CONVENTION APPLICATION FOR A STANDARD PATENT

We, ATECHEN,
a French body corporate,
of 12/16, Allee des Vosges, 92400 Courbevoie, France hereby apply
for the grant of a standard patent for an invention entitled:
"POLYMERS PRODUCED FROM POLYAMIDE Oligomers AND EPOXIDE RESINS"
which is described in the accompanying complete specification.

DETAILS OF BASIC APPLICATION

Number of Basic Application:- 8413244
Name of Convention Country in which Basic Application was filed:- France
Date of Basic application:- 27 August 1984
Our address for service is:-
C/- Spruison & Ferguson Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia

DATED this TWENTY-SIXTH day of AUGUST 1985

By:


TO: THE COMMISSIONER OF PATENTS
AUSTRALIA

SBR:JMC:12M
COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952–1973
DECLARATION IN SUPPORT OF CONVENTION OR NON–CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

In support of the Application made for a Patent
entitled: "POLYMERS PRODUCED FROM POLYAMIDE Oligomers and Epoxy Resins"
1 LEBOULENGER Jean – FONDE DE POUVOIRS
of: ATOCHEM, a French Body Corporate of:
12/16, Allée des Vosges, 92400 COURBEVOIE, France.

do solemnly and sincerely declare as follows:—

1. (a) I am the applicant....... for the Patent
or (b) I am authorized by
ATOCHEN, the applicant........ for the patent of addition to make this declaration on its behalf.

2. (a) I am the actual inventor....... of the invention
or (b) DANIEL CUZIN, a Citizen of France of:
CAPENTONNE 27300 BERNAY, FRANCE.

"The applicant would, if a patent were granted upon an application made by the inventor, be entitled to have the patent assigned to it".

3. The basic application....... as defined by Section 141 of the Act was made
in FRANCE: NO. 84-13244............. on the 27th August, 1984
by ATOCHEM, in
by
in
by

4. The basic application....... referred to in paragraph 3 of this Declaration were the first application....... made in a Convention country in respect of the Invention the subject of the application.

Declared at COURBEVOIE the 2ND day of SEPTEMBER 1985

Jean LEBOULENGER

Signature of declarant(s) (no attestation required)

Initial all alterations.
Use of polymer in the manufacture of articles, for coatings and as adhesive agent is also claimed.

Claim:

1. A polymer produced by reacting a polyepoxide compound and a polyamide oligomer, which is a primary monomaine, alpha,omega- primary or secondary diamine, alpha,omega-diacid or alpha- primary amine, omega-acid oligomer.

25. Use of a polymer according to any one of claims 1 to 23 or a composition according to claim 24 in the manufacture of articles moulded by injection, compression or reaction injection moulding technique, or in the manufacture of extruded articles.

26. Use of a polymer according to any one of claims 1 to 23 or a composition according to claim 24 in the production by the "pultrusion" method of composite articles consisting of long fibres held together by the polymer.
27. Use of a polymer according to any one of claims 1 to 23 or a composition according to claim 24 in the coating of metal articles.

28. Use of a polymer according to any one of claims 1 to 23 or a composition according to claim 24 as an adhesive agent.
The following statement is a full description of this invention, including the best method of performing it known to us.

"POLYMERS PRODUCED FROM POLYAMIDE Oligomers AND EPOXIDE RESINS"
ABSTRACT

POLYMERS PRODUCED FROM POLYAMIDE Oligomers AND EPOXIDE RESINS

A polyepoxide compound and a polyamide oligomer which is a primary monoamine, alpha,omega- primary or secondary diamine, alpha,omega-diacid or alpha- primary amine omega-acid oligomer may be reacted together to produce a polymer which may be used in moulding or extrusion or a composition containing the polyepoxide and polyamide oligomer may be used, in the form of a powder to coat metal articles.
POLYMERS PRODUCED FROM POLYAMIDE Oligomers and Epoxide Resins

It is known that epoxide resins and polyamides can react together.

Thus, polyamides can be crosslinked with small quantities of polyepoxides. Conversely, it is possible to produce thermosetting polymers by treating epoxide resins with small quantities of some polyamides, but in this case conventional methods of crosslinking epoxide resins are involved.

Crosslinking of epoxide resins by polyamides is described in the literature, particularly in the work by Lee and Neville: Handbook of epoxy resins, McGraw-Hill, New York 1967. The "polyamide" compounds employed as hardeners in epoxide resin formulations are generally amorphous and of low molecular mass. They are, for example, amidopolyamides, produced by the reaction of dimerized fatty acids with an excess of diamine or polyamine. Since dimerized fatty acids are mixtures of isomers of several diacids, with a poorly defined structure, which are produced by dimerization of mono- or polyunsaturated fatty monocarboxylic acids, the resultant polyamides themselves have a poorly defined structure, and are amorphous. Because of their high content of amine groups (more than two amine groups per molecule), they enable epoxide resins to be crosslinked, but the amide groups which they contain do not play a dominant role in the final properties of
the material. Finally, because of their amorphous nature and their low softening point, these polyamides react with epoxide resins at low temperature.

Semicrystalline polyamides of high molecular mass have been employed as additives in epoxide resin formulations to improve some of their properties but, in this case, these polyamides act rather as fillers. Furthermore, European Patent Application No. 83 1,003,311-6 (Publication No. 0,085,324) describes polyamide compositions prepared by anionic polymerization of at least 75% of lactams, with approximately 25% of an epoxide compound, but the process claimed can apply only to some polyamides, those derived from lactams and, furthermore, as it involves anionic polymerization, it has all the disadvantages therefore.

The process of the present invention produces a whole family of new, thermoplastic or thermosetting polymers, which are obtained from oligomers of polyamides derived from monomers which are not necessarily lactams, and from various compounds bearing epoxide groups.

These polyamide oligomers have a defined structure; their molecular weight, and the nature and number of the groups carried by the chain ends are controlled.

The process for the manufacture of these polymers of polyamides and of epoxide resins, consists, in effect, in reacting two principal components with each
other. These components are

(i) An oligomer of a semicrystalline poly-
amide, that is to say a polyamide as defined in the
Chapter "Polyamide" of "Encyclopedia of Polymer Science
and Technology", vol. 10, page 483 et seq. John Wiley &
Sons Inc. 1969, in contradistinction to the polyamides
derived from dimerized fatty acids such as defined
in the same work in the chapter "Polyamide from
Fatty Acids", vol. 10, page 597 et seq., the said
polyamide oligomer bearing either a single reactive
group of the primary amine type at one of its two
chain ends, the other end bearing no reactive group, or
a reactive amine (primary or secondary) group or acid
group on each of the two chain ends, the oligomer being
then alpha,omega- primary diamine or alpha,omega- secondary
diamine, or alpha- primary amine, omega- secondary amine
or alpha,omega-diacid, or a primary amine group at one
of the chain ends and an acid group at the other end, the
oligomer then being alpha-amine, omega-acid.

and (ii) a solid or liquid organic compound incorporating
at least two epoxide groups in the molecule.

The reaction between these two components may be
carried out in a common solvent for both compounds, but
it preferably takes place in the molten state, at a tem-
perature above or equal to the melting point of the higher-
melting component.

Polymers are thus obtained, the physical
properties of which will be the result of the semicrystalline structure with which they are endowed by the polyamide oligomer sequences.

In an alternative form of the invention, it is also possible to use, instead of a monofunctional polyamide oligomer, a mixture of different monofunctional polyamide oligomers (manufactured from various monomeric polyamide precursors); this is also the case for difunctional oligomers.

It is also possible to use mixtures of monofunctional and difunctional polyamide oligomers.

Preparation of the polyamide oligomer.

Regardless of whether it is monofunctional, the polyamide oligomer may be produced from one or more amino acids, lactams, salts of diacids with diamines or mixtures of diacids with diamines. This implies that the oligomer may be a copolyamide oligomer.

The hydrocarbon chain of these amino acids, lactams, diacids and diamines, preferably has from 4 to 14 carbon atoms.

Thus, use may be made of the compounds generally employed in the manufacture of polyamides, for example: caprolactam, dodecalactam, aminocaproic acid, eonantholactam, 7-aminohepanolic, 11-aminoundeconoic, N-heptyl-11-aminoundeconoic or 12-aminododecanoic acid; mixtures or salts of diamines such as hexamethylene diamine, nonamethylene diamine, undecamethylene diamine, dodecamethylene-
diamine, meta-xylylenediamine, bis-aminocyclohexylmethane, and the like, with diacids such as terephthalic, isophthalic, adipic, azelaic, sebacic, dodecanedioxylic, glutaric and the like.

These polyamide-forming compounds will therefore be melted in the presence of a chain-terminating compound the proportion of which relative to the above compounds will adjust the length of the polyamide sequence, in other words will adjust the molecular mass of the polyamide oligomer.

A first method for preparing oligoamides which are monofunctional at one amine end consists in polycondensing the polyamide monomer(s) in the presence of a specified quantity of monoamine. Preferably, a monoamine will be chosen, the physical characteristics, particularly the volatility, of which are compatible with the operating procedure chosen for the oligoamide synthesis. As an example of the monoamines which can be employed as chain-terminators, mention may be made of n-heptylamine, n-octylamine, n-dodecylamine, tetradecylamine, hexadecylamine, octadecylamine and cyclohexylamine.

A second method for preparing monoamine oligoamides consists in first preparing a monoacid oligoamide in a manner similar to that described earlier for the monoamine oligoamides, but replacing the monoamine by an organic monoacid of general formula RCOOH, where R typically denotes a straight-chain or branched alkyl radical containing from 1 to 24 carbons. This monoacid oligoamide is then reacted with a
diamine the concentration of which should be such that two amine groups are present per acid group in the medium.

The diamines which can be employed are, for example, aliphatic diamines containing 4 to 22 carbon atoms such as, for example, tetramethylenediamine, hexamethylenediamine and nona- and dodecamethylenediamines.

Cycloaliphatic or aromatic diamines may also be suitable. As in the case of the monoamines, the choice of diamines may be imposed by volatility criteria, the high vapour pressure of the low molecular mass diamines being capable of constituting a disadvantage in the synthesis of diamine oligoamides.

To prepare the alpha,omega-diacid oligoamides, the polycondensation of the polyamide monomer(s) is carried out in the presence of a suitable quantity of a dicarboxylic acid. Use may be made of aliphatic diacids containing from 4 to 20 carbon atoms such as, for example, succinic, adipic, suberic, azelaic, sebacic, undecanedioic or dodecanedioic acids. Alicyclic diacids such as 1,4-cyclohexanedicarboxylic acid, or aromatic diacids, such as terephthalic acid, may also be suitable.

Several methods of synthesis may be applied to prepare the alpha,omega-diamine oligoamides. The first resembles the method of synthesis of alpha,omega-diacid oligoamides. It consists in polycondensing the polyamide monomer(s) in the presence of the required quantity of a diamine. The diamines which can be employed are the same as those which
have been described in conjunction with the synthesis of the primary monoamine oligoamides from a monoacid oligoamide and a diamine.

It is also possible to use diamines containing a primary amine group and a secondary amine group, such as (3-aminopropyl)methylamine or (3-aminopropyl)alkylamines. In this case, the difference in reactivity between the two amine functions in the diamine results in the formation of a high proportion of alpha,omega-diamine oligoamide in which one of the ends bears a primary amine group and the other end a secondary amine group.

The second method of synthesis of alpha,omega-diamine oligoamides consists in starting with an alpha,omega-diacid oligoamide and reacting it with an excess of diamine, the concentration of the diamine being double that of the diacid oligoamide. The diamines which can be employed are the same as those which were described in connection with the synthesis of monoamine oligoamides from a monoacid oligoamide and diamine. As before, when a diamine containing a primary amine group and a secondary amine group is employed, an alpha,omega-diamine oligoamide having a secondary amine group at each end of the chain will be predominantly obtained.

This last type of alpha,omega-secondary diamine oligoamide can also be obtained by employing, as a polyamide monomer, an N-alkylated omega-aminoacid or an N-substituted lactam, alone, or mixed with an omega-aminoacid
or an unsubstituted lactam, and, as chain-stopper, a diamine, which may be e.g. a primary diamine or a diamine containing a primary amine group and a secondary amine group. For example, a mixture of 11-aminoundecanoic acid and N-heptyl-11-aminoundecanoic acid can be poly-condensed in the presence of a diamine such as hexamethylenediamine and, because of differences in reactivity already referred to, an alpha,omega-diamine oligoamide can be obtained in which the amine groups at the end of the chain are substantially secondary amine groups.

In order to illustrate the various routes, just described, for the synthesis of functional oligoamides, a number of examples are given below, which describe the preparation of polyamide oligomers bearing acid or amine reactive groups at the end of the chain.

**Example 1**

**Preparation of a primary monoamine polyamide-11 oligomer**

10.2 kg of 11-aminoundecanoic acid and 1.15 kg of dodecylamine are introduced into a steel autoclave 45 l in capacity, equipped with an anchor stirrer, an oil-bath heating, a relief valve, an electrically heated bottom valve and pipework enabling a nitrogen sweep to be carried out. In the autoclave it is pressurized with 5 bars of nitrogen and then depressurized to atmospheric pressure. The operation is repeated 5 times in succession. The reaction mixture is heated up to 240°C and maintained
at this temperature for 6 hours. With all the valves closed, the pressure in the autoclave becomes steady at 18 bars. The total duration of the operations from the start of heating is then 8 hours 15 minutes. At the end of this time, the pressure in the autoclave is gradually reduced by carrying out a controlled depressurizing from 18 bars down to atmospheric pressure over 4 hours, which permits most of the water formed by the polycondensation reaction to be removed, and then the reaction mixture is maintained for 3 hours under a nitrogen sweep of 0.5 m$^3$/h, the temperature remaining at 240°C. Stirring is then stopped and the reactor is emptied through its bottom valve. The product is collected in a steel vat filled with cold distilled water and it is then drained and dried in a vacuum oven at 80°C for 12 hours. The molecular mass of the monoamine polyamide-11 oligomer produced, determined by estimating amine groups, is 1,720.

**Example 2**

**Preparation of a primary monoamine polyamide-12 oligomer.**

14.5 kg of dodecalactam and 1.5 l of water are introduced into an autoclave similar to that employed in Example 1. An auxiliary storage vessel 3 l in capacity, capable of withstanding a pressure of 45 bars, is connected to the autoclave lid via a valve. 0.57 kg of dodecylamine is introduced into this storage vessel. The autoclave and the attached storage vessel are purged with
nitrogen, as described in Example 1.

With the autoclave valves closed, the reaction mixture is heated up to 270°C over 2 hours 30 minutes and this temperature is maintained for 6 hours, the pressure becoming steady at 20 bars. At the end of this period, the pressure is gradually reduced down to 20 bars over 1 hour. The attached storage vessel, which has been pre-heated to 100°C, is raised to a pressure of 35 bars and the valve connecting it to the autoclave is opened so as to transfer the dodecylamine into the autoclave. Once the dodecylamine has been introduced, the reaction mixture is maintained at 260-270°C for 3 hours at 20 bars and then a gradual depressurization down to atmospheric pressure is carried out, followed by a nitrogen sweep for 1 hour at a rate of 0.5 m³/h. Completion of the operation takes place in the same manner as in Example 1. The molecular mass, determined by estimating the amine groups, of the monoamine polyamide-12 oligomer produced is 5,035.

Example 3

Preparation of an alpha,omega-diacid polyamide-11 oligomer

30 kg of 11-aminoundecanoic acid, 30 l of water and 3.1 kg of adipic acid are introduced into an autoclave 100 l in capacity equipped with an anchor stirrer, an oil-bath heating, a relief valve, an electrically heated bottom valve and pipework enabling a nitrogen sweep to be carried out. The reactor is purged with nitrogen as indicated in
Example 1. The reaction mixture is heated to 180°C over 1 hour. The pressure reaches 8.5 bars. Water is then gradually removed by opening the relief valve, which results in a drop in pressure down to atmospheric pressure over 50 min; the temperature of the reaction mixture is then raised to 200°C for 1 hour, under a nitrogen sweep of 0.5 m³/h. The product is collected through the bottom valve of the autoclave into a steel vat filled with cold distilled water. The product is drained, and then dried under vacuum for 20 hours at 80°C. The molecular mass determined by estimating the acid groups in the alpha, omega-diacid polyamide-11 oligomer produced is 1,460.

By carrying out a similar operation with 30 kg of aminoundecanoic acid and 1 kg of adipic acid, an oligomer with a molecular mass of 4,080 is obtained.

Example 2

Preparation of an alpha,omega-diacid polyamide-12 oligomer

16 kg of dodecalactam, 1.68 l of water and 1.8 kg of adipic acid are introduced into an autoclave similar to that employed in Example 1. The autoclave is purged with nitrogen as indicated in Example 1 and then the valves are closed and the autoclave is heated to 270°C. The reaction mixture is maintained at this temperature for 3 h, the pressure becoming steady at 30 bars. A gradual depressurization is then carried out, reducing the pressure from 30 bars to atmospheric pressure, and enabling most of the
water to be removed, and the temperature is simultaneously lowered from 270°C to 240°C. The reaction mixture is then kept at 240°C for 3 h under a nitrogen sweep of 0.5 m³/h. The product is collected and treated as in Example 1. The molecular mass, determined by estimating the acid groups, of the alpha,omega-diacid polyamide-12 obtained is 1,542.

Example 5

Preparation of an alpha,omega- primary diamine

polyamide-11 oligomer

35 kg of 11-aminoundecanoic acid and 18 l of water are introduced into an autoclave similar to that employed in Example 3, equipped with an additional storage vessel 10 l in capacity, connected to the autoclave lid via a valve. 2.0 kg of hexamethylendiamine are introduced into the additional storage vessel. The reactor and the additional storage vessel are purged as indicated in Example 1. The reaction mixture is heated to 190°C over 1 hour, the pressure reaching 9.3 bars. Water is gradually removed by means of the relief valve over 1 hour 15 minutes, the pressure decreasing down to atmospheric pressure.

The hexamethylendiamine contained in the additional storage vessel is then introduced into the autoclave. With the valves closed again, the temperature is raised to 200°C, the pressure increasing up to 5 bars, and these conditions are maintained for 4 hours. At the end of this period, a gradual depressurization is carried out over 2 hours,
returning the pressure from 5 bars to atmospheric pressure, while the temperature is increased to 240°C and the reaction mixture is maintained for another 2 hours at this temperature under a nitrogen sweep of 0.5 m³/h. The alpha,omega-diamine polyamide-11, collected and treated as in Example 3, has a molecular mass, determined by estimating the end groups, of 1,980.

By proceeding in a similar manner with 35 kg of aminoundecanoic acid and 1.03 kg of hexamethylenediamine, an oligomer with a molecular mass of 3,700 is obtained.

Example 6

Preparation of an alpha,omega-primary diamine polyamide-12 oligomer

15.4 kg of dodecalactam and 1.68 l of water are introduced into an autoclave similar to that employed in Example 1. The autoclave is equipped with an additional storage vessel, as indicated in Example 2, into which 1.6 kg of hexamethylenediamine is introduced. The autoclave and the additional storage vessel are purged with nitrogen as indicated in Example 1. The remainder of the operations is identical to the operating procedure described in Example 2. The molecular mass of the alpha,omega-diamine polyamide-12 oligomer obtained, determined by estimating the amine groups, is 1,214.
Example 7

Preparation of an alpha,omega- secondary diamine polyamide-11 oligomer

752 g of N-heptyl-11-aminoundecanoic acid, 1,450 g of 11-aminoundecanoic acid and 116 g of hexamethylene-diamine are introduced into a steel autoclave 6 l in capacity, equipped with an anchor stirrer, an electric heating, a relief valve, an electrically heated bottom valve and pipework permitting a nitrogen sweep to be carried out. The apparatus is purged with nitrogen as indicated in Example 1.

The mixture is heated to 250°C and this temperature is maintained for approximately 2 hours, the pressure becoming steady at approximately 9 to 10 bars. At this temperature, depressurization is carried out down to atmospheric pressure and the reaction is allowed to proceed under a nitrogen sweep for 4 hours. The stirring is then stopped and the contents of the reactor are drained via the bottom valve into liquid nitrogen. The product is then ground, and dried under vacuum at 60 - 70°C for 8 hours.

The melting point of the oligoamide produced, determined by differential thermal analysis is 165°C. 13C-NMR analysis shows only traces of a primary amine group; from this it can be concluded, therefore, that the end groups are substantially secondary amine groups.

The molecular mass of the oligoamide, determined
by estimating of the amine groups, is 1,980.

Example 8

Preparation of an alpha,omega-primary diamine polyamide-6 oligomer and a monoamine polyamide-6 oligomer

The operation is carried out in the same equipment as that described in Example 2. 17 kg of caprolactam and 1.3 l of water are introduced into the autoclave, and 2 kg of hexamethylenediamine into the additional storage vessel. The whole equipment is purged with nitrogen as indicated in Example 1.

With all the valves closed, the apparatus is heated up to 260°C and the pressure becomes steady at 20 bars. These conditions are maintained for 4 hours with stirring at 30 rev/min.

A controlled depressurization is then carried out down to 2.5 bars and the temperature is lowered to 250°C.

The attached storage vessel which has been preheated to 100°C is raised to a pressure of 3 bars, and the valve which connects it to the autoclave is opened so as to transfer the hexamethylenediamine into the autoclave.

The reaction mixture is then held for 4 hours at 250°C at 5 bars, and then the pressure is gradually reduced down to atmospheric pressure. This depressurization stage lasts 2 h. The reaction is then terminated by a nitrogen sweep for 0.5 h at 250°C.

The end of the operations takes place in the same manner as in Example 1.
The molecular mass of the alpha, omega primary diamine polyamide-6 oligomer produced, determined by estimating the amine groups is 1,074.

To prepare a monoamine polyamide-6 oligomer, the operating procedure is strictly identical, the only difference being that 1.25 kg of dodecylamine are introduced into the additional storage vessel.

The molecular mass of the monoamine polyamide-6 oligomer obtained, determined by estimating the amine group, is 2,690.

Epoxide compound

This compound, which will react with the oligamide, contains at least two groups of the epoxide type in its molecule.

It may be solid or liquid.

At present there is a very large number, on the market and in the scientific and technical literature, of examples of organic compounds corresponding to this definition and whose structures are very diverse. The most widely used compounds are those derived from the reaction of bisphenol A with epichlorohydrin and, in particular, the compounds resulting from the addition of two molecules of epichlorohydrin to one molecule of bisphenol A, that is to say the diglycidyl ethers of bisphenol A (DGEBA).

For example, mention may be made of the products marketed by Shell under the reference Epikote 828, or by Dow Chemical under reference DER 332. However, in the polymers used
temperature above or equal to the melting point of the higher-melting component.

Polymers are thus obtained, the physical

in the invention it is possible to use a large number of other epoxide resins such as those resulting from the attachment of an epoxide group to both ends of a paraffinic hydrocarbon chain, for example, butanediol-derived diepoxides, or a polyether chain such as the polypropylene glycol alpha,omega-diepoxide, marketed by Dow Chemical under the reference DER 732 or DER 736. It is also possible to use individual diepoxide compounds such as vinylcyclohexene dioxide, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanemonocarboxylate, 3-(3,4-epoxycyclohexyl)-8,9-epoxy-2,4-dioxaspiro-[5,5]-undecane, bis(2,3-epoxycyclopentyl) ether, bis(3,4-epoxy-6-methylecyclohexyl) adipate and resorcinol diglycidyl ether.

When the intention is to produce a final material having a high crosslinking density it may be advantageous to employ epoxide compounds containing more than two epoxide groups per molecule, such as epoxidised soya oils, polyglycidyl ethers of phenolic resins of the novolak type, p-aminophenol triglycidyl ether or 1,1,2,2-tetra-(p-hydroxyphenyl)ethane tetracyclidyl ether. It is also possible to use different polyepoxide compounds.

In addition to these two basic components it is also possible to add other compounds to the reaction mixture, such as heat, light and oxidation stabilizers, colorants, plasticizers, various reinforcing or non-reinforcing fillers and mould release agents.
Relative proportions of the polyamide oligomer and the epoxide compound

The number-average molecular mass of the polyamide oligomers employed in the invention may vary within wide proportions generally from 400 to 10,000, but molecular masses of from 1,000 to 7,000 are preferable.

The proportion of the polyamide oligomer and of the epoxide compound should be such that the number of epoxide groups should be equal to number of the reactive end groups in the polyamide oligomer. In the case of compositions based on a diacid oligoamide, the quantity of epoxide resin is such that the composition contains one epoxide group for each acid group. However, for reasons of reaction rate and of finished product quality, it may be necessary to depart from this desirable theoretical composition and to employ compositions containing e.g. from 0.9 to 1.6 epoxide groups per acid group in the oligoamide.

In the case of monoamine oligoamides, given that the amine group is difunctional towards the epoxide group, the composition of the reaction mixture will be chosen so that there are two epoxide groups in the mixture per amine group. If the diepoxide compound employed is represented as:

$$\text{CH}_2\text{-}\text{CH} - \left[R_1\right] - \text{CH} - \text{CH}_2$$

where $R_1$ denotes an organic diradical optionally
The acid of general formula $RCOOH$, where $R$ typically denotes a straight-chain or branched alkyl radical containing from 1 to 24 carbons. This monoacid oligoamide is then reacted with a containing heteroatoms, and if $R_2 - PA - NH_2$ represents the monoamine oligoamide produced by polycondensing a polyamide precursor monomer with an amine $R_2-NH_2$, where $R_2$ denotes a monovalent hydrocarbon radical, then, by using one molecule of diepoxide compound per molecule of monoamine oligoamide, which actually corresponds to two epoxide groups per amine group, a polymer of structure:

$$
\left[ \begin{array}{c}
CH_2 - CH - [R_1] - CH - CH_2 - NH_2 \\
\bigg\uparrow \\
PA \\
R_2 \\
\bigg\downarrow
\end{array} \right] \quad n
$$

is obtained.

This is a copolymer, uncrosslinked, consisting, on the one hand, of a polyl tertiary polyamine principal chain derived from the original structure of the epoxide compound and, on the other hand, of short polyamide side chains.

When an epoxide compound containing more than two epoxide groups is employed, a crosslinked polymer can be obtained.

As in the case of the compositions based on a di-acid oligoamide, it may be necessary, for reasons of reaction kinetics, to modify slightly the relationship which exists between the epoxide group and the amine group, a relationship which can vary typically from 1.6 to 2.4.

In the case of a diamine oligoamide with a primary amine end group the relationship between the epoxide group and
the amine group can be varied in wider proportions than in the case of a monoamine oligoamide. In effect, when a diepoxide compound of structure:

\[
\text{CH}_2 - \text{CH} - \left[ \text{R}_1 \right] - \text{CH} - \text{CH}_2
\]

is polycondensed with a diamine oligoamide of structure:

\[
\text{NH}_2 - \text{PA} - \text{R}'_2 - \text{PA} - \text{NH}_2
\]

(where \( \text{R}'_2 \) denotes a divalent hydrocarbon radical), the proportion of oligoamide to diepoxide being such that there is one epoxide group per amine group in the mixture, then an essentially straight-chain polymer, of structure:

\[
\text{CH}_2 - \text{CH} - \left[ \text{R}_1 \right] - \text{CH} - \text{CH}_2 - \text{NH} - \text{PA} - \text{R}'_2 - \text{PA} - \text{NH} - \text{OH} - \text{OH}
\]

is produced at the outset of the reaction.

At the end of the reaction, for kinetic reasons (reduction in the concentrations of primary amine and epoxide groups, increase in the concentration of secondary amine), a number of bridges may form and result in a partly crosslinked polymer.

By choosing a stoichiometry such that there are two epoxide groups per amine group in the initial mixture and by allowing the reaction to continue to completion, a crosslinked polymer is obtained in which the majority of the amine groups are tertiary amines, and the idealized
This last type of alpha,omega- secondary diamine oligoamide can also be obtained by employing, as a polyamide monomer, an N-alkylated omega-aminooacid or an N-substituted lactam, alone, or mixed with an omega-aminooacid.

\[
\text{structure of which is as follows:}
\]

\[
\text{- N - CH}_2 = \text{CH} \left[ \text{R}_1 \right] = \text{CH} - \text{CH}_2 - \text{N}
\]

In the case of a primary diamine oligoamide it is therefore possible, depending on the nature of the polymer which it is intended to produce, and particularly on the crosslinked density which is aimed at in the case of thermosetting polymers, to choose a composition in which the ratio of the epoxide groups to the amine groups varies from 0.9 to 2.5. In some cases, in fact, it may be advantageous to use compositions such that there are more than two epoxide groups per amine group, so as to retain in the resin a number of free epoxide groups which may be responsible for particular properties at the time when the polymers are put to use (adhesion to various substrates, for example).

In the case of a diamine oligoamide with secondary amine end groups, of general formula:

\[
\text{[R}_1 \text{NH - PA - NH[R}_2 \text{N]}
\]

where \([R}_2 \text{N] denotes a monovalent alkyl radical containing 1 to 24 carbon atoms, the polymer obtained is substantially
straight-chain and has the structure:

\[
\begin{align*}
\text{CH}_2\text{-CH}-\left[R_1\right]-\text{CH}_2\text{-N}\text{-PA}\text{-R}_2\text{-PA}\text{-N} \\
\text{CH}_2\text{-CH}_2\text{[R''_2]}\text{-CH}_2\text{-N}\text{-PA}\text{-R''_2}\text{-PA}\text{-N}
\end{align*}
\]

since each secondary amine group is monovalent towards epoxide groups. The optional possibilities of crosslinking originate from secondary reactions, for example from the reaction between the OH groups formed and the epoxide groups which have not yet reacted, or from the polymerisation reaction of the epoxide groups with each other, catalysed by the tertiary amines formed.

The theoretical stoichiometry which makes it possible to produce a straight-chain polymer with high molecular mass is therefore that of one epoxide group per secondary amine group or, which amounts to the same thing, one molecule of alpha, omega-secondary diamine oligoamide per molecule of diepoxide compound. Nevertheless, for reasons of reaction kinetics, or to take into account secondary reactions which may entail a faster consumption of one of the reactive groups relative to the other, it may be preferred to vary the stoichiometric ratio between 0.8 and 1.15.

The reaction which leads to the polymers may be carried out in accordance with a wide variety of operating methods. In point of fact, one
of the advantageous characteristics of the two-reactant system — functional oligoamide and epoxide resin — is that it reacts rapidly at temperatures above the melting point of the oligoamide chosen, without releasing volatile compounds and without it being indispensable to add a catalyst.

The manufacture of these copolymers may be carried out in a conventional autoclave of the same type as those generally employed for the synthesis of homopolyamides or copolyamides of high molecular mass; in this case, the oligoamide chosen is charged into the reactor which is then heated to a temperature about ten degrees above the melting point of the oligoamide. The desired quantity of epoxide resin is then added and kept stirred for the time required to produce a homogeneous mixture. If the homogeneous mixture is drained out through a multiholed die, the polymer can be obtained in the form of rods, and then of granules after passing through a granulator.

These granules can subsequently be used to manufacture moulded articles with the aid of conventional machines employed for injection moulding.

Another operating method for the manufacture of the copolymer consists in carrying out the homogenization and the prepolymerization of the mixture of the two components of the system in a compounding machine. This produces a prepolymer, in the form of powder or granules, which can be employed for a subsequent use. This use,
during which the polymerization will continue, can take place in accordance with various techniques. As before, the injection moulding technique may be employed, provided that the reactivity of the system is compatible with the residence time in the injection machine. It is also possible to use the "extrusion" technique, which consists in producing a profile member with a specified cross-section, by resin-coating, in a so-called "crosshead" die, glass fibre core which passes continuously through the said die, the cross-section of which is that of the profile which is to be produced; if need be, the extruded profile, after being coated with the resin, passes through an oven in which the polymerization of the resin is taken to completion.

The manufacture of the polymer and its moulding into large-sized articles can be carried out in a single operation by employing the reaction injection moulding (RIM) technique described, for example, in Modern Plastics International, April 81.

In this case, the two components of the system - the oligoamide and the epoxide resin - are stored in liquid state in two separate storage tanks maintained at a sufficient temperature to keep the two reactants liquid; the polymerization and the moulding of the finished article are carried out simultaneously by pumping, from the two storage tanks, the required quantity of each of the two reactants, by mixing them in a special device which very rapidly produces a highly intimate mixture of the two
\text{Re
duction is then carried out, reducing the pressure from 30 bars to atmospheric pressure, and enabling most of the components, and by injecting the mixture produced into the mould. The polymerization of the resin takes place during the mixing of the two components in the mixing head and continues during the transfer into the mould, to be completed in the latter. In this type of operating method, given that the cycle time for the manufacture of the finished article is directly related to the rate of polycondensation of the mixture of the two components, the most reactive combinations of oligoamide and epoxide compound will be chosen. If need be, the rate of reaction can be increased still further by adding a catalyst such as a tertiary amine. Finished articles can be produced, of course, in a similar manner by employing the conventional techniques for the conversion of thermoplastics, such as extrusion, injection moulding, rotational moulding, heat forming, etc. Given below are several Examples which further illustrate the invention.}

The physical or mechanical properties of the polymers produced have been determined on specimens moulded or machined with the use of the following standardized methods:
- Tensile Elongation (ASTM standard D 638)
- Flexural Modulus (ASTM standard D 790)
- Heat Deflection Temperature under Load (HDT) (ASTM standard D 648)
Inherent viscosity is measured at 25°C on solutions of polymer in m-cresol at a strength of 0.5% by weight, and expressed in cm³ g⁻¹.

Example 9

370 g of the alpha,omega-diacid polyamide-11 oligomer, with a molecular mass Mn = 1,460, obtained in Example 3, are mixed in a beaker with 120 g of bisphenol A diglycidyl ether (DGEBA) with an epoxide number equal to 187 (Epikote 828 resin from Shell) and with a molecular mass equal to 374.

The epoxide/acid ratio is thus equal to 1.25.

The mixture is heated to 180°C with stirring until a homogeneous, pale yellow liquid is obtained; this liquid is poured into a circular steel mould which is then maintained for 15 minutes at 180°C between the heating platens of a hydraulic press producing a pressure of 11 tonnes.

After cooling and demoulding, a homogeneous, pale yellow disc is obtained, from which specimens which make it possible to carry out mechanical tests are cut with the aid of a punch-cutter. The values of the mechanical properties of the material are given in Table 1.

Example 10

The procedure is as in Example 9, but the relative proportions of the two reactants are modified: 132 g Epikote 828 are added to 345 g of alpha,omega-diacid poly-
amide-11 oligomer, which corresponds to an epoxide/acid ratio equal to 1.50. The subsequent procedure is identical to that in Example 9. The mechanical properties of the material produced are given in Table 1.

5 Example 11

190 g of an alpha,omega-diacid polyamide-11 oligomer, of Mn = 4,080, prepared according to the operating procedure illustrated by Example 3 are placed in a beaker and heated to 190°C with stirring. When the polyamide oligomer is molten, 26 g of Epikote 828, preheated to 90°C, are quickly added with stirring. The homogeneous mixture obtained is poured quickly into a steel mould consisting of an annular member of rectangular shape and two removable plates with plane faces defining a parallelepipedal volume 140 x 140 x 6.4 mm in size. The duration of the operations of mixing the two components of the resin and filling the mould is of the order of 1 to 2 minutes. The resin-filled mould is kept for 10 minutes at a temperature of between 190 and 200°C between the heating platens of a hydraulic press producing a pressure of 10 t.

After cooling, a yellowish, slightly translucent, homogeneous plaque is demoulded, from which specimens for mechanical tests can be cut out by machining.

A similar procedure is followed with a mould of slightly different size (165 x 165 x 4 mm) for the mechanical tests which require specimens of lower thickness.

The mechanical properties of the material obtained compounding machine, the difunctional polyamide oligomer
group; from this it can be concluded, therefore, that the end groups are substantially secondary amine groups.

The molecular mass of the oligoamide, determined appear in Table 1.

**Example 12**

170 g of an alpha,omega- primary diamine polyamide-11 oligomer, of molecular mass Mn = 1,980, prepared according to the operating procedure described in Example 5, are placed in a beaker and heated to 190°C with stirring. Once the polyamide oligomer has melted, 56 g of a polypropylene glycol alpha,omega-diepoxide resin, with Mn = 660 and an epoxide number of 330 (DER 732 from Dow Chemical), preheated to 90°C, are added very quickly with vigorous stirring. The epoxide/amine ratio is equal to 1.

The homogeneous and viscous mixture obtained is quickly poured into a steel mould similar to that described in Example 9. The total duration of the operations of mixing the two components of the resin and filling the mould should not exceed 30 seconds. The polymerization of the mixture in the mould takes place under the same conditions as in Example 9. A thinner mould is also used as in Example 9.

The plaques obtained are homogeneous, whitish and opaque. The mechanical properties of the material are given in Table 1.

**Example 13**

The procedure followed is as in Example 12, but an alpha,omega- primary diamine polyamide-11 oligomer of Mn = 3,700 is employed. The quantity of polyamide oligomer used is 190 g and that of a polypropylene glycol polymer prepared by mixing in melt form, in a suitable
alpha,omega-diepoxide (DER 732) 34 g; the epoxide/amine ratio remaining equal to 1.

The end of the operations takes place in the same manner as in Example 1.

Example 14
17.3 kg of a previously prepared alpha,omega-diacid polyamide-11, of Mn = 1,384, are introduced into an autoclave 90 l in capacity, equipped with an anchor stirrer. The material is melted at 200°C under nitrogen pressure, and then the temperature is lowered to 180°C and the nitrogen pressure is lowered to atmospheric pressure. From a storage tank fixed to the lid of the reactor via a valve, 8.275 kg of polypropylene glycol alpha,omega-diepoxide of Mn = 660 (DER 732 from Dow Chemical) are then introduced into the reactor, which corresponds to an epoxide/acid ratio equal to 1. The mixture is kept at 180°C for 30 minutes with stirring and under a nitrogen sweep.

At the end of this time the polymer is withdrawn through a multiholed bottom valve, in the form of flexible rods which, after cooling in a water bath and granulation, give 23.2 kg of granules with an inherent viscosity in meta-cresol \( \eta_i = 0.51 \).

These granules are employed to produce specimens for mechanical tests with the aid of an injection moulding machine: parallelepipedal bars 6.4 x 12.7 x 127 mm in size and dumbbell-shaped specimens 2 mm in thickness and
160 mm in length, the plasticizing temperature being 180°C and that of the mould 20°C.

The mechanical properties obtained are reported in Table 1.

Example 15

A homogeneous mixture is produced containing 68.8% of alpha,omega-diacid polyamide-11, of Mn = 1,463, and 31.2% of polypropylene glycol alpha,omega-diepoxide (DER 732 from Dow Chemical), which corresponds to an epoxide/acid ratio equal to 1, by compounding with the aid of a Werner-Pfleiderer ZSK 30 twin-screw extruder with 12 barrel units. The polyamide oligomer is introduced into the machine via the feed hopper, in the form of a coarse powder, and the epoxide-resin is introduced in liquid state into the molten polyamide, at the 4th barrel unit of the machine by means of an injection pump at a pressure of 15 to 20 bars. The material temperatures at various points of the screw are between 194 and 220°C. The throughput is 10 kg/h. The product leaving the die is collected in water. After drying, the product can be easily ground in the form of powder. Its melt viscosity at 200°C is 70 poises. When the product is maintained for 1 hour 40 minutes at 200°C, its melt viscosity rises to 10,000 poises.

Example 16

A homogeneous mixture is produced, containing 87% of alpha,omega-diacid polyamide-11 of Mn = 4,412, and
13% of polypropylene glycol alpha,omega-diepoxide, DER 732 from Dow Chemical, which corresponds to an epoxide/acid ratio equal to 1.0, by compounding with the aid of the Werner-Pfleiderer ZSK 30 machine, under the conditions of Example 15, except for slightly higher material temperatures (200 to 224°C). The melt viscosity, at 200°C, of the product collected is 400 poises; it rises to 800 poises at the end of 1 hour 40 minutes at this temperature.

The oligomer of a viscosity of 400 poises, ground into powder form, is employed to produce mechanical test specimens by means of an injection press in the same manner as in Example 12; the mechanical properties are listed in Table 1.

Example 17

A homogeneous mixture is produced, containing 64.2% by weight of alpha,omega-dicarbonyl-12 oligomer, \(M_n = 1,542\), produced in Example 4, and 35.8% by weight of polypropylene glycol alpha,omega-diepoxide (DER 732 from Dow Chemical) with an epoxide number of 330, which corresponds to an epoxide/acid ratio equal to 1.3.

The mixture is produced by compounding with the aid of a Werner-Pfleiderer ZSK 30 twin-screw extruder with 12 barrel units, under conditions which are similar to those described in Example 13. The material temperatures at various points of the screws are between 187°C and 220°C. The throughput is 10 kg/hour. The polymer obtained, ground into powder form, is employed to produce
mechanical test specimens with the aid of an injection press, in the same manner as in Example 14. The mechanical properties of the specimens are listed in Table 1.

**Example 18**

51,230 g of polyamide-11 monoamine of Mn = 1,720, prepared according to the operating method described in Example 1, and 270 g of DGEBA (Epikote 828 from Shell), with an epoxide number of 187, which corresponds to an epoxide/amine ratio equal to 2, are introduced into a steel autoclave 6 l in capacity, equipped with an anchor stirrer, electric heating, an electrically heated bottom valve and a pipework device enabling a nitrogen sweep to be carried out. The weight proportions of each component are 82% of monoamine polyamide-11 oligomer and 18% of epoxide resin. The reactor is closed, the mixture is heated for 1 hour 30 minutes at 210°C, while being stirred and swept with nitrogen. At the end of this reaction time, there is recovered, by means of the reactor bottom valve, a homogeneous, whitish, rigid polymer with an inherent viscosity in meta-cresol \( \eta_i = 0.87 \text{ cm}^3 \text{ g}^{-1} \) and an intrinsic viscosity \( \eta = 1.06 \text{ cm}^3 \text{ g}^{-1} \).

Mechanical properties listed in Table 1.

**Example 19**

The procedure as in Example 18 is followed, but using 1,395 g of monoamine polyamide-12 oligomer of Mn = 5,035, obtained according to the operating method described in Example 12, and 105 g of DGEBA (Epikote 828 from Shell).
with an epoxide number of 187. The epoxide/amine stoichiometry is equal to 2 and the weight proportions of each component are 92% of polyamide-12 oligomer and 8% of epoxide resin. After 30 minutes' reaction at 200°C, there is withdrawn via the reactor bottom valve a whitish, rigid and opaque polymer with a homogeneous appearance, an inherent viscosity in meta-cresol of 1.45 cm³ g⁻¹ and an intrinsic viscosity \( \eta = 1.55 \text{ cm}^3 \text{ g}^{-1} \).

Mechanical properties listed in Table 1.

**Example 20**

By compounding with the aid of a Werner-Pfleiderer ZSK 30 twin-screw extruder a homogeneous mixture is produced, containing 86% by weight of primary monoamine polyamide-11 oligomer of Mn = 2,191, obtained according to the method described in Example 1 and 14% by weight of DGEBA epoxide resin (DER 332 from Dow Chemical, with an epoxide number of 176), the epoxide/amine ratio in the mixture being equal to 2.

The operating conditions for the compounding are the same as those described in Example 15. The throughput is 10 kg/h and the residence time in the machine 1 min 30 s. A homogeneous, viscous liquid is obtained at the die, solidifying at ambient temperature and lending itself readily to being ground into powder form. The inherent viscosity of this prepolymer, in m-cresol, is 0.73. The prepolymer is used to feed an injection press and to mould mechanical test specimens as indicated in Example 14. The mechanical
a crosslinked polymer is obtained in which the majority of
the amine groups are tertiary amines, and the idealized

properties determined on the moulded specimens are given
in Table 1.

Example 21

The procedure as in Example 20 is followed but
5 with a monoamine polyamide-11 oligomer of Mn = 4,265. The
weight proportion of polyamide oligomer is 2.4\% and that
of DER 332 7.6\%. The product obtained at the die exit,
much more viscous than in the preceding example, can be
granulated under the conditions which are usually employed
10 for thermoplastic polymers. Its inherent viscosity in m-
cresol is 1.06.

The granules obtained are used as in the preceding
example, to mould mechanical test specimens under the
following conditions:
15 - plasticizing temperature : 220°C
 - injection temperature : 250°C
 - mould temperature : 20°C

The mechanical properties determined on the moulded
specimens are given in Table 1.

Example 22

180 g of alpha,omega- secondary diamine polyamide-
11 oligomer of Mn = 1,980, prepared according to the oper-
ating procedure described in Example 7 are weighed into a
beaker and heated to 190°C with stirring. Once the
polyamide oligomer has melted, 350 g of DER 332, preheated
to 150°C, are added quickly with vigorous stirring. The
epoxide/amine ratio is equal to 1. The homogeneous mixture
thus obtained is used to produce moulded plaques under the same conditions as in Example 11. The plaques obtained are homogeneous and translucent and have excellent mechanical strength. The material has a melting point of 151°C and a crystallinity of 16.6%, as determined by DSC.

Example 23

48.6 g of the monoamine polyamide-6 oligomer of Mn = 2,690, prepared in Example 8, are introduced into the mixing trough of a Haake kneader, maintained at 230°C. At a speed of rotation of the kneader blades of 60 rev/min, the torque, in g m, is zero. 6.4 g of DGEBA epoxide resin (DER 332 from Dow Chemical) of Mn = 352, preheated to 160°C, are then added, which corresponds to an epoxide/amine ratio = 2. After 15 minutes' kneading, the torque recorded by the apparatus is 55 g m, which corresponds to a polyamide Mn = 10,000. It is double the torque recorded when kneading a commercial polyamide-6 at the same temperature.

Glass transition temperature 50°C
Melting point 212°C
Crystallinity 33%

Examples 24 to 28

A Martin Sweats reaction injection moulding (RIM) machine, of the Flexamatic RHPI type, is used to produce moulded plaques, by reacting an alpha,omega- primary diamine polyamide-11 oligomer, or an alpha,omega- primary diamine polyamide-6 oligomer, with the epoxide resin DER 332.

The machine consists of the following components:

- a double-entry mixing head which, in open
position, ensures intimate mixing of the two reactants and their transfer towards the mould described below, and, in closed position, ensures the recirculation, without mixing, of each of the reactants towards the lines A and B described below;

- a square mould, 305 x 305 x 3 mm in size, supplied with the mixture originating from the mixing head;
- two lines A and B connected to the mixing head, each incorporating a storage volume for one reactant or the other, and a hydraulically controlled metering unit. This metering unit permits either the recirculation in a closed circuit between the storage volume and the mixing head in closed position, of the line reactant, without mixing with the reactant in the other line, or the injection of the reactant into the mixing head in open position, the delivery pressure simultaneously permitting the intimate mixing with the reactant coming from the other line and the flow of the mixture into the mould. A detailed description of the principle of the RIM machines will be found in the work: Introduction to Reaction Injection Molding, Technomic Publ. Co. Inc. 1979 - pages 77 to 126.

All the components of the machine can be regulated up to a temperature of 235°C and the operating temperature of each component can be set independently of that of the other components.
The stoichiometric ratio between the two reactants and the homogeneity of the mixture are determined by acting on, on the one hand, the settings of the metering units in each line and, on the other hand, the diameter of the valve connecting each line to the mixing head.

The conditions in the various tests carried out on the RIM machine are collated in Table 2. Three tests were carried out without glass fibre reinforcement, and two other tests were carried out by placing in the mould, before the injection of the mixture of reactants, a glass mat from Vetrotex, having the reference Unifilo U 816 (375 g m\(^{-2}\)), which represents 12.3% by weight of glass fibre filler and 87.7% by weight of resin. In all the cases, the mould is perfectly filled and the plaques produced have an excellent appearance. Their properties are given in Table 3.

Example 29

Using a Brabender extruder equipped with a 5 D double screw 42.4 mm in diameter, a homogeneous mixture is produced by compounding 80 parts by weight of an alpha,omega-diacid polyamide-11 oligomer of Mn = 4,080 and 20 parts by weight of DGEBA epoxide resin (Epikote 1001 from Shell) of Mn = 978, which corresponds to an epoxide/acid ratio = 1.

The material temperature is 200°c and the residence time 30 s. The viscosity of the homogeneous mixture produced at the die exit differs little from that of the
reactants, by mixing them in a special device which very rapidly produces a highly intimate mixture of the two starting polyamide oligomer, which shows that the degree to which the reaction has progressed is very low. The reactant mixture is then cooled in water, ground into the form of a fine powder with a mean particle size of 100 µ, and then stoved under vacuum. The fine reactant powder thus produced is deposited by sprinkling onto a glass fibre cloth with a 16 satin weave (from Stevens Genin, ref. 374, 240 g m⁻²). A stack of 15 layers of glass cloth sprinkled with resin is produced in an identical manner.

The whole is then compressed between the platens of a press at 200°C under 14 bars for 5 minutes, and then cooled to 80°C under pressure. A composite material 2.42 mm in thickness is thus obtained, where the impregnation of the fibre reinforcement is perfectly produced by virtue of the fluidity of the reactant system. The mechanical flexure tests have given the following results:

- porosity volume ratio in % : < 0.3
- fibre volume ratio in % : 55.6

- flexure 23°C (ASTM D 790):
  - maximum stress : 506 ± 9 Mpa
  - elasticity modulus : 23,600 ± 300 Mpa

Example 30

A carbon fibre cloth with an 8 satin weave (Stevens Genin ref. 40830, 364 g m⁻²) is impregnated using the same reactant mixture as in Example 29. A stack of 8 layers of carbon cloths, preimpregnated with powder by
sprinkling, is produced. The whole is then compressed between the platens of a press at 200°C under 5 bars for 15 minutes, and then cooled to 80°C under pressure.

A composite material which is perfectly impregnated, 2.15 mm in thickness, is obtained. The mechanical flexure tests have given the following results:
- porosity volume ratio in % : < 3
- fibre volume ratio in % : 52.3
- flexure 23°C (ASTM D 790):
  - maximum stress : $577 \pm 31$ MPa
  - elasticity modulus : $40,300 \pm 6,000$ MPa

**Example 3**
A homogeneous mixture of 61 parts by weight of an alpha,omega- primary diamine polyanamide-11 oligomer of $M_n = 1,535$ and 39 parts by weight of Epikote 1001 resin, which corresponds to an epoxide/amine ratio = 1, is produced as in Example 29 by compounding in a Brabender extruder. The mixture is ground into fine powder form and stored under vacuum.

The fine powder produced is deposited by sprinkling onto a glass fibre cloth with a 16 satin weave (from Stevens Genin, ref. 374, 240 g m⁻²), and a stack of 10 layers of glass cloths impregnated with powder in this way is produced. The whole is then compressed between the platens of a press at 200°C, under 12 bars for 12 minutes, and then cooled to 80°C under pressure. A composite plaque 2.2 mm in thickness, suitably impregnated by virtue...
of the high fluidity of the reactant system, and having the following properties, is thus produced:
- porosity volume ratio in %: $\leq 3$
- fibre volume ratio in %: 42.6
- flexure $23^\circ C$ (ASTM D 790):
  - maximum stress: 338 Mpa
  - elasticity modulus: 13,700 Mpa
- HDT 1.8 Mpa (ASTM D 648): 176$^\circ$C

The methods of use which have just been described, illustrated by the preceding examples, permit the production of moulded articles in which the constituent material is the thermoplastic or thermosetting resin of the invention. However, this same resin, owing to the properties of adhesion to a large number of substrates, with which it is endowed by the epoxide compounds which it contains, can find advantageous applications in the field of coatings and in that of adhesives.

In the field of coatings, it is possible to apply to the resins according to the invention the same techniques as those employed for polyamide powders. In contrast to the latter, it is possible to produce coatings with a high adhesion to steel without the need to pretreat the metal substrate with an undercoat intended to permit good bonding of the polyamide coating. Various techniques are possible for producing these coatings: it is possible to employ a powder produced by grinding the homogeneous prepolymer produced by mixing in melt form, in a suitable
compounding machine, the difunctional polyamide oligomer and the epoxide compound as defined above. It is also possible to use a powder consisting of a mechanical mixture, produced cold, of, on the one hand, the difunctional polyamide oligomer and, on the other hand, the epoxide compound. The coating of the substrate using these powders can be carried out in accordance with the known coating methods, for example, by electrostatic spraying followed by a cure of several minutes at a high temperature, of between 200 and 250°C, or by dipping the substrate, pre-heated to a high temperature, in a fluidized bed in which the powder is kept in suspension.

In the field of adhesives, the thermoplastic or thermosetting polymers according to the invention are particularly highly suitable for gluing metal structures, provided that the substrates to be assembled by gluing can withstand the high temperature required to ensure the polymerization of the system; this is particularly the case for assemblies employing metals such as steel or aluminium. Depending on the nature of the oligoamides and the epoxide compounds employed, the temperature at which the gluing is carried out may be between 100 and 250°C, but in most cases the operation will be carried out between 150 and 220°C. As in the case of the coatings, gluing can be carried out with the aid of the polymers of the invention in accordance with various methods of application. It is possible to use the homogeneous pre-
polymer prepared by mixing in melt form, in a suitable compounding machine, the functional oligoamide and the epoxide compound. It is also possible to use a powder consisting of a mechanical mixture, produced cold, of, on the one hand, the epoxide compound and, on the other hand, the functional oligoamide. The gluing may be carried out by heating, between both platens of a heating press, the two metal surfaces which are to be assembled, separated by the required quantity of the prepolymerized or non-prepolymerized mixture of oligoamide and diepoxide compound. This mixture can be used in the form of powder or film.

An alternative form of utilization consists in depositing the molten mixture on one of the surfaces to be assembled, applying the other surface and subjecting the assembly to the combined effect of pressure and temperature with the aid of a suitable device.

Several examples will be found below, illustrating the applications of the polymers of the invention in the fields of coatings and adhesives.

Example 32

An alpha-omega-diamine polyamide-11 oligomer of Mn = 2,040 and, separately, DGEBA resin (Epikote 1004 from Shell) with an epoxide number of 1,045 and a molecular mass of 2,090, are reduced, by being passed through a grinder, to a fine powder of particle size distribution (measured with a Coulter counter) of between 10 and 80 microns, and a mean diameter of 30 to 35 microns.
and dumbbell-shaped specimens 2 mm in thickness and

39.5 parts by weight of alpha, omega-diamine polyamide-11 powder and 60.5 parts by weight of Epikote 1004 resin powder are carefully mixed with the aid of a Henschel blade mixer with a capacity of 2 kg, to produce a homogeneous mixture of the two compounds, with an epoxide/amine ratio = 1.5.

The mixture is applied to a steel plate 180 x 180 x 1 mm in size, pretreated by sandblasting; the application is made in accordance with the electrostatic coating method, with a positive potential difference of 30 kV.

The powder-coated plate is then placed in an oven maintained at 220°C for a period of 4 minutes. This cure treatment converts the powder into a polymer film with an average thickness of 50 μ.

According to an empirical test which permits the adhesion of the polyamide powder coatings to be classified against a rating scale ranging from 0 (zero adhesion) to 4 (excellent adhesion), the coating produced is given the rating 4.

After the substrate has been bent over a curvature radius of 5 mm, no crack appears on the coating.

Examples 33 to 36

The procedure as in Example 32 is followed, but using various mixtures of alpha, omega-diamine polyamide-11 oligomer and DGEBA resins (Epikote 1004 or 1001, the latter having a molecular mass equal to 978), mixtures whose composition is given in Table 4 below.
In all cases, the coatings produced under the operating conditions described in Example 32 have satisfactory appearance and quality and do not give rise to the appearance of cracking on being bent.

Example 37

The prepolymer prepared, in accordance with the operating procedure described in Example 14, by reacting in the molten state in an autoclave an alpha,omega-diacid polyamide oligomer of Mn = 1,384 with a polypropylene glycol alpha,omega-diepoxide resin (DER 732 from Dow Chemical), with an epoxide number of 330, is reduced by cryogenic grinding into the form of powder with a particle size distribution of between 10 and 100 μ, and a mean particle diameter of 56 μ.

This powder is applied to a steel plate in accordance with the operating procedure described in Example 32 and, after a heat treatment of 4 minutes in an oven at 220°C, a film is obtained with an average thickness of 60 μ, an adhesion 3 on the rating scale defined in Example 32 and with good bending strength.

Example 38

The prepolymer prepared according to the operating method described in Example 14 by reacting in the molten state form an alpha,omega-diacid polyamide oligomer of Mn = 1,384 with the DER 732 resin with an epoxide number of 330, ground into fine powder form according to the operating method described in Example 37, is employed to produce glue.
joints on aluminium and steel specimens.

The glued specimens, conforming to the ISO standard 4587, are 100 x 25 x 1.6 mm in size, with a joint covering area of 25 x 12.5 mm. They are degreased beforehand in a bath of 1,1,1-trichloroethane with ultrasonic agitation, and then dried in air.

The bonds are produced by depositing the required quantity of powder on the covering surface of the assembly, which is then heated for 2 minutes at 200°C under a pressure of 1 bar. The specimens are then subjected to a heat treatment for 2 h 30 min at 230°C, in an oven.

The shear strength of the assemblies is measured using a J.J. Lloyd T20 K tensometer equipped with a thermostatic enclosure permitting the measurement to be carried out at various temperatures. Each of the results assembled in Table 5 below is the average of 5 measurements carried out on 5 different specimens.

Example 39

40 parts by weight of an alpha,omega- primary diaminopolyamide-11 oligomer of Mn = 4,066 are ground into a finely powdered state. The powder obtained is mixed intimately with 10 parts by weight of powdered DGEBA epoxide resin of Mn = 978 (Epikote 1001 from Shell, epoxide number 489), which corresponds to an epoxide/amine ratio = 1. The mixture of powders thus prepared is employed to produce glued bonds on aluminium specimens of the same type as those described in Example 38.
The glued bonds are produced at 200°C, under a pressure of 1 bar for 15 minutes. There is no subsequent heat treatment. The shear strengths, measured at various temperatures, are as follows:

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Shear Strength (daN cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200°C</td>
<td>346</td>
</tr>
<tr>
<td>800°C</td>
<td>194</td>
</tr>
<tr>
<td>1400°C</td>
<td>61</td>
</tr>
</tbody>
</table>
### TABLE 1

| Oligoamide | Epoxide resin | Epoxide or epoxide \n| Nature | Epoxide or amine ratio | Tensile test (ASTM D 638) | HDT (ASTM D 648) | Flexural modulus Mpa (ASTM D 790) at 20°C | Hardness Shore D (150° D 868) |
|-----------|-----------------|--------------------------|----------------|--------------------------|-------------------|
| Example 9 | PA1,diCOOH 1460 | DGEBA (1) 374           | 1.25          | 36                        | 1210              | 74                |
| Example 10| PA2,diCOOH 1460| DGEBA (1) 374           | 1.50          | 30                        | 1115              | 73                |
| Example 11| PA3,diCOOH 4080 | DGEBA (1) 374           | 1.50          | 47                        | 1100              | 71                |
| Example 12| PA4,diNH, 1980  | PPG, di- 660 epoxide (3)| 1             | 41                        | 215               | 55                |
| Example 13| PA4,diNH, 3700  | PPG, di- 660 epoxide (3)| 1             | 31                        | 510               | 66                |
| Example 14| PA5,diCOOH 1384 | PPG, di- 660 epoxide (3)| 1             | 13                        | 209               | 49                |
| Example 15| PA6,diCOOH 4412 | PPG, di- 660 epoxide (3)| 1             | 27                        | 469               | 61                |
| Example 16| PA7,diCOOH 1542 | PPG, di- 660 epoxide (3)| 1             | 24.5                      | 193               | 47                |
| Example 17| PA8,monoNH, 1720| DGEBA (1) 374           | 2             | -                         | -                 | -                 |
| Example 18| PA9,monoNH, 5035 | DGEBA (1) 374           | 2             | 46.3                      | 1183              | -                 |
| Example 19| PA10,monoNH, 2191| DGEBA (2) 352           | 2             | 26.4                      | 1248              | 68                |
| Example 20| PA11,monoNH, 4265| DGEBA (2) 352           | 2             | 43.1                      | 1248              | 73                |

(1) Bisphenol A diglycidyl ether - Epikote 828 (Shell)  
(2) PPG alpha,omega-diepoxide - DER 332 (Dow Chemical)  
(3) PPG alpha,omega-diepoxide - DER 732 (Dow Chemical)  

- Epoxide number = 187  
- Epoxide number = 176  
- Epoxide number = 330
### TABLE 2

<table>
<thead>
<tr>
<th>Nature</th>
<th>Flow rate, g/s</th>
<th>( \varphi )</th>
<th>Flow rate, g/s</th>
<th>( \varphi )</th>
<th>( D_{\text{c}} )</th>
<th>( \varphi )</th>
<th>Filling time</th>
<th>Hold time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 24</td>
<td>PA-d/DMH</td>
<td>1074</td>
<td>95</td>
<td>190</td>
<td>350</td>
<td>21</td>
<td>140</td>
<td>200</td>
</tr>
<tr>
<td>Example 25</td>
<td>PA, d/DMH</td>
<td>1239</td>
<td>85</td>
<td>180</td>
<td>24</td>
<td>140</td>
<td>200</td>
<td>180</td>
</tr>
<tr>
<td>Example 26</td>
<td>1239</td>
<td>85</td>
<td>180</td>
<td>24</td>
<td>140</td>
<td>200</td>
<td>4 s</td>
<td>10 min.</td>
</tr>
<tr>
<td>Example 27</td>
<td>1978</td>
<td>93</td>
<td>190</td>
<td>16.8</td>
<td>140</td>
<td>200</td>
<td>3.3 s</td>
<td>10 min.</td>
</tr>
<tr>
<td>Example 28</td>
<td>1978</td>
<td>93</td>
<td>190</td>
<td>16.8</td>
<td>140</td>
<td>200</td>
<td>4 s</td>
<td>10 min.</td>
</tr>
</tbody>
</table>

### TABLE 3

<table>
<thead>
<tr>
<th>Composition, % weight</th>
<th>Glass fibre</th>
<th>Epoxide matrix</th>
<th>Tg, ( ^{\circ} \text{C} )</th>
<th>% crystallinity</th>
<th>Mechanical properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Flexural modulus MPa(1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( 25^{\circ} \text{C} )</td>
</tr>
<tr>
<td>Example 24</td>
<td>75.6</td>
<td>24.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Example 25</td>
<td>78.0</td>
<td>22.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Example 26</td>
<td>66.4</td>
<td>19.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Example 27</td>
<td>84.7</td>
<td>15.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Example 28</td>
<td>74.2</td>
<td>23.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(1) Determined by DMA. *Dupont Apparatus DMA 981*
diamine polyamide-6 oligomer, with the epoxide resin DER 332.

The machine consists of the following components:

- a double-entry mixing head which, in open

---

### TABLE 4

<table>
<thead>
<tr>
<th>Polyamide 11</th>
<th>DGEBA</th>
<th>Epoxide</th>
<th>Coating thickness</th>
<th>Adhesion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecule</td>
<td>Nature</td>
<td>Number</td>
<td>Quantity</td>
<td>Microns</td>
</tr>
<tr>
<td>Test 33</td>
<td>4066</td>
<td>56.5 parts</td>
<td>1045</td>
<td>43.5 parts</td>
</tr>
<tr>
<td>Test 34</td>
<td>4066</td>
<td>81 parts</td>
<td>489</td>
<td>19 parts</td>
</tr>
<tr>
<td>Test 35</td>
<td>4066</td>
<td>75.5 parts</td>
<td>489</td>
<td>26.3 parts</td>
</tr>
<tr>
<td>Test 36</td>
<td>6321</td>
<td>85.5 parts</td>
<td>489</td>
<td>44.5 parts</td>
</tr>
</tbody>
</table>

---

### TABLE 5

<table>
<thead>
<tr>
<th>Substrates</th>
<th>Shear strength (daN cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aluminium</td>
</tr>
<tr>
<td>Traction temp.</td>
<td></td>
</tr>
<tr>
<td>- 40°C</td>
<td>240</td>
</tr>
<tr>
<td>20°C</td>
<td>237</td>
</tr>
<tr>
<td>80°C</td>
<td>133</td>
</tr>
<tr>
<td>140°C</td>
<td>59</td>
</tr>
</tbody>
</table>
CLAIMS
1. A polymer produced by reacting a polyepoxide compound and a polyamide oligomer which is a primary monomaine, alpha, omega—primary or secondary diamine, alpha,omega-diacid or alpha—primary amine, omega-acid oligomer.

2. A polymer according to claim 1, in which the polyepoxide compound is a bisphenol A diglycidyl ether or polypropylene glycol alpha,omega-diepoxide.

3. A polymer according to claim 2, in which the bisphenol A diglycidyl ether has a number-average molecular mass of from 300 to 2,100 and an epoxide number of from 150 to 1,100.

4. A polymer according to any one of claims 1 to 3, in which the said polyamide oligomer is produced by polycondensation of one or more monomer which is an amino acid, lactam, salt of a diacid with a diamine or mixture of a diacid with a diamine.

5. A polymer according to claim 4 in which the monomer has a hydrocarbon chain of from 4 to 14 carbon atoms.

6. A polymer according to any one of claims 1 to 5, in which the said polyamide oligomer has an average molecular mass of from 400 to 10,000.

7. A polymer according to claim 6 in which the average molecular mass is from 1,000 to 7,000.

8. A polymer according to any one of claims 1 to 7, in which the said polyamide oligomer is produced by
same reactant mixture as in Example 29. A stack of 8 layers of carbon cloth, preimpregnated with powder by

polycondensation of one or more of caprolactam, dodecylactam, 11-aminoundecanoic acid or hexamethylenediamine adipate.

9. A polymer according to any one of claims 1 to 8, in which the said polyamide oligomer is a monoamine oligomer produced by polycondensation of at least one polymerizable monomer in the presence of a primary mono-amine.

10. A polymer according to claim 9, in which the said monoamine is dodecylamine.

11. A polymer according to claim 9 or 10, in which the proportion of polyepoxide compound to monoamine oligomer is such that there are 1.6 to 2.4 epoxide groups per amine group.

12. A polymer according to any one of claims 1 to 8, in which the said polyamide oligomer is an alpha,omega-diamine oligomer produced by polycondensation of at least one monomer in the presence of a primary or secondary diamine containing 4 to 22 carbon atoms.

13. A polymer according to claim 12, in which the said primary diamine is hexamethylene diamine.

14. A polymer according to claim 12 or 13, in which the proportion of polyepoxide compound to alpha,omega-diamine oligomer is such that there are 0.9 to 2.5 epoxide groups per amine group if the latter is a primary amine, and 0.8 to 1.15 if the latter is a secondary amine.

15. A polymer according to any one of claims 1 to 8, in which the said polyamide oligomer is an alpha,omega-diacid oligomer produced by polycondensation of at least
one monomer in the presence of a dicarboxylic acid containing from 4 to 22 carbon atoms.

16. A polymer according to claim 15 in which the carboxylic acid is aliphatic.

17. A polymer according to claim 15 or 16, in which the said diacid is adipic acid.

18. A polymer according to any one of claims 15 to 17, in which the proportion of polyepoxide compound to alpha, omega-diacid oligomer is such that there are 0.9 to 1.6 epoxide groups per acid group.

19. A polymer according to any one of claims 1 to 8, in which the said polyamide oligomer is an alpha-amine, omega-acid oligomer produced by polycondensation of at least one monomer in the absence of a chain terminator.

20. A polymer according to claim 1 in which the polyamide oligomer is substantially as described in any one of Examples 1 to 8.

21. A polymer according to claim 1 substantially as described in any one of Examples 9 to 39.

22. A polymer according to claim 1 which is thermoplastic.

23. A polymer according to claim 1 which is thermosetting.

24. A reactive composition comprising a polyepoxide compound and a polyamide oligomer which is a primary monoamine, alpha,omega-primary or secondary diamine, alpha,omega-diacid or alpha-primary amine omega acid
oligomer, which is capable of reacting to form a polymer according to any one of claims 1 to 23.

25. Use of a polymer according to any one of claims 1 to 23 or a composition according to claim 24 in the manufacture of articles moulded by injection, compression or reaction injection moulding technique, or in the manufacture of extruded articles.

26. Use of a polymer according to any one of claims 1 to 25 or a composition according to claim 24 in the production by the "pultrusion" method of composite articles consisting of long fibres held together by the polymer.

27. Use of a polymer according to any one of claims 1 to 23 or a composition according to claim 24 in the coating of metal articles.

28. Use of a polymer according to any one of claims 1 to 23 or a composition according to claim 24 as an adhesive agent.

29. A polymer according to claim 1 in all its new and useful aspects.

DATED this TWENTY THIRD day of AUGUST 1985

ATOCHEM

Patent Attorneys for the Applicant
SPRUSON & FERGUSON