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Rubber-toughened curable compositions have an epoxy resin containing oligomeric epoxy species and a reaction product of solid rubber and the epoxy resin. The resin has two epoxy monomeric components, one having an epoxy functionality of greater than three and the other having an epoxy functionality of greater than one but not more than three. The resin is cured preferably using a combination of two curing agents, the first being capable of reacting with epoxy groups and of promoting reaction between hydroxyl and epoxy groups and the second being capable of reacting with epoxy groups. The solid rubber has reactive groups and is swellable by or soluble in a reaction mixture in which the reaction product is formed. The reaction product is formed in situ in the composition.

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Rubber-toughened curable compositions have an epoxy resin containing oligomeric epoxy species and a reaction product of solid rubber and the epoxy resin. The resin has two epoxy monomeric components, one having an epoxy functionality of greater than three and the other having an epoxy functionality of greater than one but not more than three. The resin is cured preferably using a combination of two curing agents, the first being capable of reacting with epoxy groups and of promoting reaction between hydroxyl and epoxy groups and the second being capable of reacting with epoxy groups. The solid rubber has reactive groups and is swellable by or soluble in a reaction mixture in which the reaction product is formed. The reaction product is formed *in situ* in the composition.

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Curable Compositions

This invention relates to curable compositions.

The use of curable compositions such as epoxy, cyanate, phenolic and like resins, both reinforced and unreinforced, has been known for a long time in a wide variety of commercial and military applications. Of particular importance is the use of such resins reinforced with continuous fibres, both unidirectional and woven, for structural applications such as aerospace vehicle parts such as aircraft tail assemblies and wing structures. Many such applications involve the use of multifunctional epoxy resins such as tetraglycidyl compounds cured using diamine hardeners.

However, whilst composite materials made from these resins have a relatively high modulus and Tg, they are usually brittle. A number of approaches have been used to improve the mechanical properties of the resin systems both in the bulk resin system and in the interlaminar regions in laminated fibre-reinforced composite materials. Typically, to improve toughness, for example, these include the addition of rubbers, thermoplastics, particulate fillers, interlaminar tougheners etc, often in combination.

Examples of toughened resin systems are to be found in US-A-4482660, US-A-4500660, US-A-4680076, US-A-4783506, US-A-4863787, US-A-4977215, US-A-4977218, EP-A-71197 and EP-A-559437. Brief details of the disclosures of these documents is given below.

US-A-4482660 and US-A-4500660 both disclose epoxy resin systems which are derived from epoxy resins, a reaction product of an epoxy resin and a butadiene/ acrylonitrile copolymer having carboxylic groups and a curing agent such as dicyandiamide or 4,4'-diaminodiphenylsulphone. Whilst there are no specific details disclosed, both documents suggest that using a reaction product of an epoxy resin and a solid rubber does not give rise to useful properties either in the curable composition or in the cured articles made therefrom. It is suggested that the viscosity of the curable composition can be adjusted by the addition of solid rubber particles, eg nitrile rubbers having carboxylic groups, thereto.

US-A-4680076 discloses a tough cured resin system having a phase-inverted morphology derived from a polyepoxy resin, an aromatic oligomer (ie thermoplastic), an aromatic diamine hardener and a reactive liquid rubber.

US-A-4783506 and US-A-4863787 disclose a curable composition based on a polyepoxy resin, an aromatic oligomer, a diamine hardener for the epoxy resin and a reactive (eg carboxyl functionality) solid rubber, the latter being present as infusible particles having a median size between 10μ and 75μ. The conversion of the rubber into infusible particles is preferably achieved in situ by removing solvent from the epoxy/ oligomer/rubber mixture whilst heating it. In using the composition to form fibre-reinforced composite materials, a large proportion of the particles are filtered by the fibres and remain on the prepreg surface to act as interlaminar toughening agents. Alternatively, the particles, presumably preformed, may be applied directly to the surface of the prepregs.

US-A-4977215 and US-A-4977218 disclose similar resin systems to US-A-4783506 and US-A-4863787 but in which the infusible rubber particles are preformed, have a Tg above 15°C, a size in the range 1μ to 75μ and comprise cross-linked carboxylated diene rubbers or carboxylated acrylic rubbers. Again, in using the composition to form fibre-reinforced composite materials, a large proportion, if not all, of the particles remain on the prepreg surface to act as interlaminar toughening agents.

EP-A-71197 is primarily concerned with novel diamine hardeners for curable compositions but again discloses the use of what is termed flexibilizing agents or elastomeric compounds such as rubbers and thermoplastics.

EP-A-559437 is concerned with a particular problem arising when fabricating honeycomb reinforcing structures which are covered with resin-impregnated fabrics; that is porosity in the fabrics which it solves by crushing the impregnated fabric to achieve a certain cover factor K_p as defined therein. As EP-A-559437 discloses, the liquid rubber systems, whether present as added or as a reaction product or alone or together with a solid rubber, or solid rubber systems do not adequately overcome the problem of porosity. EP-A-559437 discloses crushing fabrics impregnated with a composition of epoxy resin, pre-curing agent and solid rubber either without reactive groups or with reactive groups. The preferred composition adds the solid rubber in a lightly cross-linked state.

In these known resin systems, the toughening effect is achieved by the generation of relatively large, infusible rubber particles which phase separated from the epoxy resin during curing. When curable compositions which have pre-formed rubber particles, eg US-A-4977215 and US-A-4977218, are used to make prepreg materials, the fibres have a filtering effect on the particles which effectively limits the toughening effect of the rubber to the interlaminar regions of the composite materials. Consequently, the intralaminar properties of such composite materials are enhanced, as a result of the presence of the rubber toughening agent, to a considerably lesser extent.

Furthermore, as discussed in relation to EP-A-559437, the fabrication of honeycomb and like load-bearing structures present particular difficulties. One such proposed application of honeycomb structures involves aerospace vehicle components, eg aircraft tail units, in which prepregs will be used to form a continuous skin over a honeycomb reinforcing member. Such structural components are required inter alia to have high low temperature tensile strength. As discussed above, EP-A-559437 proposes to overcome the problem of porosity by crushing the fabric. However, in all instances, it is necessary to use relatively low moulding pressures, eg approximately 0.3MPa, to avoid crushing the honeycomb material.

Consequently, the rheological properties of the curable compositions considered for such use are critical since too high a viscosity will prevent resin flow into air pockets under the applied pressure, and thus will entrap volatile vapour which will nucleate to form voids, and too low a viscosity will cause the resin to flow out of the fibres even under the modest pressure applied.

The known proposed curable compositions discussed above have serious disadvantages when considered for such applications. For example, the use of thermoplastic tougheners results in a significant increase in the viscosity, and hence the elasticity, of the composition. The use of liquid rubbers alone does not significantly affect the viscosity, and hence the elasticity, of the compositions including them. The use of infusible particles alone has no significant effect on the viscosity of the composition and thus the elasticity is too low. The use of solid rubbers which are capable of cross-linking, ie when the infusible particles are formed in situ, results again in relatively high viscosity as the composition is heated sufficiently for the rubber to react. The use of lightly cross-linked solid rubbers, eg as in EP-A-559437, also gives rise to high viscosity compositions, hence the need to crush the fabric under high pressure to achieve high coverage. Additionally, in EP-A-559437, the use of non-reactive solid rubbers requires the use of special closely-woven fabrics and, again, hence the need to crush the fabric to achieve impregnation. Furthermore, in the crushed fabrics of EP-A-559437, the low pressures may result in poor bonding of the fabrics to the honeycomb structures by preventing sufficient flow of the composition to form adhesive fillets with the honeycomb walls.

In one broad aspect of the invention, there are provided curable compositions utilising a solid rubber wherein the compositions give rise to cured polymer matrices throughout which the rubber is substantially dispersed to give homogeneous or fine particulate morphology.

In another broad aspect of the invention, there is provided such curable compositions in which the requisite rheological properties are generated for selected applications.

Thus, in one embodiment of the invention there is provided a curable composition in which a solid rubber has been pre-reacted *in situ* with at least a proportion of an epoxy resin present in the composition.

In accordance with a more particular embodiment of the present invention, there is provided a curable composition comprising: (a) an epoxy resin comprising (i) at least one first epoxy resin monomeric component comprising monomers having an epoxy functionality of greater than three, having at least 0.05% by weight (based on said epoxy resin) of oligomeric epoxy species, and being a polyglycidyl derivative or an oligomer of a polyglycidyl derivative of at least one compound selected from aromatic diamines, aromatic monoprimary amines and aminophenols, and (ii) at least one second epoxy resin component comprising monomers having an epoxy functionality of greater than one but not more than three; (b) at least one curing agent for the epoxy resin and (c) a reaction product formed *in situ* by pre-reaction between (i) a solid rubber, which has at least 1.0 wt% of reactive groups and which is swellable by or soluble in a reaction mixture in which said reaction product is formed, and (ii) at least a portion of oligomers present in the first epoxy resin monomeric component, wherein the solid rubber to first epoxy resin weight ratio is between 1:1 and 1:20, and wherein the pre-reaction is conducted in the presence of a catalyst. The catalyst is preferably an alkyl triphenyl phosphonium iodide, bromide or chloride, stannous octoate or chromium octoate.

By reacting the rubber with the epoxy resin components prior to the addition of the remaining components of the curable composition, it has been found that the resultant curable composition is substantially homogeneous to look at, i.e. the rubber is not visibly detectable. In matrices obtained by curing the compositions according to the invention, the morphology is generally homogeneous but, if the rubber is detectable, i.e.

particulate morphology, it is as very fine particles, ie substantially less than 5µ and, more especially, not more than 1µ.

Additionally, as will be discussed in greater detail below, the viscoelastic properties of the curable composition are controllable to enable impregnation and subsequent fabrication of structures such as fabric-reinforced honeycomb structures to occur.

It has been found that the reaction producing the reaction product occurs primarily between the rubber and oligomeric epoxy species present in the epoxy resin. Provided such oligomeric species are present, the reaction product comprises either rubber reacted with at least a proportion of a mixture of both of said epoxy resin components; or, alternatively, rubber reacted with at least a proportion of one or other of said epoxy resin components. In a particularly preferred form of the invention, the reaction product comprises rubber reacted only with at least a proportion of said first epoxy resin component.

The amount of such oligomeric species present in the epoxy resin is at least 0.05% by weight, preferably at least 0.5%. In practice, however, epoxy resin systems contain significant quantities of oligomeric species which are created during the manufacture of said resins. The minimum quantities of such oligomeric species quoted above are derived from consideration of stoichiometric requirements based on potential reaction mechanisms. However, the types of oligomeric species present in the epoxy resin may differ from resin to resin depending upon the manufacturing route and, consequently, higher quantities of oligomeric species (to ensure the presence of sufficient quantities of appropriate reactive species) may be required. Thus, in practice, based on commercially-available epoxy resins, it is preferred that the epoxy resin has at least 5% by weight, preferably at least 7.5% by weight and especially at least 15% by weight of oligomeric species.

In making the reaction product, the rubber to epoxy resin ratios are between 1:1 and 1:20, preferably between 1:2.5 and 1:17 and especially between 1:2.5 and 1:16.5.

Preferably, the epoxy resin components comprise glycidyl derivative of one or more of:

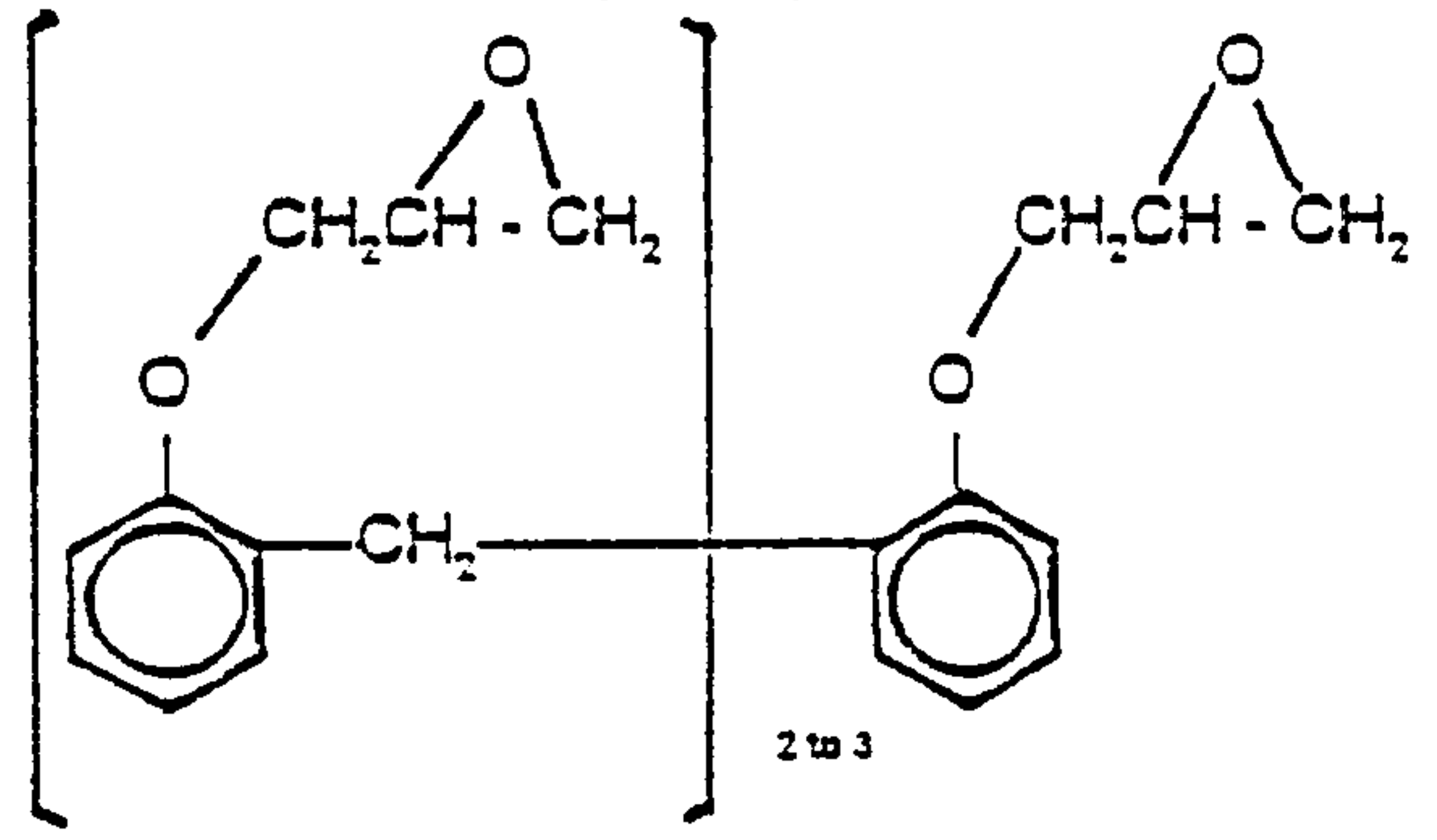
aromatic diamines
aromatic monoprimary amines
aminophenols
polyhydric phenols

polyhydric alcohols

polycarboxylic acids.

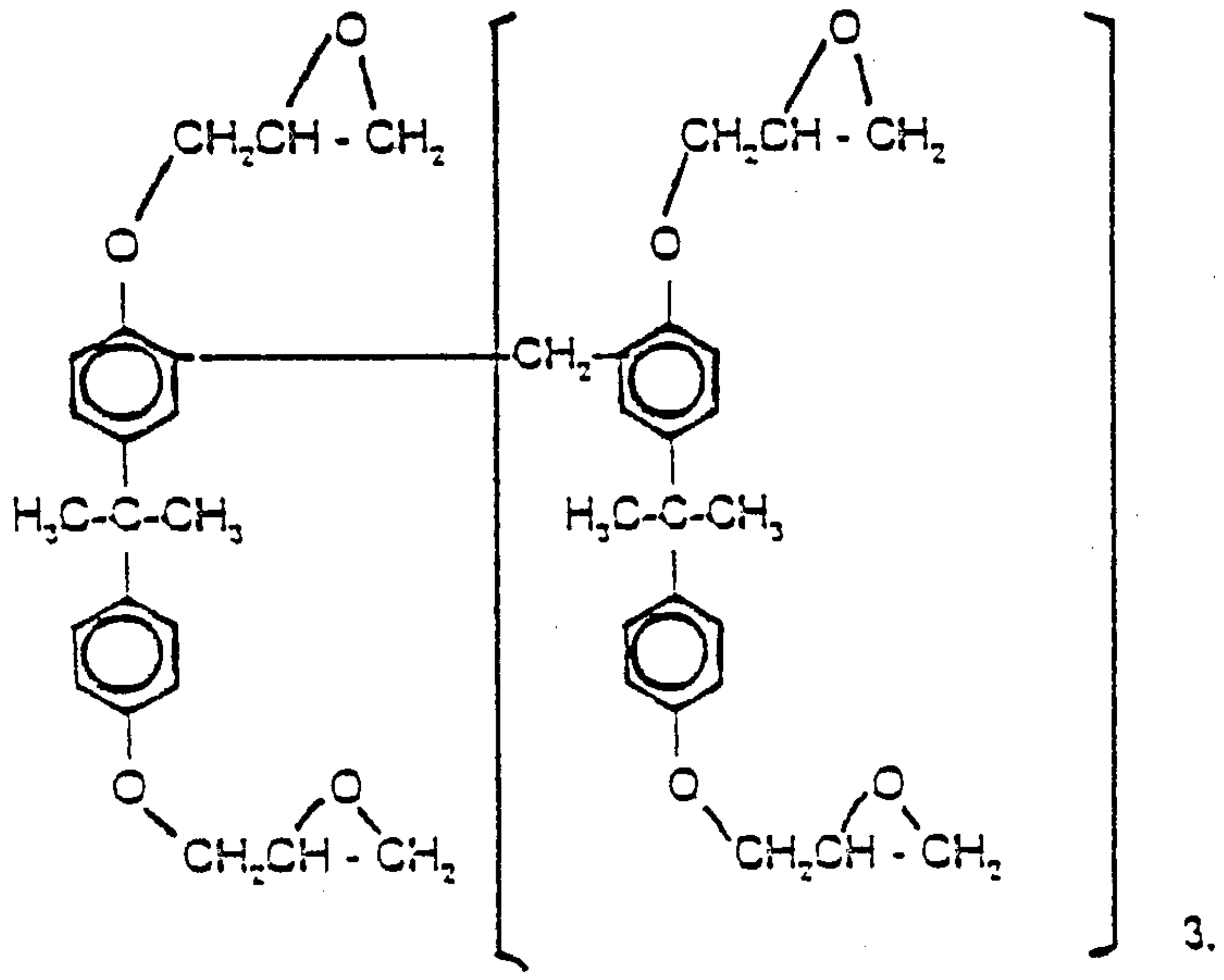
Examples of such compounds, which are useful as said first epoxy resin component, are as follows:-

- N, N, N', N'-tetraglycidyldiaminodiphenylmethane, eg "MY 9663" sold by Ciba-Geigy;
- N, N, N', N'-tetraglycidyl-bis(4-aminophenyl)-1,4-diiso- propylbenzene, eg EPON* 1071 sold by Shell Chemical Co, viscosity 18-22 Poise at 110°C;
- N, N, N', N'-tetraglycidyl-bis(4-amino-3,5-dimethylphenyl)- 1,4-diisopropylbenzene, eg EPON 1072 sold by Shell Chemical Co, viscosity 30-40 Poise at 110°C;
- gylcidyl ethers of phenol novolak resins, eg "DEN* 438" sold by Dow, varieties in the low viscosity class of which are preferred in making compositions according to the invention and which are typically of formula:-



and

- gylcidyl ethers of bisphenol A novolac resins which are typically of formula:-



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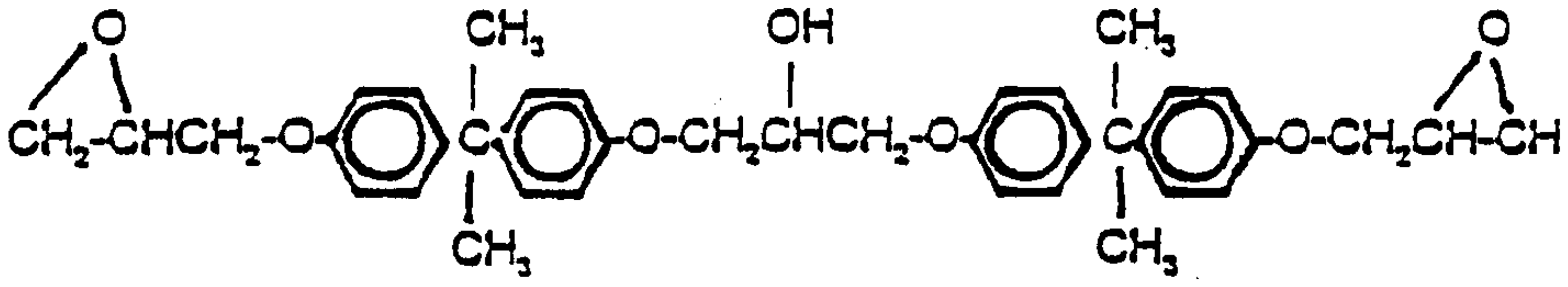
*Trade-mark

Particularly preferred for said first epoxy component is N, N, N', N'-tetraglycidyl diaminodiphenylmethane with an epoxide equivalent weight of 112 to 125.5.

Examples of gylcidyl derivatives which are useful as said second epoxy resin component are as follows:-

- digylcidyl ethers of bisphenol A based materials, eg DER* 661 sold by Dow, which have the formula:-



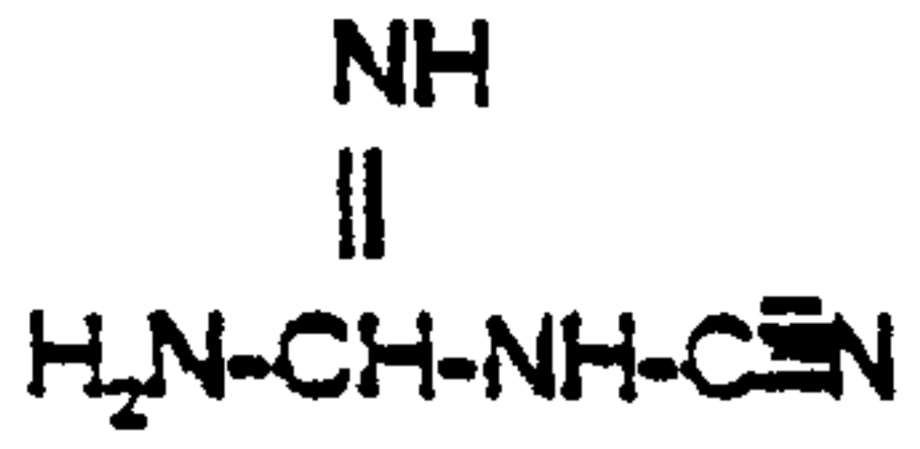
- triglycidyl ethers of 4-aminophenol (eg "MY 0510" sold by Ciba-Geigy), viscosity 0.55 - 0.85 Pa s at 25°C;
- diglycidyl ether of bisphenol A (eg "Epikote 828" sold by Shell), which has a viscosity 8-20 Pa s at 25°C;
- digylcidyl 1,2-phthalate, eg GLY CEL A-100.

Particularly preferred for said second epoxy component are digylcidyl ethers of bisphenol A based materials having the formula given in the preceding paragraph and having an epoxide equivalent weight of 188 to 500.

Preferably, at least two curing agents are used, the first of the curing agents being capable of reacting with epoxy groups and of promoting reaction between hydroxyl groups and epoxy groups.

The curing agents are preferably an amino compound having a molecular weight up to 500 per amino group, for example an aromatic amine or a guanidine derivative. Particular examples suitable for use as the second curing agent are:-

- dicyanodiamide, ie:-



$$H_2N-\overset{\overset{NH}{\|}}{CH}-NH-C\equiv N$$

available as Amicure CG 1200 from Pacific Anchor Chemical;

- 4-chlorophenyl-N,N-dimethyl-urea, eg Monuron;
- 3,4-dichlorophenyl-N,N-dimethyl-urea, eg Diuron.

Preferably, said second curing agent is dicyanodiamide.

Particular examples suitable for use as the first curing agent are:-

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*Trade-mark

- 3,3'- and 4,4'-diaminodiphenylsulphone;
- methylenedianiline;
- bis(4-amino-3,5-dimethylphenyl)-1,4-diisopropylbenzene available as EPON 1062 from Shell Chemical Co; and
- bis(4-aminophenyl)-1,4-diisopropylbenzene available as EPON 1061 from Shell Chemical Co.

Preferably, said first curing agent is 4,4'-diaminodiphenylsulphone.

The total amine content of the curing agent is in the range 70-110% of the stoichiometric requirement of the epoxy resin component.

If desired, a catalyst for the epoxy resin component/curing agent reaction may also be used. If such a catalyst is used, it is typically a Lewis acid, for example boron trifluoride, conveniently as a derivative with an amine such as piperidine or methyl ethylamine. Alternatively it can be basic, for example an imidazole or amine.

The rubber used to prepare the reaction product is selected from olefin, diene and nitrile rubbers and copolymers and terpolymers thereof which have pendant reactive groups, especially carboxylic groups. Particularly preferred are diene-nitrile copolymers having carboxylic groups. A particular preferred rubber is acrylonitrile/butadiene rubber having carboxylic groups. Preferably, the carboxylic groups are provided by a termonomer such as methacrylic acid. Preferably, the rubber contains at least 1 wt % preferably at least 2 wt % and more especially at least 2.25wt % of carboxylic groups; and preferably upto 5 wt % carboxylic groups. The carboxylic group content is expressed as a weight % derived from the molecular weight of a carboxyl group divided by the molecular weight of the length of polymer chain to which it is attached expressed as a percentage. This translates as follows: 1 wt % is equivalent to 1 carboxylic group per 4500 M_w (M_w = weight average molecular weight of the polymer chain); 2 wt % is equivalent to 1 per 2250 M_w; 2.25 wt % is equivalent to 1 per 2000 M_w. Particularly preferred rubbers are the acrylonitrile/butadiene/ methacrylic acid rubbers available from Nippon* Zeon under the trade name HYCAR*, especially HYCAR 1472 (now available under the trade name NIPOL* 1472) which has 3.75 wt % of carboxylic groups (ie 1 per 1200 M_w).

Preferably, the rubber has an M_w of at least 30000, preferably at least 100000 and especially at least 150000.

Preferably, the rubber is soluble or at least highly swellable in the epoxy resin.

*Trade-mark

Preferably, the curable composition comprises 1 to 20 wt %, preferably 1 to 10 wt %, and more especially 3 to 6 wt %, of rubber based on the total weight of epoxy resin, curing agent and reaction product in said composition.

In the preferred curable composition according to the invention wherein said reaction product is rubber reacted with said first epoxy component, the curable composition comprises 4.0 to 8.0 wt %, more especially 4.5 to 7.0 wt %, of rubber based on the total weight rubber and said first epoxy resin component. In this instance, said reaction product may contain all of said first epoxy resin; alternatively, said reaction product may contain only a proportion of said first epoxy resin.

The prereaction of the rubber with at least a proportion of said epoxy resin *in situ* enables a significant degree of control over the viscoelastic properties of the resultant curable composition to be exercised. The viscoelastic properties can be varied by varying the ratio of rubber to epoxy resin. As previously mentioned, the rubber to epoxy resin ratios of between 1:1 and 1:20, preferably between 1:2.5 and 1:17 and especially between 1:2.5 and 1:16.5 are to be used. Surprisingly, small variations in the rubber to epoxy resin ratio have a significant effect on the viscoelastic properties of the resultant curable composition.

A measure of the viscoelastic properties of the curable composition is possible by determining the rheological properties of the composition especially the storage or elastic modulus, G'. This is determined as described below in the Examples. In the curable compositions used for those applications in which significant moulding pressure cannot be used, the G' minimum of the curable composition is controlled within the range 20 Pa to 200 Pa, preferably within the range 40 Pa to 160 Pa and, more especially, within the range 80 Pa to 110 Pa.

The curable composition according to the invention may also contain other toughening agents such as thermoplastics optionally having reactive groups; other fillers such as fumed silica; aggregates, eg glass beads; polytetrafluoroethylene; graphite; boron nitride; mica; talc; vermiculite; nucleating agents; and stabilisers. However, such additional components will have an effect on the viscoelastic properties of the composition which has to be taken into account when formulating the reaction product.

Preferably, the invention includes composite material comprising the curable composition according to the invention and fibre reinforcement. Although the fibres may be any suitable fibres such as glass, carbon or organic polymers, preferably, the fibres are carbon fibres, especially graphite fibres. Graphite fibres which have been found to be especially useful in the invention are those supplied by Amoco under the trade designations T650-35, T650-42 and T300; those supplied by Toray under the trade designation T800-HB; and those supplied by Hercules under the trade designations AS4, AU4, IM 8 and IM 7.

The fibres may be short or chopped fibres, typically of mean fibre length not more than 20 mm, for example about 6mm. Alternatively, and preferably, the fibres are continuous and may, for example, be unidirectionally-disposed fibres or a woven fabric, ie the composite material comprises a prepreg. Combinations of both short and/or chopped fibres and continuous fibres may be utilised. The fibres may be sized or unsized.

The total of the aforementioned other toughening agents, fillers, aggregates etc in the curable composition and the fibre reinforcement of any composite material comprising said curable composition should be such that the curable composition or composite material contains at least 20% by volume of such materials and/or reinforcing fibres. The percentages of fibres and such other materials are calculated on the total composition after curing.

The invention also includes composite materials comprising prepregs according to the invention laminated together by heat and pressure, for example by autoclave, compression moulding or by heated rollers, at a temperature above the curing temperature of the curable composition.

When the fibres of the reinforcement are continuous and unidirectional, the resulting multi-ply laminated composite material may be anisotropic in which the fibres are oriented essentially parallel to one another or quasi-isotropic in each ply of which the fibres are oriented at an angle, conveniently 45° as in most quasi-isotropic laminates but possibly for example 30° or 60° or 90° or intermediately, to those in the plies above and below. Orientations which are between anisotropic and quasi-isotropic, and combination laminates, may be used. Suitable laminated composite materials contain at least four, preferably at least eight, plies. The number of plies is dependent on the application for the laminated composite material, for example the strength required, and laminated composite materials containing thirty-two or even more, for example several hundred, plies may be desirable. There may be aggregates, as mentioned above, in interlaminar regions.

When the prepreg comprises woven fabric, structures may be quasi-isotropic or between anisotropic and quasi-isotropic.

The invention also includes a composite material comprising prepreg according to the invention laid up on at least one side, and preferably with both opposed sides, of a honeycomb reinforcing component such as Nomex* honeycomb available from Hexel, optionally with an adhesive layer interposed between the prepreg and the honeycomb component.

Also according to the invention, a process for making a curable composition as hereinbefore defined comprises forming a reaction mixture of said rubber, at least a proportion of said epoxy resin, a catalyst capable of promoting a reaction between epoxy groups and the reactive groups of said rubber and a polar solvent , said rubber, said epoxy resin and said catalyst comprising between 25 and 75 wt %, preferably between 35 and 65 wt %, more especially between 40 and 50 wt %, of the reaction mixture, heating the mixture to effect said reaction, cooling the resultant mixture to substantially ambient temperature and adding the remaining proportion of the epoxy resin and curing agents to the mixture and substantially removing the solvent therefrom.

Preferably, the mixture is heated to a temperature in the range 40°C to 80°C, preferably under reflux.

The catalyst is preferably selected from the group consisting of alkyl triphenyl phosphonium iodide, bromide or chloride, wherein alkyl is methyl, ethyl, propyl, n-butyl, iso-butyl, n-pentyl or n-decyl, triphenyl phosphine, stannous octoate, chromium octoate, boron trifluoride, boron trifluoride monoalkyl (eg monoethyl) amine, especially ethyl triphenyl phosphonium iodide.

Composite materials according to the invention which comprise continuous fibres are made by preimpregnating the continuous fibres with the curable composition prior to removal of the solvent to form prepregs and removing the solvent from the prepreg, said prepreg optionally being consolidated between nip rollers.

The invention will now be illustrated by reference to the accompanying drawings and the following Examples. In the accompanying drawings:-

*Trade-mark

Figure 1	is a graphical representation of resin viscosity for a number of epoxy resin samples;
Figure 2	is a graphical representation of G' minimum against resin viscosity of formulations using the resins shown in Figure 1;
Figure 3	is a schematic drawing of a drumwinding mechanism used to prepare prepregs;
Figure 4	is a schematic cross-sectional drawing of a layup and tool used to prepare consolidated samples for testing;
Figure 5	is a schematic drawing of prepregging equipment used to prepare pregpregs;
Figure 6	is a schematic perspective drawing of a layup used to prepare consolidated honeycomb-reinforced samples for testing; and
Figure 7	is a schematic cross-sectional drawing of a layup and tool used to prepare the samples shown in Figure 6.

Example 1

A curable composition was made using the following components and formulation (pbw = parts by weight):-

First epoxy resin component - N, N, N', N' - tetraglycidyldiaminodiphenylmethane as MY 9663 sold by Ciba-Geigy	76.53 pbw
Second epoxy resin component - digylcidyl ether of bisphenol A as DER 661	12.72 pbw
Curing agent - dicyanodiamide ("DICY")	6.0 pbw
Rubber - an acrylonitrile/butadiene/methacrylic acid rubber as HYCAR 1472 from Nippon Zeon, Mn = 50000 to 53000, Mw = 156000, Tg = -18°C, acrylonitrile content = 29%, butadiene content = 67% and methacrylic acid content = 4%.	varying pbw - see table below
Catalyst - ethyl triphenyl phosphonium iodide ("ETPI")	0.5 pbw

The curable composition was made by preparing the reaction product *in situ* from a reaction mixture containing:-

a) the rubber and all of the first epoxy resin component (Reaction Route A);

b) the rubber and all of the second epoxy resin component (Reaction Route B); or

c) the rubber and all of both the first and the second epoxy resin components (Reaction Route C);

followed by the addition of the remaining ingredients. The method was as follows:-

a) the respective epoxy resin component(s) was predissolved in acetone together with ETPI and the rubber;

b) the solution was stirred and heated under reflux for 2 hours;

c) the solution was then cooled to <40°C and the remaining first epoxy resin component, if any, together with the second epoxy resin component was added and allowed to solubilise with stirring for 30 minutes;

d) DICY was then added to the mixture and it was stirred for a further 30 minutes; and

e) the solvent was then removed by placing the solution in a vacuum oven for 30 minutes at 50°C and <10 mm Hg.

Using this method, samples of curable compositions were made in which the reaction route was varied and the rubber content was varied within some of the reaction routes.

The viscoelastic properties of samples of the curable compositions were assessed rheologically. Typical conditions used to evaluate 2ml samples, using a RMS 800 rheometer manufactured by Rheometrics Limited, were:-

Plate size	40mm
Gap	1.6mm
Initial Temperature	70°C
Final Temperature	170°C
Heating rate	2.0°C/min
Strain rate	10.0%
Oscillation	10 rads/sec
Data Points	One every 30 sec.

Details of the samples of curable compositions and the viscoelastic properties are given in Table 1 below.

Table 1

SAMPLE	1	2	3	4	5	6	7	8
1/1	A	5	76.53	15.31	5	75	13	130-150
2/1	A	4.75	76.53	16.11	4.76	60	8	130-150
3/1	A	4.25	76.53	18.01	4.28	40	5.5	130-150
4/1	A	4	76.53	19.13	4.04	30	5	130-150
5/1	A	3.75	76.53	20.41	3.79	13	3.1	130-150
6/1	A	3	76.53	25.51	3.06	3.5	1.5	130-150
7/1	B	4.75	12.72	2.68	4.76	200	22	100-140
8/1	C	5	89.25	17.85	5	15	-	140
9/1	C	4.75	89.25	18.79	4.76	6	-	140
10/1	C	4.25	89.25	21	4.28	5	-	140

Column 1	Reaction Route.
Column 2	Rubber content - pbw.
Column 3	Amount of epoxy resin component prereacted with rubber - pbw.
Column 4	Ratio of column 2:column 3.
Column 5	Rubber content - % based on all components except ETPI.
Column 6	G'minimum - Pa
Column 7	η^*- complex viscosity - Pa.s
Column 8	Temperature (°C) at which G'minimum is attained.

Example 2

A curable composition was made using the following components and formulation:-

First epoxy resin component - N, N, N', N' - tetraglycidyldiaminodiphenylmethane as MY 9663 sold by Ciba-Geigy	63.75 pbw

Second epoxy resin component - digylcidyl ethers of bisphenol A as EPON 291 (a 50:50 mixture of EPON 1001F and EPON 828 sold by Shell Chemical Co	12.0 pbw
First curing agent - dicyanodiamide ("DICY")	2.5 pbw
Second curing agent - 4,4'-diaminodiphenylsulphone ("DDS")	17.0 pbw
Rubber - an acrylonitrile/butadiene/methacrylic acid rubber as HYCAR 1472 from Nippon Zeon, Mn = 50000 to 53000, Mw = 156000, Tg = -18°C, acrylonitrile content = 29%, butadiene content = 67% and methacrylic acid content = 4%.	varying pbw - see table below
Catalyst - ethyl triphenyl phosphonium iodide ("ETPI")	0.5 pbw

The curable composition was made by prereacting the rubber with all or part of the first epoxy resin component using the method described in Example 1 (both DDS and DICY were added at step d)).

Using this method, samples of curable compositions were made in which the rubber content was varied; in which the amount of first epoxy resin component was varied; and in which the rubber and the first epoxy resin component were varied but the ratio between them was held constant.

The viscoelastic properties of samples of the curable compositions were assessed rheologically as described in Example 1.

Details of the samples of curable compositions and the viscoelastic properties are given in Table 2 below.

Table 2

SAMPLE	1	2	3	4	5	6	7	8
1/2	4.75	63.75	13.42	4.75	6.9	150	18	100-130
2/2	4.5	63.75	14.17	4.51	6.59	100	8	100-130
3/2	4.25	63.75	15	4.27	6.25	65	-	130-150
4/2	4	63.75	15.94	4.03	5.9	40	2.5	130-150
5/2	3.75	63.75	17	3.79	5.55	22	2	130-150
6/2	3.5	63.75	18.21	3.54	5.2	15	1.5	130-150
7/2	3.25	63.75	19.62	3.3	4.85	8	1	130-150

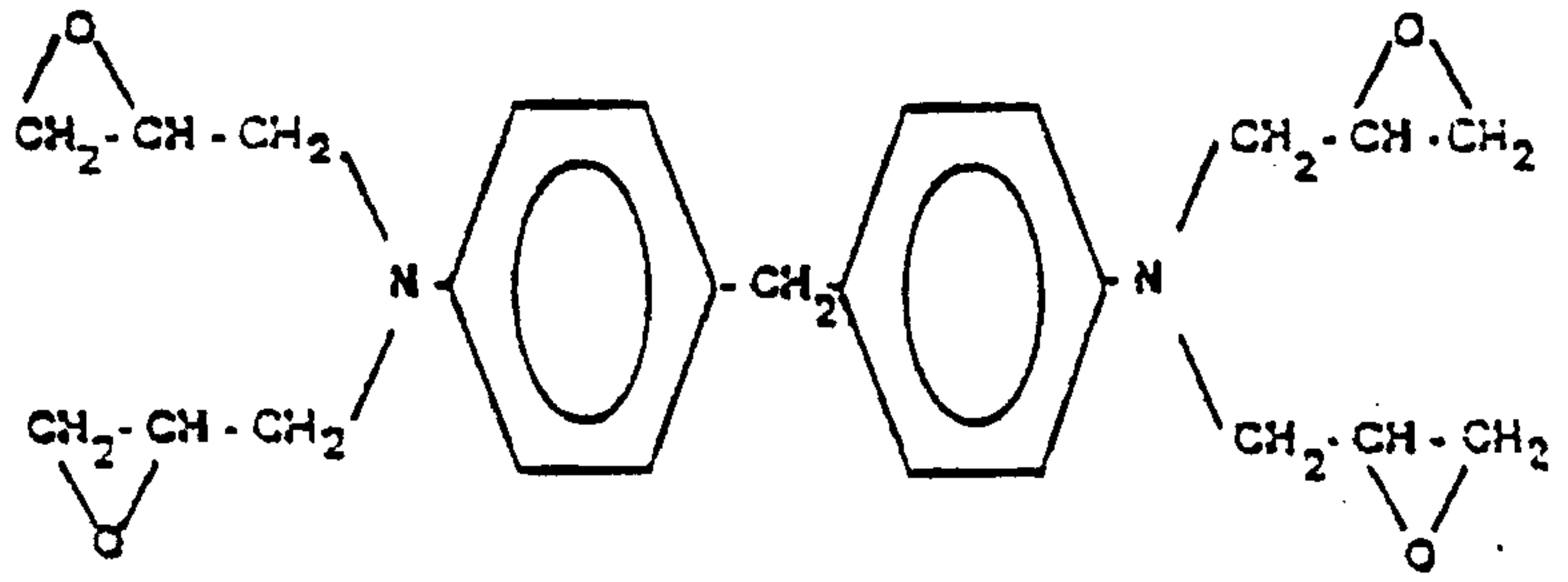
8/2	3.25	53.63	16.5	3.3	5.71	33	3.5	130-150
9/2	3.25	43.5	13.38	3.3	6.95	62	5	120-140
10/2	3.25	36	11.08	3.3	8.28	120	5	100-130
11/2	3.25	30	9.23	3.3	9.77	180	10	100-130
12/2	3.75	50	13.33	3.3	5.55	90	10	100-130

Column 1	Rubber content - pbw.
Column 2	Amount of epoxy resin component prereacted with rubber - pbw.
Column 3	Ratio of column 1:column 2.
Column 4	Rubber content - % based on all components except ETPI.
Column 5	Rubber content - % based on rubber + total amount of first epoxy resin component.
Column 6	G'minimum - Pa
Column 7	η'- complex viscosity - Pa.s
Column 8	Temperature (°C) at which G'minimum is attained.

Example 3

The effect of oligomer content of the epoxy resin was investigated as follows:-

The viscosity of various MY epoxy resin grades available from Ciba-Geigy were determined using a CARIMED* viscometer at 50°C using a shear rate of 0.5 and the results are given in Figure 1. The viscosity of the epoxy resins is directly attributable to the level of higher oligomeric species of the monomeric material present in the resins, ie oligomers of pure glycidyl methylenedianiline (epoxide equivalent weight =125.5), ie



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*Trade-mark

This was confirmed using high pressure liquid chromatography (HPLC).

63.75 pbw of some of the resins were then reacted with 5.0 pbw of NIPOL 1472 (Mw = 170000) and 0.5 pbw of ETPI in acetone, the mixture having a pre-reaction solids content of 45%. The reaction mixture was then heated and held at reflux for 2 hours before being cooled to room temperature. To the mixture was added 17.0 pbw of DDS, 2.5 pbw of DICY, 6.0 pbw of EPON 828 (a difunctional epoxy resin based on bisphenol A supplied by Dow Chemicals - epoxide equivalent weight = 344), 6.0 pbw of EPON 1001F (a difunctional epoxy resin based on bisphenol A supplied by Dow Chemicals - epoxide equivalent weight = 500; this is a higher molecular weight analogue of EPON 828) and sufficient acetone to give a prepreg solution having a solids content of 50% by weight.

Resin samples for rheological examination were taken and placed in a vacuum oven at 60°C for 30 min to remove acetone. The samples were then rheologically tested to determine the G'minimum.

This investigation revealed that the "purer" resin MY721, ie low oligomer content, produced a significantly lower rheological response, ie G' minimum, after the reaction product is formed than the other resins. This was repeated for several batches of NIPOL 1472 (varying molecular weight) with similar results. The results are plotted in Figure 2 giving high/low figures (which result from the variations in molecular weight). In Figure 2 the resin viscosities are quoted and, thus, the resin is identifiable from the following Table 3:-

Table 3

Resin	Viscosity (Pa.s)
MY721	4.4
MY9655	9.4
MY9512	11.39
MY9634	15.5
MY9663	19.2

HPLC was used to examine some of the resins both before and after the reaction with the rubber. The results are given in Table 4.

In Table 4, the figures in the rows are the areas of the peaks obtained using HPLC for the various components of the resins and they are proportional to the quantities of the resin components present. The large figures, eg 68.4 etc, represent the amount of monomer present; the figures in the rows above the monomer row are derived from remnant starting materials from which the monomer is made; and the figures in the rows below the monomer row are derived from oligomeric species that are present.

As can be seen, in each instance, the post-reaction oligomeric levels have dropped significantly compared to the pre-reaction levels.

Table 4

MY	9663		MY	9512		MY	721
Prior to Pre-reaction	Post Pre-reaction		Prior to Pre-reaction	Post Pre-reaction		Prior to Pre-reaction	Post Pre-reaction
0.4	0.2		0.4	0.2		1.7	1.1
2.3	1.9		0.3	0.3		1.8	1.2
68.4	74.9		1.5	1.3		1	1.5
6.2	5.3		75.4	80.1		86.6	89.1
0.4	0.2		6.3	4.7		4	3.4
17.8	14.8		2	0.8		1.1	0.6
3.9	2.5						

Example 4

The procedure described in Example 3 was used to determine G' minimum for samples made using varying weights of NIPOL 1472 of differing molecular weights (determined using Gel Permeation Chromatography using tetrahydrofuran as the solvent phase and at 40°C and a polystyrene calibration curve). The results are listed in Table 5 below.

Example 5

A formulation, Sample 1/5, as used in Example 2 but using 5.0 pbw of rubber was prepared along with two further samples in one of which, Sample 2/5, the catalyst ETPI was omitted and in the other of which, Sample 3/5, the ingredients were merely blended together, again the catalyst ETPI being omitted. The rheological properties of the formulations were assessed and are given in Table 6.

Table 5

NIPOL 1472 Batch	Mw of NIPOL 1472 Batch	G' minimum (Pa) - 4.25 pbw	G' minimum (Pa) - 5.0 pbw	G' minimum (Pa) - 5.25 pbw
1	155600	55.5	360	515
2	164000	46	130	200
3	170000	9.3	100	202
4	171000	38.5	-	136
5	178000	16	90	183
6	184000	17.5	86.5	136.5
7	185000	12	75	128

Table 6

SAMPLE	G' minimum (Pa)	η^* (Pa.s)
1/5	130	13
2/5	2	0.6
3/5	6	1.3

Example 6

A variety of formulations, see Table 7, were used to impregnate unidirectional fibres to produce prepregs which were laid up, consolidated and subjected to mechanical property assessment, the results from which are given in Table 8 (which includes -75°F (-60°C) Tensile results obtained in Example 8 but reproduced in Table 8 for convenience).

Method for Blocking Carboxylic Groups

Into a 1,000ml reaction flask equipped with a paddle stirrer, thermometer, nitrogen inlet and condenser was charged NIPOL 1472 rubber (128.2og, 0.000706 mols , this weight includes 6.4wt% talc) and 950mls methylethylketone (MEK). Once solution was complete, phenylglycidylether (32.00g, 0.2131 moles) and ETPI (5.36g, 0.0128 moles) were added to the NIPOL 1472 rubber solution. The reaction temperature was raised by means of an oil bath, so that the MEK was gently refluxing. The reaction temperature was maintained for 2 hours and then cooled to room temperature.

Table 7

SAMPLE	FORMULATION	G' minimum (Pa)	η* (Pa.s)
1/6	As Sample 1/5 (ie in accordance with the invention).	100	12
2/6	As Sample 2/5 (ie without EPTI).	2	0.7
3/6	As Sample 3/5 (ie blended).	6	1.5
4/6	As Sample 1/6 but without any NIPOL 1472 present.	*	*
5/6	As Sample 1/6 but using NIPOL 1472 in which 20% of the carboxylic groups have been blocked**.	70	8
6/6	As Sample 1/6 but using NIPOL 1472 in which 40% of the carboxylic groups have been blocked**.	3	1
7/6	As Sample 1/6 but using NIPOL 1472 in which 55% of the carboxylic groups have been blocked**.	2	0.8
8/6	As Sample 1/6 but using NIPOL 1472 in which 100% of the carboxylic groups have been blocked**.	2	0.6
9/6	As Sample 1/6 but using NIPOL DN 300 W 45 (available from Nipon Zeon; M_w = 240000; an acrylonitrile/butadiene rubber having no reactive functionality) instead of NIPOL 1472.	0.4	0.2
10/6	As Sample 1/6 but substituting CTBN 1300 x 13 (available from Nipon Zeon; M_w = 13700; an acrylonitrile/butadiene/acrylic acid rubber) 50% by weight of the NIPOL 1472.	0.1	0.3
11/6	As Sample 1/6 but using CTBN 1300 x 13 (available from Nipon Zeon; M_w = 13700; an acrylonitrile/butadiene/acrylic acid rubber) instead of NIPOL 1472.	0.2	0.2
12/6	As Sample 1/6 but using E2016 (available from ICI Acrylics; M_w = 13700; an acrylic polymer containing 0.6 wt % of carboxylic groups) instead of NIPOL 1472.	1	0.35
13/6	As Sample 1/6 but using E2016 (available from ICI Acrylics; M_w = 13700; an acrylic polymer containing 20 wt % of carboxylic groups) instead of NIPOL 1472.	2	0.35

* - unable to measure owing to extremely low viscosity.

** - see method for blocking carboxylic groups below.

During the reaction, 5ml samples were withdrawn at various intervals. These samples were then titrated with 0.01N potassium hydroxide to ascertain the degree of reaction.

The reaction solution, on cooling to room temperature, was poured into a large crystallising dish to allow the bulk of the MEK to evaporate off. The resultant blocked rubber was then leached with propan-2-ol to remove the excess phenylglycidylether. Finally, the blocked rubber was dried for 20 hours at 60°C in a vacuum oven.
The degree of reaction (100% in this case) was assessed by titration as described above and by FTIR.

The 20%, 40% and 55% blocked rubbers were obtained by a similar procedure.

Formulation of Prepregging Solution (Samples 1/6, 3/6 and 5/6 to13/6)

Into a 700ml reaction flask equipped with a metal paddle stirrer, nitrogen inlet and condenser was charged MY 9663 (255.00g), ETPI (2.00g) and NIPOL 1472 (20 .00g) dissolved in 250g of acetone. A further 80g of acetone was then added to make the solids content of the reaction mixture up to 45%w/w.

The temperature of the reaction flask raised by means of an oil bath to reflux the acetone. This temperature was then maintained for 2 hours following which the heat was switched off and the temperature was allowed to drop to 40°C. An EPON 1001F/EPON 828 (50:50) epoxy mixture (48.00g) was then added. The temperature of the reaction flask was then allowed to cool to room temperature at which time DDS (68.00g) and DICY (10.00g) were added.

The reaction mixture (DICY is insoluble in acetone) was allowed to stir for a further 10 to 15 minutes or until all the DDS was in solution. Finally a further amount of acetone was then added so that the resin solids content measured between 54%w/w and 60%w/w depending on the resin density.

Formulation of Prepregging Solution (Samples 2/6 and 4/6)

Into a 700ml reaction flask equipped with a metal paddle stirrer, nitrogen inlet and condenser was charged MY 9663 (255.00g), NIPOL 1472 (20.00g) dissolved in 280g of acetone and EPON 1001F/EPON 828 (50:50) epoxy mixture (48.00g). A further 50.00g of acetone was then added to make the solids content up to 45%w/w.

The temperature of the reaction mixture was raised to 50°C to aid solubility of the MY 9663 and EPON epoxy mixture in the acetone. Once solution was complete the heat was removed. Then DDS (68.00g) and DICY (10.00g) were added. The reaction mixture was allowed to stir at room temperature for 1/2 hour or until all the DDS was in solution. Acetone was then added to give the required resin solids content for prepregging (55%w/w - 60%w/w).

Unidirectional Carbon Fibre Impregnation by Drumwinding (Wilton).

The formulated resin solution (1 litre) was poured into a resin pump (see Figure 3) of a drumwinder. The drum on the drumwinder was set to a temperature of 55°C to ensure complete volatilisation of the solvent. Each run on the drumwinder produced 1m^2 of prepreg. Two runs were carried out for each of the formulated Samples 1/6 to 13/6. The following process conditions were utilised so that a resin content on the prepreg of between 35%w/w and 42%w/w (determined gravimetrically) was achieved:-

Fibre	Amoco* T300 (12K).
Drum Temperature	55°C
Drum Speed	10 rpm
Pump Speed	5.2 rpm

Unidirectional Composite Fabrication

The appropriate number of plies were cut to size from the prepreg and laid up. The number of plies and their dimensions were dependant on the type of mechanical test to be performed. Transflexural Strength (TFS), Modulus, Tg determination, Short Beam Shear (SBS) and morphology required a test panel of 16 plies ($[0]_{16}$) and dimensions of 6 inches by 4 inches (152.4mm by 101.6mm). Toughness (G_{1c}) measurement required a test panel of 20 plies ($[0]_{20}$) with dimensions of 14 inches by 6 inches (355.6mm by 152.4mm). The plies were laid up by sequentially ironing them together with an iron set at 50°C.

The laid up plies were then inserted into a pressclave and bagged up according to the arrangement shown in Figure 4. The composite panels in this study were pressclaved according to the BMS 8 256 moulding cycle outlined below:

1. Room temperature start.
2. Ramp at 2°c per min to 180°C.
3. Hold at 180°c for 120 minutes.
4. Ramp at 2°C per min to Room Temperature.

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*Trade-mark

Vacuum is applied at the start to consolidate the lay up and is then released so that the panel is left open to vent. A pressure of 45psi (0.31MPa) is also applied at the start and held at this pressure through out the moulding cycle .

Transflexural Strength was determined using test specimens obtained from a $[0]_{16}$ panel with a nominal thickness of 2mm. The specimen size used was 10mm x 70mm and these were cut using a diamond saw. The test was carried out on a Instron 6022 machine using a standard 3 point bend arrangement with a support span of 50mm and tested at a speed of 1mm/min. The stress to cause failure was recorded. An average of 8 samples was taken to give a final TFS value for each of the composite systems studied. Fracture surfaces were examined both visually, to check for fibre mis-orietation and by SEM to discover the nature of failure.

Flexural Modulus was determined using test specimens were cut from a $[0]_{16}$ panel that had a nominal thickness of 2mm. The dimensions of the specimens were 140mm x 10mm . Testing was carried out on an Instron 6022 machine set up in 3 point bend mode with a support span of 100mm , thus giving a span to depth ratio of 50:1. The test was performed at a rate of 1mm/min. The test was manually stopped when the central deflection was equal to the specimen thickness(approx 2mm). An average of 4 specimens was taken as the final result.

Tg Measurement by DMTA - the samples were run on a power head, P1 DMTA under nitrogen with a heating rate of 2°C per minute. A single cantilever method was employed, the sample is clamped at one end and oscillated at the other end with a frequency of 10Hz.

Short Beam Shear was determined using test specimens which were machined from a $[0]_{24}$ panel with a nominal thickness of 3mm. The specimen size used was 25mm x 10mm (0° in 25mm direction) and these were cut using a diamond saw. The test was carried out on a Instron 6022 testing machine with a three point bend set up using a support span of 15mm giving a span to depth ratio of 5:1. The test speed used was 1mm/min and an average of 8 samples was taken to give the final result. The mode of failure was also recorded.

G_{1c} Testing The G_{1c} testing was determined using panels used for this test were $[0]_{20}$ 6inch x 14inch (152.4mm by 101.6mm) that had a crack starter (FEP - 0.02mm thick) 3inch x 6inch (76.2mm x 152.4mm) placed in between plies 10 and 11. Prior to testing the panels were C-scanned then samples were cut to a size of 1"x14" for double cantilever beam testing. Specimens were precracked by loading them at a crosshead rate of 0.05inch/min until the crack reached a length of 1inch beyond the FEP crack starter. Specimens were then tested at a rate of 0.05inch/min in tension. Results quoted are G_{Ic} of propagation.

Morphology was determined using $[0]_{16}$ unidirectional panels. Small samples of the composites were cut and mounted in cold-curing epoxy resin. These samples were then polished to a fine finish using a Buehler Metserv automatic polishing machine. To reveal the morphological structure samples were etched in a 1% w/v solution of $KMnO_4$ in "super acid" (which is a mixture of 5:5:2 by volume of conc. sulphuric acid: phosphoric acid : distilled water respectively). Samples were etched in this solution for 10 minutes then washed under flowing water for 30 mins. The samples were then cut from the mounting epoxy resin and attached to stubbs for SEM analysis. SEM samples were gold coated prior to analysis.

Example 7

Certain of the formulations used in Example 6 were repeated using the methods described below and for convenience the same sample numbering is utilised.

Formulation of Prepregging Solutions

The rubber to be used was solvated in acetone. The rubber solution, MY9663 and ETPI were mixed for 10 minutes until homogeneous. This mixture was then heated to reflux (approx 57°C) and held for 2 hours. The solution had approximately 45% resin solids during the reflux. After the two hour reflux, the heating apparatus was removed and the EPON 828 and EPON 1001F were added immediately to the solution. This was allowed to mix until the solid 1001F had completely dissolved into the solution. With the solution mixed well and cooled to approaching room temperature, the DDS and DICY were added to the mixture. 0.01% by weight AEROSIL* 974 (fumed silica available from De Gussa) was also added at this point and allowed to mix until homogeneous. All additions to the solution are washed with acetone. The final solution had approx. 55% resin solids content. This was adjusted (as needed) during impregnation.

Samples 1/6, 3/6 and 5/6 to 7/6 were prepared using this process.

Samples 2/6 and 8/6 were prepared using the process just described except that there was no reflux of the rubber solution and MY 9663 epoxy. The components were all simply added to the vessel and mixed at room temperature.

*Trade-mark

Sample 4/6 was prepared similarly to Samples 2/6 and 8/6 except that there was no rubber added to the mix. The percent amounts of each component was altered somewhat to compensate for the 5% lost from the rubber as follows: MY9663 - 66.32; EPON 828 - 6.32; EPON 1001F - 6.32; DDS - 17.89; DICY - 2.63; ETPI - 0.53; AEROSIL 974 - 0.05.

Table 8

SAMPLE	TFS (MPa)	SBS (MPa)	MODULUS (MGa)	T_g (°C)	G_{1c} (KJm^{-2})	MORPHOLOGY	-75°F TENSILE STRENGTH
1/6	82.32 (9.20)	56.6 (2.10)	44.90 (0.98)	152.81	0.228 (0.026)	Homogeneous	579.3
2/6	151.90 (6.00)	66.33 (4.40)	70.50 (0.87)	206.52	0.177 (0.019)	2-phase fine particulate	533.9
3/6	97.24 (5.23)	87.11 (2.40)	77.00 (0.40)	204.26	0.191 (0.013)	2-phase relatively coarse particulate	NA
4/6	90.88 (8.90)	53.66 (7.10)	87.90 (0.62)	187.83	0.371' (0.093)	homogeneous	498.8
5/6	110.9 (4.90)	107 (6.20)	63.20 (0.57)	201.59	0.329 (0.014)	coarse irregular particulate	586.2
6/6	83.02 (5.20)	50.39 (2.10)	70.40 (0.91)	191.47	0.203 (0.023)	coarse irregular particulate	570.3
7/6	83.23 (6.54)	51.22 (3.10)	69.60 (0.21)	201.52	0.337 (0.033)	coarse irregular particulate	517.4*
8/6	110.8 (6.24)	59.6 (2.40)	81.90 (0.90)	176.19	0.212 (0.046)	large particulate	482.9
9/6	74.71 (0.89	46.60 (6.80)	58.34 (0.30)	179.36	0.298' (0.056)	coarse irregular particulate	494.7 (80.5)
10/6	84.23(6.10)	49.77 (3.20)	43.90 (0.90)	174.29	0.694' (0.120)	NA	NA
11/6	103.1 (7.40)	74.21 (0.10)	90.69 (0.57)	181.99	0.236 (0.039)	large particulate	NA
12/6	105.6 (16.9)	77.41 (2.10)	85.80 (0.80)	184.25	0.277 (0.034)	gross phase separation owing to immiscibility/ insolubility of acrylic polymer in epoxy resin	NA
13/6	75.2 (3.7)	72.3 (3.10)	80.70 (0.20)	166.16	0.229 (0.044)	gross phase separation owing to immiscibility/ insolubility of acrylic polymer in epoxy resin	NA

Standard deviations are in brackets.

* A 85% blocked HYCAR 1472 was used.

[1] Panel gave poor C-Scan result.

Fabric Impregnation

The formulated Samples (2-5 litres) were poured into an impregnation bath contained within a solution impregnation semi-technical unit and outlined below in Figure 5:

The following process conditions were used to achieve a final resin solids content on the prepreg of 40% + 2%:-

Fabric	W-322/70C, Amoco T300, 3K, Plain weave.
Width	30 inches (762mm).
Line speed	18 inches per min (7.62mm/sec).
Resin concentration	50%w/w in acetone.
Resin specific gravity	1.000 - 1.005
Oven Bay Temperatures	Bays 1&2 set to 60°C, bay 3 set at 116°C.

The impregnated fabric was then transferred to the tape line and compacted under the following set of conditions:

Line speed	35 inches per min (14.8mm/sec).
1st Nip Temperature	Room Temperature
1st Nip Pressure	5psi (0.034MPa)
Hot Plate Temperature	88°C
2nd Nip Temperature	88°C
2nd Nip Pressure	20psi (0.14MPa)

The plies were cut from the prepreg and a $[0,90]_8$ was prepared using 12inch by 12inch (304.8mm by 304.8mm) squares for testing -75°F (-60°C) Tensile test and moulded similarly to the test composites prepared in Example 6. This test was performed using a 9 inch (228.6mm) tensile bar, ie waisted, held at -75°F (-60°C) on a standard test machine at a load rate of 1.27mm/min. The results of this test are quoted in Table 8 above. As can be seen, compositions according to the invention perform surprisingly well in this test which is considered especially important in the aerospace industry since aerospace vehicles are frequently subjected to very low temperatures during flights.

A porosity panel was also prepared in which fabric was bonded to a honeycomb structure using the layup illustrated in Figure 6. The panel was consolidated by being placed into a bag, as illustrated in Figure 7, and autoclaved. The panels are sectioned into two equal halves from which a 1 inch (25.4mm) wide strip is then cut and mounted in epoxy resin. The specimen is then polished to a high surface finish and the number of pores along the length of the panel are counted using a light microscope. If any significant pores are observed, the panel is failed. The results are given in Table 9.

Table 9

SAMPLE	EDGEBAND	BAGSIDE	TOOLSIDE	PASS/ FAIL
1/6	Good, some small porosity near chamfer tip	Chamfer - Good 3-ply area - Good 2-ply area - Good	3-ply area - 1 medium void at interface 2-ply area - Good	PASS
2/6	Good	Chamfer - Several small voids 3-ply area - 2 big voids 2-ply area - 2 big voids	3-ply area - 1 large void + 6 medium voids 2-ply area - Poor - repeating pores	FAIL
4/6	Repeating voids	Chamfer, 3-ply and 2-ply area - Repeating voids	3-ply area and 2-ply area - Repeating pores	FAIL
5/6	8 Medium voids	Chamfer - 4 voids 3-ply area - OK 2-ply area - 4 medium voids	3-ply area - > 8 medium/large voids 2-ply area - Good	FAIL
6/6	2 Medium voids	Chamfer - 1 void 3-ply area and 2-ply area - Repeating pores	3-ply area - > 10 repeating voids 2-ply area - > 5 medium/small voids	FAIL
7/6 - but 0.85 blocked	>15 voids, poor	Chamfer - Poor 3-ply area and 2-ply area - Poor	3-ply area and 2-ply area - Poor	FAIL
8/6	Poor	Chamfer - OK 3-ply area - 2 small voids 2-ply area - Good	3-ply area and 2-ply area - Poor	FAIL
9/6	Poor - large voids	Chamfer, 3-ply and 2-ply area - Repeating voids	3-ply area - 7 large voids and 2-ply area - 6 small voids	FAIL

CLAIMS:

1. A curable composition comprising:

(a) an epoxy resin comprising:

(i) at least one first epoxy resin monomeric component comprising monomers having an epoxy functionality of greater than three; having at least 0.05% by weight, based on a total weight of the epoxy resin, of oligomeric epoxy species; and being a polyglycidyl derivative or an oligomer of a polyglycidyl derivative of at least one compound selected from aromatic diamines, aromatic monoprimary amines and aminophenols, and

(ii) at least one second epoxy resin component comprising monomers having an epoxy functionality of greater than one but not more than three;

(b) at least one curing agent for the epoxy resin and

(c) a reaction product formed *in situ* by pre-reaction between

(i) a solid rubber, which has at least 1.0 wt% of reactive groups and which is swellable by or soluble in a reaction mixture in which the reaction product is formed, and

(ii) at least a portion of oligomers present in the first epoxy resin monomeric component,

wherein the solid rubber to first epoxy resin weight ratio is between 1:1 and 1:20, and

wherein the pre-reaction is conducted in the presence of a catalyst, which catalyst is an alkyl triphenyl phosphonium iodide, bromide or chloride, stannous octoate or chromium octoate.

2. The curable composition according to claim 1, wherein the at least one first epoxy resin monomeric component comprises monomers having an epoxy functionality of four.

3. The curable composition according to claim 1 or 2 in which the amount of oligomeric species present in the epoxy resin is at least 0.5% by weight.

4. The curable composition according to any one of claims 1 to 3 in which the reaction product comprises solid rubber reacted only with at least a portion of the first epoxy resin monomeric component.

5. The curable composition according to any one of claims 1 to 4 in which the second epoxy resin component comprises a glycidyl derivative of one or more of:

aromatic diamines,

aromatic monoprimary amines,

aminophenols,

polyhydric phenols,

polyhydric alcohols, and

polycarboxylic acids.

6. The curable composition according to any one of claims 1 to 5 in which the first epoxy resin monomeric component is selected from the group consisting of N,N,N',N'-tetraglycidyl diamino diphenylmethane, N,N,N',N'-tetraglycidyl-bis(4-aminophenyl)-1,4-

diisopropylbenzene, N,N,N',N'-tetraglycidyl-bis(4-amino-3,5-dimethylphenyl)-1,4-diisopropylbenzene, glycidyl ethers of phenol novolak resins, and glycidyl ethers of bisphenol A novolak resins.

7. The curable composition according to claim 6 in which the first epoxy resin monomeric component is N,N,N',N'-tetraglycidyl diamino diphenylmethane.

8. The curable composition according to any one of claims 1 to 7 in which the second epoxy resin component is selected from the group consisting of diglycidyl ethers of bisphenol A based materials, triglycidyl ethers of 4-aminophenol, diglycidyl ether of bisphenol A, and diglycidyl 1,2-phthalate.

9. The curable composition according to claim 8 in which the second epoxy resin component is a diglycidyl ether of bisphenol A.

10. The curable composition according to any one of claims 1 to 9 in which the at least one curing agent is an amino compound having a molecular weight up to 500 per amino group.

11. The curable composition according to any one of claims 1 to 9 in which at least first and second curing agents are used, wherein the first curing agent is reactive with epoxy groups and promotes reaction between hydroxyl groups and epoxy groups.

12. The curable composition according to claim 11, wherein the first curing agent is an amino compound having a molecular weight up to 500 per amino group.

13. The curable composition according to claim 11 in which the first curing agent is selected from the group

consisting of 3,3'- and 4,4'-diaminodiphenylsulphone, methylenedianiline, bis(4-amino-3,5-dimethylphenyl)-1,4-diisopropylbenzene and bis(4-aminophenyl)-1,4-diisopropylbenzene.

14. The curable composition according to claim 13 in which the first curing agent is 4,4'-diaminodiphenylsulphone.

15. The curable composition according to any one of claims 11 to 14 in which the second curing agent is selected from the group consisting of dicyanodiamide, 4-chlorophenyl-N,N-dimethyl-urea, and 3,4-dichlorophenyl-N,N-dimethyl-urea.

16. The curable composition according to claim 15 in which the second curing agent is dicyanodiamide.

17. The curable composition according to any one of claims 10 to 16 in which total amine content of curing agents is in the range 70-110% of the stoichiometric requirement of the epoxy resin components.

18. The curable composition according to any one of claims 1 to 17 in which the solid rubber is soluble in the epoxy resin.

19. The curable composition according to any one of claims 1 to 18 in which the solid rubber is selected from the group consisting of olefin, diene and nitrile rubbers and copolymers and terpolymers thereof which have pendant reactive groups.

20. The curable composition according to any one of claims 1 to 19 in which the solid rubber has at least 2.5 wt% of reactive groups.

21. The curable composition according to any one of claims 1 to 20 in which the solid rubber has reactive carboxylic groups.

22. The curable composition according to any one of claims 1 to 21 in which the solid rubber is a diene-nitrile copolymer having carboxylic groups.

23. The curable composition according to any one of claims 1 to 22 in which the solid rubber is an acrylonitrile/butadiene rubber having carboxylic groups.

24. The curable composition according to any one of claims 1 to 23 in which the reactive groups are carboxylic groups and are provided by a methacrylic acid termonomer.

25. The curable composition according to any one of claims 1 to 24 in which the solid rubber contains up to 5 wt% carboxylic groups.

26. The curable composition according to any one of claims 1 to 25, comprising 1 to 10 wt% of solid rubber based on a total weight of epoxy resin, curing agent and reaction product of the composition.

27. The curable composition according to any one of claims 1 to 26, comprising 3 to 6 wt% of solid rubber based on a total weight of epoxy resin, curing agent and reaction product of the composition.

28. The curable composition according to any one of claims 1 to 27, comprising 4.0 to 8.0 wt% of solid rubber based on a total weight solid rubber and the first epoxy resin monomeric component.

29. The curable composition according to any one of claims 1 to 28, comprising 4.5 to 7.0 wt% of solid rubber

based on a total weight solid rubber and the first epoxy resin monomeric component.

30. The curable composition according to any one of claims 1 to 29 in which the catalyst alkyl group is selected from methyl, ethyl, propyl, n-butyl, iso-butyl, n-pentyl and n-decyl.

31. The curable composition according to any one of claims 1 to 30 in which the catalyst is ethyl triphenyl phosphonium iodide.

32. A prepreg comprising the curable composition according to any one of claims 1 to 31 and continuous fibre reinforcement.

33. A shaped article comprising the curable composition according to any one of claims 1 to 31, wherein the composition has been cured and forms a matrix having a homogeneous morphology, or a particulate morphology in which the solid rubber is present as particles having a mean size of less than 5 micron.

34. The shaped article according to claim 33, wherein the matrix has a particulate morphology in which the solid rubber particles have a mean size of not more than 1 micron.

35. A shaped article comprising the prepreg of claim 32, wherein the curable composition has been cured and forms a matrix having a homogeneous morphology, or a particulate morphology in which the solid rubber is present as particles having a mean size of less than 5 micron.

36. The shaped article according to claim 35, wherein the matrix has a particulate morphology in which the solid rubber particles have a mean size of not more than 1 micron.

37. A process for making the curable composition of any one of claims 1 to 31, comprising:

forming a reaction mixture of the solid rubber, at least a portion of the first epoxy resin monomeric component, the catalyst and a polar solvent, the catalyst promoting reaction between the first epoxy resin monomeric component and the reactive groups of the solid rubber, and the solid rubber, the first epoxy resin monomeric component and the catalyst comprising between 25 and 75 wt% of the reaction mixture;

heating the reaction mixture to effect the reaction;

cooling the resultant mixture to substantially ambient temperature;

adding any remaining portion of the first epoxy resin monomeric component and adding the second epoxy resin component and curing agents to the mixture; and

substantially removing the solvent therefrom.

38. The process according to claim 37 in which the reaction mixture is heated to a temperature in the range 40°C to 80°C.

39. The process according to claim 37 or 38 in which the reaction mixture is under reflux.

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PATENT AGENTS

Fig.1.

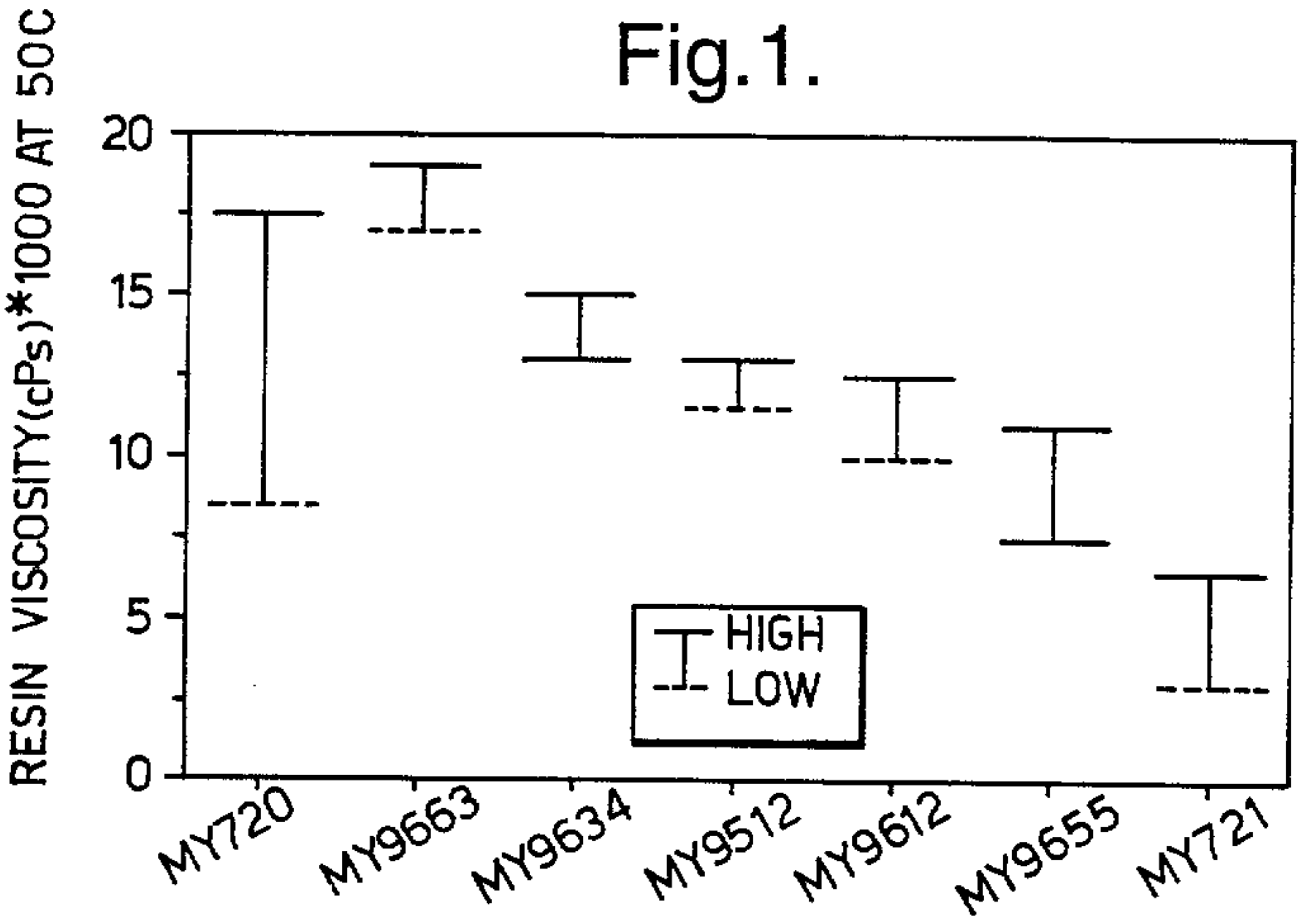

RESIN VISCOSITY(cPs)*1000 AT 50C
0
5
10
15
20
HIGH
LOW
MY720
MY9663
MY9634
MY9512
MY9612
MY9655
MY721

Fig.2.

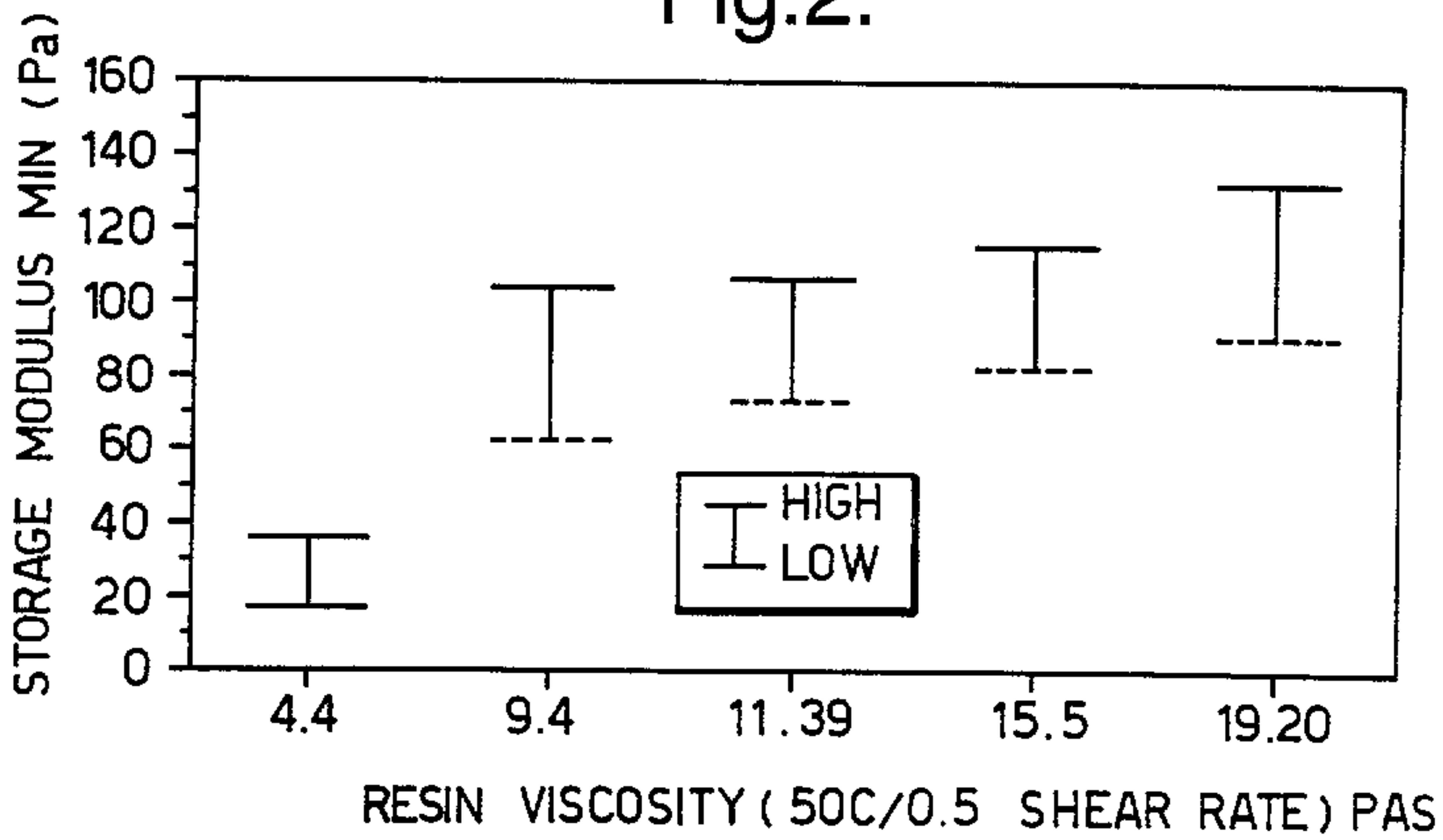

STORAGE MODULUS MIN (Pa)
0
20
40
60
80
100
120
140
160
HIGH
LOW
4.4
9.4
11.39
15.5
19.20
RESIN VISCOSITY (50C/0.5 SHEAR RATE) PAS

Fig.3.

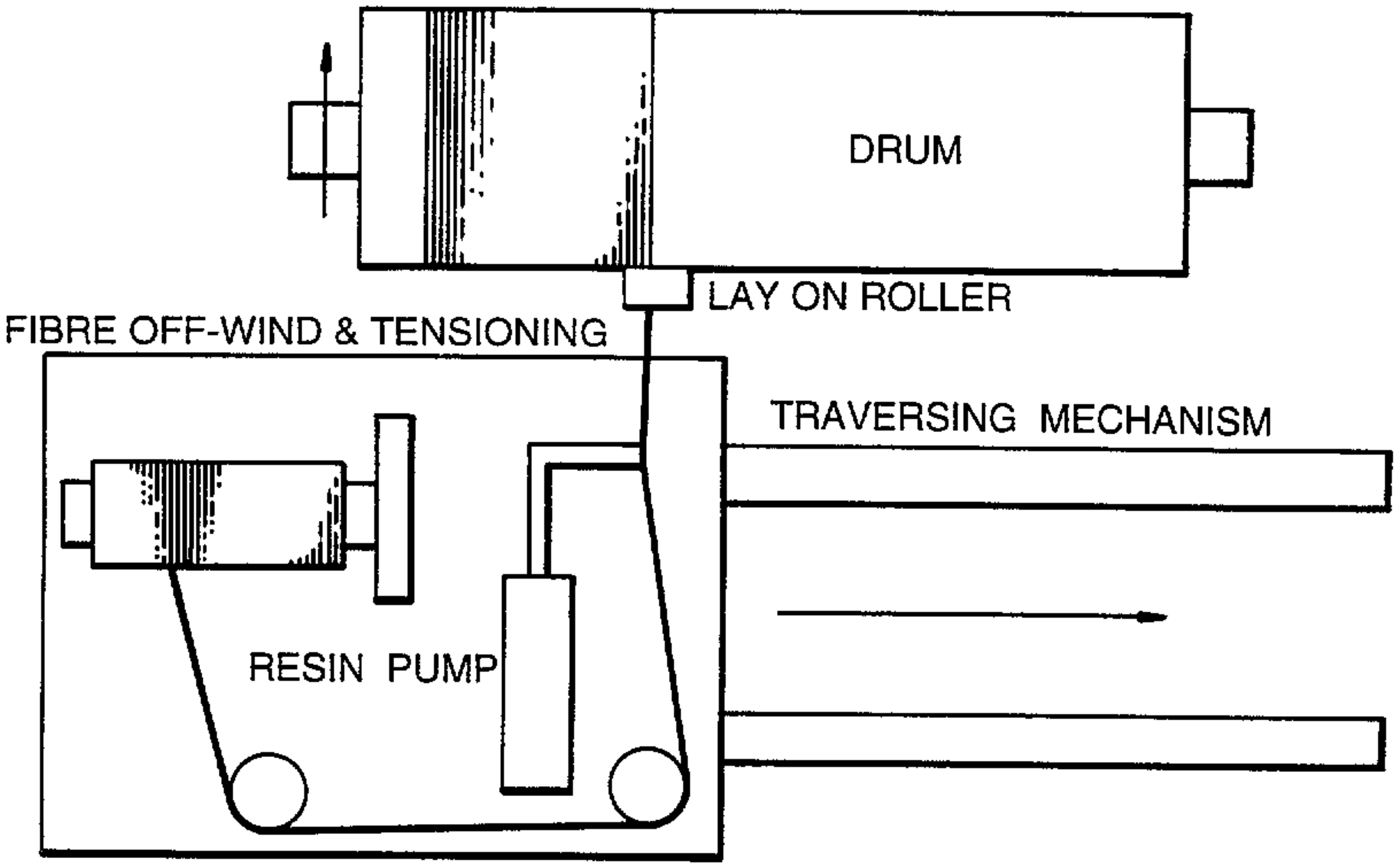

DRUM
LAY ON ROLLER
FIBRE OFF-WIND & TENSIONING
TRAVERSING MECHANISM
RESIN PUMP

Fig.4.

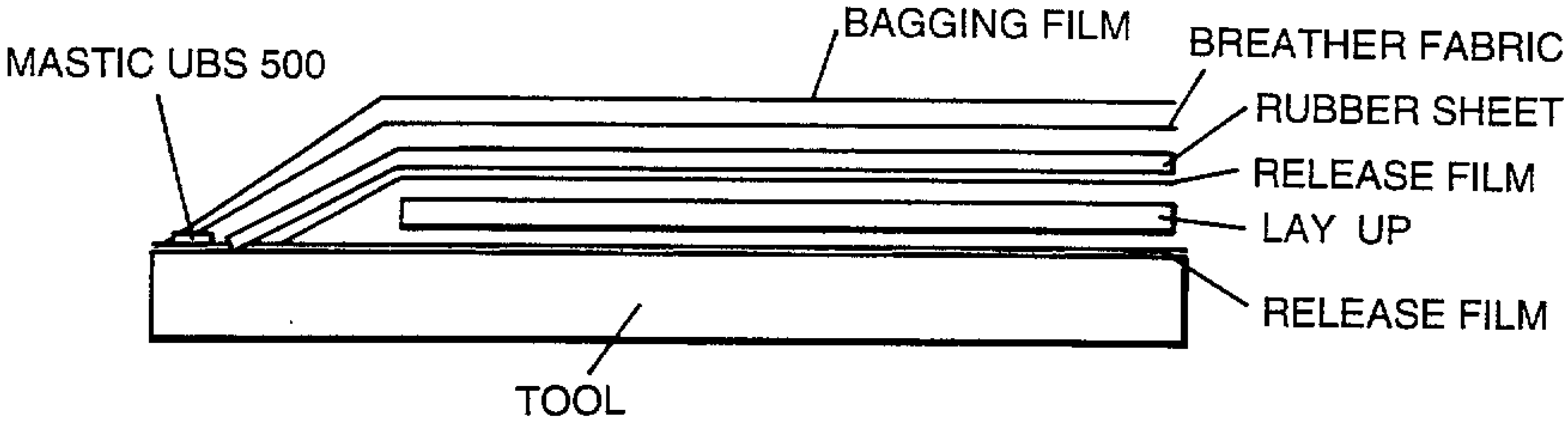

BAGGING FILM
MASTIC UBS 500
BREATHER FABRIC
RUBBER SHEET
RELEASE FILM
LAY UP
RELEASE FILM
TOOL

Fig.5.

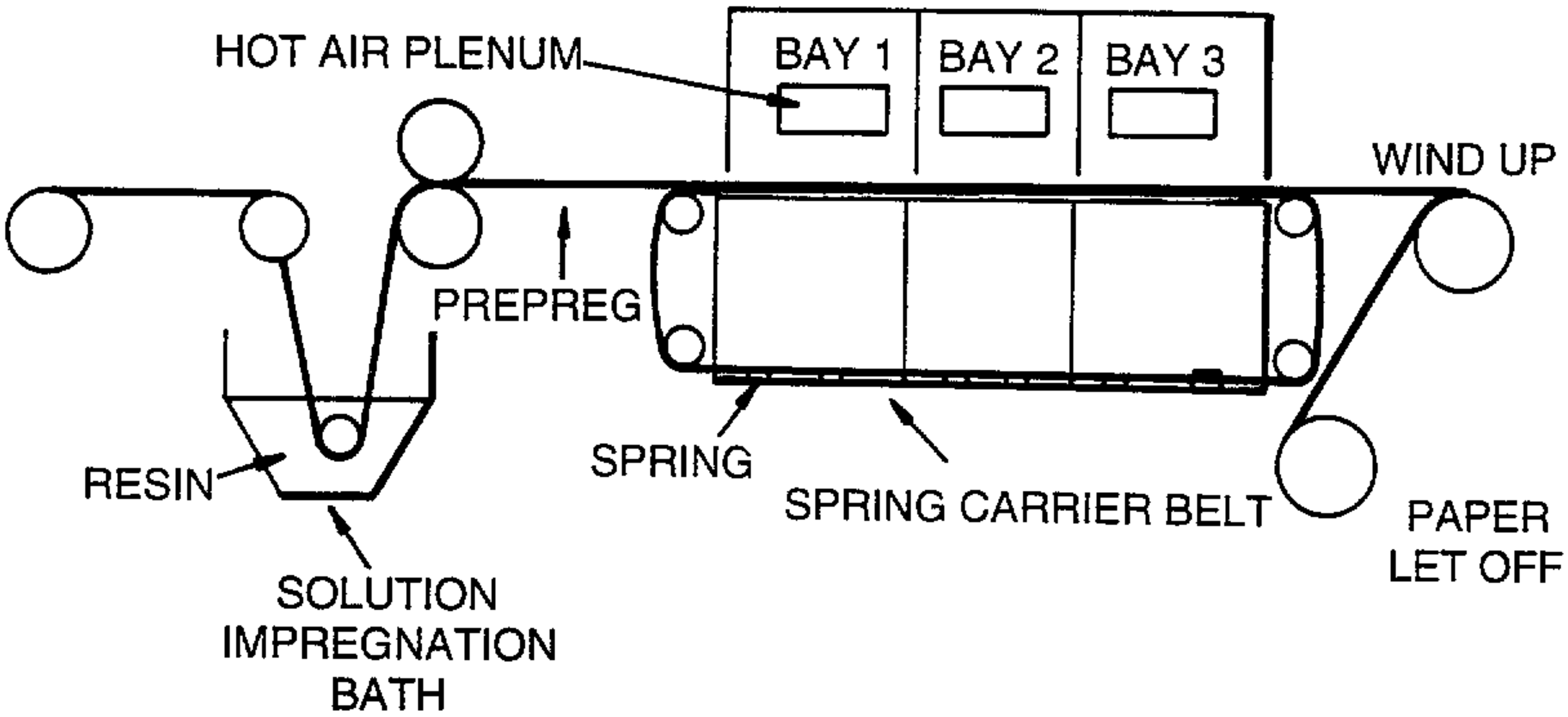

HOT AIR PLENUM
BAY 1
BAY 2
BAY 3
WIND UP
PREPREG
RESIN
SPRING
SPRING CARRIER BELT
PAPER LET OFF
SOLUTION IMPREGNATION BATH

Fig.6.

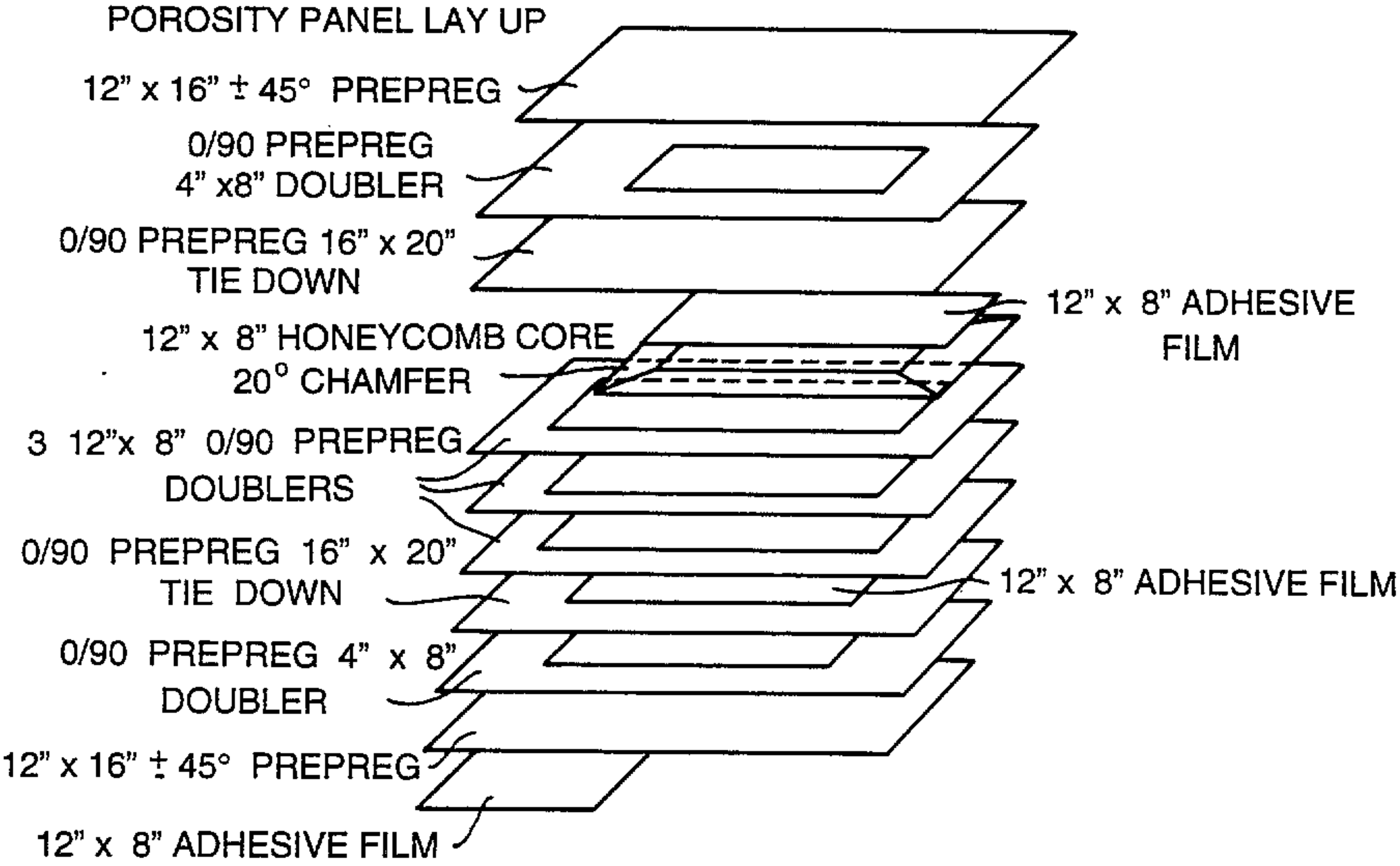
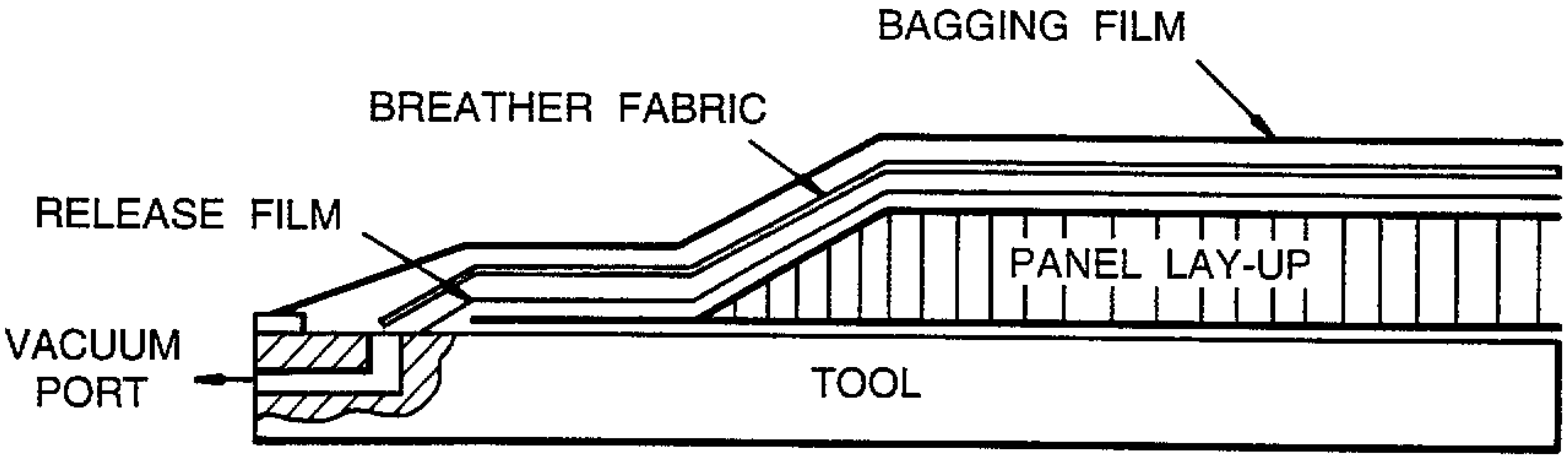

POROSITY PANEL LAY UP
12" x 16" ± 45° PREPREG
0/90 PREPREG 4" x8" DOUBLER
0/90 PREPREG 16" x 20" TIE DOWN
12" x 8" ADHESIVE FILM
12" x 8" HONEYCOMB CORE 20° CHAMFER
3 12"x 8" 0/90 PREPREG DOUBLERS
0/90 PREPREG 16" x 20" TIE DOWN
12" x 8" ADHESIVE FILM
0/90 PREPREG 4" x 8" DOUBLER
12" x 16" ± 45° PREPREG
12" x 8" ADHESIVE FILM

Fig.7.


BAGGING FILM
BREATHER FABRIC
RELEASE FILM
PANEL LAY-UP
VACUUM PORT
TOOL