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Development and Fabrication
of
Bismaleimide-Graphite Composites

by

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ABSTRACT

The successful fabrication of high temperature resistant composites depends mainly on the processability of the resin binder matrix. For two new bismaleimide type resins the processing of graphite fabric prepregs to composites is described. One resin coded M 751 has to be processed from N-Methylpyrrolidone, the other resin evaluated is a so-called "hot melt" solvent-less system. Commercial T300/3000 Graphite fabrics were used as reinforcement.

M 751 - Resin is a press grade material and laminates are therefore moulded in high pressure conditions (400 N/cm^2). The solvent-less resin system H 795 is an autoclave grade material and can be cured at 40 N/cm^2. The cure cycles for both the press grade and the autoclave grade material (Fiberite W 134 fabric prepregs) are provided and the mechanical properties of laminates at low (23°C) and high (232°C) temperatures were measured. For comparison the neat resin flexural properties are also presented. The water absorption for the neat resins and the graphite fabric laminates after a 1000 hour period has been evaluated.

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DEVELOPMENT AND FABRICATION OF BISMALEIMIDE-GRAPHITE COMPOSITES

1. INTRODUCTION

Synthesis and application of high temperature non-flammable resins and polymers has been extensively investigated during the last decade. An advancing field of research is the application for structural composites in combination with high modulus high-strength fibres. Morphologically linear high polymers, such as Polyimides, Polybenzimidazoles, Polyphenylquinoxolines and Aramides, are difficult to process into composites, since soluble precursors cure by condensation reactions causing voids in laminates and consequently low mechanical properties are obtained. Usual solvents for prepregging are N-Methylpyrrolidone-2 (NMP), Dimethylformamide (DMF) and Dimethylacetamide (DMAC) and the like, which show an extremely good affinity to the resin and are therefore difficult to remove from the composite during postcure. Residual solvent prevents the development of good high temperature mechanical properties because of its plasticizing effect. Also the thermal-oxidative stability is reduced by residual solvents in composites.

To overcome processing disadvantages, many different synthetic approaches for new resins have been developed. The most promising concept is based on low molecular weight prepolymers which can be cured by addition type and/or polymerization type reactions that produce no volatiles during the final cure. The high temperature mechanical properties of these thermosetting polymers are extremely good, but thermal oxidative stability is lower as compared with wholly aromatic polymers mentioned above.

A popular chemical concept is based on bismaleimides which undergo thermal polymerization at temperatures between 150 - 400°C (1). The great advantage of this approach is that low molecular weight imide prepolymers endcapped with reactive maleimide rings are polymerized into highly

(1) Grundschober, F., J. Sambeth U.S. Patent 3.380.964 (1968)
Bergain A., A. Combet, P. Grosjean U.S. Patent 3.562.223 (1971)
H.D. Stenzenberger, J.Appl.Polym.Symp. 22, 77-88 (1973)
H.D. Stenzenberger, J.Appl.Polym.Symp. 31, 91-104 (1977)
G.T. Kwiatkowski, L.M.Robenson, G.L.Brode and A.W. Bedwin J. Polymer Sci.Polym.Chem.Ed. 13, 961 (1975)

cross-linked thermally stable polyimides without the evolution of byproducts. Another type of thermosetting polyimide resin was developed by TRW-system (2). The terminating nadic imide endgroups undergo pyrolytic polymerization during cure. More recently, polyimide prepolymers with acetylenic endgroups were developed (3). These resins cure by a cyclotrimerization reaction forming a totally aromatic polymer.

1.1 Maleimide type resins

The first serious interest in maleimide type resins for high temperature applications is reflected by the US-Patent 3.380.964 (4) assigned to Rhone-Poulenc, France. Bismaleimides are polymerized to dense, voidfree plastic articles by simply heating the monomers to temperatures between 180 - 260°C. The resulting materials show good high temperature mechanical properties and are attractive from the commercial point of view, because the starting materials are easily available and low-priced (5). The synthesis starts from aromatic diamino-compounds which are reacted with maleic acid anhydride forming the corresponding bismaleamic acid, which is cyclodehydrated with acetic acid anhydride (6). It has been recognised by the various users that the applicability of unmodified Bismaleimides is somewhat limited due to their brittleness. A technical resin modification with improved flow properties and somewhat better extensibility is available from Rhone-Poulenc under the trademark Kerimid 601 (Fig. 1) (7). The resin is made by reacting a bismaleimide with an aromatic diamino-compound to form a prepolymer which is meltable (80 - 105°C) and soluble. Prepregs can be fabricated via NMP-solution techniques.

(2) H.R. Lubowitz (assigned to TRW), U.S. Patent 3.528.950 (1970)

(3) Bilow N., A.L. Landis, Polymer Preprints Vol.19, No.2 p.23-28

(4) F. Grundschober, J. Sambeth, U.S. Patent 3.380.964

(5) W.J. Gilwee, R.W. Rosser, J.A. Parker
High temperature composites from Bismaleimide Resin, Proceedings of the 18th National Sampe Symposium, Los Angeles, California 1973

(6) N.D. Cole, W.F. Gruber, U.S. Patent 3.127.414 (1964)

(7) "Kerimid 601" Rhodia Technical Information Bulletin, Rhodia Inc., New York
See also M.Bergain, A.Combet, P. Grosjean U.S.Patent 3.562.223

Many resin formulations are possible by varying the molecular weight and the structure of the diamino-compounds used for the Bismaleimide synthesis. The patent literature of the last 8 - 10 years is extremely voluminous. Two types of resins which differ in their processing characteristics have been accepted by the industry, e.g. "solvent-resin-systems" and "solvent-less" resins.

1.2 Processing of maleimide type resins to composites

Generally there are two basic methods for fabricating advanced composite fibre reinforced structures; i.e. filament winding and hand lay-up of prepreg materials. The combination of the two methods is sometimes necessary to meet fabrication requirements. Filament winding is the most direct approach for laying the fibres in the desired direction. The direct winding approach in the final structure is limited to cylindrical and conical bodies. Prepregs and broad goods are best fabricated by filament winding techniques.

The first operation necessary during composite fabrication is the application of the selected resin onto the fibres. Liquid or liquefiable binders need no solvent for impregnation ("solvent-less" resin), while high molecular weight prepolymers, that fuse by forming high viscosity melts, need to be dissolved to wet the fibres uniformly (Fig. 2). Maleimide type resins are preferably dissolved in NMP (N-Methyl-pyrrolidone) forming low viscosity solutions. The wetting is easily performed by using impregnation bath techniques, and fibre placement into unidirectional orientation can be done by filament winding of the "on line" impregnated fibres. The prepregs thus obtained are consolidated to obtain precise fibre orientation and uniform tape thickness. The prepregs contain a large amount of solvent which has to be evaporated prior to composite fabrication. During the drying operation the resin on the prepreg polymerizes simultaneously, forming a "B" stage prepreg. This prepolymerization during solvent removal has to be controlled carefully to obtain the optimal flow properties necessary for laminate consolidation. The aspired advancement of the resin on the prepreg depends on the pressure used during composite moulding.

It has to be considered that for autoclave moulding at low pressure (50 - 100 psi) high flow prepregs are necessary. To obtain drape and tackiness a relatively high solvent content is also requested (10 %). Many resins like K 601 show the tendency to polymerize (advance) in solution, which significantly increases the solution viscosity. Therefore prepregs containing a high amount of solvent show a limited storage life. Furthermore entrapped solvent in the laminate leads to a thermoplastic failure mode at high temperatures. Therefore new resins with improved processing characteristics are still requested.

Recently Technochemie GmbH - Verfahrenstechnik developed two new bismaleimide type resins for composites. Up until now no graphite fabric-polybismaleimide composites have been evaluated.

1.3 Programme objectives

a. Develop basically the process of fabricating structural composites, using commercially available graphite fabric T-300 and a bismaleimide resin which is soluble in low boiling solvents.

b. Develop a B-stage bismaleimide/graphite prepreg for improved processibility.

c. Evaluate the adhesive performance of the graphite/bismaleimide composites by determining the lap shear tensile strength at 25°C and 232°C. One or more of the following resins will be utilized:

Resin A :	This resin is soluble in low boiling solvent.
Resin B :	Code M 751.
Resin C :	Hot melt bismaleimide resin.

1.4 Proposed Development (specific tasks)

1.4.1 Develop, prepare, characterize and deliver graphite/polybismaleimide composites consisting of a minimum of 18 plies of style 134, 5.5 oz/yd Thornel T-300 graphite fabric impregnated with the resin

1.4.1.1 Code M 751.

1.4.1.2 Hot melt maleimide type resin.

The resin solids content in the composites should be approximately 30 - 50 percent by weight. In addition to the specimens utilized for testing, 20 (twenty) flat specimens (6" x 6") with each resin will be delivered to NASA-AMES (Total minimum samples: 40).

1.4.2 Characterization of Prepregs

The following properties of the prepregs will be specified.

1.4.2.1 Resin Code M 751
- a) Resin content (% by weight)
- b) Fibre content (% by weight)
- c) Prepreg solvent content
- d) Area weight (g/m^2)
- e) Cured ply thickness (mm)

1.4.2.2 Hot melt maleimide type resin
- a) Resin content (% by weight)
- b) Fibre content (% by weight)
- c) Area weight (g/m^2)
- d) Cured ply thickness (mm)

1.4.3 Laminate fabrication

The curing cycles for both prepreg types will be evaluated for

1.4.3.1 Platen press moulding (pressure 20 - 50 kp/cm^2)

1.4.3.2 Autoclave moulding (pressure max. 4 kp/cm^2)

The data provided are to be time-temperature and time-pressure profiles and all other processing parameters (vacuum etc.).

1.4.4 Mechanical and Environmental Properties of Cured Laminates

The following mechanical properties for both laminate types have to be evaluated.

Test temperatures 25°C and 232°C (450°F)

  1.4.4.1 Density

  1.4.4.2 Resin content

  1.4.4.3 Flexural strength

  1.4.4.4 Flexural modulus

  1.4.4.5 Interlaminar shear strength (short beam shear test)

  1.4.4.6 Moisture absorption

1.4.5 Prepare and deliver a process specification for the fabrication of the laminates. Specification shall include as minimum : methods for preparing prepregs, moulding of laminates and curing schedules.

1.4.6 Prepare and deliver Quarterly Reports on contract work progress and a Final Report detailing results of the entire contract effort.

2. RESINS INVESTIGATED

Two resin types differing in chemical structure and processing characteristics have been investigated during the course of this work. One resin has to be processed from NMP as a solvent (Code M 751) and the second resin is a "solvent-less system", which can be used for fibre and fabric impregnation without dilution (Code H 795).

2.1 Resin Chemistry

2.1.1 Resin Code M 751 : The chemistry of Resin M 751 is outlined in Figure 3. m-Maleimidobenzoic acid chloride (m-MIC) is reacted with an aromatic diamino compound in such a way that the molar proportion of the difunctional amine to the acid halide is 1.4 : 2. The resulting resin consists of a mixture of a bismaleimide and an amino-terminated monoimide. This close to eutectic mixture melts at 120 - 140°C, and then polymerizes by a

a) Michael addition of the free amino groups to maleimide double bonds followed by a

b) vinyl polymerization of the terminating maleimide double bonds.

The Michael addition reaction leads to a macro-bismaleimide which has a molecular weight (FMW-formulated molecular weight) of 1128 according to the molar proportion of the reactants. The advantage of the new chemical concept is that the properties e.g. the crosslink density of the finally cured resin can simply be adjusted by varying the FMW. The special molar proportion between m-MIC and MDA of 1 : 0.7 has been found advantageous with respect to the mechanical properties of the neat resin at both low (25°C) and high (250°C) temperatures.

2.1.2 Resin Code H 795 : The basic chemistry for this resin is provided schematically in Figure 4. An eutectic ternary mixture of bismaleimides is reacted with a chain extender by a Michael addition type reaction (the chosen extender is not a diamino-compound). This reaction provides after prepolymerization a high viscosity melt on the prepreg.

2.2 Curing behaviour

Differential scanning calorimetry is used as a tool to characterize the curing behaviour of the resins. Figures 5 and 6 provide the DSC traces obtained for the two resin types. For comparison some characteristic temperatures of the DSC trace have been defined.

- T_B	Temperature at which the first energy release can be detected (start of polymerization, heating rate 20°C/min)
- T_{BEX}	Extrapolated polymerization start
- T_{MAX}	Peak temperature
- T_{EEX}	Temperature of polymerization termination

Also the heat of polymerization has been determined which is in correlation with the formulated molecular weight. The numerical values are given in Table 1.

Table 1 : DSC temperatures for thermosetting bismaleimide resin

Resin	T_B (°C)	T_{BEX} (°C)	T_{MAX} (°C)	T_{EEX} (°C)	ΔH J/g
M 751	181	200	265	325	60.04
H 795	175	205	245	280	214.30

According to the prepolymer molecular weight and according to the lower concentration of maleimide groups M 751 resin shows only a low heat of polymerization.

The onset temperatures (T_B) for both resins are very similar, also the peak temperatures. The temperature T_{EEX} which characterizes the temperature of polymerization termination is higher for M 751 resin. Therefore the postcuring temperature for M 751 resin needs to be higher as compared with H 795.

2.3 TGA Stability

Figures 7 and 8 provide the TGA stabilities of the two resins investigated. To compare different resins the following different temperatures were defined.

- T_{ZB} Temperature at which the first detectable weight loss is obtained
- T_{ZE} Decomposition temperature extrapolated
- $T_{10\%}$ Temperature at which 10% weight loss has occurred
- Char yield at 750°C.

Table 2 : TGA stablilities of bismaleimide resins

(Heating rate 10°C/min, N_2, powdered polymer)

Resins	T_{ZB} (°C)	T_{ZE} (°C)	$T_{10\%}$ (°C)	Char Yield (%)
M 751	280	360	417	56
H795	295	435	450	47

The TGA behaviour of the resins is quite different as indicated by the shape of the TGA curve. H 795, which is a highly cross-linked resin (FMW 400), seems to be more stable because of the high T_{ZB} and $T_{10\%}$ temperatures. The much higher char yield of M 751 resin is an indication that this resin has a higher aromaticity (FMW 1128).

2.4 Resin-solution characteristics

Since Resin M 751 is to be processed from N-Methylpyrrolidone, the varnish stability has to be known because solution viscosity and concentration will influence the prepregging conditions. Figure 9 provides the viscosity-time properties of various batches and solvent-resin combinations. From the curves obtained it is evident that the solutions are quite stable and can be stored for more than 3 weeks when cooled to 4°C.

2.5 Gelation of H 795 Resin

Gel times of the solvent-less system H 795 were determined according to ASTM D2471-68 for two typical laboratory batches (Figure 9).

Table 3 : Gel times for H 795 Resin

Temperature (^{o}C)	Gel time (minutes) Batch M 1268	Batch M 1335
160	60	70
170	31	35
180	16	22

Resin H795 is prepared by mixing the components in toluene as a diluent, followed by distilling off the solvent and degassing in vacuum. The resin, as it is obtained, contains about 6% by weight of residual toluene, which helps to reduce the viscosity of the resin for optimum fibre impregnation. It has been found that also Ether type solvents like Diethyleneglycoldiethylether (DEDEE) can be used as viscosity regulators because these solvents can easily be removed from prepregs because of their high fugacity. Therefore H 795 Resin can be processed in the presence of 30% DEDEE at around 80^{o}C, providing a prepreg which contains only a very little residual solvent. Advantageously this solvent does not degrade the high temperature mechanical properties of the cured carbon fibre laminate. The viscosity-time profile for this resin is given in Figure 10.

2.6 Neat resin density

The density of M 751 Resin was determined from a disk prepared by pressing M 751 powder in a heated platen press. Sample preparation: see paragraph 2.8 (neat resin flexural properties). Typical values are 1.30 - 1.32 g/cm^{2}. The density of H 795 Resin was determined from a cast cube which was prepared by mixing the components in a ball mill followed by melting the composition at 150^{o}C, degassing it for two minutes at 150^{o}C, and casting the hot resin into a stainless steel mould. Curing was performed at 180^{o}C for two hours, and two hours at 220^{o}C. The resulting bar was postcured for 15 hours at 240^{o}C.
The density of H 795 Resin is 1.32 g/cm^{3}.

2.7 Neat resin expansion

The expansion coefficient of the neat resin contributes to the overall properties of the carbon fibre composite. As a result of the high cure temperatures, the coefficient of thermal expansion (CTE) contributes to a major extent to in-built stresses during carbon fibre composite cure. To select optimum postcure temperatures and times it is of value to know the CTE temperature dependency of the neat resin. CTE values for M 751 and H 795 Resins were determined by use of the Thermal Mechanical Analyser (TMA)-941 of Du Pont's Thermal Analysis System. The following Table 4 summarizes the results.

Table 4 : CTE values for Bismaleimide Resins

Temperatures (^{o}C)	Expansion coefficient (cm/cm x 10^6) M 751	 H 795
30	31.7	35.6
50	39.2	40.8
75	42.8	42.6
100	47.7	47.1
125	51.5	52.4
150	56.2	54.6
175	55.0	55.1
200	58.0	55.3
225	63.9	58.7
250	84.0	73.4
x 30 - 250	52.4	51.6

x - average value

2.8 Neat resin flexural properties

The high temperature mechanical properties of carbon fibre composites depend on the mechanical performance of the resin matrix at high temperatures. For thermosetting resins the high temperature mechanical properties depend mainly on the curing and post-curing temperatures which influence the crosslink density and the glass transition temperature (Tg) of the resin.

The two resin systems of this work differ extremely in their prepolymer molecular weights. The M 751 resin has a formulated molecular weight of 1128 and therefore needs to be processed to composites from solution. The autoclave grade resin H 795, which has a formulated molecular weight of 395, forms a low viscosity fluid after being molten. As a consequence, both resins behave differently in cure and differ significantly in their mechanical properties.

The mechanical properties for both resins at room temperature are given in Table 5. The values given in Table 5 have been obtained for 10 different mouldings (M 751) or castings (H 795) respectively.

Table 5 : Room temperature mechanical properties of bismaleimide resins (postcured 15 hours at 250°C)

Resin	Density g/cm^3	Property	
		Flex. strength$^+$ N/mm^2	Flex. modulus$^+$ N/mm^2
M 751	1.31	200 - 250	4300 - 5400
H 795	1.32	90 - 110	4400 - 4500

+ - Span to depth ratio 10:1, DIN 53452 (Feb. 1952)

These preliminary results indicate that H 795 is a highly crosslinked resin with only low flexural strength, conversely M 751 resin has a much lower crosslink density and therefore a much higher flexural strength and a much higher extensibility. Additional flexural property data, especially high temperature values, became of interest because the M 751-Graphite fabric laminates degraded significantly and it had to be elucidated if these mechanical property losses are the consequence of neat resin property losses or residual prepregging solvent in the laminate. Therefore new samples of both M 751 and H 795 resins were prepared.

Sample preparation:

M 751 Tooling : heated platen press, the resin can be pressed either as a pre-formed M 751 tablet or as powder between aluminium foils.

1. Preheat mould parts or platen press to 180°C.
2. Preform the resin powder at room temperature at 300 - 400 kg/cm^2
3. Add the pre-formed M 751 tablet to the heated mould or between the platen press.
4. Heat the pre-formed M 751 tablet for 10 minutes at 180°C.
5. Apply pressure (20 - 50 kg/cm^2). (The pressure should be applied slowly to prevent squeeze-out of resin.)
6. Hold for 5 minutes at 180°C.
7. Heat to 220°C and cure for one hour.
8. Post-cure for 15 hours at 250 - 265°C.

H 795 This hot melt type Bismaleimide resin was cast between glass plates spaced by Teflon washers and cured by heating in stages from 140 to 200°C. After demoulding the plate was postcured at 250°C for 15 hours.

The mechanical properties of the new samples are provided in Table 6. The highly crosslinked PI-Resin Code H 795 showed a very good mechanical property retention up to 250°C, only a ~ 40 % reduction of the flexural strength and flexural modulus is obtained for samples that were post-cured at 250°C.

Resin M 751 showed a higher mechanical property reduction which was expected. Post-cure at 280°C improves mainly the modulus values due to crosslinking. If we compare the M 751 and H 795 mechanical properties at 250°C, it becomes apparent that both resins show nearly equal properties; they should therefore perform similarly in graphite composites at high temperatures.

Table 6 : Mechanical properties of Bismaleimide resins

Property	Test temp. °C	Unit	Value		Procedure
			Resin M 751	Resin H 795	
Density	23	g/cm^3	1.32	1.32	
Flexural strength	23	N/mm^2	211.-	97.1	DIN 53452
	250	N/mm^2	78.5-100.7	61.1	
	250^x	N/mm^2	102.1	---	
Flexural modulus	23	N/mm^2	5027.-	5028.-	DIN 53452
	250	N/mm^2	1970-2659	2977.-	
	250^x	N/mm^2	3164.5	---	
Linear expansion coefficient	23	cm/cm. 10^6/°C	31.-	37.-	TMA
	250	"	84.-	73.-	
Water absorption^{xx} after 1000 h immersion	23	%	4.27	4.99	DIN 53495 ASTM D570-63
PDT	dT/dt = 10°C/min.	°C	360.-	435.-	TGA

x - Postcured at 280°C for 15 hours

xx - see paragraph 5.6 of this report

TMA = Thermal Mechanical Analysis
TGA = Thermal Gravimetric Analyis
PDT = Polymer Decomposition Temperature

3. CARBON FIBRE PREPREGS

3.1 Prepreg fabrication technology

The typical prepreg fabrication technology used for the laboratory work consists of passing the carbon fabric through a solution of the resin and removal of excess resin by passing the impregnate between a pair of steel rollers. The wet impregnate thus obtained is dried in a circulating air oven to adjust the desired wet solvent content (volatile content). Prepregs are preferably clamped into frames to obtain good air circulation from both sides. The drying conditions used will of course provide a defined residual solvent content in the resulting prepreg.

The usual technology at the prepregger consists of passing the Graphite fabric through the impregnation batch followed by passing the coated fabric through a vertical drying tower providing a programmed drying procedure for the prepreg. The tower used for this programme at the prepreg company was 3 metres high and the maximum temperature in the tower was 170°C. The impregnation speed was 0.6 metres per minute.

3.2 Prepreg properties - test methods

3.2.1 Resin content

Both resin types (M 751 and H 795) are easily soluble in dimethylacetamide (DMAc), therefore the resins plus the residual solvent (volatile content) can be determined by extracting them with DMAc.

Specimen : A small piece of prepreg material ($\sim$ 3.5 g total weight)

Method : Weigh the prepreg material accurately to the nearest 0.01 g(w_1). Put the prepreg in a glass sintering funnel and extract the resin with 150 cc of DMAc. Suck off the solvent and wash the fibrous residue with a further 100 ml of DMAc. Wash with 150 cc of acetone and dry the fibrous residue to constant weight in a circulation air oven at 100°C.

$$\text{Resin \& Volatile content } ({}^{w}/{}_{o}) = \frac{w_1 - w_2}{w_1} \cdot 100$$

w_1 = weight of prepreg
w_2 = weight of graphite fibres

$$\text{Resin content } ({}^{w}/{}_{o}) = \frac{w_1 - w_2}{w_1} \cdot 100 - \text{Volatile content } ({}^{w}/{}_{o})$$

3.2.2 Fibre content

See paragraph 2.2.1. The fibre content is calculated in the following way:

$$\text{Fibre content } {}^{w}/{}_{o} = 100 - \frac{w_1 - w_2}{w_1} \cdot 100$$

3.2.3 Residual solvent

The weight loss of a prepreg test specimen dried at 240°C for 120 mins is defined as the residual solvent content.

Specimen : A 10 cm x 10 cm prepreg square is used for the determination.

Method : Weigh a prepreg piece approximately 10 cm x 10 cm (w_3). The prepreg is clamped on a frame and dried in a circulating air oven at 240°C for 120 minutes, then cooled to room temperature and weighed (w_4). Calculate the volatile content as follows :

$$\text{Volatile content } ({}^{w}/{}_{o}) = \frac{w_3 - w_4}{w_4} \cdot 100$$

3.2.4 Area weight

Specimen : A 20 cm x 20 cm prepreg square is used for this determination.

Method : The accurately cut 20 cm x 20 cm prepreg is weighed (w_5) and the area weight calculated in the following way :

$$\text{Area weight } (g/m^2) = w_5 \times 25$$

3.2.5 Flow characteristics

The flow properties of a prepreg are of main interest because this test provides an insight into the state of advancement of the resin and they are therefore used as a quality control. The resin flow of a prepreg material is defined as the amount of resin, expressed in weight percent ($^w/_o$), which can be pressed out from a flow test lay up at 170°C, at a pressure of 40 N/cm^2.

Specimen : The flow test lay up consists of five layers of prepreg 6.5 cm in diameter sandwiched between two glass fabrics (style US 7628, area weight 195 g/m^2)

Method : Set the temperature platen press to 170 ± 3°C
Place the flow test lay up between two aluminium foils on the press and immediately apply 40 N/cm^2 to the specimen.
After 10 minutes remove the specimen (total lay up) from the press and cool to room temperature.
Remove specimen from lay up and trim excess resin which has extruded around the edges. Calculate the resin flow in the following way.

$$\text{Flow } ^w/_o = \frac{w_6 - w_7}{w_6} \cdot 100$$

w_6 = initial weight of specimen (5 layers of prepreg)
w_7 = final weight of specimen after pressing.

3.2.6 Prepreg shelf life

Commercial graphite fibre prepregs based on epoxy resins have to be stored at low temperatures, preferably at -18°C to get adequate shelf life. Bismaleimides are solid substances at room temperature and can be stored in dry environment without change in their properties. Since they are prepregged from solutions, the resin composition of the prepreg, which consists of resin plus residual solvent, has to be considered as a solution. Therefore changes of the flow properties with time can occur and have to be tested (shelf life).

Method : Flow test samples are prepared from the prepreg material and the flow is determined as a function of time (paragraph 3.2.5). The flow test samples are altered at room temperature.

Initially after the fabrication of the prepregs at the prepregger, flow test samples were prepared and stored at room temperature. At the end of this contract, the storage life, with respect to changes in the flow properties of prepregs, will be discussed.

4. PREPREG FABRICATION

The fabrication of prepregs with both resin types was performed at the prepregger in January 1979. The resin M 751 is processed from a NMP-toluene solution in the usual way. Resin H 795 was initially designed to be used as a hot melt resin to be processed without the use of a solvent. Therefore processing was planned to be performed with a 20 inch wide graphite cloth (Fiberite F 134 - T 300-3000). Because of the technical problems that arose at the prepregger in establishing an impregnation bath heatable to around 120°C, it was tried in the laboratory to use special types of solvents for prepregging. As a result of an extended laboratory investigation, it was found that resin H 795 can be processed to prepregs from various ether type solvents at low temperatures (around 30 - 40°C).

It is well stated in the literature that solvents like NMP, DMAc and DMF have disadvantages when they are used as prepregging solvents. Residual solvent, which remains in the laminate after moulding, degrades the high temperature mechanical properties. Conversely, it was found that ether-type solvents can be used for prepregging and advantageously, these solvents do not degrade the high temperature mechanical properties of the laminates even when the prepreg contains 3 - 4% of residual solvent. Therefore H 795 resin was processed from a dioxane-diethyleneglycol monoethyl ether mixture. The solution is stable at 35°C, cooling to lower temperatures will crystallize parts of the resin.

4.1 Resin solution preparation

M 751 resin solution:

A resin solution consisting of 16 kg of resin M 751, 16 kg of NMP and 8 kg of toluene, was prepared by heating the components in a glass enamelled vessel to 90°C and constant stirring. The solution was further diluted at the prepreg company, providing a 35 weight percent solution (a solution viscosity of 45 mm/sec was obtained).

H 795 resin solution:

A resin solution consisting of 17.45 kg of resin H 795, 5.25 kg of diethyleneglycolmonoethylether and 12.25 kg of dioxane was prepared by heating the components at a temperature of 100°C for 2 hours. The solution had a viscosity of 24.7 mm/sec.

4.2 Prepreg fabrication

As indicated in paragraph 3.1, the prepregs have been fabricated by use of standard prepregging equipment using dip coating techniques for wetting the fabric, followed by drying in a vertical 3 m drying tower with a maximum temperature of 170°C. The prepregging speed was 0.6m/min. M 751 resin solution was further diluted at the prepregger to provide a 30 - 32% by weight solution. Since the volatile content of the prepreg was too high after passing the drying tower, the material was allowed to pass the drying tower twice (speed 0.6 m/min.).

H 795 prepreg was fabricated in the same manner. The impregnation bath was heated to 40°C to prevent resin from crystallization. H 795 prepreg was prepared from a 20 inch wide Fiberite Style 134 (5.5 oz/yd^2) graphite fabric material.

4.3 Prepreg characterization

The prepregs delivered by the prepregger were characterized according to the test methods given in paragraph 3. Table 7 summarizes the properties obtained.

Table 7 : Prepreg properties of bismaleimide resins

Property		Resin	
		M 751	H 795
Resin content	($^w/_o$)	33.46	42.38
Fibre content	($^w/_o$)	57.29	49.36
Volatile content	($^w/_o$)	9.25	8.26
Area weight	(g/m^2)	343.08	399.24
Flow 170°C, 40 N/cm^2	($^w/_o$)	19.83	32.87
Shelf life		6 months	6 months

5. LAMINATE FABRICATION

Two typical laminate fabrication procedures were used to produce flat 6" x 6" test panels from the prepreg materials described in paragraph 4.

5.1 Cure cycle development

The prepregs of the M 751 resin are to be processed by a high pressure platen press method as a consequence of the resin flow properties. The prepreg of the "hot melt" resin H 795 is designed to be processable in an autoclave at low pressure conditions.

5.1.1 Platen press moulding of M 751-Fiberite W 134 prepregs

Preliminary tests to mould small test coupons from M 751-Fiberite W 134 prepregs showed that the preferred temperature to cure under pressure (350 - 400 N/cm^2) is between 170-180°C. It was also found that the cure time under pressure need not exceed two hours. A laminate (sixe 50 x 50 cm) consisting of 18 layers of prepreg (properties - see paragraph 4.3, Table 7) having a residual solvent content of 9.25% by weight was moulded in a heated platen press by using the following cure cycle:

- Preheat platen press to 170°C.
- Insert the prepreg lay up between Al-foils into the preheated press.
- Kiss contact for 30 seconds.
- Apply pressure of 350-400 N/cm^2.
- Cure 2 hours at 170°C and at a pressure of 350-400 N/cm^2.
- Cool to room temperature and demould laminate.

It is well stated in the literature that it is very difficult to strip off or dry off residual prepregging solvent from the cured laminate. It is also well known that residual solvent acts as a plasticizer and degrades the high temperature mechanical properties. Nevertheless, it was tried to postcure the moulded laminate at a temperature of 250°C in a circulating air oven but the laminate delaminated catastrophically after 15 hours. So it again became apparent that residual solvent is the reason for

this behaviour. Surprisingly this delamination did not occur when the laminates were postcured at 225°C.
To prevent delaminations during postcure, the residual solvent content in the prepregs, as delivered by the prepreg company, had to be reduced. Because of the resins' curing behaviour a drying temperature had to be chosen, which provided the necessary solvent content reduction without advancing the resin too far. It was found that a drying temperature of 150°C was optimal. Figure 12 provides the residual solvent content of the prepreg as a function of the drying time. It is apparent that after 10 minutes the solvent content could be reduced to around 3.3 to 3.4% by weight. Also these prepregs did show enough flow during moulding under pressure to provide high quality laminates free of voids. The same cure cycle as given above was used to mould laminates from dried prepregs having a controlled solvent content of less than 3.5% by weight.

Laminates obtained again were postcured at 250°C for 15 hours without delamination. The weight loss for 6" x 6" laminates was 2.1 - 2.2% by weight. Additional postcure at 265°C resulted in a loss on weight of 0.48 - 0.60%. Postcure at 280°C showed visual degradation on the laminates' surface, whereas the mechanical properties at room temperature were not degraded. It has to be noted that neat resin samples which were moulded from the solvent-less resin powder could be postcured at 280°C for 15 hours without any visual and mechanical property change (see Table 6, this report). Therefore, again, even a small amount of residual solvent (NMP) of about 1% led to a laminate degradation during postcure at 280°C (delaminations).

To further improve the mechanical properties at high temperatures of M 751 laminates, it was tried to further decrease the residual solvent content in the prepregs by increasing the drying time. It was mentioned above that this led to a loss of the resin flow due to prepolymerization. Consequently the following cure cycle was found to the best for the prepreg material specified in Table 7.

- Dry prepregs at 150^{o}C in a circulating air oven for 5 minutes to reduce the residual solvent content to less than 3.5% by weight.
- Preheat platen press to 170^{o}C.
- Insert prepreg lay-up between Al-films into the press - kiss contact for 30 seconds.
- Apply pressure of 350-400 N/cm^2.
- Cure 2 hours at 170^{o}C and 350-400 N/cm^2.
- Cool to room temperature and demould.
- Postcure 15 hours at 250^{o}C (weight loss during postcure is 2.1 - 2.2%).
- Post cure 15 hours at 265^{o}C (weight loss $<$ 0.5%)

5.1.2 Autoclave moulding

The usual technology to mould large spherical parts is based on low pressure autoclave procedures. Prepregs need to have high flow properties to obtain adequate laminate consolidation. Bleed fabrics are used to adjust the fibre content to around 50-60% by volume and the cure is performed in a high temperature nylon vacuum bag pressure membrane.

The prepregs of resin H 795, as delivered by the prepregger, contained 8.26% by weight of residual solvent (see table 7, paragraph 4.3). These prepregs were tacky enough and drapeable, and showed good handling properties. They were cured by use of the cure cycle given in Figure 13. (This cure cycle has been evaluated for unidirectional prepregs with the same resin matrix). The maximum cure temperature in the autoclave was 210^{o}C. Of main importance for the high temperature mechanical properties was the postcuring cycle. The first laminate was postcured at 250^{o}C in a circulating air oven for 15 hours. The mechanical properties measured before and after postcure showed a significant reduction of the flexural and the shear strength properties after postcure. (Weight loss during postcure 2.13%). Again it was anticipated that this degradation is the consequence of the residual solvent in the prepreg.

A drying procedure (Figure 14) was found which allowed the reduction of the residual solvent content to less than 3.5% and simultaneously did not alter the flow properties too much. In Table 8, a comparison is given of the prepreg properties before and after drying.

Table 8 : Properties of H795-Fiberite W 134 prepregs

Property	Prepreg A	Prepreg B
Resin content	42.38%	44.63%
Fibre content	49.36%	51.97%
Volatile content	8.26%	3.40%
Area weight	399.24 g/m^2	376.8 g/m^2
Flow 170°C, 40 N/cm^2	32.87%	19.07%
Shelf like	---	6 months

A. as delivered by the prepregger

B. after drying for 15 minutes in cirulating air oven at 120°C.

The dried prepregs of course lost their tackiness during solvent removal and became boardy and had to be warmed up to 50°C to be plied. The same autoclave cure cycle as given in Figure 13 could be used for moulding. Postcuring at 250°C was now possible without significant reduction of the mechanical strength properties. Consequently the H 795 prepregs could be cured by using the following cycle (see also figure 13) :

- Dry prepregs (H 795 - Table 7) in a circulating air oven at 120°C for 15 minutes to adjust a solvent content of less than 3.5% by weight.
- Prepare a prepreg lay up consisting of 18 plies of dried prepregs, one Teflon peel ply on top and bottom and 2 layers of bleed fabric on top and bottom.

  Peel ply material : Release ease 234 TEP from Airtech
  International Inc., San Bernardo, Ca.

Bleeder material : Bleeder lease C, from Airtech International Inc., San Bernardo, Ca.

- Dam edges of lay up and use an Al-caul plate, seal lay up in the usual way.
- Cure lay up by following the time-temperature and time-pressure profile given in Figure 13.
- Postcure laminates at 250°C for 15 hours.

Notice : The two prepreg materials (see Table 7, p. 20, this report) were delivered by the prepregger with a high residual solvent content. It was the first time that these two resins types were fabricated to prepregs by use of a commercial prepregging equipment. It was stated by the prepregger that of course the solvent content can be adjusted to a lower level by using either a 6 m drying tower or a lower drying speed.

6. MECHANICAL AND ENVIRONMENTAL PROPERTIES OF CURED GRAPHITE LAMINATES

The cure cycles as given in Chapter 5 were used to mould flat 20" x 20" panels. H 795 prepregs were processed by use of a production-like autoclave.

6.1 Densities

Were determined according to DIN 53479 at room temperature. Since resin and fibres have different densities, the density of the composite depends on the fibre volume fraction. The values obtained for the PI-composites are provided in Table 9.

6.2 Resin content (respectively fibre content)

The resin content for both laminate types was determined by a concentrated sulphuric acid digestion method :

> ~ 1 g of composite material is digested with concentrated sulphuric acid for 8 hours at 200 - 210°C. After cooling to room temperature the fibrous residue is filtered (glass sinter funnel), washed with water and finally with acetone followed by drying to constant weight at 150°C.

The values obtained for the PI-composites are provided in Table 9.

6.3 and 6.4

The flexural properties of the PI-composites were determined at a span to depth ratio of 32:1, all samples had a width of 10 mm (support radius 5 mm, loading rod radius 12.5 mm, crosshead speed 4 mm/minute).

6.5 Interlaminar shear strength :

Sample width 10 mm, span to depth ratio 5:1, support radius 3 mm, loading rod radius 3 mm, crosshead speed 0.5 mm/min.

All the properties for the fabric-type laminates with both resins are provided in Table 9.

Table 9 : Laminate properties

Property to be tested	Unit	Test temp. (°C)	Resin system M 751	 H 795
Fibre content	% by volume	23	57.9	51.-
Density	g/cm^3	23	1.50	1.52
Flexural strength	N/mm^2	23	780-905	615.-
		100	439.-	---
		150	249.-	---
		200	89.-	---
		232	72.-	550.-
Flexural modulus	KN/mm^2	23	76.78	76.35
		100	45.20	---
		150	44.28	---
		200	24.63	---
		232	16.53	78.73
Interlaminar shear strength	N/mm^2	23	60.61	36.70
		232	2.45	30.00

Discussion : The mechanical properties (flexural properties) of M 751 graphite laminates show the expected values at room temperature. A significant degradation of these good values is apparent at 150°C. Since the neat resin only shows a 50% property loss up to 232°C, when postcured at 250 - 280°C, this drastic property loss is the consequence of residual solvent. It has to be remembered that the prepregs used for moulding contained around 3.5% of N-Methylpyrrolidone which presumably cannot be dried off quantitatively during the cure and postcure cycle.

The H 795 hot melt resin laminates show only a 10% property loss up to 232°C, so it is again apparent that hot melt resins, when used in composites, offer the advantage of good high temperature mechanical properties.

5.6 Moisture (water) absorption

To get an insight into the moisture (water) absorption of bismaleimide type composites, samples of both laminates were immersed in distilled water at room temperature (DIN 53495, ASTM D 570, immersion temperature 23°C) and the water take-up was measured over a period of 1000 hours. Simultaneously equivalent values were measured for neat resin samples.

Sample dimensions :

M 751 - Resin (cured)	40 x 10 x 2.0 mm
H 795 - Resin (cured)	53.3 x 10 x 4.0 mm
M 751 - W 134 - Composite	150 x 10 x 3.64 mm
H 795 - W 134 - Composite	150 x 10 x 4.26 mm

The exact values are tabulated in Table 10 and presented in Figure 13.

Table 10 : Water absorption of Bismaleimide resins and graphite fabric composites

Immersion time (hours)	Water absorption (%)			
	H 795	M 751	H 795-W 134	M 751-W 134
24	1.07	1.06	1.71	0.17
168	2.87	2.64	2.29	0.43
336	3.76	3.37	2.36	0.59
648	4.60	4.02	2.44	0.80
1032	4.99	4.27	2.44	0.96

Resin H 795 has a water absorption of around 5% after 1000 hours immersion in water. Since the composite fabricated with this resin contains 50% by volume of resin, the laminate absorbs around 2.5%. The absorption of both the neat resin and the composite is almost complete after 1000 hours. The very rapid water pick-up of the composite during the first 150-hour period could be the result of micro-cracks.

Resin M 751 absorbs around 4.3% by weight after 1000 hours. The composite with this resin only shows a slow water take-up. Equilibrium conditions are not reached after 1000 hours of water immersion.

7. DELIVERY OF FLAT TEST SAMPLES TO NASA-AMES

20 samples of H 795-Fiberite W 134 laminates and 20 samples of M 751-Fiberite W 134 laminates prepared according to the procedures described in this report were delivered to NASA-Ames Research Center - Chemical Research Projects Office, on May 21st, 1979.

8. RECOMMENDATIONS FOR FUTURE DEVELOPMENTS

It has been demonstrated that the resin M 751 is a high performance material as far as the neat resin mechanical properties are concerned. Processing to composites via prepregs which were fabricated by N-methylpyrrolidone solution technics provide prepregs which show a high residual solvent content (3.5%), therefore residual solvent is also contained in the cured laminates causing thermoplastic failure at high temperature (232°C) under load. Therefore a technology to fabricate prepregs that contain no or only traces of prepregging solvent need to be developed.

Some preliminary tests were performed with the aim of obtaining graphite prepregs with low residual solvent content. A resin was synthesised by use of the M 751-chemistry concept. The only modification was that the molar ratio between m-MIC and MDA was changed from 1:0.7 to 1:0.6. This resin was processed to prepregs (Fiberite W 134) by using the usual dip coating technology. A low concentration solution was used (28% by weight) and impregnation was made twice to obtain the desired resin content. Between the two impregnation steps the prepregs were dried (15' at 140°C), thus we obtained prepregs that had only 1.7% of residual NMP-solvent. A laminate was pressed by use of the standard curing cycle for M 751 prepregs (see page 21, paragraph 5.1.1) and postcured at 265°C. This laminate showed a 50% mechanical property retention up to 232°C.

As a consequence of the experiment we recommend the development of a graphite prepreg material with low residual solvent by using a modified prepregging procedure and a slightly modified M 751-resin system.

August 23rd, 1979
Stz/gy

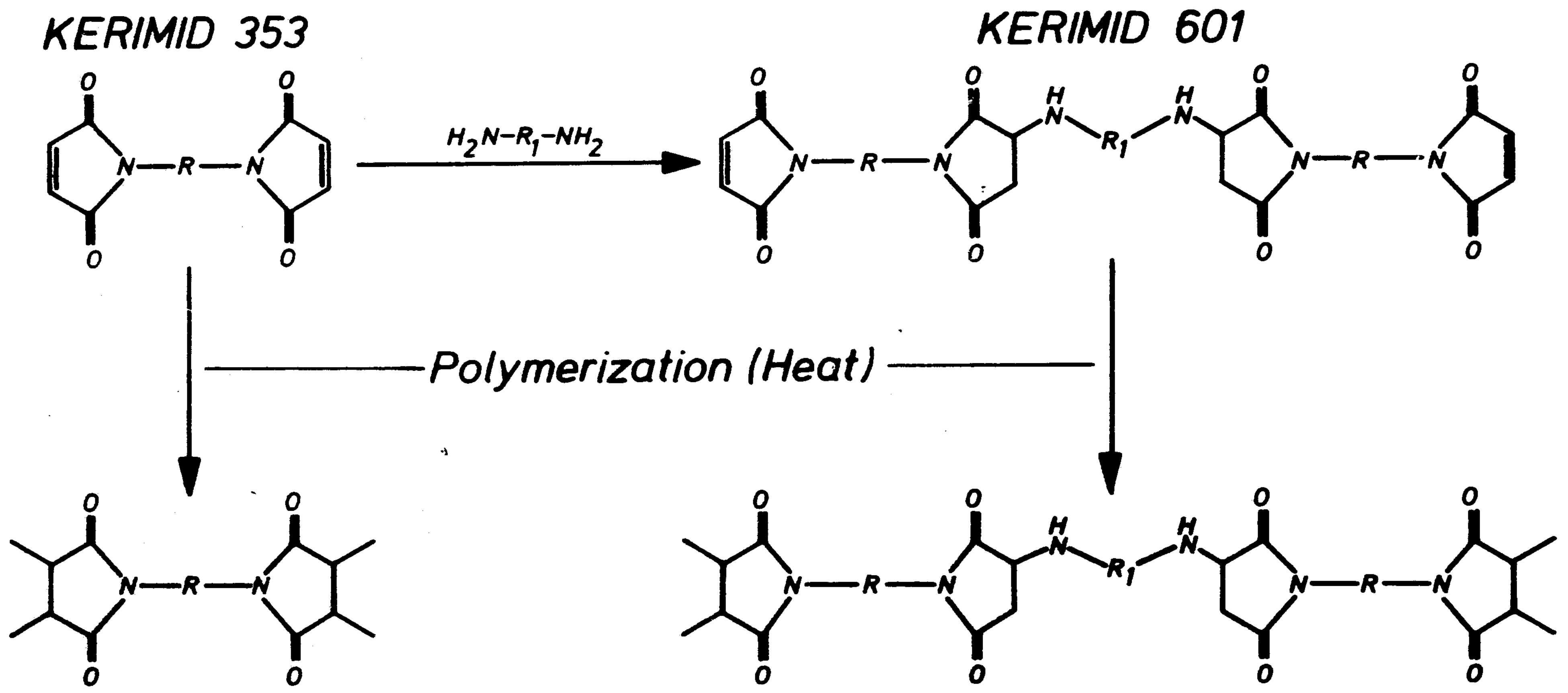

Figure 1: Maleimide resin chemistry

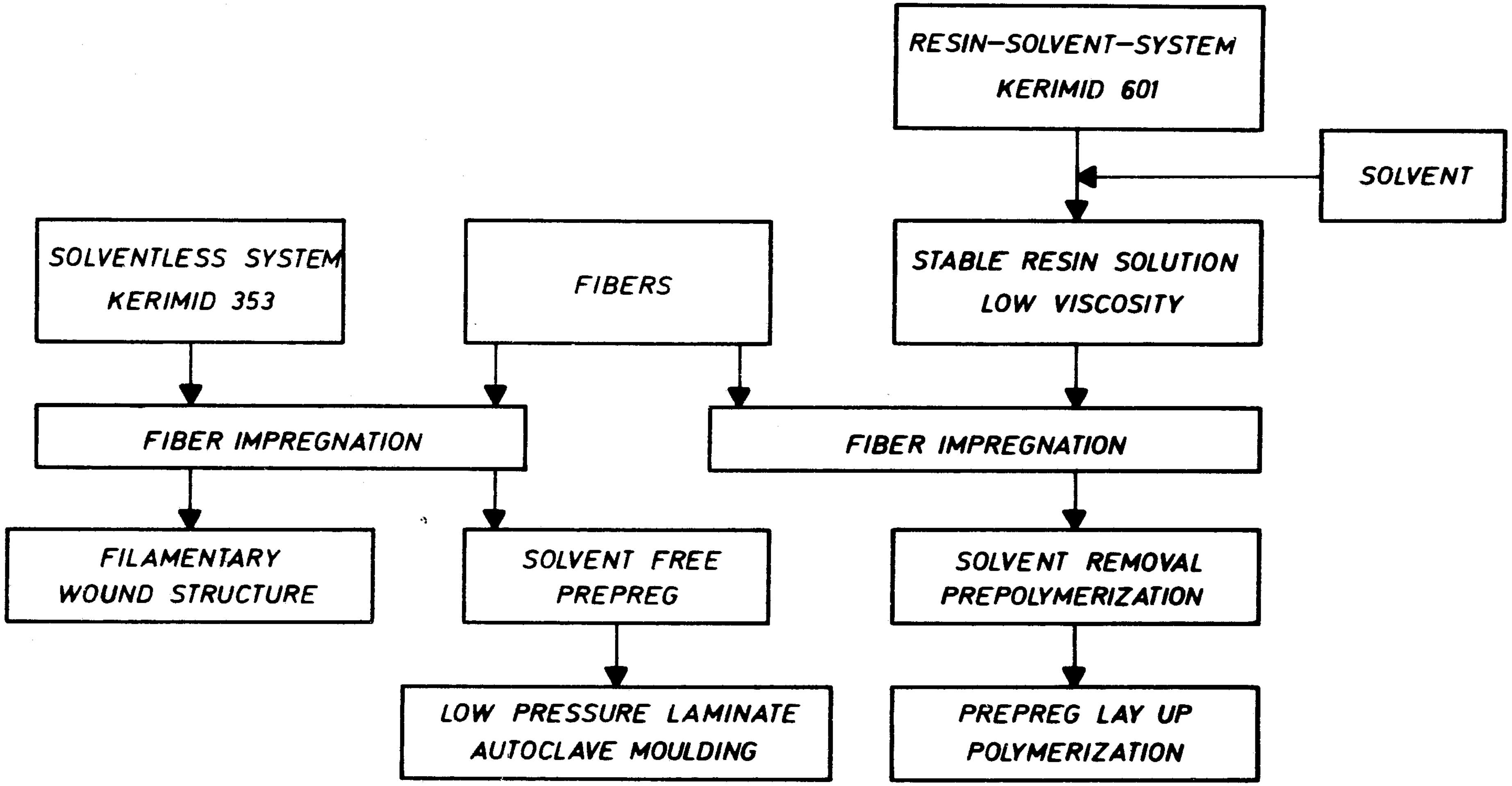

Figure 2: Processing of bismaleimide resins

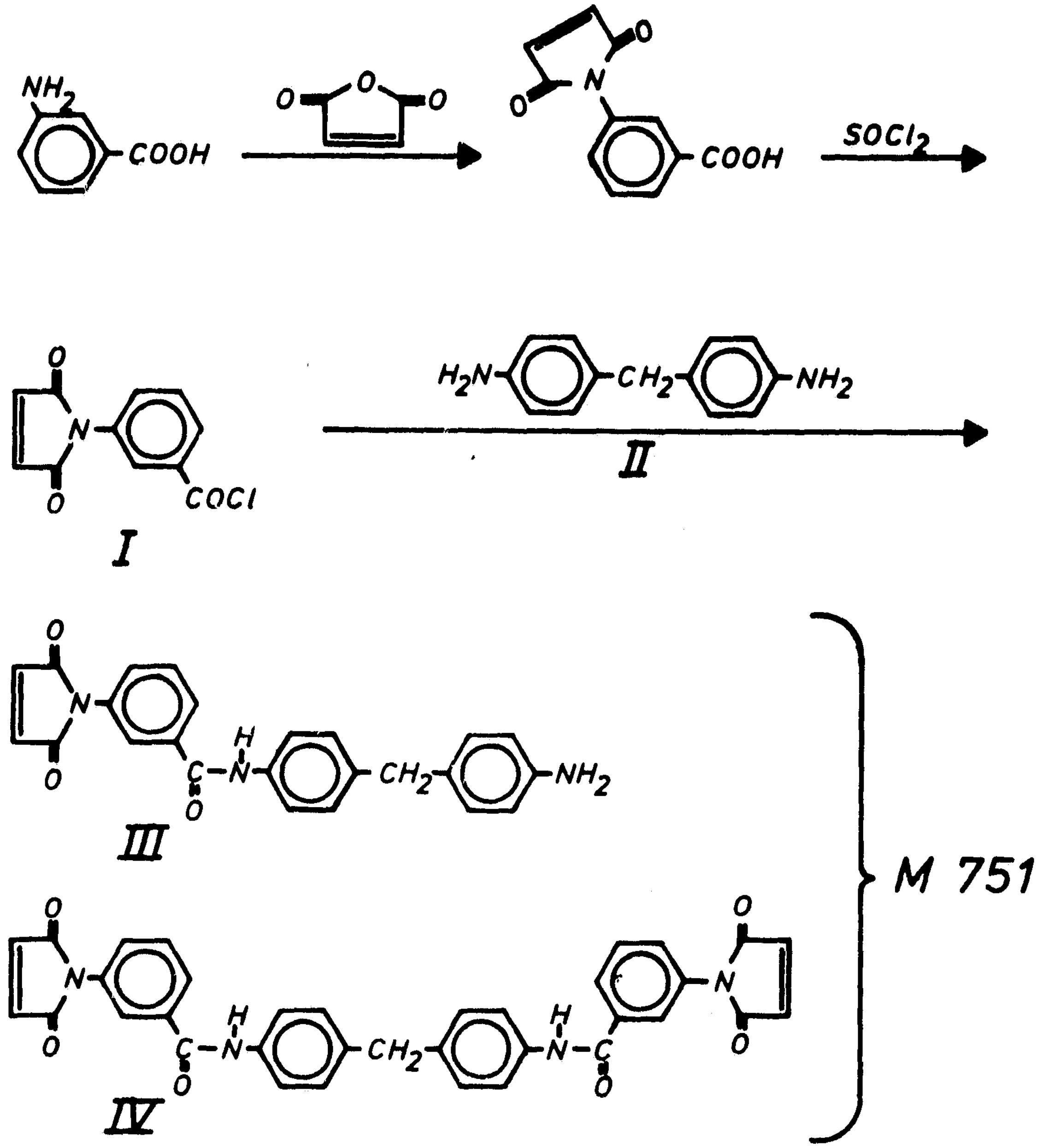

Figure 3: Chemistry of M 751 - resin

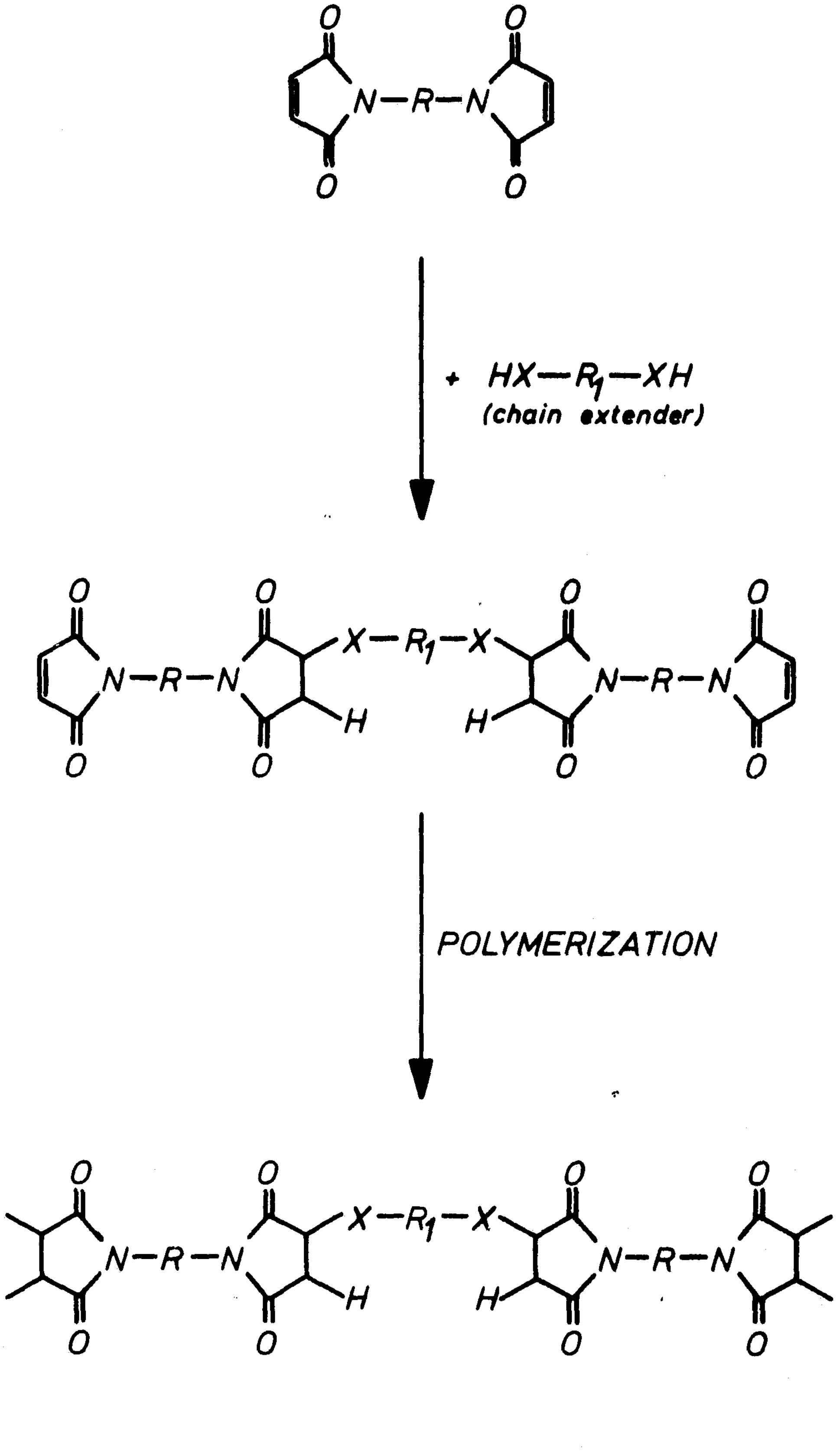

Figure 4: Chemistry of H 795-resin

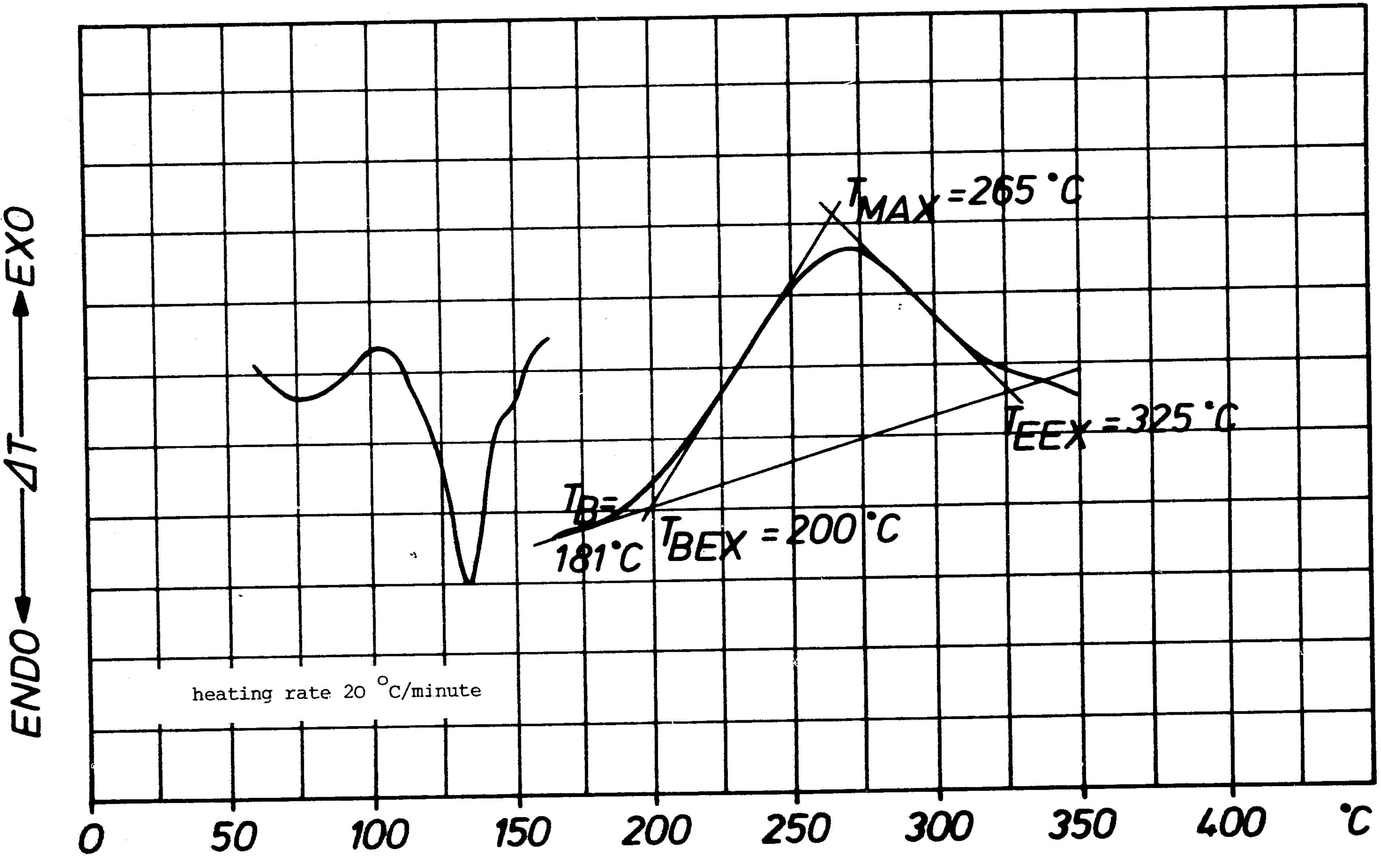

Figure 5: Melting and polymerization behaviour of bismaleimide resin M 751

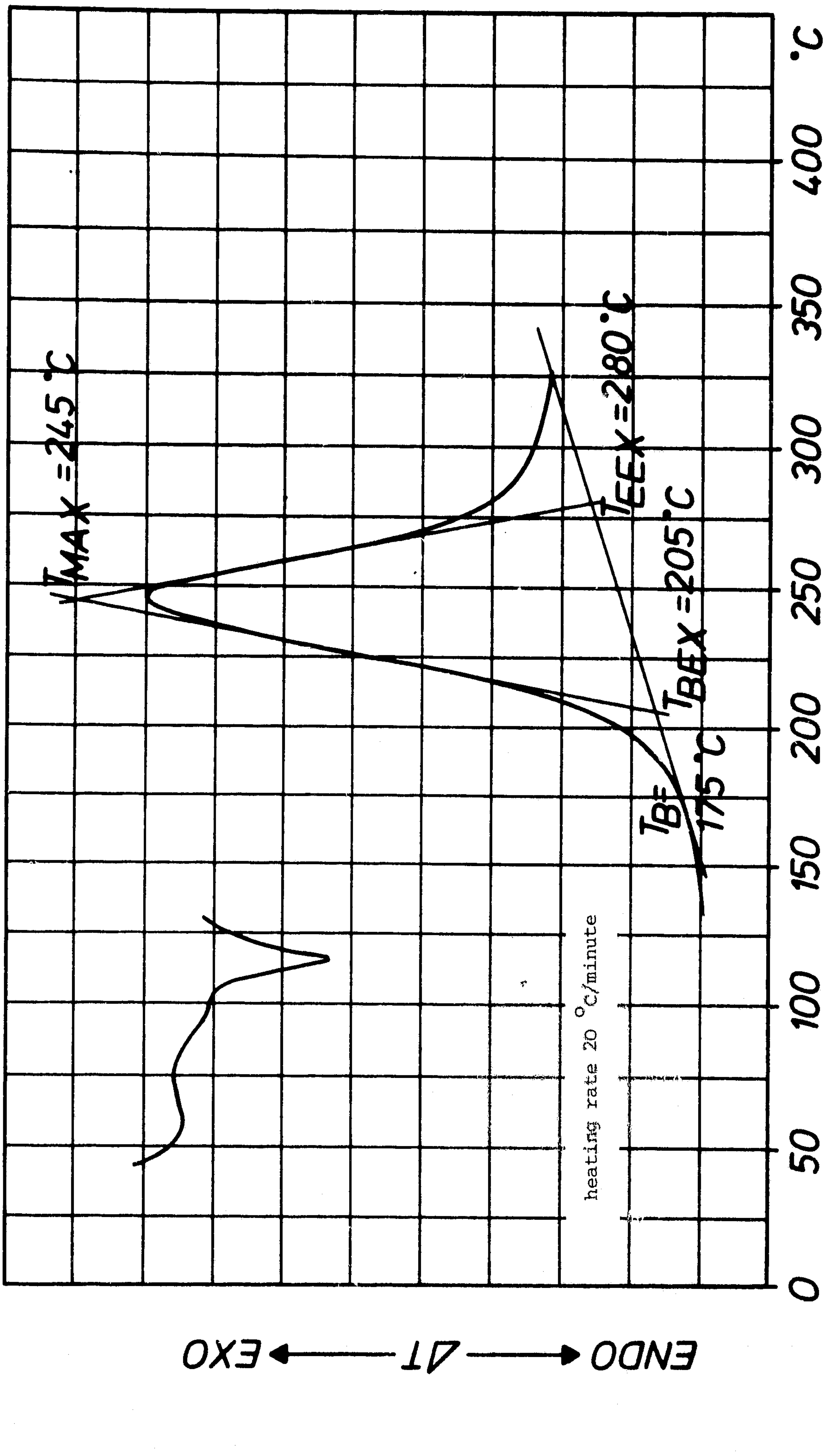

Figure 6: Melting and polymerization behaviour of hot melt bismaleimide resin H 795

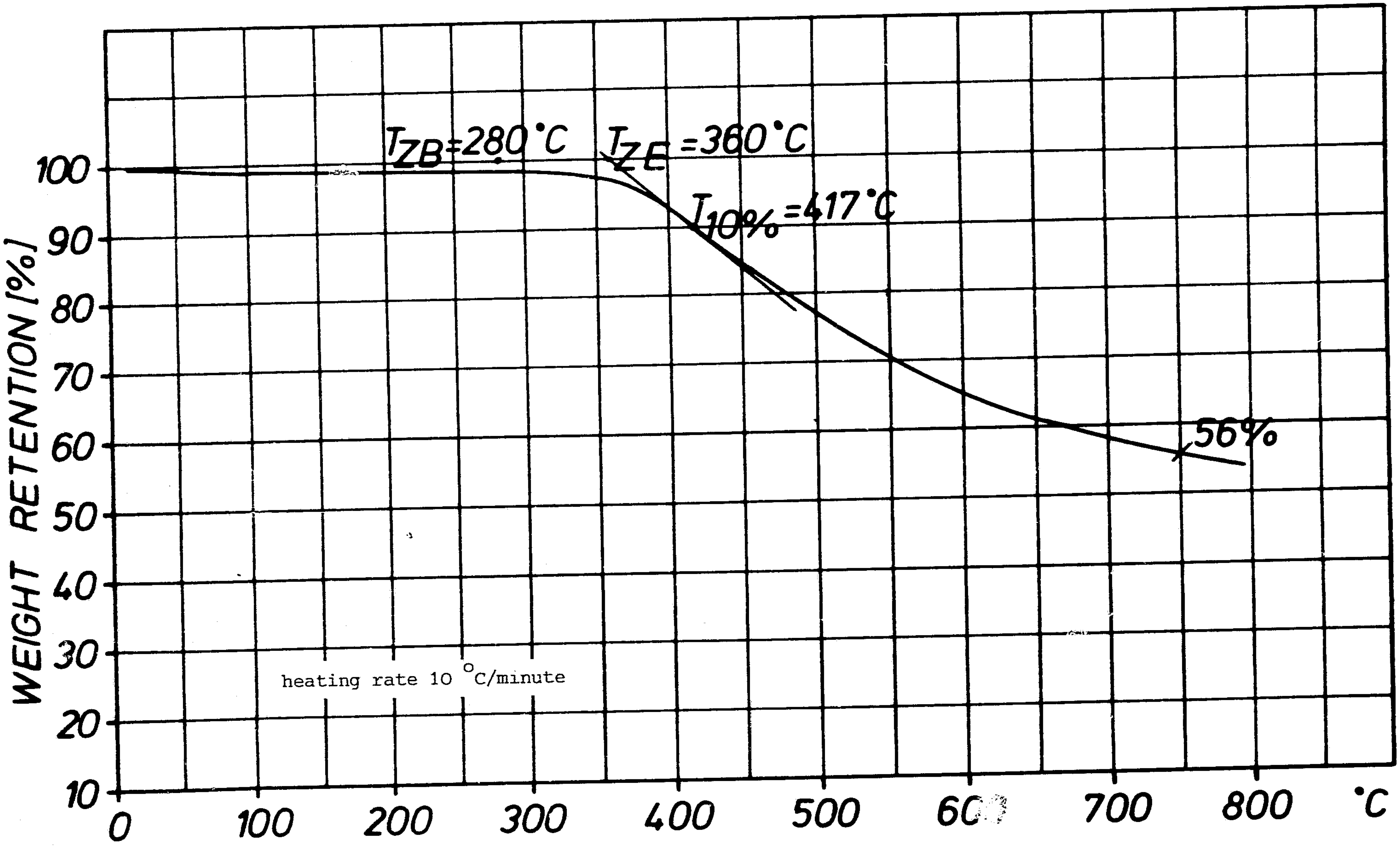

Figure 7: TGA-Thermogram of bismaleimide resin M 751

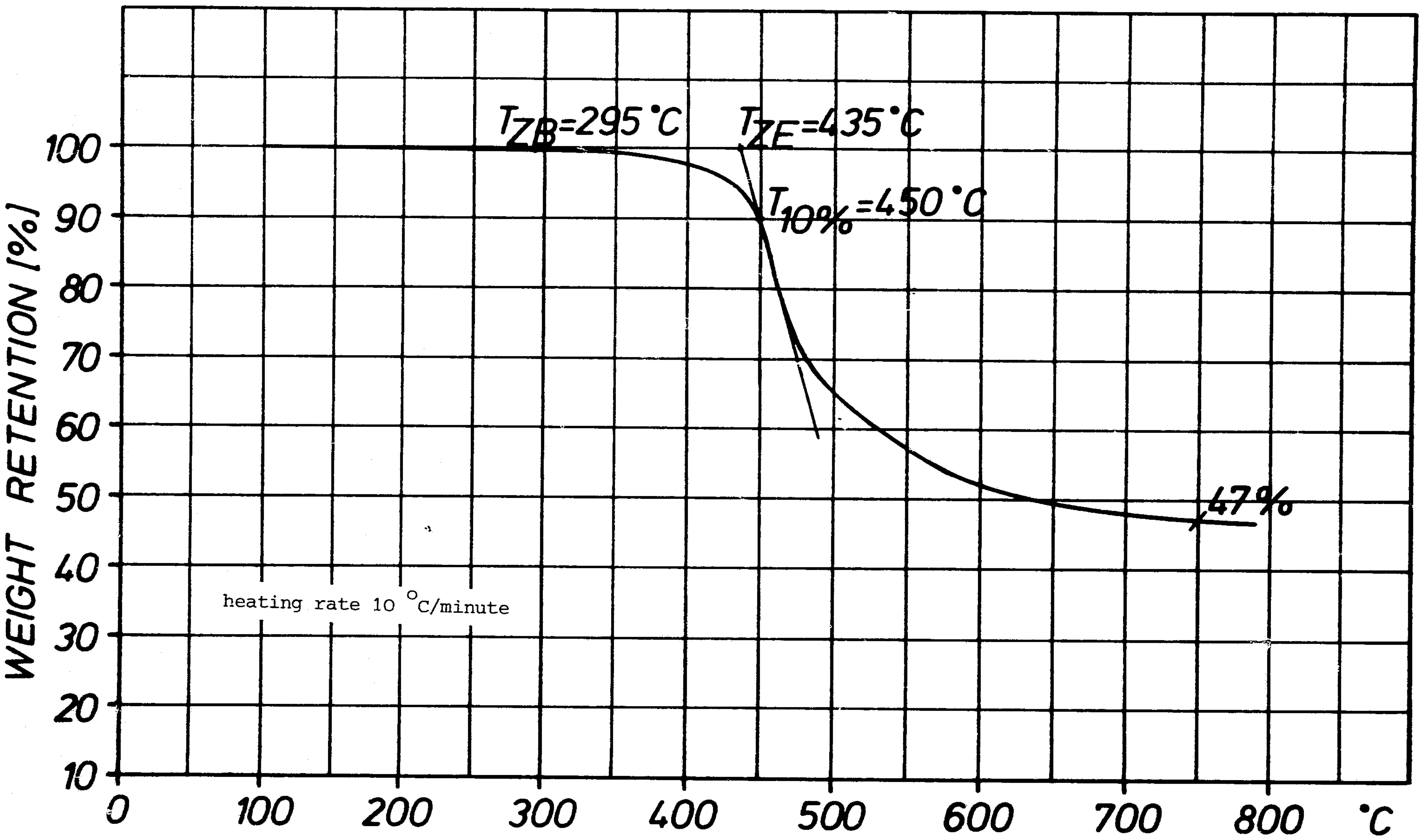

Figure 8: TGA-Thermogram of hot melt bismaleimide resin H 795

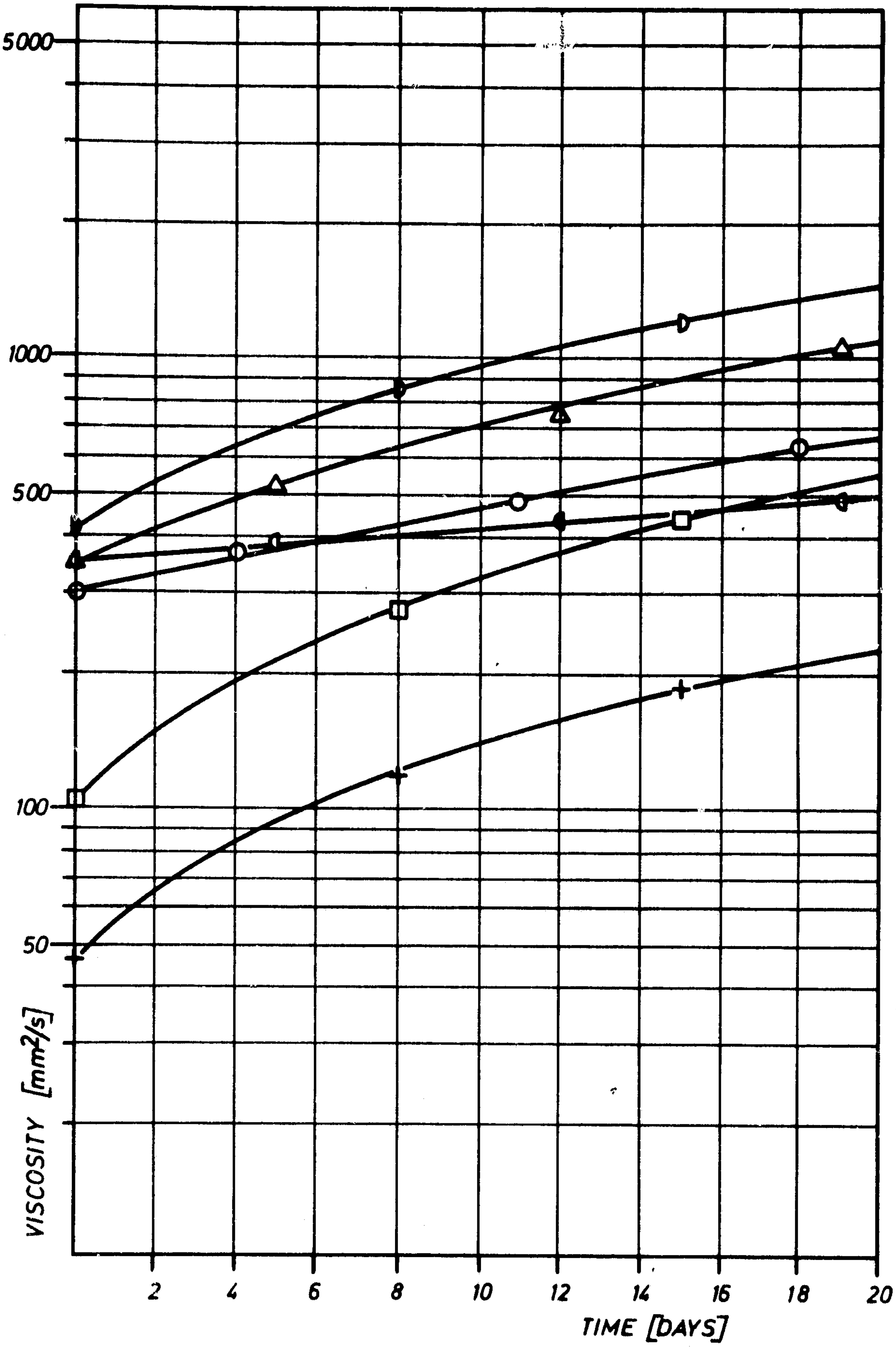

Figure 9: VISCOSITY-TIME profiles of M 751-resin solutions

○ T4 in NMP 50%ig	□ T8 in DMAc 50%ig
+ T8 in DMF 50%ig	D T8 in NMP 50%ig
△ T9 in NMP 47%ig, aging at 20°C	
◖ T9 in NMP 47%ig, aging at 4°C	

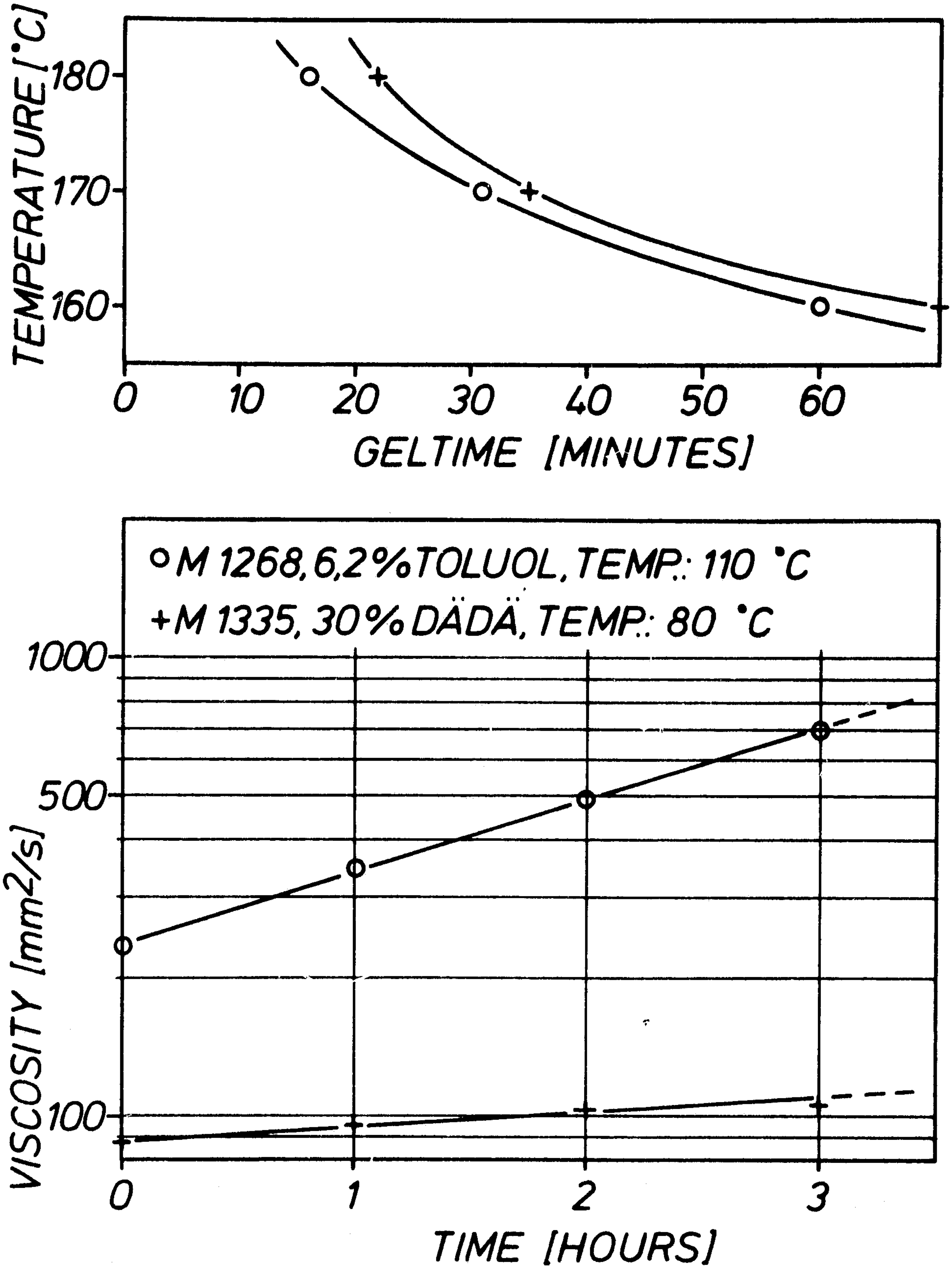

Figure 10: Viscosity and gelation behaviour of resin H 795

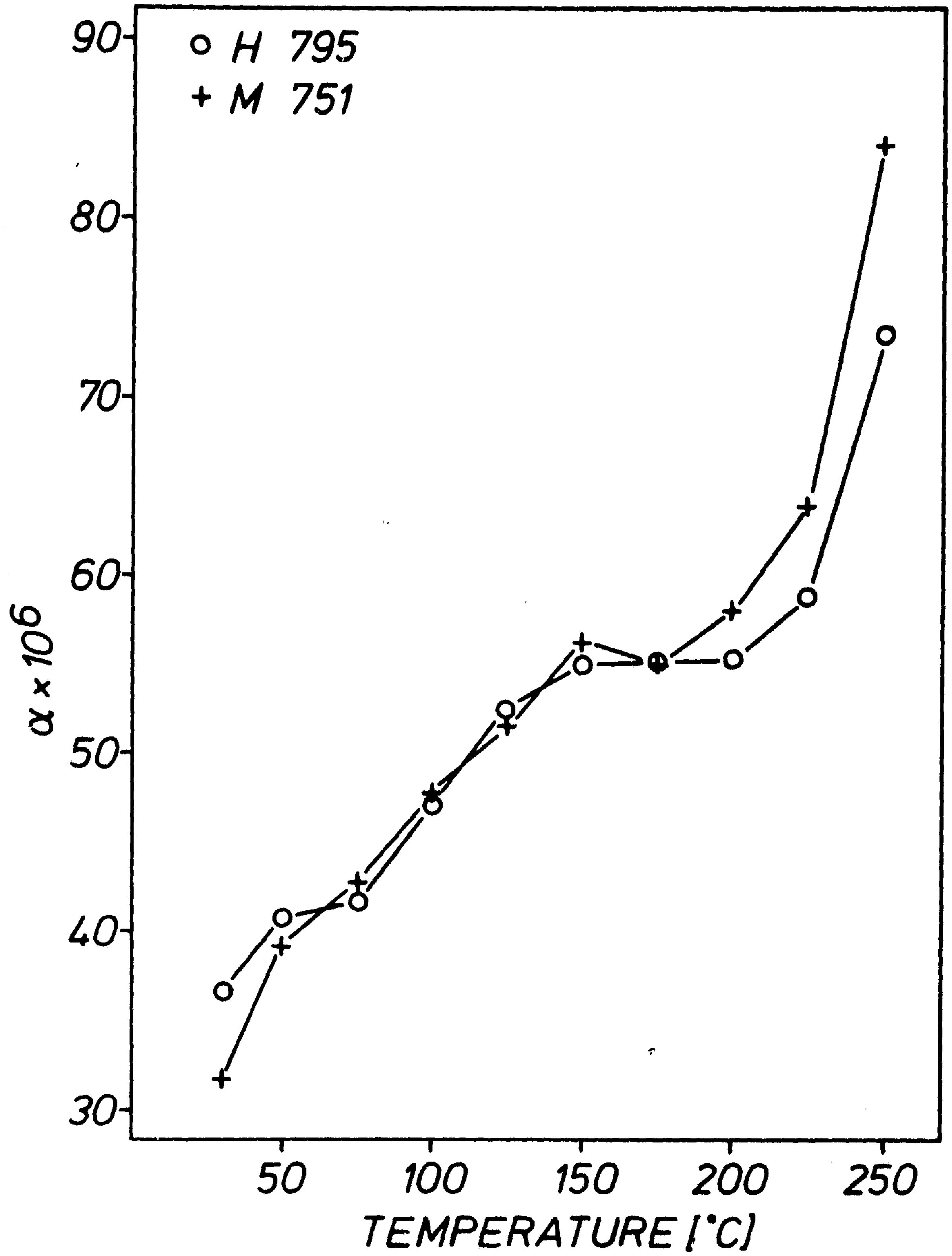

Figure 11: Expansion characteristics of bismaleimide resins

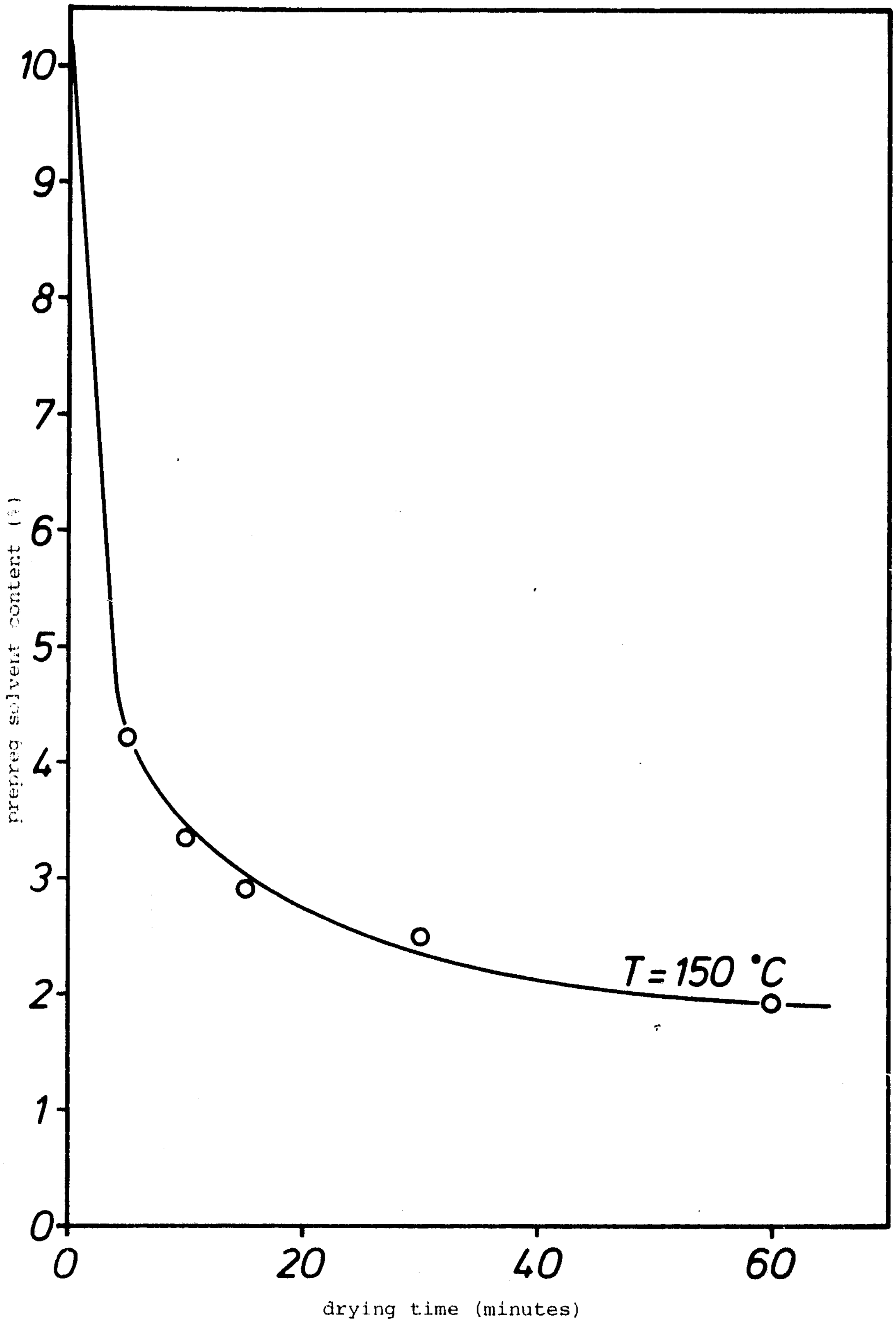

Figure 12: Residual solvent in prepreg M 751 - Fiberite W 134 as a function of drying time (temperature 150 °C, circulating air oven)

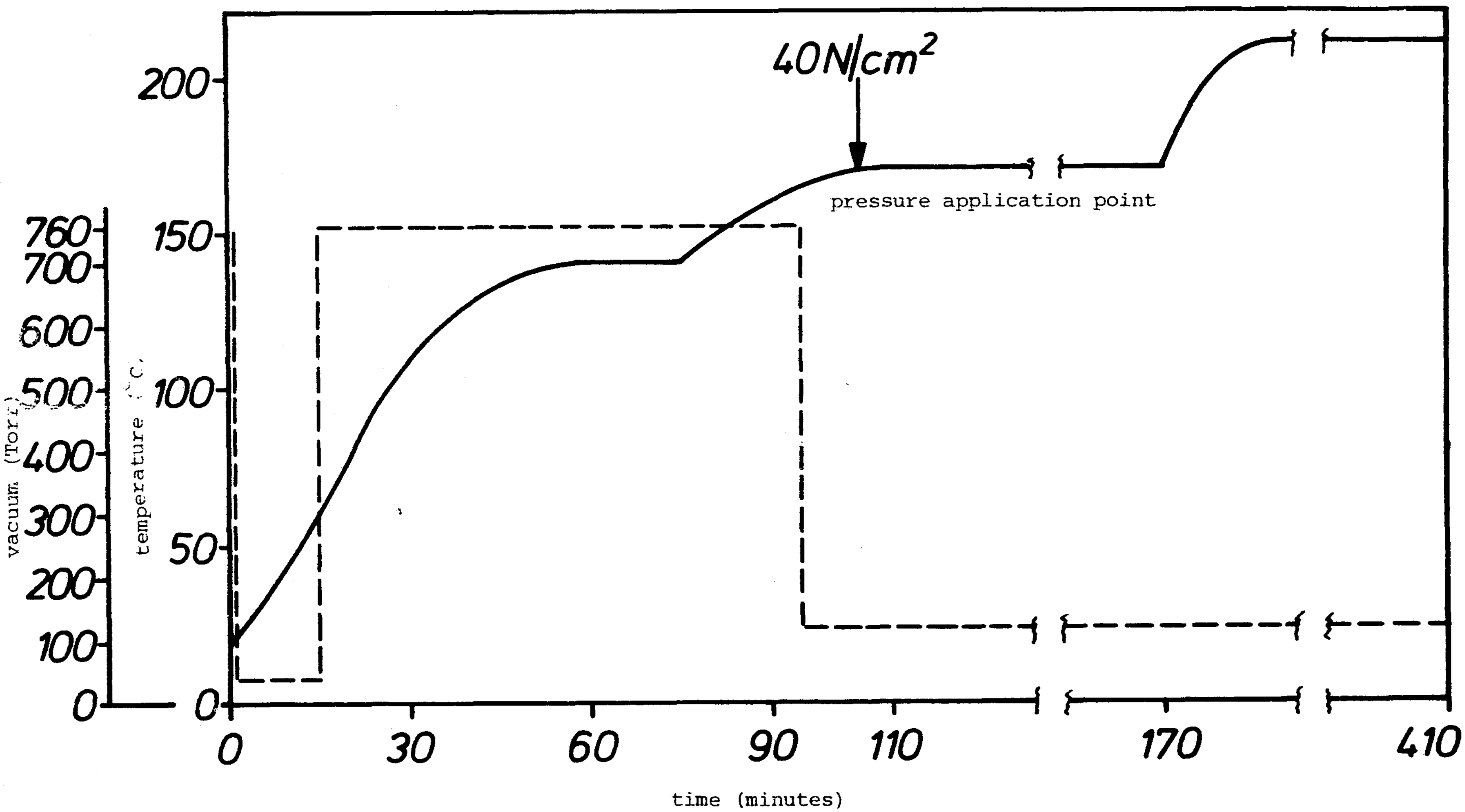

Figure 13: Autoclave cure cycle for H 795 - Fiberite W 134 - Prepregs

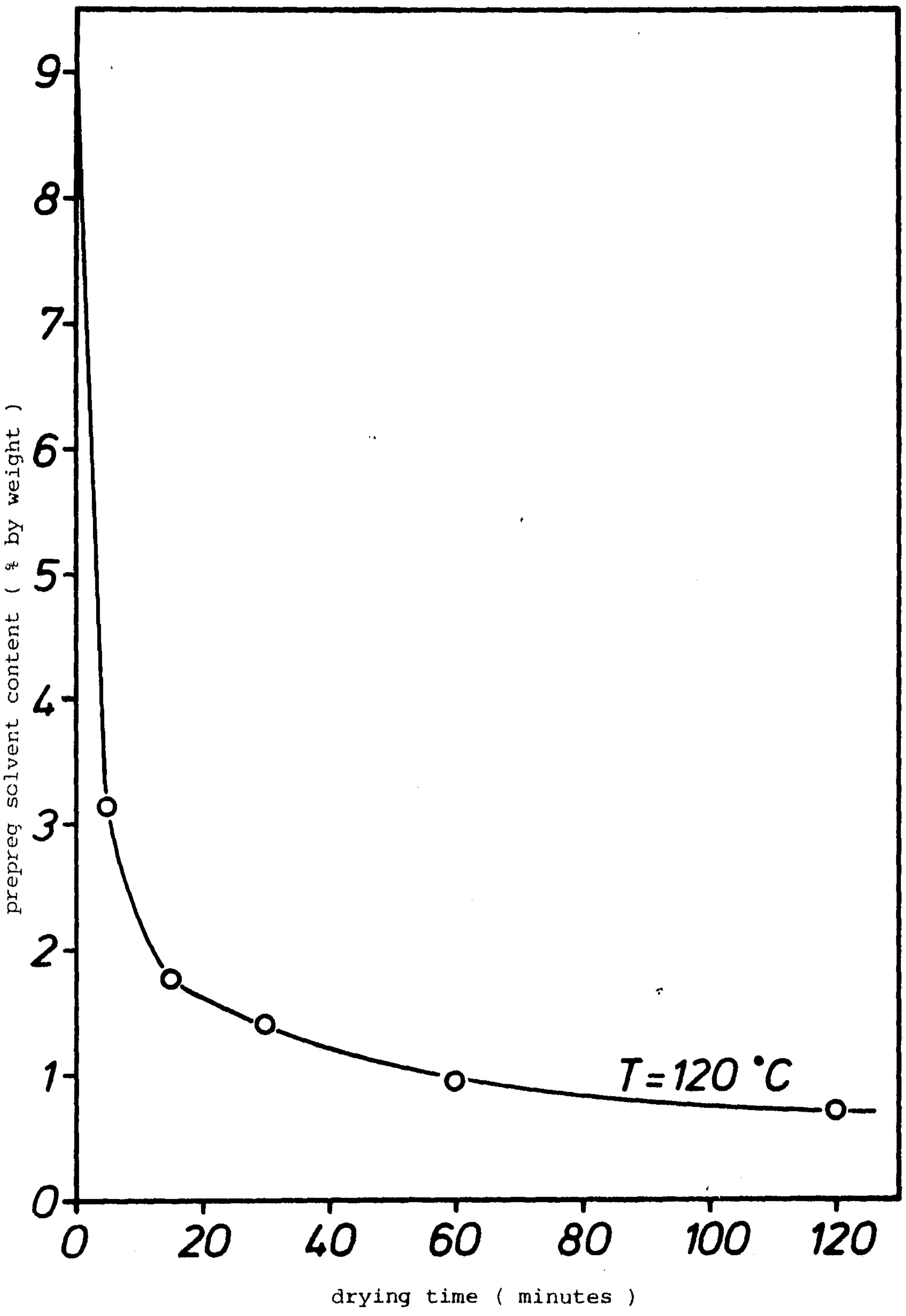

Figure 14: Residual solvent in prepreg H 795 - Fiberite W 134 as a function of drying time (temperature 120 °C, circulating air oven)

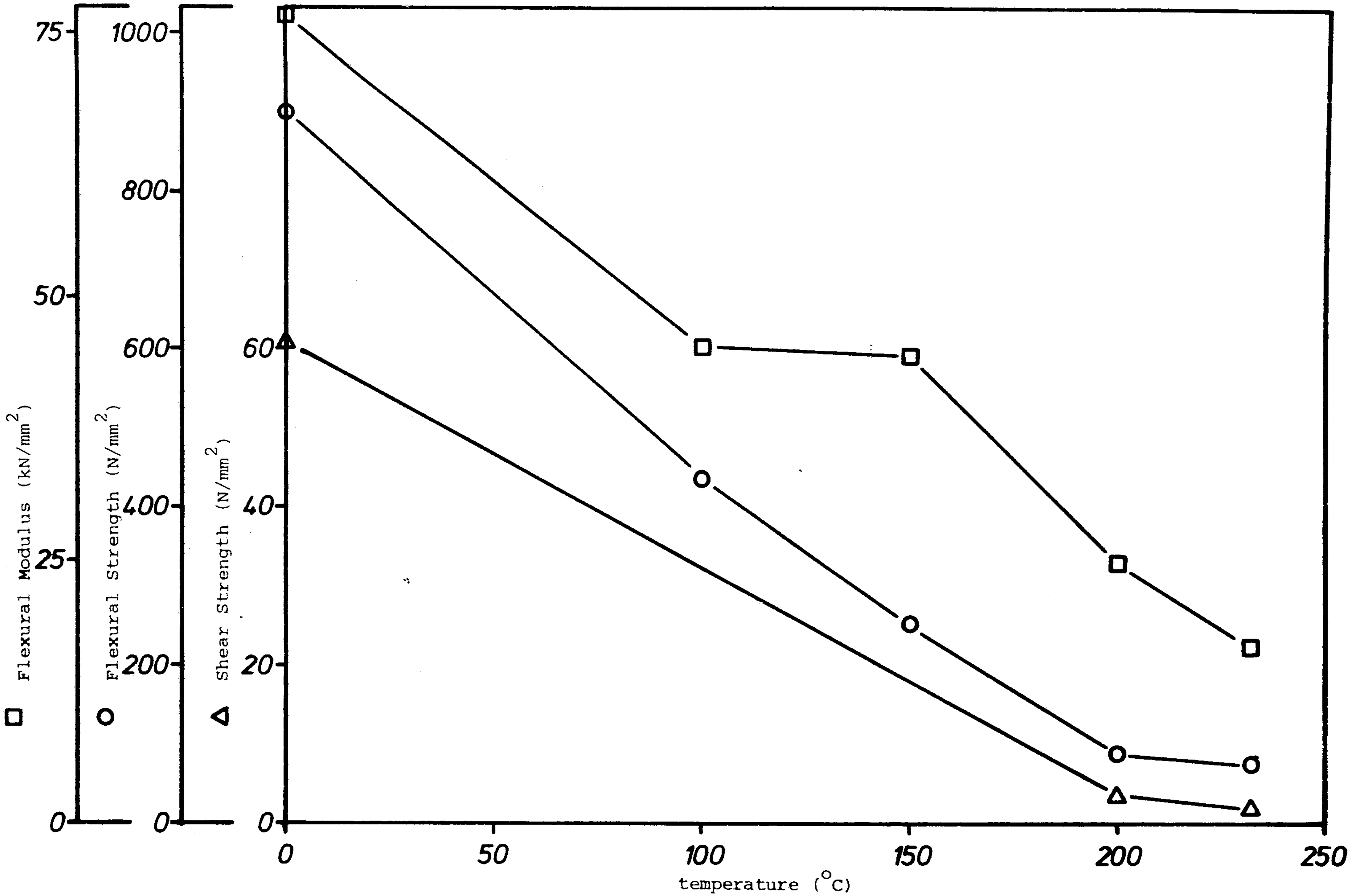

Figure 15: Mechanical properties of M 751 - Fiberite W 134 - laminates

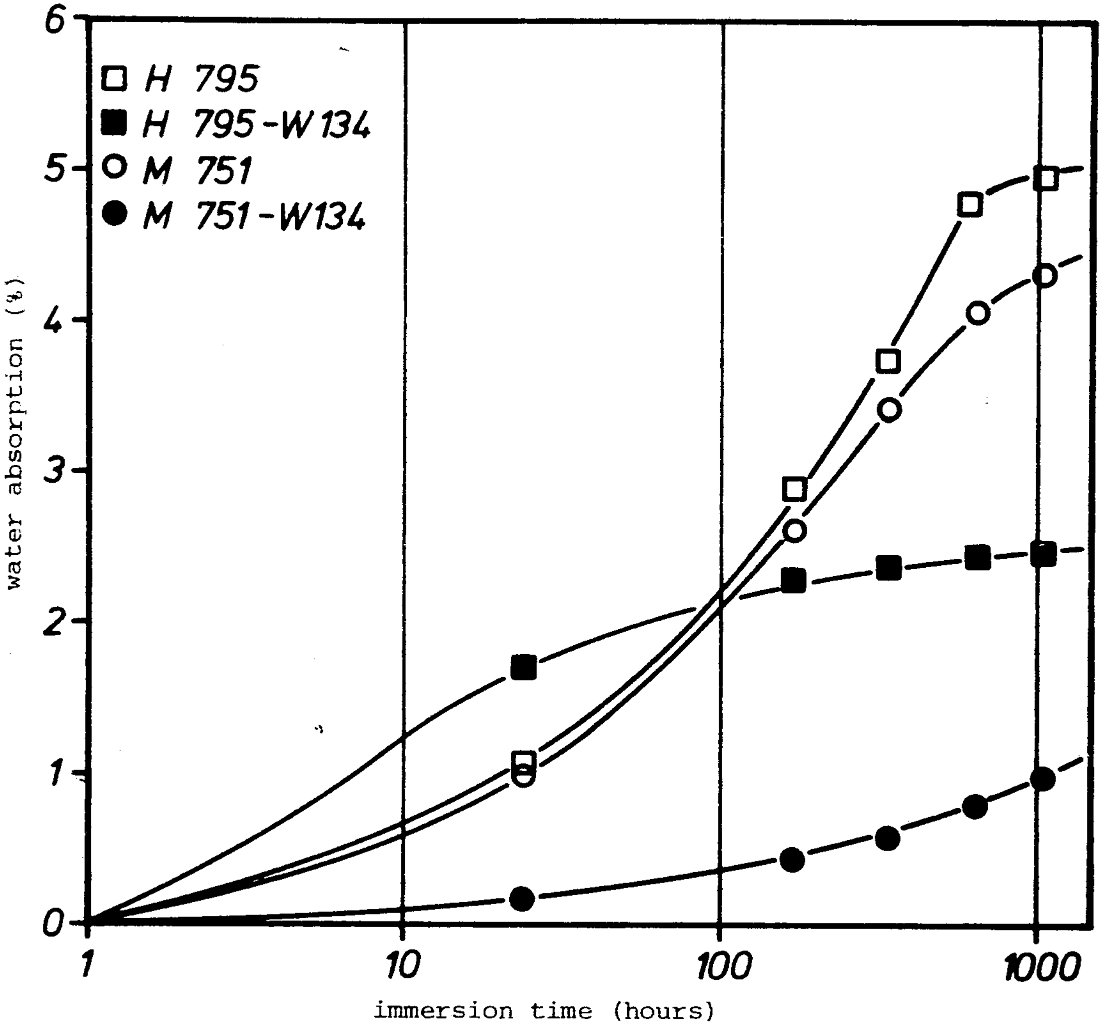

Figure 16: Water absorption of M 751- and H 795-neat resins and Fiberite W 134 - laminates