows solubility in acetone,methyl-ethyl ketone or methylene chloride.The molar proportion of the bismaleimide and the amino acid hydrazide is such that bismaleimide (I),the idealized bismaleimide III and intermediates are present in the reaction mixture providing the solubility characteristics discussed and in addition providing low melt viscosity which is necessary for low pressure autoclave moulding (Resin specification,see Figure 10).

Neat resin properties (Figure 11).

The bismaleimide resin TECHNOCHEMIE H 795 as supplied shows the differential scanning calorigramme given in Figure 11.The heat of polymerization of 265±20 Joules/g reflects the concentration of reactive maleimide groups, e.g. the state of advancement.The cured resin like all other bismaleimides provides a TGA-thermogramme indicating initial weight loss between 300 and 400°C and maximum weight loss occurring between 400 and 500°C.The unmodified resin shows no glass transition below 300°C as indicated by the torsional modulus curve.The mechanical properties of the unreinforced resin are typical for a highly crosslinked resin.The flexural strength of 100N/mm^2 at room temperature only decreases to 60N/mm^2 at 250°C.

Only a few data about the thermal oxidative stability of bismaleimide resins are available in the open literature.According to our experience with bismaleimides,these resins fill the gap between totally aromatic polyimides and epoxies,which is confirmed by the results obtained for TECHNOCHEMIE H 795 air ageing.Figure 12 summarizes the air ageing result obtained for samples which were cast by use of a steel mould and cured under a pressure of 6 bars at temperatures up to 210°C and which were postcured at 240°C for 12 hours.The room temperature mechanical properties, flexural strength,flexural modulus were not at all degraded after 500 hours of 200°C,220°C and 250°C in circulating air.The high temperature flexural modulus of the aged material is increased while simultaneously the high temperature flexural strength is decreased when aged at 250°C after 500 hours.Contrary to that at 200°C,we can see a simultaneous increase in both the high temperature strength and the high temperature modulus after ageing at 200°C.These observations indicate that,during air ageing,both postcure and thermal oxidative attack occur simultaneously.

Moisture absorption of bismaleimide type resins.

During the last three years extensive attention has been paid to moisture properties of matrix resins and composites.The state of the art high temperature epoxies based on tetraglycidylmethylenedianiline cured with 4,4'-diaminodiphenylsulfane show moisture absirption of up to 6 % by weight (neat resin).When used in graphite composites,this limits their use in so-called "hot wet " applications because the glass transition temperature of the resin is shifted dramatically to lower temperatures. Therefore polyimides are favoured for these applications because of their high glass transition temperature even when loaded with moisture.

Figure 13 summarizes the water absorption of bismaleimides (cured).Samples of TECHNOCHEMIE M751 and TECHNOCHEMIE H 795 were immersed in distilled water for 1000 hours after which time saturation at room temperature was nearly obtained.For comparison neat resin moisture absorption of Kerimide 601 is also presented.All the resins show a moisture absorption of about 4-5 % by weight.TECHNOCHEMIE H 795 was also moisturized at 70°C at 98 % relative humidity under which condition moisture absorption takes place much more rapidly but the saturation level is very similar to the cold water immersion.At this point it is of interest to note that bismaleimides absorb moisture much more rapidly than epoxy resins.

Processing of TECHNOCHEMIE H 795.

Prepregging of TECHNOCHEMIE H 795-resin.

Prepregging can be performed either from the melt or from solution. TECHNOCHEMIE H 795 resin,which is delivered as a resolidified melt,shows viscosities between 400-2800 mPa.s at 110°C and the viscosity and the processing temperature of the resin can be reduced further if necessary by blending the resin with "indifferent" solvents like toluene,2-ethoxyethylacetate,diglyme and the like in quantities up to between 10-20 % by weight.These solvents show a very low affinity to the resin and can therefore be easily stripped off at low temperatures (50-70°C).

The bismaleimide resin TECHNOCHEMIE H 795 can also be processed from 70 % by weight solutions.This concentration allows the reduction of the impregnation temperature to 50-60°C but the 70 % by weight resin solution has to be kept at a temperature of 50-60°C during impregnation to prevent the resin from crystallization.The preferred solvent is a 2-ethoxyethylacetate (EEA) - methylene chloride (MC) mixture.The EEA-MC ratio should be between 1:1 and 3:1.Excess EEA prevents skin trapping.Other solvent combinations like EEA and methyl-ethyl ketone (9:1,8:2) have also been tried successfully-N-methylpyrrolidone is not recommended because it cannot be dried off satisfactorily.

50-55 % by weight solutions are used for prepregging when fibre impregnation is performed by the dip-coating technology and excess resin is allowed to drain back into the resin reservoir.The preferred solvents for 50-55 % by weight solutions are 2-ethoxyethylacetate (EEA) - methylene chloride (MC) mixtures.The ratios can vary between 20:80 and 80:20.Preferably higher EEA concentrations are used to prevent skin trapping.

Moulding of TECHNOCHEMIE H 795 resin laminates.

TECHNOCHEMIE H 795 is designed to meet low pressure autoclave moulding procedures.A typical cure cycle is given in Figure 15 for the basic TECHNOCHEMIE H 795 resin and for an elastomer modified version coded TECHNOCHEMIE H 795E.The cycle is self-explanatory indicating a maximum cure temperature of 210°C in the autoclave and a maximum pressure of 4 bars.This cure cycle has been tested successfully within an industrial production-sized autoclave for the manufacture of a complex graphite component.Nevertheless it is possible to reduce the autoclave processing temperature further by using cure accelerators for the bismaleimide resin (H 795EK, H 795EKR).When diaza-bicyclo-octane (DABCO) is employed as a catalyst,the autoclave temperature can be reduced to 170-180°C to provide an "epoxy-like" cure (Figure 15).

At this point it should be mentioned that bismaleimide cure can be accelerated by many catalysts,examples of which are tertiary amines like trimethylamine,dimethylbenzylamine or diaza-bicyclo-octane,or all types of peroxides.Catalyst type and concentration influence the gel characteristics (e.g. gel times) and the flow properties during moulding. Adversely affected by catalysts is the shelf life of the prepreg,therefore type and concentration of the catalyst employed have to be balanced to obtain the right compromise between shelf life and processing temperature. For TECHNOCHEMIE H 795 we used concentrations up to 0.25 % by weight of diaza-bicyclo-octane to obtain the desired reductions of the cure and postcure temperature without losing sufficient shelf life.

Postcure of TECHNOCHEMIE H 795 resin laminates.

Processing autoclaves are designed for maximum cure temperatures of 170-210°C for big parts.These temperatures are not high enough to develop good high temperature mechanical properties in laminates prepared from bismaleimides.Therefore a free standing postcure at high temperatures is necessary.

Practical laminate build-ups consist of symmetric $0^{\pm}45,90^{\circ}$ lay-ups and we therefore tested the interlaminar shear strength without postcure and after postcure at 210°C and 250°C of multidirectional laminates (Figure 16).Main attention has been paid to the high temperature properties and,as can be seen from Figure 16,the increase of the postcure temperature increases the high temperature (250°C) shear strength while simultaneously the room temperature strength is decreased.This reflects the change of the neat resin properties during postcure,in particular the increase of the neat resin elastic modulus.

Similar experiments were performed with the catalyzed TECHNOCHEMIE H 795 resin version (coded TECHNOCHEMIE H 795EK) and it was found that postcure temperatures of 210°C are sufficient when the resin is properly catalyzed to develop the high temperature mechanical properties fully.

Laminate properties.

Mechanical properties of laminates prepared from TECHNOCHEMIE H 795E resin and Celion 6000 (standard epoxy-sized) fibres are given in Figure 17.Of course the properties at high temperature (250°C) are of main interest.The matrix dependent properties like the 0°-flexural strength,the 90°-flexural strength and the short beam shear strength are in correlation with the neat resin mechanical properties,e.g. about 60-70 % property retention at 250°C is obvious. The room temperature properties could be expected according to the fibre properties of Celion 6000.The horizontal shear strength of a $0^{\pm}45^{\circ}$ fibre lay-up shows only a very low property loss as compared with the room temperature value when properly postcured.All multidirectional laminates prepared from TECHNOCHEMIE H 795E resin are free of microcracks and the void content was found to be negligible.

The mechanical properties of laminates are influenced also by the sizing used on the carbon fibre.It is known that epoxy sizing contributes negatively when used in combination with polyimide matrix resins mainly when these laminates are aged at high temperatures in air.For the bismaleimide resin TECHNOCHEMIE H 795 we tested the standard epoxy-sized fibres and fibres which are sized with a polyimide finish.In this search we employed also the elastomer modified resin TECHNOCHEMIE H 795E,either catalyzed or non-catalyzed.The results obtained are summarized in Figure 18.It is obvious that the shear properties of laminates prepared from Pi-sized fibres are higher as compared with laminates made with the standard epoxy-sized fibres.Also the flexural properties perpendicular to the fibre direction are slightly improved when polyimide is used as a fibre sizing demonstrating good compatibility between the polyimide sizing and the poly (bismaleimide) resin TECHNOCHEMIE H 795 or its elastomer modified version TECHNOCHEMIE H 795E.

Recent research in the area of high temperature epoxy resins indicated negative influence of absorbed moisture on mechanical properties of laminates at high temperatures.Moisture (water) acts as a plasticizer in the laminating resin and degrades the high temperature mechanical properties because of the reduction of the glass transition temperature of the resin.Bismaleimides do like many polar resins absorb moisture to a high degree (see Figure 13),but because of their extremely high glass transition temperature (Tg) in the dry state their Tg is still very high when saturated with water.This property makes them prime candidates for application in composites for the so-called hot wet environment.

We therefore were interested in the moisture behaviour of TECHNOCHEMIE H 795 laminates either prepared from standard epoxy-sized fibres or polyimide (Pi) sized fibres.The results are given in Figure 19.Dry laminates of Pi-sized fibres show extremely high shear properties.The shear strength at 150°C is around 80-85N/mm^2 for dry unidirectional laminates.The moistured laminate (1.7 % moisture absorption) shows a reduced shear strength at both room temperature and 150°C.At 150°C the reduction is around 30 % as compared with the RT value.It is interesting to note that the epoxy-sized fibres provide shear strength values of around 65-70N/mm^2 at 150°C when dry and the shear strength is degraded to around 45-48 when wet.The percentage of property loss is the same as for the polyimide sized fibres which shows that the reduction in shear strength of wet laminates is a matrix dominant property.It is of main importance,according to our observation,that the initial shear values are sufficiently high to provide satisfactory wet shear properties in laminates.

Because of its outstanding high temperature mechanical properties and its good hot/wet properties TECHNOCHEMIE H 795 resin was selected as matrix resin to build a demonstration component,the air brake of the Alpha jet, a picture of which is given in Figure 20.The component development was performed by Dornier GmbH-Friedrichshafen and the prepregs for this programme were supplied by TECHNOCHEMIE GMBH-Verfahrenstechnik.The demonstration part was tested statically successful at 200°C and TECHNOCHEMIE H 795 resin will therefore be evaluated further for hardware production.

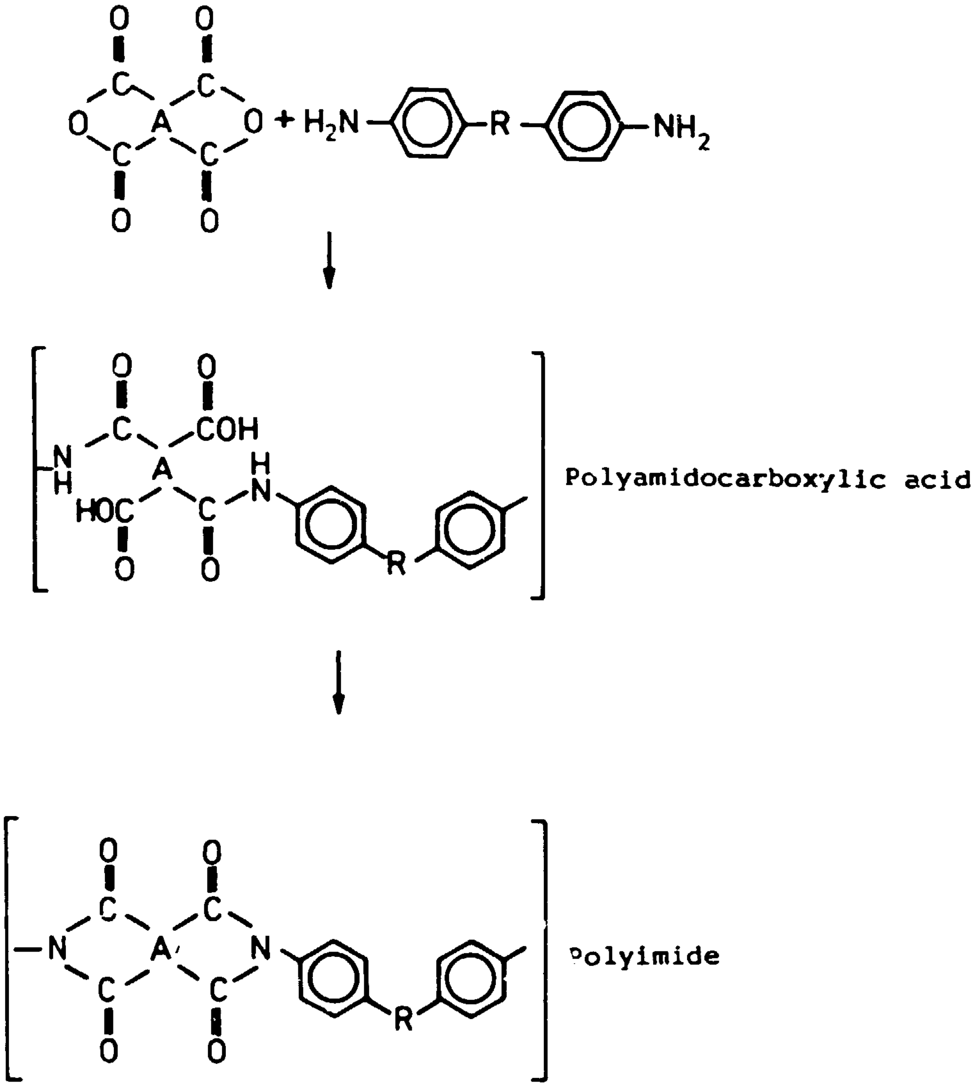
Concluding remarks.

Bismaleimide type resins are prime candidates as matrix resins for graphite fibre laminates for

(a) high temperature applications (170-220°C)
(b) applications in hot wet environment (because of their high Tg in the dry and moistured state).

Because of their easy processability and the chemistry involved,the curing conditions can easily be adjusted by employing curing catalysts,reactive diluents and elastomers.Of main importance is the improvement of the fracture toughness without the reduction of the high temperature properties.

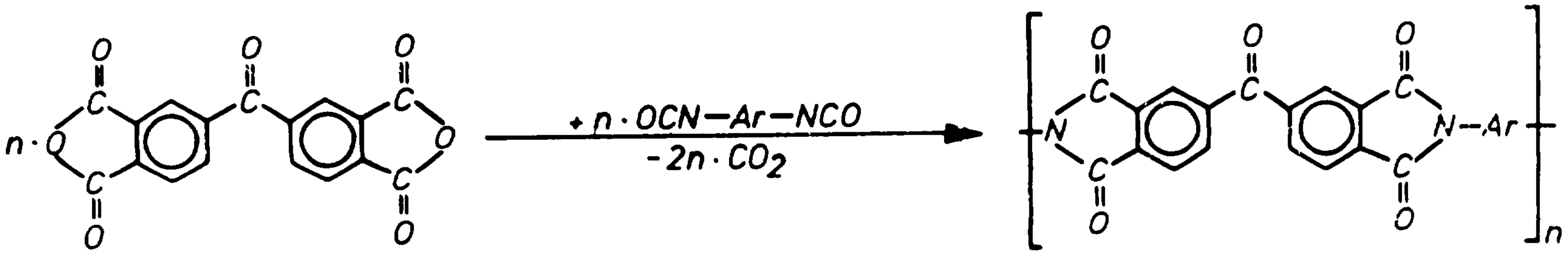
Slide 1: Synthesis of totally aromatic Polyimides

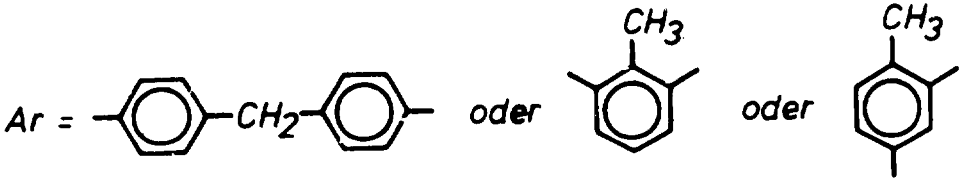


Lit.: C.E. Sroog et al, J. Polymer Sci., Part A, 3 (1965) 1373

- Excellent thermal oxidative stability
- Condensation Polyimide
- Processed from N-Methylpyrrolidone - solvent
- Processing includes 350 °C-temperature cure

Slide 2: Synthesis of thermoplastic Polyimides

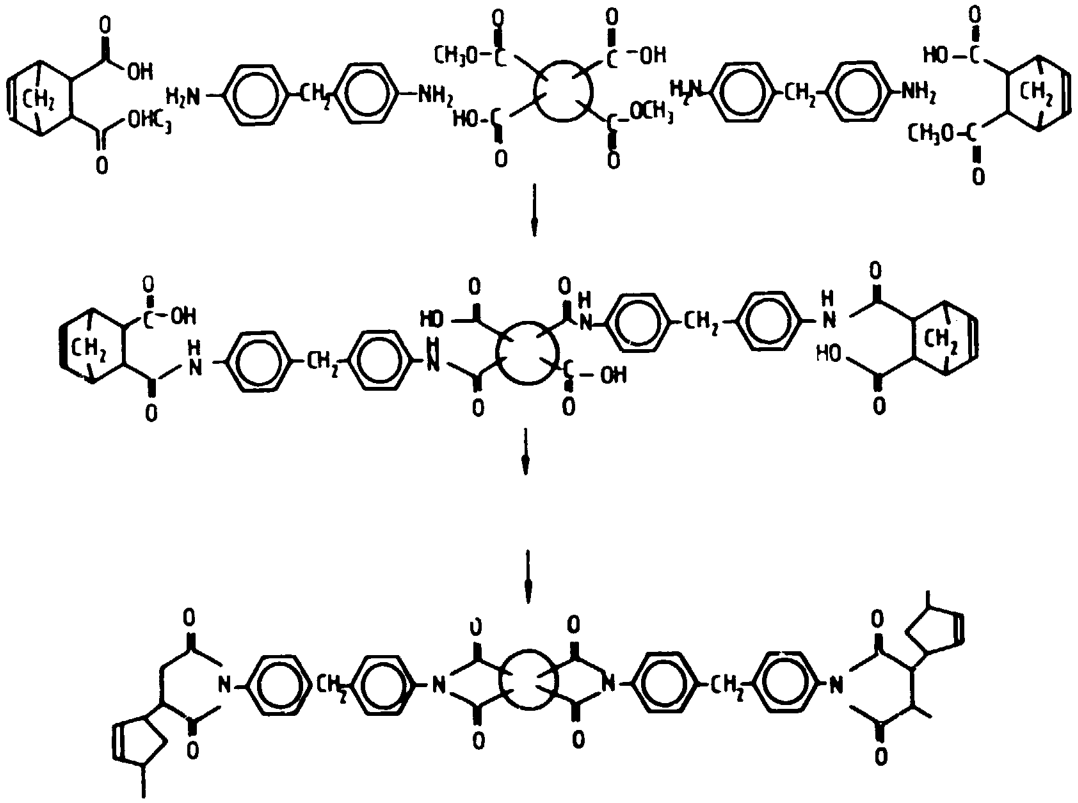




Lit.: L.M. Alberino, W.J. Farrisey jr, J.S. Rose, US P 3708458 (1973, to Upjohn)

- Excellent thermal oxidative stability (260 °C)
- High viscosity solution
- Processed from N-Methylpyrrolidone - solvent
- Processing includes high temperature (320 °C) and high pressure (7 bars)

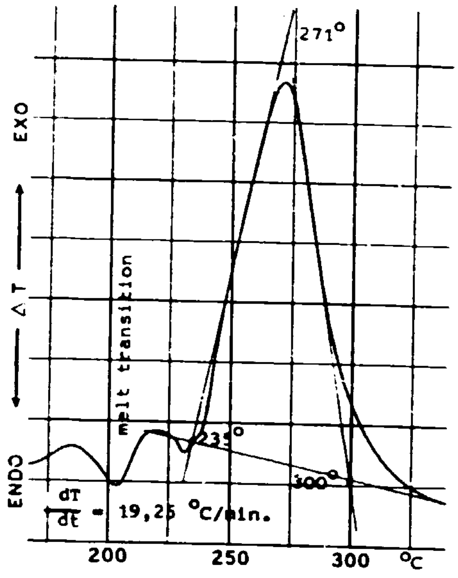
Slide 3: PMR-Polyimide concept

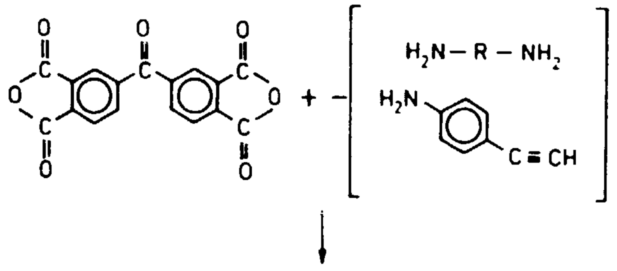


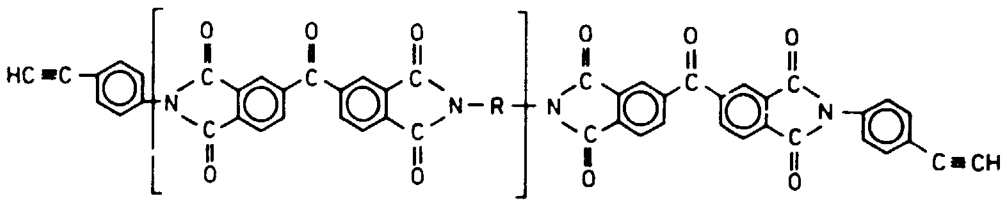
Lit.: T.T. Serafini, P. Delvigs, W.B. Alston, SAMPE Vol. 27, 320

- Excellent thermal stability (230-280 °C)
- Condensation addition Polyimide
- Processed from Methanol or Ethanol
- Processing includes high temperature (285 °C) and high pressure (14 bars)

Slide 4: Thermosetting Polyimides with acetylene endgroups



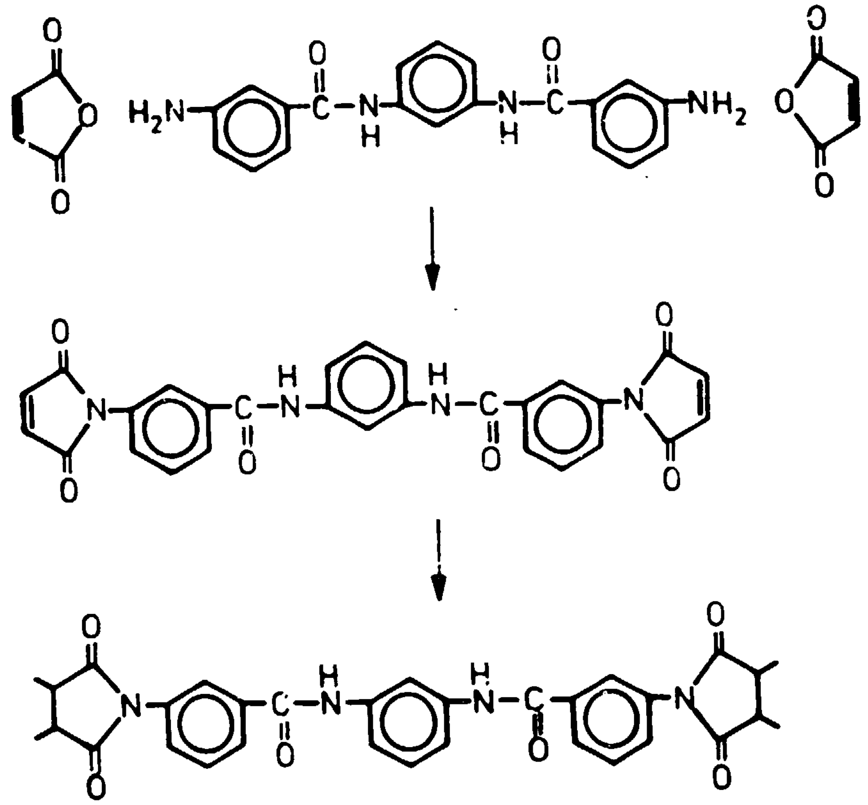




Lit.: A.L. Landis et al, ACS Polymer Preprints 15 (1974) 2, 537
N.A. Bilow, US P 3845018 (to Hughes Aircraft Company)

- Excellent high temperature ageing properties
- Addition type Polyimide
- Processed from N-Methylpyrrolidone
- Processing includes high temperatures (350 °C) and high pressure (14 bars)

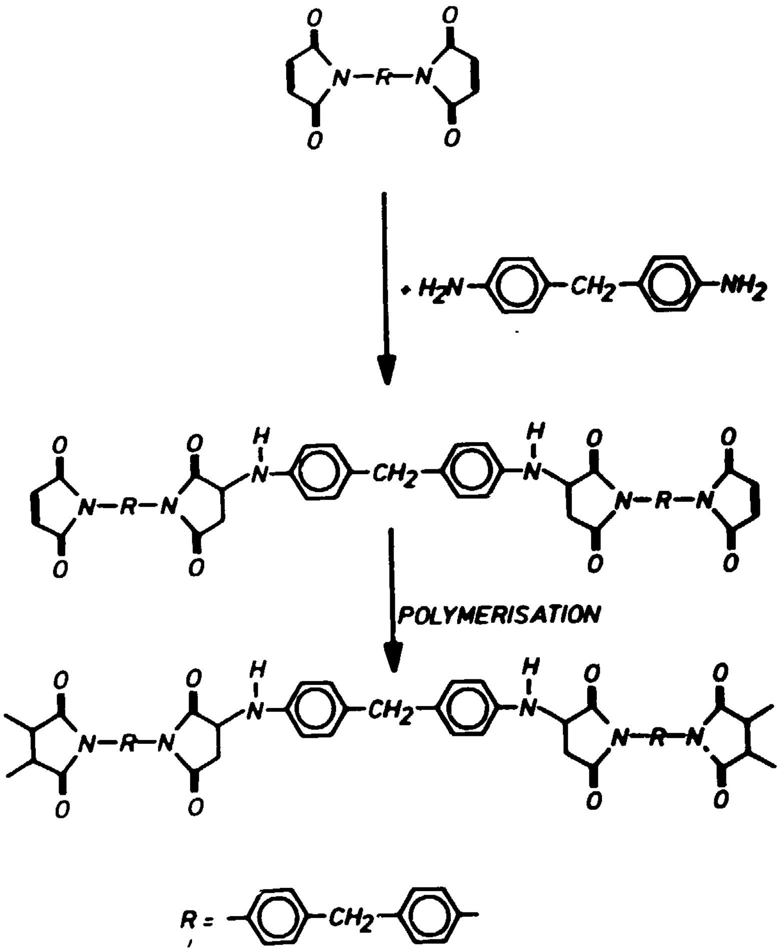
Slide 5: Synthesis of Bismaleimides



Lit.: US P 2444536 (1948)
US P 3018290 (1962)
US P 3127414 (1964)
Brit. Patent Spec. 1137592 (1968)

- Addition type Bismaleimides
- Processed from solution or from the melt
- Processability similar to Epoxies (170-200 °C, 4-7 bars)
- Temperature capability 130-230 °C
- Hot wet properties superior to Epoxies

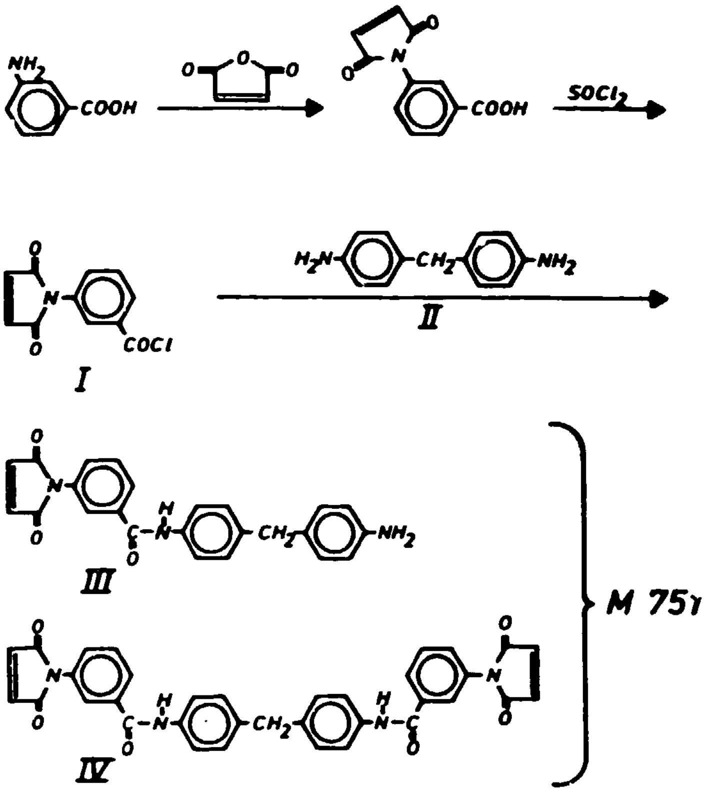
Slide 6: Polyamino bismaleimide resin concept



Lit.: M. Bergain et al, Brit. Patent 1190718 (1968, to Rhone Poulenc)

- Addition type Polybismaleimide .
- Processed from N-Methylpyrrolidone - solvent
- Processing includes 170 °C-temperature and 15-30 bar pressure
- Good mechanical property retention up to 200 °C

Slide 7: TECHNOCHEMIE M 751 - Bismaleimide resin concept



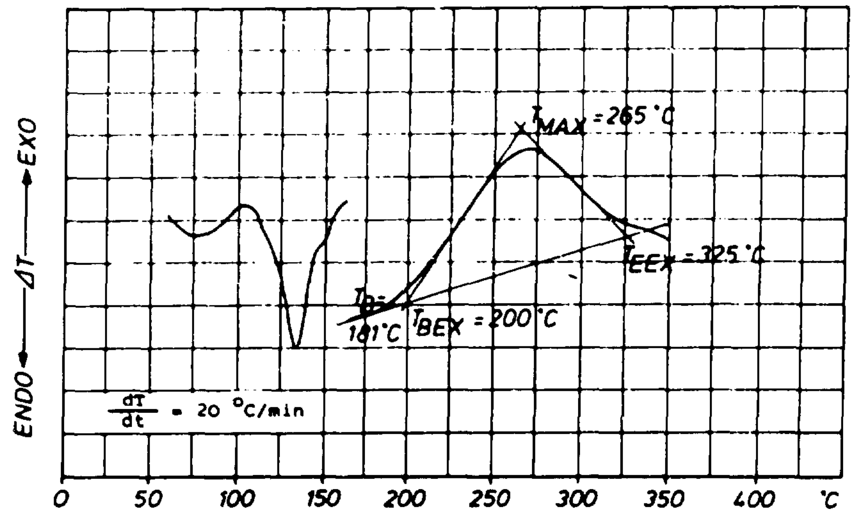
Lit.: H. Stenzenberger, Brit. Patent 1501606 (1976, to Technochemie)

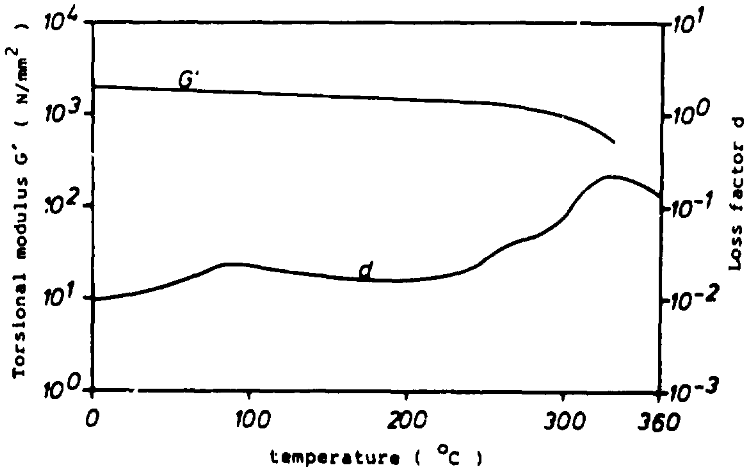
Mechanical properties for resins based on M 751-Bismaleimide concept

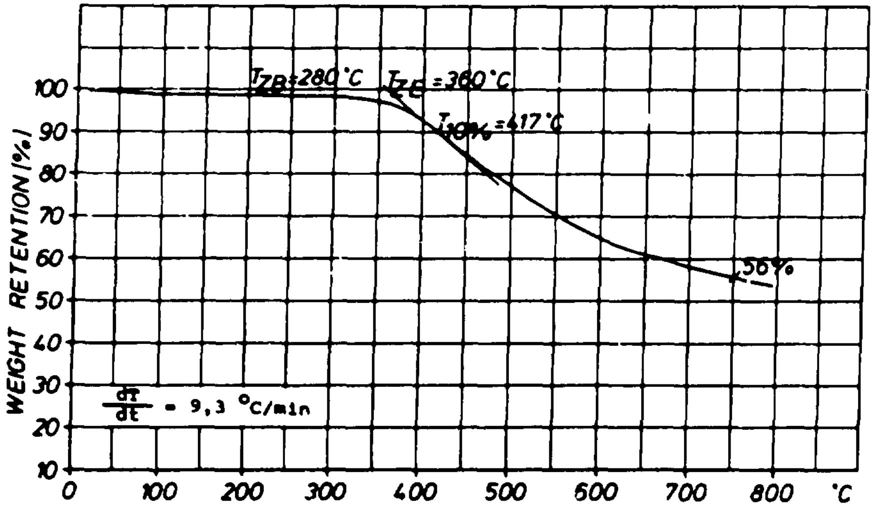
Resin No.	FMW	Flex. Strength N/mm^2	Flex. Modulus kN/mm^2	ϵ %
M 751 - 1	1140	220	4,38	4,81
M 751 - 2	790	180	4,65	3,71
M 751 - 3	670	121	4,28	2,68

FMW = formulated molecular weight

Slide 8: Properties of TECHNOCHEMIE M 751 resin



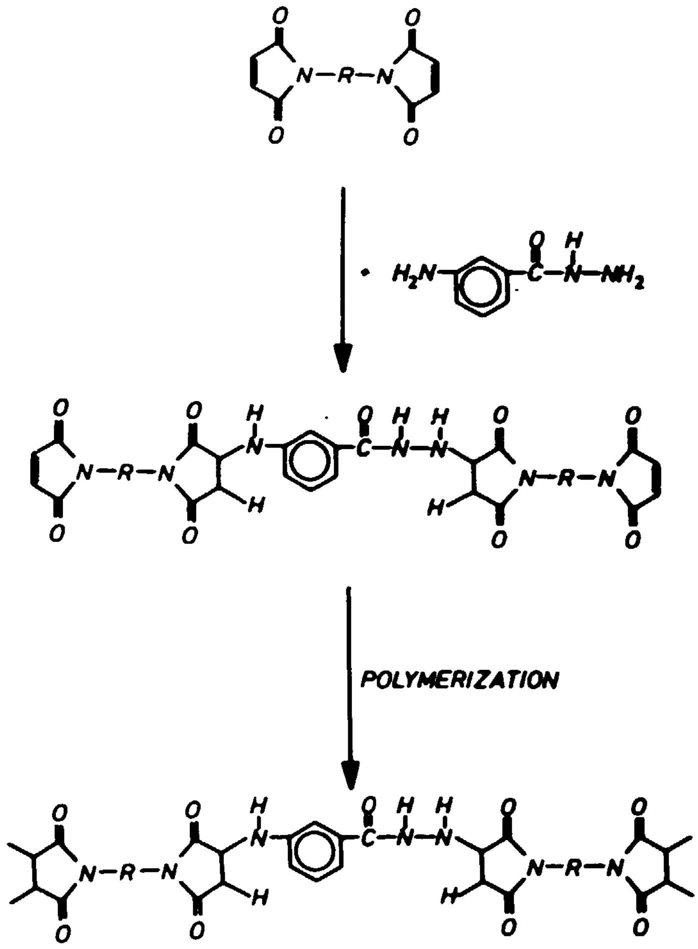




Mechanical Properties of neat Bismaleimide resin

Property	Unit	M 751 RT	 250 °C
Density	g/cm^3	1,32	
Flex. Strength	N/mm^2	210	102
Flex. Modulus	kN/mm^2	5,02	3,17
Flex. Elongation	%	4,8	
Expans. Coeff.	10^6 cm/cm/°C	31	84
Moist. Absorption	%	4,5	
T_g	°C	240	

Slide 9: TECHNOCHEMIE H 795 - Bismaleimide resin concept



Lit.: H. Stenzenberger, US P 4211861 (1980, to Technochemie)

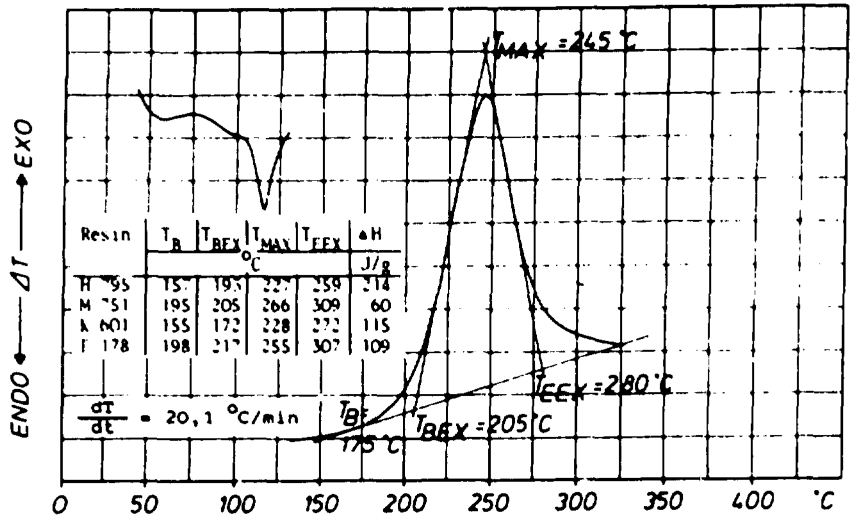
- Addition type Polybismaleimide
- Processed from melt or from solution
- Low temperature autoclave cure (170-210 °C, 4 bars)
- Temperature capability 150-220 °C
- High mechanical property retention up to 250 °C
- Component fabrication experience

Slide 10: TECHNOCHEMIE H 795 resin specification

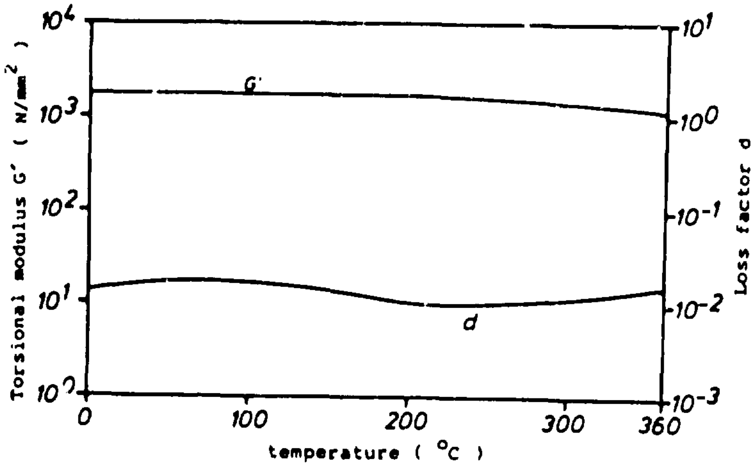
PROPERTY	TEST METHODE	VALUE	COMMENT
Gel time	DIN 16954	25 - 3 mins	test temperature 170° C
Viscosity	DIN 16954	400 - 2800 mPa.s	complex viscosity
Viscosity build up at 110° C/180 mins	DIN 16954	1200-5750 mPa.s	complex viscosity obtained after aging at 110° C for 3 hours
Residual solvent	-	2 - 6 %	Weight loss at 140° C in vacuum (20 Torr) after 30 minutes
Solubility	-	50 % MEK 50 % Acetone 40 % CH_2Cl_2	clear soluble clear soluble clear soluble
Differential Scanning Calorigramme	DSC	T_B 146 ± 4° C T_{BEX} 179 ± 4° C T_{MAX} 230 ± 6° C T_{EEX} 277 ± 7° C	Heating rate 10° C/min
Polymerization Energy	DSC	265 ± 20 J/g	from DSC-Analysis $\frac{dT}{dt} = 10^\circ$ C/min
Composition	HPLC	comparison with standard	

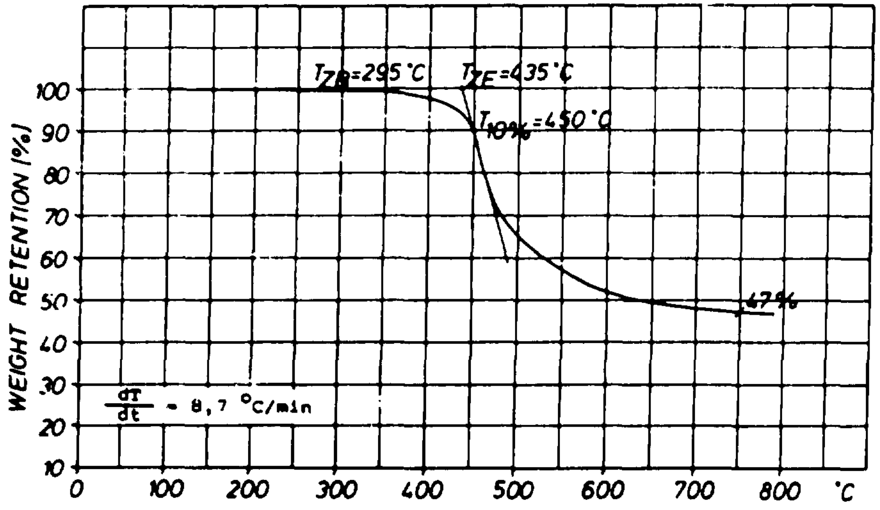
Abbreviations :		
	m Pa . s	millipascals . seconds
	MEK	Methyl-ethyl-ketone
	CH_2Cl_2	Methylene chloride
	T_B	onset temperature
	T_{BEX}	extrapolated onset temperature
	T_{MAX}	exotherm peak temperature
	T_{EEX}	complete reaction temperature
	DSC	Differential Scanning Calorimetry
	J/g	Joule/gramm

Slide 11: Properties of TECHNOCHEMIE H 795 resin



Resin	T_B	T_{BEX}	T_{MAX}	T_{EEX}	ΔH
	°C				J/g
H 795	157	193	227	259	214
M 751	195	205	266	309	60
K 601	155	172	228	272	115
F 178	198	217	255	307	109

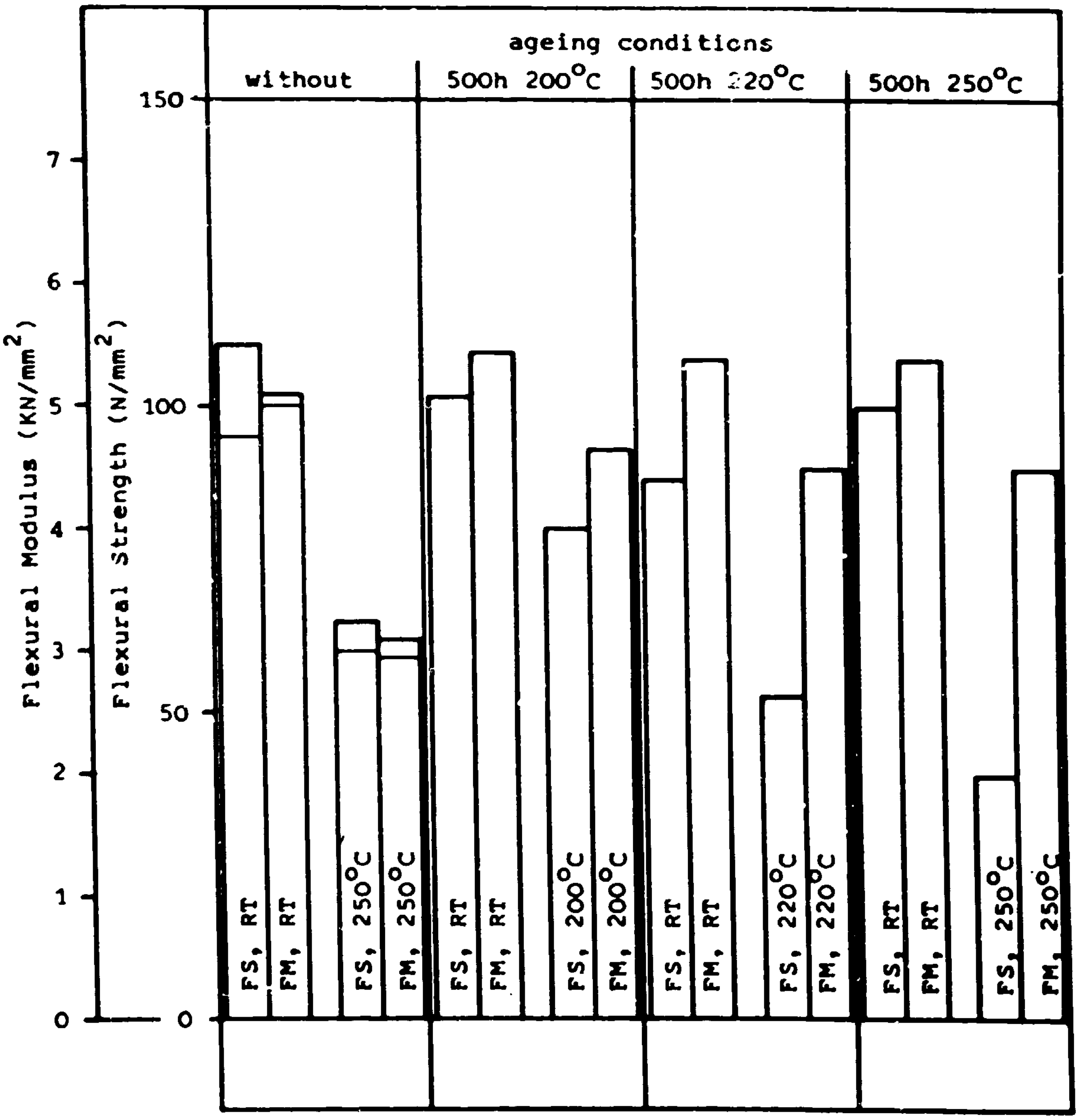




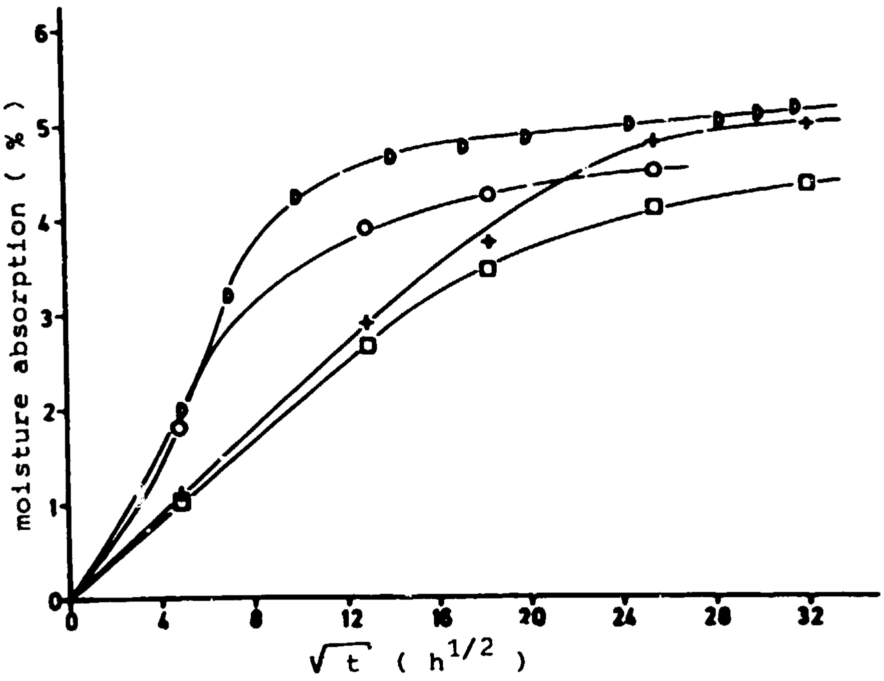
Mechanical Properties of neat Bismaleimide resin

Property	Unit	H 795 RT	H 795 250 °C
Density	g/cm^3	1,32	
Flex. Strength	N/mm^2	90-110	60-65
Flex. Modulus	kN/mm^2	5,3-5,5	3,2-3,4
Flex. Elongation	%	2,2-2,4	2,0-2,2
Expans. Coeff.	10^6 cm/cm/°C	36,6	73,4
Moist. Absorption	%	4,85	

Slide 12: Ageing of TECHNOCHEMIE H 795 neat resin



Slide 13: Moisture absorption of Bismaleimide type resins



○ K 601, cold water
□ M 751, "
+ H 795, "
◗ H 795, 70 °C, 98 %rF

Polyimide resins and prepregs : terminology

I. Low pressure processing (autoclave moulding)

a. resins:

Base resin	Modification	Purpose of modification
TECHNOCHEMIE H 795		
	elastomer	a) elastification b) reduction of microcracks in C-fibre laminates
TECHNOCHEMIE H 795 E		
	reaktive diluent	viscosity modifier
TECHNOCHEMIE H 800 (H 795 ER)		
	catalyst	processing temperature reduction

b. prepregs:

TECHNOCHEMIE T300 EP/H 800-0,1 K/38UD

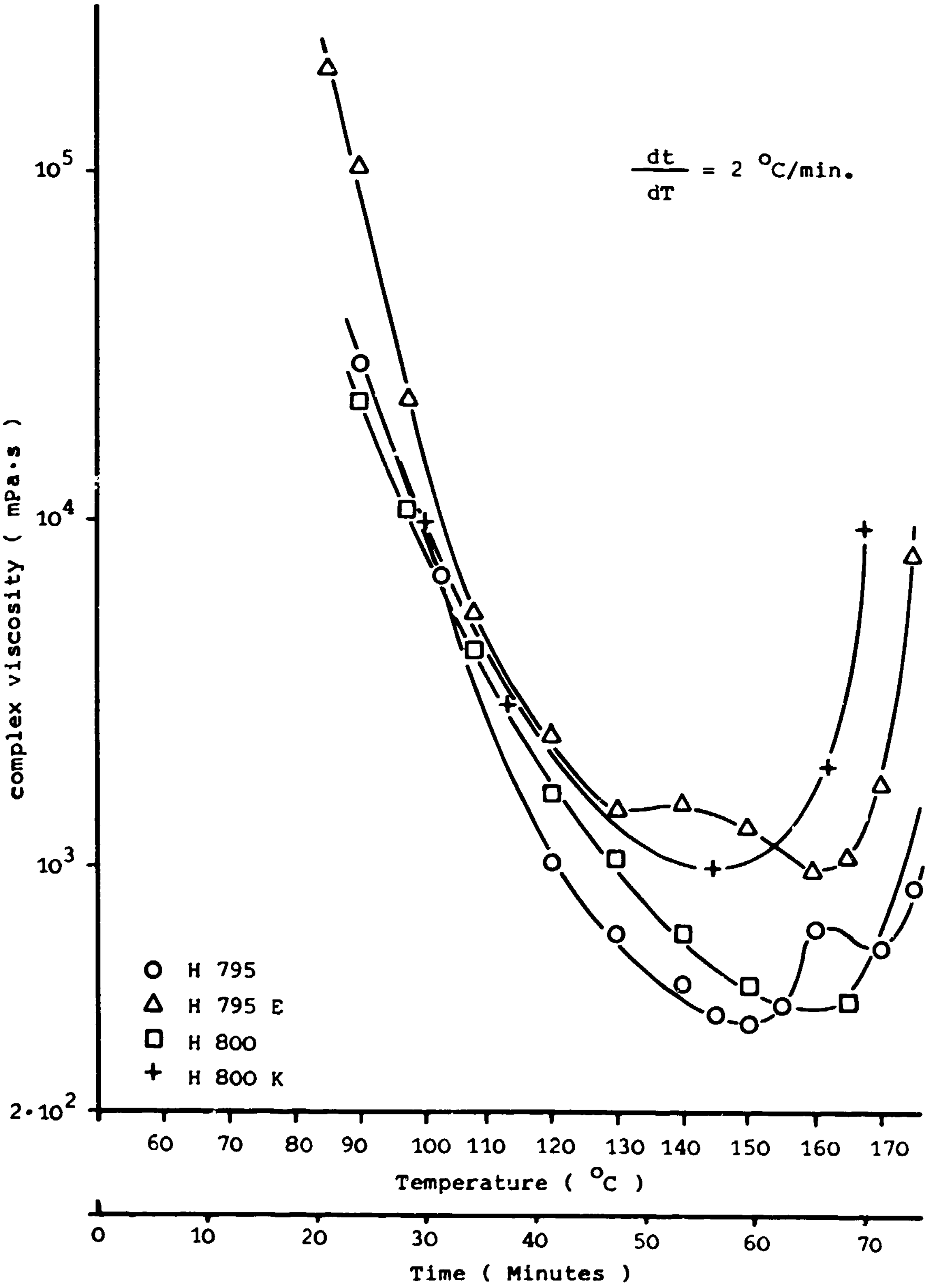
TECHNOCHEMIE C6000 EP/H 800-0,25K/38UD

resin content, fibre orientation
type of resin, catalyst quantity
type of fibre, type of size

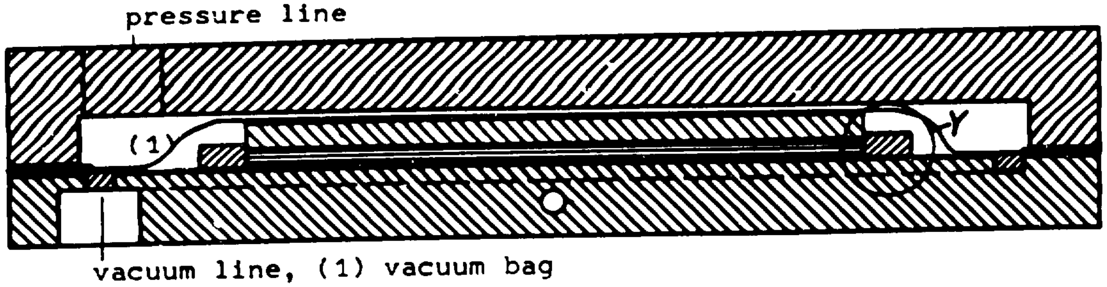
II. High pressure processing (press moulding, injection moulding, ram extrusion)

TECHNOCHEMIE M 751		
	NMP solvent	
TECHNOCHEMIE M 751-L40		varnish for impregnation

Dynamic viscosity-temperature - profile

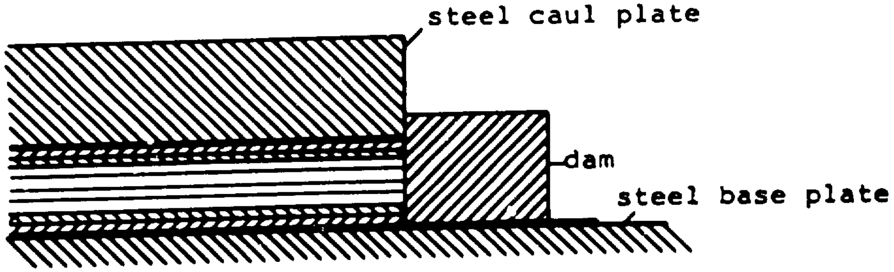


Slide 14: Processing of TECHNOCHEMIE H 795 resin prepregs

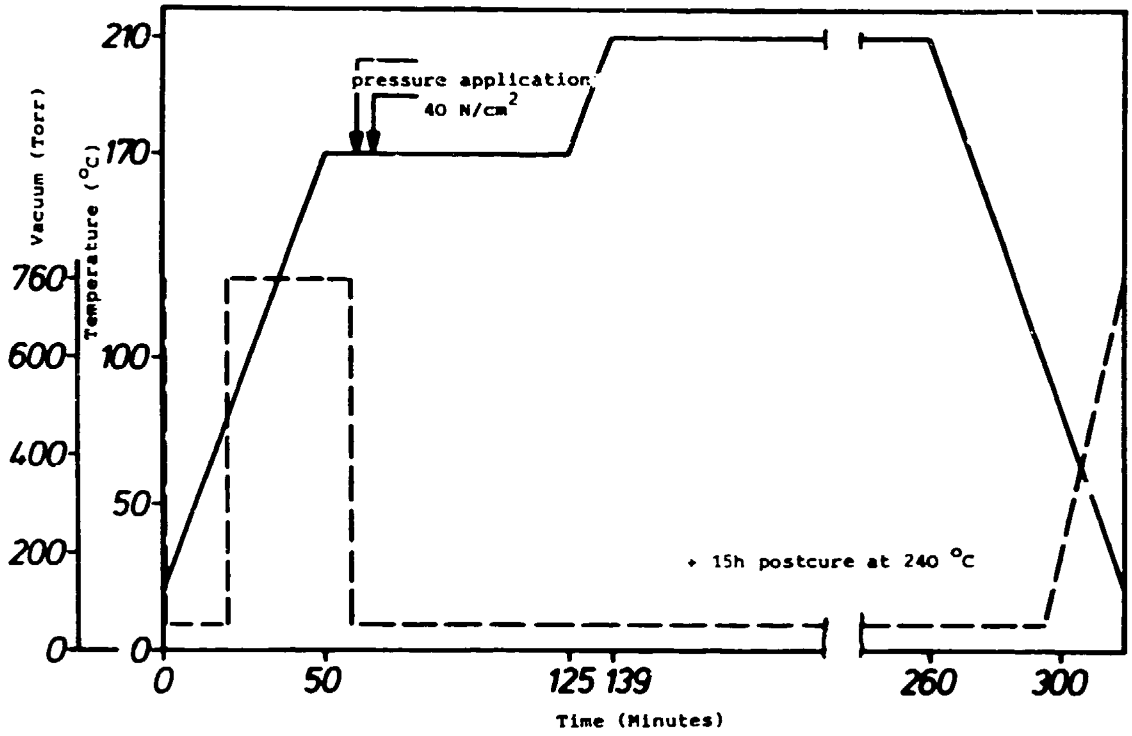


▬ Alu-foil
▨ glass fabric
▧ Teflon release fabric
▤ laminate

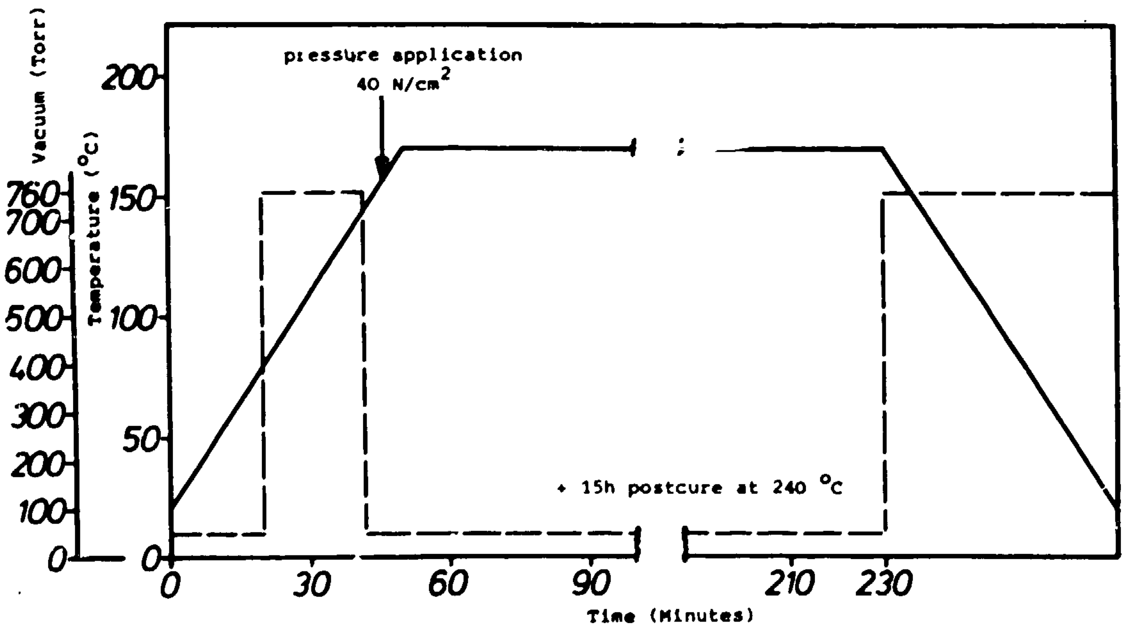
enlargement Y



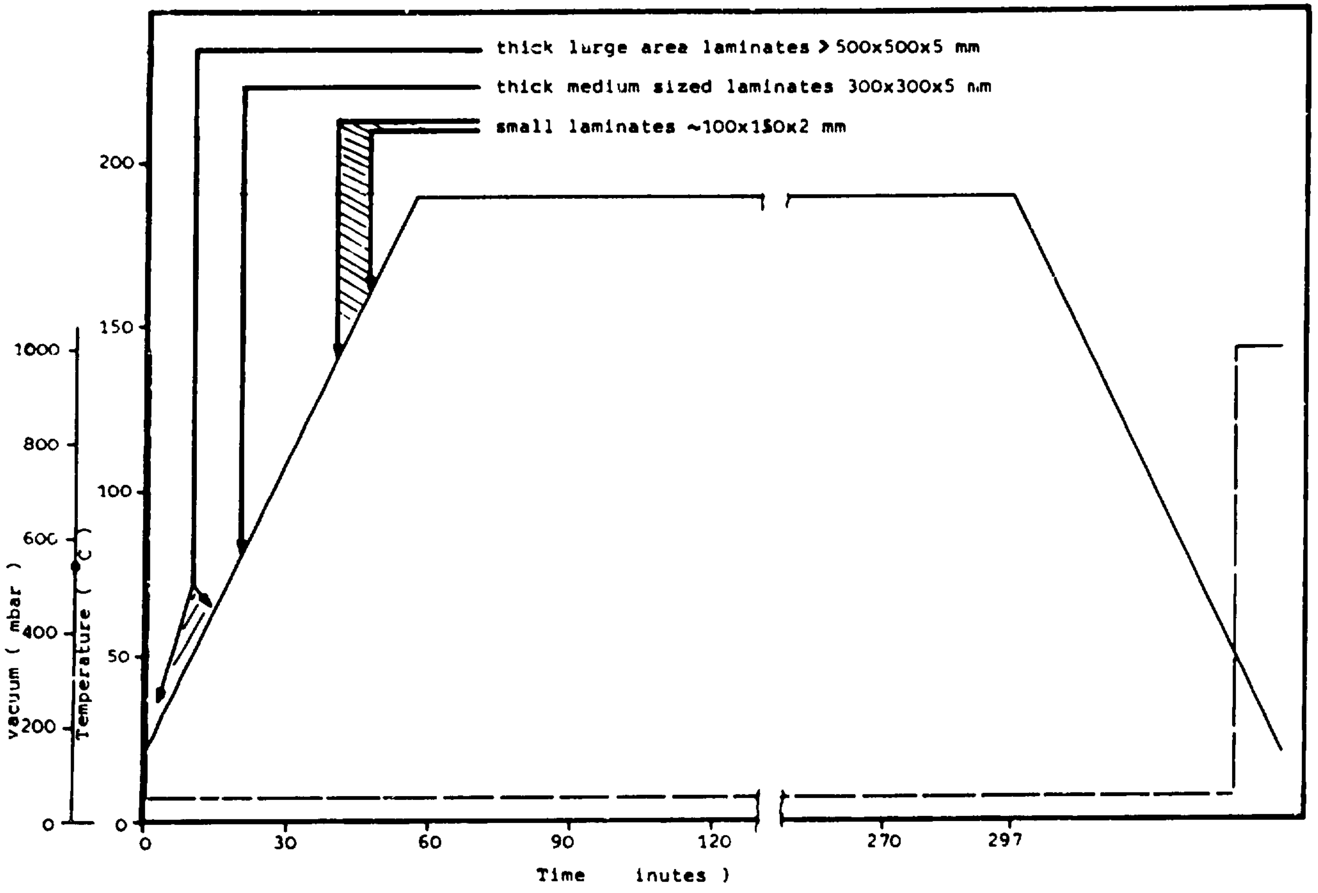
Slide 15: Cure cycle for H 795 and H 795 E - laminates



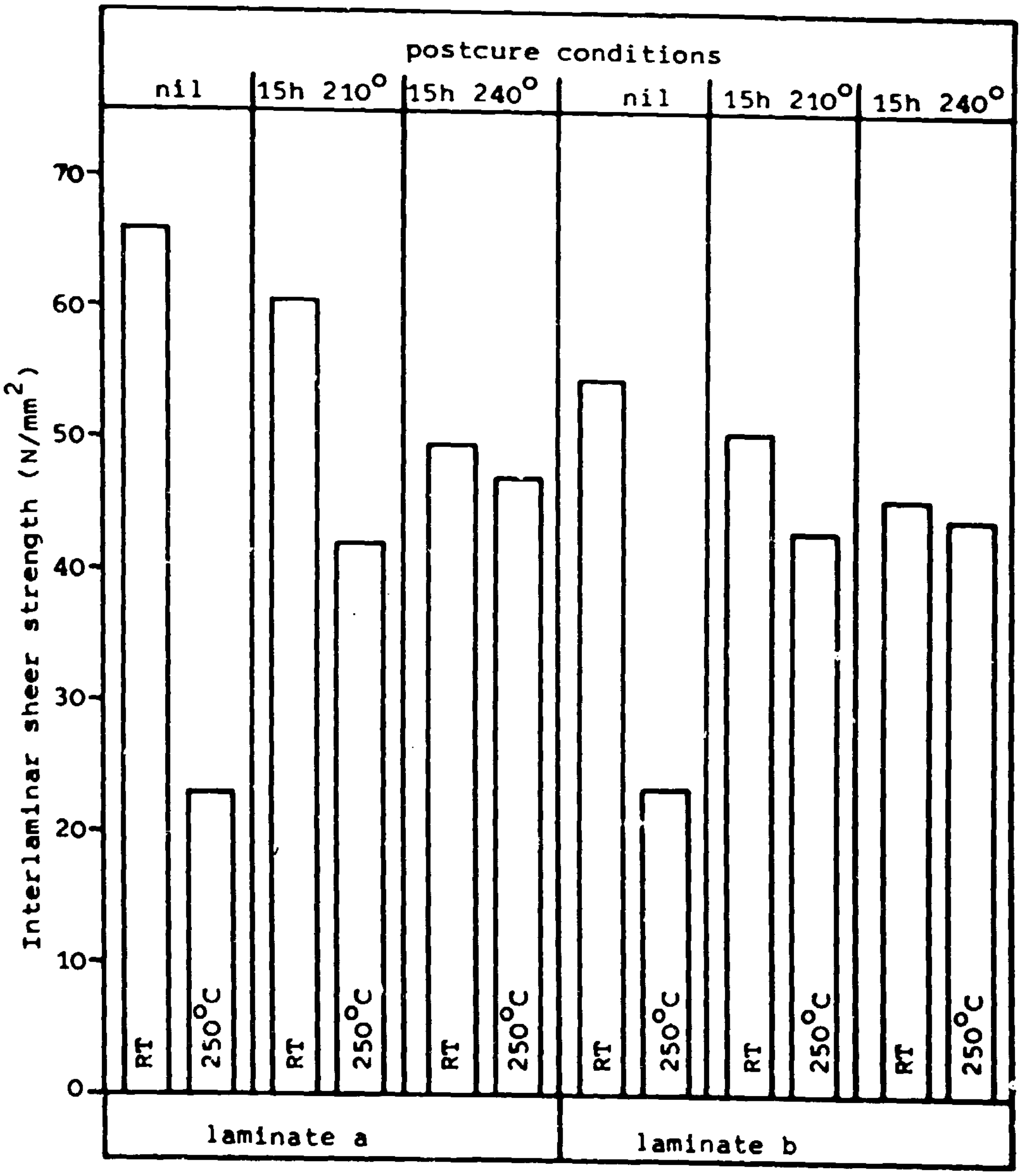
Cure cycle for H 795 EK and H 795 EKR - laminates



Processing of TECHNOCHEMIE H 795 ERK - prepregs



Slide 16: Interlaminar shear strength of multidirectional laminates as a function of postcure conditions
resin: TECHNOCHEMIE H 795
fibre: T 300/3000



Prepreg lay up:
laminate a: $(0,+45,0,-45,0,+45,0,-45,0)_s$
laminate b: $(0,0,+45,-45,0,0,-45,+45,0)_2$

Slide 17: Properties of TECHNOCHEMIE H 795 E Celion-6000+ laminates

Property	Fibre Direction	Unit	Value	
			20°C	240°C
Flexural Strength	0	N/mm^2	1850	1240
Flexural Modulus	0	kN/mm^2	117	120
Flexural Strength	90	N/mm^2	53	29
Flexural Modulus	90	kN/mm^2	7,4	5,3
Tensile Strength	0	N/mm^2	1450	1300
Tensile Modulus	0	kN/mm^2	119	128
Compressive Strength	0	N/mm^2	1400	800
Compressive Modulus	0	kN/mm^2	128	120
Horizontal Shear (short beam shear, span to depth ratio 5:1)	0	N/mm^2	96	53
Horizontal Shear	0±45	N/mm^2	48	42

+ Standard Epoxy-sizing (1,1-1,3 % by weight)

Slide 18: Properties of various TECHNOCHEMIE H 795 resin formulations

Property	Fibre Direction	Unit	Test Temp. (° C)	H 795 T 300/EP	H 795 E C 6000/EP	H 795 EK C 6000/EP	H 795 E C 6000/PI	H 795 EKR C 6000/PI
Prepreg Batch No.				X	X	8225	8230	8235
Fibre Content		v/o		61	64	62	67	67
Flexural Strength	0	N/mm^2	23	1646	1850	1761	1992	1957
			250	1378	1240	1217	1575	-
Flexural Modulus	0	KN/mm^2	23	121	117	116	117	121
			250	120	120	114	121	-
Flexural Strength	90	N/mm^2	23	81	53	60	81	62
			250	31	29	37	36	-
Flexural Modulus	90	KN/mm^2	23	8,7	7,4	8,0	8,5	8,2
			250	7,6	5,3	6,3	6,1	-
Horizontal Shear	0	N/mm^2	23	81	96	95	104	109
			250	49	53	53	51	59
Horizontal Shear	0±45	N/mm^2	23	48	48	51	45	54
			250	44	42	43	38	49

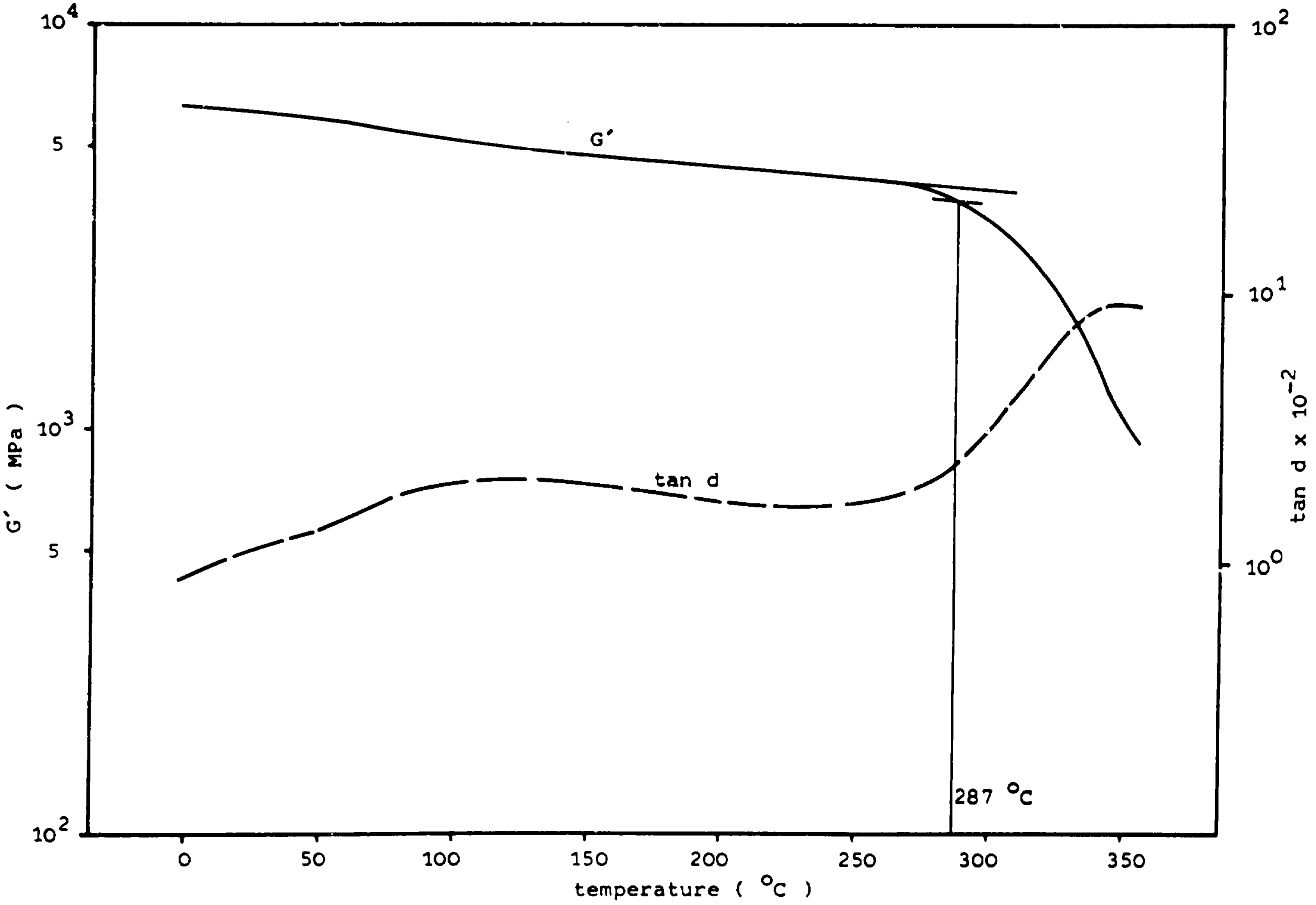
H 795 Basic hot melt BMI-resin formulation, E = Elastomer, K = Catalyst, R = Reactive diluent

X average of 3 different Prepreg batches

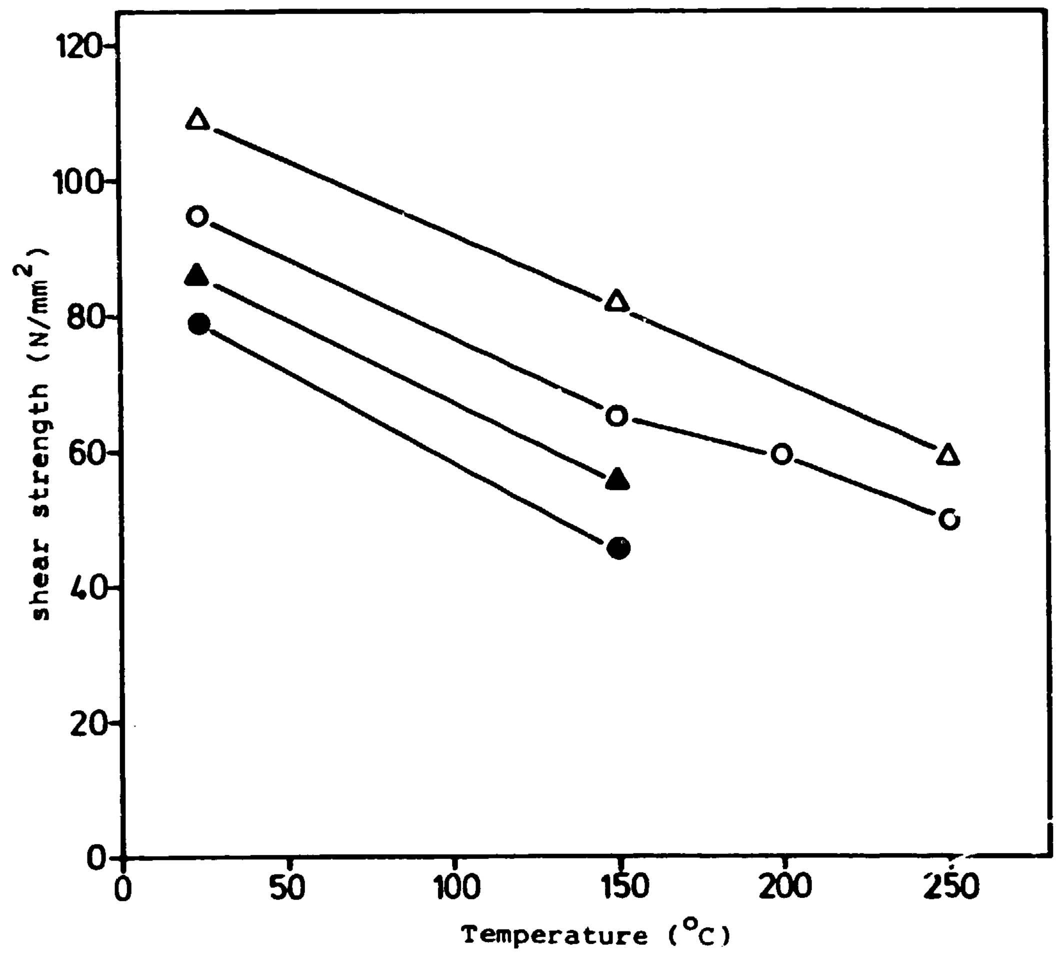
EP = Epoxy

PI = Polyimide

Glass transition temperature of H 795 ERK/T300 - laminates (according to DIN 29971)



Slide 19: Short beam shear properties of TECHNOCHEMIE H 795 resin laminates



△ H 795 EKR Celion 6000/PI, dry laminate

▲ H 795 EKR Celion 6000/PI, wet laminate (1,71 % moisture)

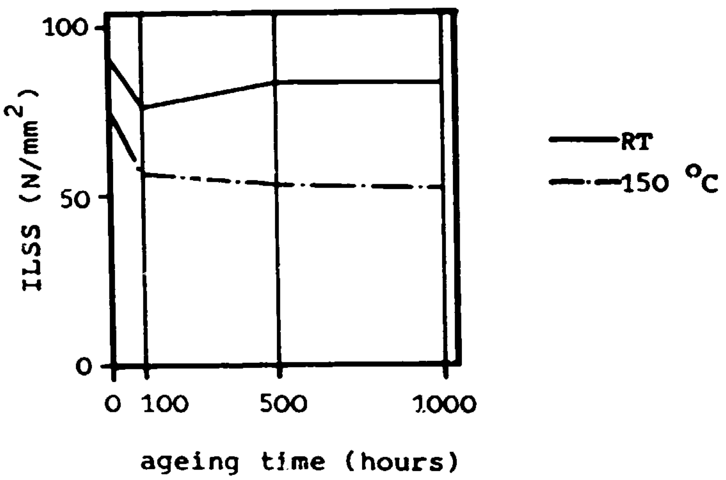
○ H 795 EK Celion 6000/EP, dry laminate

● H 795 EK Celion 6000/EP, wet laminate (1,61 % moisture)

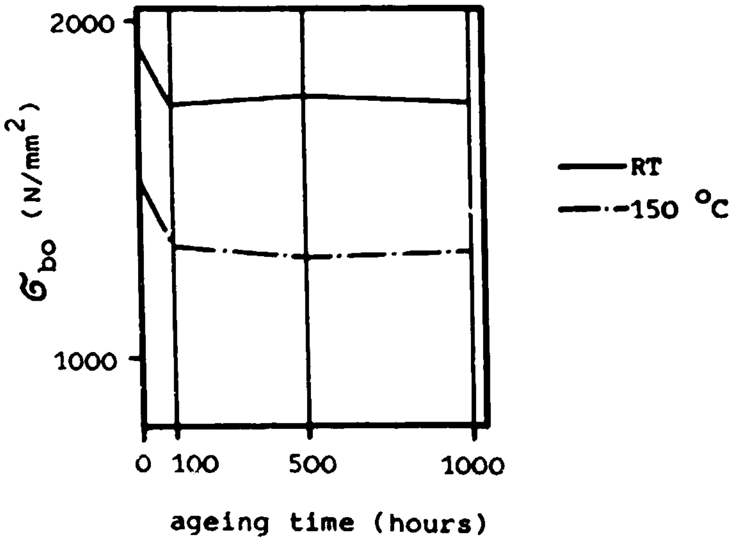
Property retention of H 795 ERK/C6000 - laminates

ageing conditions: at 70 °C and 94 % relative humidity

interlaminar shear strength



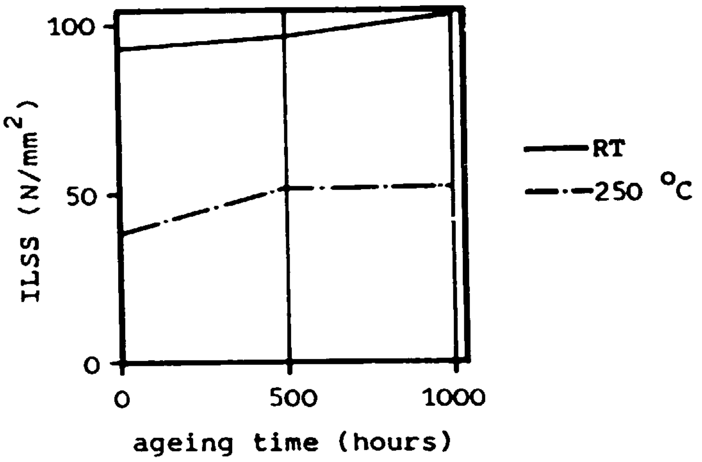
flexural strength



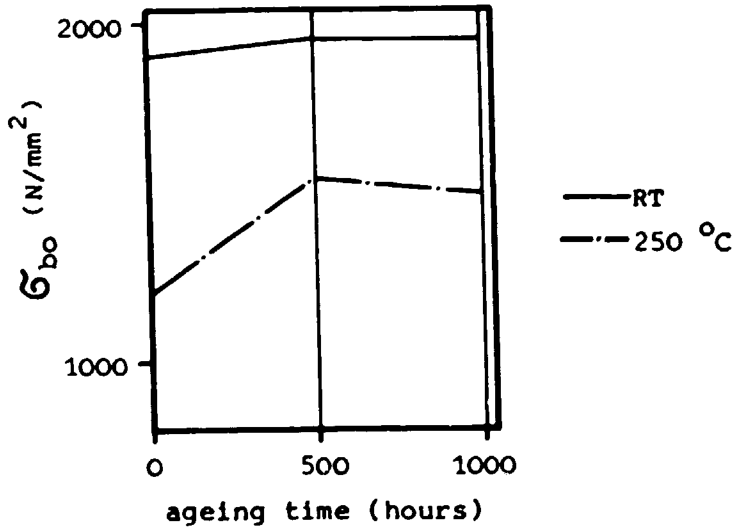
Property retention of H 795 ERK/C6000 - laminates

ageing conditions: at 250 °C in circulating air

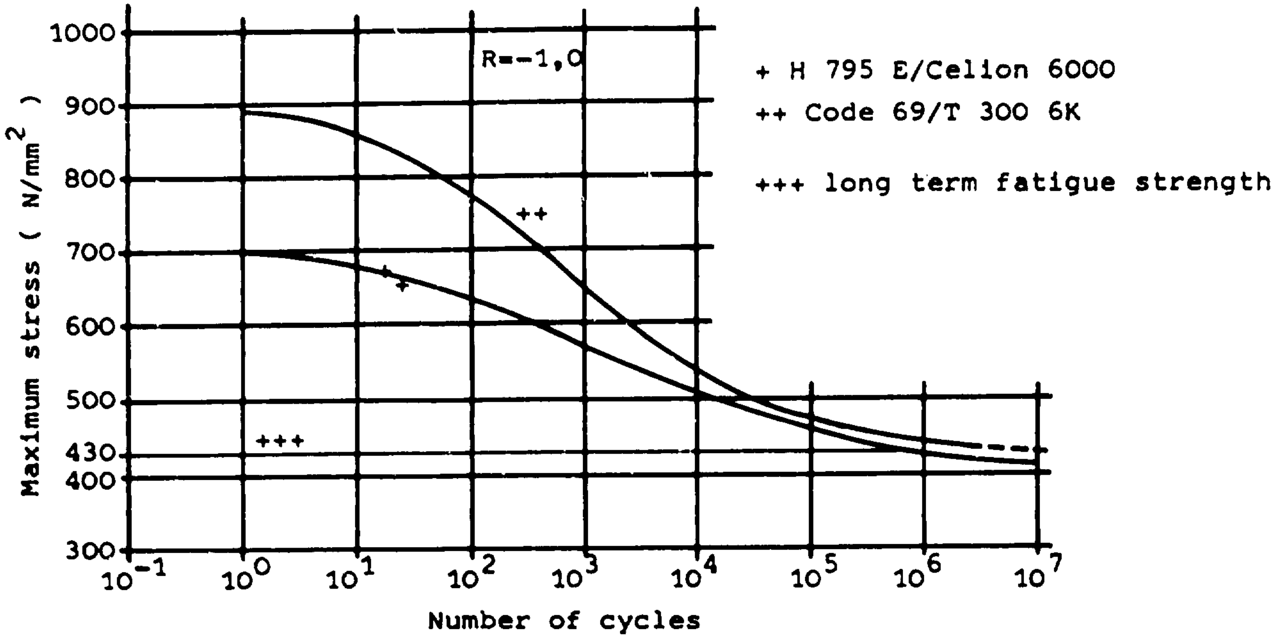
interlaminar shear strength



flexural strength

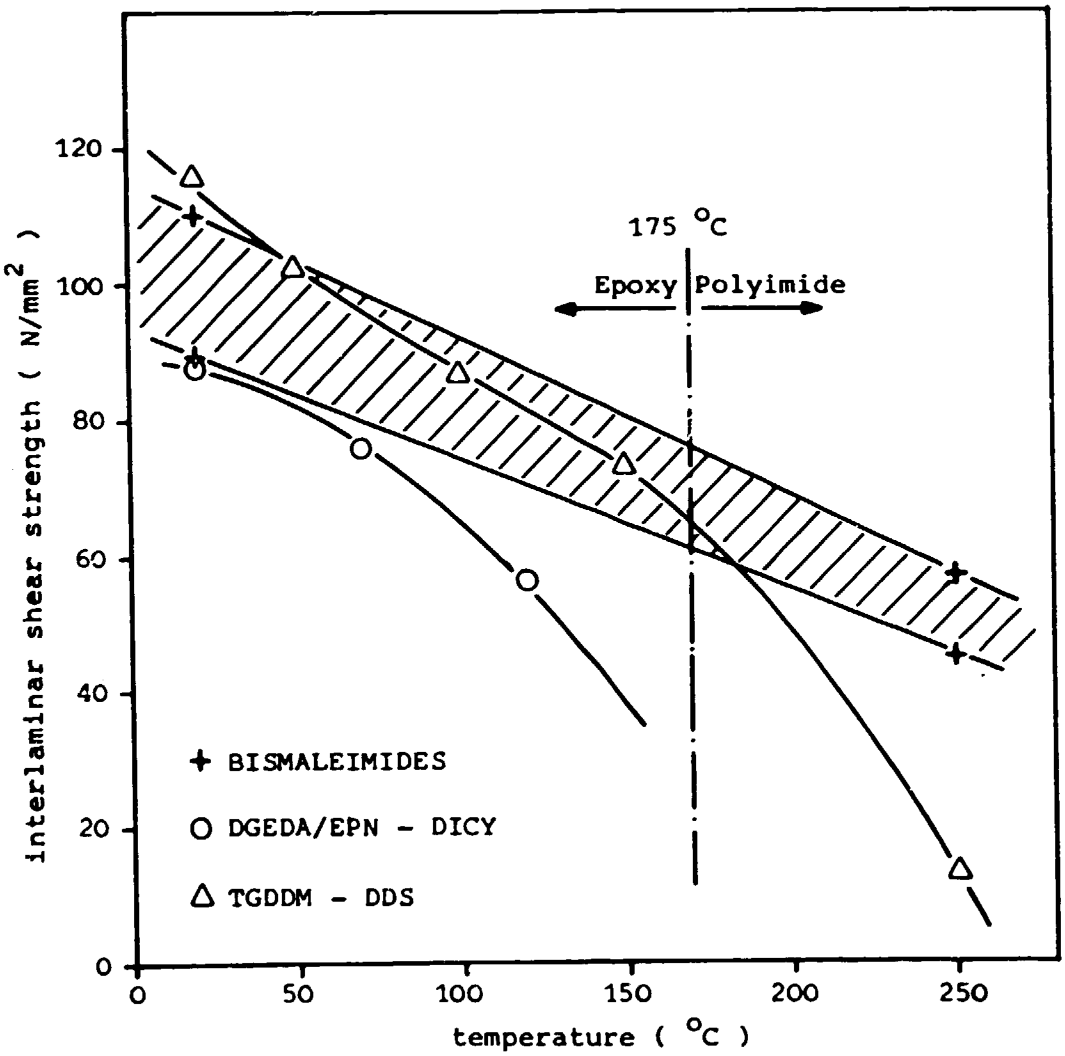


Fatigue characteristic of H 795 E - laminates



fibre lay up:$(0/0/\pm 45/0/0/\pm 45)_s$ 90

Interlaminar shear strength - temperature correlation
unidirectional Celion 6000 - laminates



Target Properties for New Technology Prepreg and Composites

I. General Properties

- A. Room temperature mechanical properties of composites superior to epoxy/graphite composites
- B. Processability of prepreg at least equivalent to epoxy/graphite
- C. 350°F service capability of composites after 75% RH exposure to equilibrium moisture content
- D. Fracture toughness of composites superior to epoxy/graphite

II. Processability/Handleability

- A. Graphite fiber/resin prepreg
  1. Self adhesion tack
  2. Nonirritating to operators (e.g., no objectionable odors/vapors)
  3. Cure with present equipment (375°F/100 psi max)
  4. Fourteen days out-time at 80°F
- B. Graphite fiber/resin composites
  1. Unrestrained postcure (max 650°F/6 hrs./air) resulting in crack-free $(+30_2, -30_2, 90_2)_S$ laminates

III. Physical/Mechanical Properties of Composites

- A. Environmental
  1. Glass transition temperature (Tg)
     - (a) Min dry = 450-550°F
     - (b) Min wet (75% RH) = 350°F
  2. Thermal spikes
     - (a) Max wt gain of 0.15% when exposed intermittently to 75% RH and 350°F spikes
- B. Flexure and Shear
  1. 0° flexure
     - (a) Min RT dry flex strength = 250 ksi
     - (b) Min 350°F dry flex strength = 200 ksi
     - (c) Min 350°F wet (75% RH) flex strength = 150 ksi
     - (d) Min RT dry modulus = 18.5 msi
  2. Four-point interlaminar shear
     - (a) Min RT dry = 14 ksi
     - (b) Min 350°F dry = 10 ksi
     - (c) Min 350°F wet (75% RH) = 7.5 ksi
  3. 90° flexure (four-point)
     - (a) Min RT dry, tensile-face strain-to-failure = 1.0%
- C. Critical strain energy release rate
  1. Min RT dry G_{Ic} = 1.0 in-lbs/in^2
- D. Edge delamination strength
  1. $(+30_2, -30_2, 90_2)_S$ edge delamination coupon
     - (a) Min RT dry, edge delamination strength = 90% ultimate