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(21) International Application Number: PCT/NL98/00469 (22) International Filing Date: 19 August 1998 (19.08.98) (30) Priority Data: 1007001 11 September 1997 (11.09.97) NL (71) Applicant (for all designated States except US): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): NUSSELDER, Jan, Jacob, Hendrik [NL/NL]; Kerkstraat 20, NL-6174 RE Schinnen (NL). BONEKAMP, Karel, Franciscus, Hubertus [NL/NL]; Brederodestraat 21, NL-6181 BE Stein (NL). (74) Agent: VAN BOKHOVEN, Petrus, Hubertus, Maria; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HR, HU, ID, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, SL, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>	
(54) Title: LAMINAR PREPREG			
(57) Abstract Laminar prepreg comprising one or more layers of a laminar carrier, which carrier is impregnated with an as yet uncured resin, the carrier being a laminar porous polymer and the elongation at break of the prepreg and of the separate impregnated laminar carrier being greater than 10 %.			

LAMINAR PREPREG

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The invention relates to a laminar prepreg comprising one or more layers of a laminar carrier, which carrier is impregnated with an as yet uncured resin.

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Laminar prepregs comprising a plurality of mutually stacked layers of α -cellulose impregnated with the reaction product of formaldehyde and melamine are disclosed, for example, in US-A-3730828. According to said patent publication, paper is first impregnated with
15 a melamine-formaldehyde resin. Then a prepreg is made by precuring layers and thereafter stacking a few layers of said impregnated paper on top of one another. The resin is then cured in a press under a pressure of, for example, 6 MPa and at a temperature of approximately
20 150°C. The conversion of the reaction between formaldehyde and melamine in the laminar product thus obtained is complete (completely cured). The laminar products described in said patent publication appear to have good postforming properties. Postforming is
25 understood as meaning that the laminar product can be bent at an elevated temperature which is between 160 and 180°C, it being possible to bend the laminar product along one axis without the laminar product breaking/cracking.

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A disadvantage is that, starting from a prepreg according to US-A-3730828, it is not possible to

obtain laminar products which can be bent into complex shapes along two (or more) mutually intersecting axes without breaking/cracking. Complex shapes may be considered to be, for example, a saddle-type pattern, a small tub, a sickle pattern or a satchel.

5 The object of this invention is a prepreg with which more complex shapes can be obtained.

According to one embodiment of this invention there is provided a laminar prepreg comprising one or more layers of a laminar carrier, which carrier is impregnated with an as yet uncured resin, characterised in that the carrier is a laminar porous polymer and in
10 that the elongation at break of the prepreg and of the separate impregnated laminar carrier is greater than 10% in accordance with ISO 37 and for a residual volatility of approximately 5%.

According to another embodiment of this invention there is provided a process of making a prepreg according to the invention, the polymer carrier being impregnated with
15 water-fluid resin, optionally in the presence of a wetting agent, after which the carriers impregnated in this way are dried (precured), with the water being evaporated, so that the prepreg has a residual volatility of 2-20%, after which stacking of the prepreg is optionally carried out.

According to a further embodiment of this invention there is provided a process for
20 the processing of a prepreg according to any one of claims 1-10 into a shaped product, the prepreg being deformed at a temperature between room temperature and 200°C with the resin being cured either in a subsequent step or during the deformation.

According to yet a further embodiment of this invention there is provided a laminar prepreg made by the process of the invention.

25 According to yet another embodiment of this invention there is provided a processed prepreg made by the process of the invention.

It has been found that, proceeding from the prepreg according to the invention, laminar products can be made in the most diverse shapes without cracks occurring in the laminar product during the deformation. Laminar products are now possible which have
30 shapes in which the prepregs are locally stretched from 10% to more than 400% during the shaping. A further advantage is that the further curing of the resin and the deformation can be performed in one step. This is in contrast to the method described in the above-mentioned US-A-3730828 where, proceeding from the prepreg, two steps are necessary to arrive at a shaped final product. An additional advantage is that the prepreg



can be processed by a multiplicity of techniques, as a result of which the most optimum technique can be used for each final product.

Proceeding from the prepreg according to the invention, it is furthermore possible to make laminar products which are bent into an acute angle, for example along one axis.

5 Proceeding from the known preregs based on a paper carrier, this is impossible.

JP-A-7002119 discloses a prepreg made up of a carrier of a polyamide nonwoven material and a carrier of kraft paper, which carriers are impregnated with a melamine-formaldehyde resin. An impregnated polyamide nonwoven carrier has, as a rule, an elongation at break of more than 10%. However, impregnated kraft paper has an
10 elongation at break of less than 10%, as a result of which the elongation at break of the prepreg as a whole is less than 10%.

A laminar porous polymer carrier is understood as meaning any polymer which comprises a high degree of porosity. The porosity of the polymer carrier is essential for obtaining the advantageous properties of the prepreg as described above.

15 As a result of the high porosity, the laminar polymer carrier can, as it were, be mixed almost homogeneously with the resin. Preferably, the porosity is obtained in the form of microscopically small, mutually communicating cavities and there are preferably few larger cavities and holes present. Larger holes result in loss of resin during the further processing of the prepreg to its final shape. Preferably, the porosity is sufficiently
20 high for at least 30% by volume of the final shaped part to consist of resin. The porosity is the ratio between the density of the porous polymer carrier with respect to that of the corresponding bulk polymer (no cavities). Typically the density of the porous polymer carrier is less than 70% of the density of the corresponding bulk polymer.

The porous polymer carrier may, for example, be a nonwoven laminar polymer, a
25 laminar open polymer foam or a microporous membrane. Preferably, the fibres



of the nonwoven are smaller than 0.1 mm. Nonwovens having very small-diameter fibres are also referred to as open films. This class of nonwovens has, as a result of the small thread diameter, few larger meshes and many microscopically small, mutually communicating cavities. The fibres of said nonwovens lie, as a rule, parallel to the plane of the laminar porous polymer. Polymer foams inherently have a reasonably definable and uniform size of the mutually communicating cavities. The cavities preferably have a diameter of less than 1 mm. Larger cavities may occasionally be present in the foam provided more than 80% by volume of the cavities have said smaller diameters.

The porous polymer carrier may in principle be any porous polymer which meets the requirement that the impregnated carrier has an elongation at break of more than 10%. Examples of porous polymers are porous polyethylene, porous polypropylene, porous polystyrene, porous ethylene/propylene copolymers, porous EPDM, porous polyamides, for example, porous nylon 6,6, porous nylon 6, porous ethylcellulose, porous cellulose acetates, for example porous cellulose diacetate, porous SMA/SAN, porous polyesters, for example porous polyethylene terephthalate (PET), porous polybutylene terephthalate (PBT), porous polyethers. Also possible are combinations of different porous polymers or combinations of porous polymers with paper. As porous polymer carrier, the above-mentioned polymers can be used as nonwoven, open film or open polymer foam.

Examples of an open-film polyethylene are the polyethylene types which are known under the name of

Solupor[®] (Solupor[®] is a DSM N.V. brand name). Nonwovens based on various polymers are suitable to be used as carrier. An example of a nonwoven polyethylene is Tyvek[®] (Tyvek[®] is a DuPont de Nemours brand name). An example of a nonwoven polypropylene is Lutrasil[®] (Lutrasil[®] is a Freudenberg brand name). An example of a nonwoven polyester is Viledon[®] H1206. An example of a nonwoven polyamide is Viledon[®] FS2118 (Viledon[®] is a Freudenberg brand name). An example of an open polymer foam is Calligan[®] open-cell foam standard 1.17 polyether (Calligan[®] is a Calligan Europe B.V. brand name). An example of a cellulose filled nonwoven polypropylene is Workhouse[®] (Workhouse[®] is a Kimberly-Clark brand name). An example of a nonwoven cellulose acetate is TAT 2121 which is a product of Freudenberg.

The polymer may have either polar or apolar properties. As a result of making use of suitable wetting agents, the desired degree of impregnation of the polymer sheet by the resin can be obtained. As a rule, all the wetting agents known to the person skilled in the art can be used. Examples of wetting agents are PAT[®] 523W, PAT[®] 959 (PAT[®] is a Würtz brand name), Nonidet[®] P40 (Nonidet[®] P40 is a Sigma Chemie brand name) and Aminol[®] N (Aminol[®] is a Chem-Y brand name).

The resin may in principle be any known thermosetting resin. Examples are aminoplast formaldehyde resin, phenol-formaldehyde resin (PF resin), epoxy resin or unsaturated polyester resin.

Preferably, an aminoplast-formaldehyde resin is used as resin. Urea, melamine or benzoguanamine, for example, can be used as aminoplast. Preferably, melamine

is used because of its superior mechanical properties. The resin can be prepared in a process known to the person skilled in the art by reacting aminoplast and formaldehyde in water. The ratio of, for example, 5 formaldehyde:melamine is normally speaking between 1:1 and 6:1, preferably between 1.2:1 and 2:1. Optionally, the aminoplast can be partially replaced by, for example, phenol, but this may have adverse effects on the colour. Modifiers, such as sorbitol, ϵ -caprolactam, 10 ethylene glycol, trioxitol, toluenesulphonamide, and benzo- and acetoguanamine can also be added.

Mechanical properties which can be used well in practice are achieved if 10-70% by weight of porous polymer and 90-30% by weight of resin are used. The 15 resin may contain the known fillers such as lime, clay, glass, carbon, silica or metal particles. It has been found, however, that the best results are achieved in the absence of fillers or at any rate with less filler than has been usual hitherto. The filler and resin 20 weight ratio is preferably between 0:1 and 0.5:1. These ratios relate to the cured, final laminar product.

→ The prepreg comprises one or more stacked sheets of the impregnated porous polymer carrier. The number of laminar carriers is, as a rule, 10 or lower, 25 and preferably 5 or lower. The thickness of the prepreg can vary from 100 μm to approximately 3 cm. The degree to which the resin is cured in the prepreg can be determined for melamine-formaldehyde (MF) and PF resins by determining the residual volatility. Said residual 30 volatility is the loss in mass of the prepreg during 7 minutes at 160°C. The residual volatility of the prepreg

is, as a rule, between 2 and 20%. The elongation at break of the prepreg as used in the description is defined as the elongation at break for a residual volatility of approximately 5%.

5 The prepreg is made under the conditions which are already known for making prepreps based on a paper carrier, as described, for example, in the above-mentioned US-A-3730828 or JP-A-7002119. The resin is preferably dissolved in water and is 'water-fluid', the
10 resin preferably having a viscosity of 1-1000 Pa.s. The viscosity can be influenced by varying the amount of solvent. The solvent will vary depending on the chosen resin. Still uncured aminoplast-formaldehyde is preferably dissolved in water. Preferably solvents are
15 used in which the polymer carrier does not dissolve or swell. The temperature during the impregnation may be between 15 and 60°C and, for practical reasons, is often room temperature. Higher temperatures are less practical because the resin partially cures during the
20 impregnation. The pressure during the impregnation is not critical and, for practical reasons is, as a rule, atmospheric.

 The carriers impregnated in this way are dried until the residual volatility is reached, as
25 described above for the prepreg. The drying preferably takes place at a temperature of 100-160°C. Higher temperatures are less practical because the drying times then become too short, resulting in a less controllable process. The temperature will in practice also be
30 determined by the type of oven. Preferably, the carrier is stacked after the drying.

The elongation at break of the separate impregnated carrier (residual volatility = approximately 5%) and of the prepreg obtained is greater than 10% and preferably greater than 50%. The prepreg may optionally
5 also comprise layers of a non-porous polymer in addition to the porous polymer carriers provided these polymers also have an elongation at break which is greater than or equal to that of the prepreg.

→ The prepreg can be processed into a shaped
10 final product by first deforming the prepreg and then curing the shaped intermediate product at elevated temperature or by combining the deformation and the curing in one step.

The deformation, optionally in combination
15 with the curing, can be performed by means of bending, embossing, stamping, pneumatically stretching or mechanically stretching.

The temperature during the deformation will depend on the yield stress of the prepreg. The yield
20 stress is the stress at which the material begins to flow. Said yield stress is determined by the resin composition, resin content, polymer type and water content. In principle, said temperature may be between room temperature and 200°C. At temperatures higher than
25 100°C, the resin will already (partially) cure during the deformation, as a result of which the deformation and curing of the resin will take place simultaneously.

The shaped product obtained in this way can be used as final product or as protective layer around
30 an object having a core material of, for example, wood, metal, glass or plastic, for example polyethylene,

polypropylene, ABS, polyamide and MF resins, PF resins and epoxy resins.

Examples of final products of the shaped product are serving trays, washing-up basins, crockery, doors, kitchen worktops, furniture, wall panels. Examples of end products where the shaped product is used as protective layer for a wooden core are worktops having, for example, an acute angle, (kitchen) cupboards particularly the fronts of (kitchen) cupboards consisting of for example milled MDF (= medium density fibre board) or window frames. Examples of articles in which the shaped product serves as protective layer for a plastic core are bumpers, petrol tanks, garden furniture, worktops or car bodywork components.

The protective layer may be glued to the core material. Another possibility is that the shaped product is applied to the core while the resin is still incompletely cured. The resin then serves as glue joint when it is subsequently cured. Then curing and deformation takes place in one process step.

The invention will be described by means of the following, non-limiting examples.

Example 1

Preparation of resin

In a reactor, 24 parts of water and 135 parts of formaldehyde (30% formaldehyde in water adjusted to a pH of 9.3 using 50% NaOH) were added to 100 parts of melamine. The F/M ratio of the resin was 1.7 (F/M ratio is the formaldehyde-melamine molecular ratio). The condensation reaction was performed at 95°C

until the water dilutability of the resin at 20°C was 1.5 g of resin per g of water. The water dilutability is the amount (g) of water which can be added to a resin solution (g) at 20°C before the solution becomes turbid.

- 5 The resin was made reactive (catalyzed) with a 50% (by weight) p-toluenesulphonic acid solution to a pH of 8.1.

Preparation of laminar product

- Four 10 by 10 cm sheets of Solupor[®] (type 10 16P03; DSM) were impregnated at room temperature with the above-mentioned resin solution, to which 1% (m/m) of Nonidet[®] P40 (Sigma Chemie) had been added as wetting agent. After a few minutes, the sheets impregnated with resin were removed from the resin set-up and the excess 15 resin was removed with the aid of a "wringer". The sheets were dried in a ventilated oven for 4 minutes at 100°C.

Characterization of the prepreg

- 20 Resin content: the resin content of the prepreg was determined by weighing the prepreg and the polymer carrier and was 440%. The resin content is defined as:

25
$$(g(\text{prepreg}) - g(\text{polym})) / g(\text{polym}),$$

$g(\text{prepreg})$ and $g(\text{polym})$ are the weights of the prepreg and of the Solupor polymer carrier, respectively.

- Residual volatility content: the residual 30 volatility content was determined by measuring the weight loss after drying and curing the prepreg further

for 7 minutes in an oven at 160°C and was 3.5%. The residual volatility content is defined as:

$$(g(\text{before}) - g(\text{after})) / g(\text{before}),$$

5

$g(\text{before})$ and $g(\text{after})$ are the weights of the prepreg before and after treatment at 160°C, respectively.

Characterization of the laminate:

10 Resin content: the resin content of the laminate was determined by weighing the laminate and the starting polymers and was 406%. The resin content is defined as:

15 $(g(\text{laminate}) - g(\text{polym})) / g(\text{polym}),$

$g(\text{laminate})$ and $g(\text{polym})$ are the weights of the laminate and of the polymer carrier, respectively.

Elongation at break: the elongation at break was

20 measured on test pieces (dimensions 4.0*50.0*0.07 mm) at 140°C with the aid of a standard Zwick tensile test bench in accordance with ISO 37 type 3 and was more than 400%, the maximum value measurable with said equipment. The tensile strength was 5.4 MPa. The rate of
25 deformation was 100 mm/min.

- 2D pressing:

Four 10*10 cm sheets of the prepreg were pressed into a laminate by the following high-pressure laminate

30 pressing cycle: the sheets are placed in the press (of the type Fontijnen SRA 100) at 60°C and the press is

brought to a pressure of 80 bar and the press is further heated in approximately 15 minutes to 130°C, said temperature is maintained for 30 minutes and then cooling to 60°C takes place in approximately 15 minutes, after which the pressure is let down.

- 3D pressing:

A few sheets of Solupor prepreg were pressed on a high-density polyethylene core material in an S-shaped mould at 140°C for 20 minutes. The mould clamping force was 9 MPa. Cooling was then carried out for 10 minutes to 40°C. The results are further reported in Tables 1 and 2.

15 Example 2

The process of Example 1 was repeated, but Tyvek[®] L1058D (DuPont) was used instead of Solupor. Table 1 shows the resin content, the residual volatility content, the pressing conditions of the prepreg and the resin content of the laminate. Table 2 shows the elongation at break and the tensile strength of the prepreg at the stated test temperature.

Example 3

25 The process of Example 1 was repeated, but Lutrasil[®] 3450 (Freudenberg) was used instead of Solupor. See Tables 1 and 2 for further conditions and results.

30 Example 4

The process of Example 1 was repeated, but

cellulose diacetate (CD) nonwoven was used instead of Solupor. See Tables 1 and 2 for further conditions and results.

5 Example 5

The process of Example 1 was repeated, Viledon[®] FS2118 being used instead of Solupor[®]. See Tables 1 and 2 for further conditions and results.

10 Example 6

The process of Example 1 was repeated, Viledon[®] H1206 being used instead of Solupor[®]. See Tables 1 and 2 for further conditions and results.

15 Comparison Experiment A

The same process as in Example 1 was used, but a decorative paper (80 g/m²) was used instead of Solupor. See Tables 1 and 2 for further conditions and results.

Table 1

Example	Polymer	Drying time, min (100°C)	Prepreg resin content, % (m/m)	Residual volatility, % (160°C, 7 min)	Pressing conditions			Laminate resin content, % (m/m)
					Time, min	Temp., °C	Press., kN	
1	Solupor [®]	4	440±10	3.5±1.5	30	120	16	406±10
2	Tyvek [®] 1058D	2	115±15	4±1.5	30	120	20	76±30
3	Lutrasil [®] 3450	10	371±30	8.6±2.0	15	140	8	270±50
4	CD nonwoven	8	175±30	12.5±2.0	15	140	2	141±30
5	Viledon [®] FS2118	10	260±20	7.5±1.5	15	140	8	203±20
6	Viledon [®] H 1206	2	90±10	6.4±1.5	15	140	8	42±20
A	Paper	2.5	70±10	5.6±1.5	15	140	80	70±10

Table 2

Example	Polymer	Test temp., °C	Elongation at break, %	Tensile strength, MPa
1	Solupor	140	> 400	5.4±0.5
2	Tyvek 1058D	140	90±10	1.5±0.3
3	Lutrasil 3450	140	167±15	2.5±0.2
4	CD nonwoven	160	> 400	0.56±0.10
5	Viledon FS2118	140	72±8	7.5±0.5
6	Viledon H1206	190	31±3	17.4±1
A	Paper	140	0.8±0.1	17.1±1

The claims defining the invention are as follows:

1. A laminar prepreg comprising one or more layers of a laminar carrier, which carrier is impregnated with an as yet uncured resin, characterised in that the carrier is a laminar porous polymer and in that the elongation at break of the prepreg and of the
5 separate impregnated laminar carrier is greater than 10% in accordance with ISO 37 and for a residual volatility of approximately 5%.

2. A laminar prepreg according to claim 1, characterised in that the elongation at break of the separate impregnated laminar carrier and of the prepreg is greater than 50%.

3. A laminar prepreg according to any one of claims 1-2, characterised in that
10 the density of the porous polymer carrier is less than 70% of the density of the corresponding bulk polymer.

4. A laminar prepreg according to any one of claims 1-3, characterised in that the porous polymer carrier is a laminar nonwoven, open-film or open-foam polymer carrier.

5. A laminar prepreg according to claim 4, characterised in that the porous
15 polymer carrier is a nonwoven or open-film carrier.

6. A laminar prepreg according to any one of claims 1-5, characterised in that the resin is an aminoplastic formaldehyde resin, a phenol-formaldehyde resin, an epoxy resin or an unsaturated polyester resin.

7. A laminar prepreg according to claim 6, characterised in that the resin is an
20 aminoplastic formaldehyde resin.

8. A laminar prepreg according to claim 7, characterised in that the aminoplastic is urea, melamine or benzoguanamine.

9. A laminar prepreg according to any one of claims 7-8, characterised in that
25 the residual volatility is between 2 and 20%.

10. A laminar prepreg according to any one of claims 1-9, characterised in that a filler is added to the prepreg and that a resin weight ratio between 0:1 and 0.5:1 is used.

11. A process of making a prepreg according to any one of claims 7-9, the polymer carrier being impregnated with water-fluid resin, optionally in the presence of a
30 wetting agent, after which the carriers impregnated in this way are dried (precured), with the water being evaporated, so that the prepreg has a residual volatility of 2-20%, after which stacking of the prepreg is optionally carried out.

12. A process for the processing of a prepreg according to any one of claims 1-10 into a shaped product, the prepreg being deformed at a temperature between room



temperature and 200°C with the resin being cured either in a subsequent step or during the deformation.

13. A process according to claim 12, characterised in that the prepreg has locally been stretched at least 50% during the shaping.

14. Use of the shaped product obtained by the method according to any one of claims 12-13 as protective layer for a wooden, plastic, glass or metal object.

15. A laminar prepreg comprising one or more layers of a laminar carrier, which carrier is impregnated with an as yet uncured resin, substantially as hereinbefore described with reference to any one of the examples.

16. A process of making a prepreg, substantially as hereinbefore described with reference to any one of the examples.

17. A laminar prepreg made by the process of claim 11.

18. A processed prepreg made by the process of claim 12 or 13.

19. A prepreg made by the process of claim 16.

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