We, ATOCHEM, 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 OBTAINED FROM OLIGOMERS OF ANHYDRIDE-GRAFTED POLYPROPYLENE, MANUFACTURING PROCESS AND USES"

which is described in the accompanying complete specification.

DETAILS OF BASIC APPLICATION

Number of Basic Application: - 8414880

Name of Convention Country in which Basic Application was filed: - France

Date of Basic application: - 27 September 1984

Our address for service is: -

C/- Spruson & Ferguson
Patent Attorneys
Level 33 St Martins Tower
31 Market Street
Sydney New South Wales Australia

DATED this TWENTY SIXTH day of SEPTEMBER 1985

ATOCHEM

By:


TO: THE COMMISSIONER OF PATENTS
AUSTRALIA

SBR: JMC: 74T
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 OBTAINED FROM Oligomers of
ANHYDRIDE-GRAFTED POLYPROPYLENE, MANUFACTURING PROCESS AND
USES

of ATOCHEM, a French Body Corporate of:
12/16, Allee des Vosges, 92400 COURBEVOIE, France.

I, (a) the applicant, or (b) the person to whom
the applicant has authorized to make this declaration on its behalf,
do solemnly and sincerely declare as follows:—

1. (a) I am the applicant for the Patent
or (b) I am authorized by

ATOCHEM, the applicant,...... for the Patent
or (b) the person to whom

the applicant has authorized to make this declaration on its behalf.

2. (a) I am the actual inventor...... of the invention
or (b) I am a French citizen, of: Residence

Saint-Germain, Boulevard de Normandie, 27000 FLEURY, France.

3. The basic application...... as defined by Section 141 of the Act
made in FRANCE: No. 84.14880 on the 27th September, 1984
by ATOCHEM......

by...... in...... on the......
by...... in...... on the......
by...... in...... on the......
by...... in...... on the......

4. The applicant is referred to in paragraph 3 of this Declaration...... as
the applicant in respect of the invention...... in respect of the Application

day of......

Michel ROCHET

Declarant No. 16, Allee des Vosges
92400 Courbevoie (France)
RCS Nanterre B 319 632 700
Te (I) 359.70.88 - Teleo

POLYMERS OBTAINED FROM Oligomers of ANHYDRIDE-GRAFTED
Claim 1. A polymer obtained from the association of two reactive components having a low melt viscosity, one of the components being a grafted polypropylene (as hereinbefore defined) obtained using a grafting monomer an unsaturated compound bearing an acid anhydride group and the other component being a compound possessing at least two identical or different groups which react with such an anhydride group, the molar ratio of the components, defined as the ratio of the number of said reactive groups carried by the said compound to the number of anhydride groups carried by the grafted polypropylene being from 0.01:1 to 2:1.

9. A polymer according to any one of Claims 1 to 4, in which the said compound is a polysul, polyamine, polyepoxide or polyisocyanate and has a molecular weight not exceeding 50,000.

15. A composite article comprising long fibres connected by a polymer as claimed in any one of Claims 1 to
Complete Specification for the invention entitled:

"POLYMERS OBTAINED FROM OLIGOMERS OF ANHYDRIDE-RAFTED POLYPROPYLENE, MANUFACTURING PROCESS AND USES"

The following statement is a full description of this invention, including the best method of performing it known to us.
ABSTRACT

POLYMERS OBTAINED FROM OLIGOMERS OF ANHYDRIDE-GRAFTED POLYPROPYLENE, MANUFACTURING PROCESS AND USES

Polymers resulting from the association of two reactive components having a low melt viscosity are disclosed in which one of the components is a polypropylene modified by grafting an unsaturated monomer bearing an acid anhydride group and the other is a compound possessing at least two groups which are reactive towards this anhydride group. These are useful in the manufacture of moulded articles by the reaction-injection-moulding technique or of composite materials and also as coatings for metallic articles.
POLYMERS OBTAINED FROM OLIGOMERS OF ANHYDRIDE- GRAFTED POLYPROPYLENE, MANUFACTURING PROCESS AND USES

It is known that certain of the physical or mechanical properties of polyolefins can be advantageously modified by creating active sites on the polyolefins and crosslinking them with polyfunctional compounds capable of reacting with these active sites. These grafting reactions concern polyolefins of high molecular weight.

On the other hand, the present invention relates to polypropylene of low molecular weight and hence of low melt viscosity.

The present invention provides polymers which are produced by merely mixing two components, thereby causing them to react with each other, these two components both having a low melt viscosity, one of them being a polypropylene modified by grafting a monomer bearing an acid anhydride group, and the other a compound possessing at least two groups which are reactive towards this anhydride group, a compound which, for the sake of convenience, we shall refer to as "a reactive compound" or "compound R".

Both of these components, taken in isolation relatively low molecular masses and, consequently, exceedingly poor mechanical properties; this is not so in the
case of the products resulting from their reaction, polymers which, because of their advantageous physical and mechanical properties, find application in the usual fields where plastics are employed.

Numerous methods have been suggested for preparing the first component, grafted polypropylene.

By "grafted polypropylene" (PPg) we mean all the propylene homopolymers or copolymers with various monomers (be they block or random, provided that these copolymers contain at least 50 mole % of propylene) on which an unsaturated monomer bearing an acid anhydride group has been grafted.

This grafting monomer is a compound bearing at least one double bond which is active in radical polymerization, and at least one 5-membered cyclic acid anhydride group with five centres.

This monomer may be maleic, citraconic, 2-methylmaleic, 2-chloromaleic, 2-methoxycarbonylmaleic, 2,3-dimethylmaleic, 2,3-dichloromaleic, 2,3-dimethoxycarbonyl-maleic, bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic, or 4-methylcyclohex-4-ene-1,2-dicarboxylic anhydride, for example.

To produce the grafting, sites may be prepared on the polypropylene chain by treatment with initiators of the peroxide or diazo type, or by electromagnetic treatment, sites at which the anhydride can be grafted by a radical mechanism.
The activation and the grafting may also be carried out simultaneously by subjecting a suspension of polypropylene powder in a liquid, or a solution of polypropylene in a suitable solvent, to the action of a peroxide (see USP 2,970,129); it is also possible to carry out the operation in a gas stream (see USP 3,414,551), the solvent or the gas stream containing the appropriate quantity of the grafting monomer defined earlier.

It is also possible to carry out the operation in a molten state.

It is well known that these reactions with the polypropylene or propylene copolymer chain are accompanied by chain-scission reactions and as a result reduce the molecular mass of the polymer and, consequently, its melt viscosity.

This degradation effect may be restricted by involving the reactions of the monomer to be grafted or, on the other hand, may be increased by the disproportionation and transfer reactions of this same monomer.

However, in the majority of cases, PPg's are produced with much lower melt viscosities than those of the polymers from which they originated, in other words oligomers.

The PPg's employed for the manufacture of the polymers which are the subject of the present invention should generally have a melt viscosity below 500 Pa s, measured at 200°C at a shear rate of 10 s⁻¹, using a viscometer with two
coaxial cylinders, specifically Rheomat 30, which is manufactured by the Swiss company Contraves.

The compound R of which the molecular weight is generally less than 50,000 bears at least two identical or different groups which are reactive towards the acid anhydride group of the PPg; among these reactive groups there may be mentioned the alcohol group, the amine group, the epoxide group and the isocyanate group. It may therefore be a diol or a triol, or a diamine or triamine, or a compound containing an alcohol group and an amine group at the same time, or two amine groups and one alcohol group, for example.

Among the compounds R which contain at least two alcohol groups there may be mentioned: ethylene glycol, propylene glycol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol, 2-butene-1,4-diol, 1,4-(2-hydroxyethoxy)-1-butanol, 1,2,6-hexanetriol, erythritol, sucrose, glucose, dihydroxyacetone, polyoxyalkylene glycols such as polyoxyethylene glycols, polyoxymethylene glycols of various molecular weights and hydroxy derivatives of ethylene/vinyl acetate copolymers.

Among the compounds R containing at least two amine groups, there may be mentioned:

- alpha,omega-diamino polyamide oligomers of various
molecular weights, the synthesis of which has been described in French Patent Applications Nos. 83/15,859 and 84/13,244.

- aliphatic or aromatic diamines such as hexa-
  methylenediamine, nonamethylenediamine, undecamethylenediamine, dodecamethylenediamine, meta-xylenediamine, and bis-p-aminocyclohexylmethane.

Among the polyepoxy compounds \( R \), the most widely used compounds are those produced by the reaction of bisphenol \( A \) with epichlorohydrin and, in particular, the compounds produced by the addition of two molecules of epichlorohydrin to one molecule of bisphenol \( A \), that is to say bisphenol \( A \) diglycidyl ethers (BADGE). However, it is possible to use, as the polymers according to the invention, a large number of other epoxy resins such as those produced by attaching an epoxy group at both ends of a paraffinic hydrocarbon chain (for example diepoxy derivatives of butanediol), or of a polyether chain, such as alpha, omega-diepoxy polypropylene glycol, marketed by the Dow Chemical Company under the reference DER 732 or DER 736. It is also possible to employ more specific diepoxy compounds, such as vinylcyclohexene dioxide, 3,4-epoxycyclohexymethyl 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-methylcyclohexyl) adipate and resorcinol diglycidyl ether.
Among the compounds R which contain at least two isocyanate groups there may be mentioned:

- 2,4- or 2,6-tolylenedimethane diisocyanate,
- 4,4'-diphenylmethane diisocyanate,
- 1,4- or 1,6-hexamethylenediisocyanate,
- 1,4-cyclohexylene diisocyanate,
- 3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate,
- Triisocyanates such as triphenylmethane triisocyanate, for example.

The respective quantities of the two main components: PPG and compound R which will react together to give the polymers according to the invention is such that their molarity ratio (MR) defined as follows:

\[
MR = \frac{\text{Concentration of reactive groups carried by R}}{\text{Concentration of acid anhydride groups carried by the PPG}}
\]

\[
= \frac{\text{Number of reactive groups in R}}{\text{Number of acid anhydride groups in PPG}}
\]

is from 0.01 to 2 and, preferably, from 0.1 to 1, one acid anhydride group corresponding to two carboxylic acid groups.

The reaction will occur on mere mixing of the two components PPG and compound R in the molten state; any plastics conversion equipment which ensures good blending is suitable, such as a Brabender or Buss blender, a single-screw extruder, or a double-screw extruder of the Werner and Pfleiderer type. The operation may also be
carried out in a simple autoclave with good stirring.

Since both components have a low melt viscosity, it is advantageous to use the Reaction Injection Moulding (RIM) technique, as described in Modern Plastics International, 5 April 81, to produce the polymer and its moulding into large-sized articles in a single operation. Thus, this technique makes it possible to obtain large mouldings from modified polypropylene having good mechanical properties, while it would be very difficult, if not impossible, to obtain the same articles by injection moulding of ordinary polypropylene, which is too viscous, while with crosslinked polypropylene it would be impossible.

In this case, the two components of the system - PPg and R - are conveniently stored in a liquid state in two separate containers maintained at a temperature which is sufficient for the two reactants to remain liquid; the polymerization and the moulding of the finished article can be produced simultaneously by pumping the required quantity of each of the two reactants from the two containers, mixing them in a special device producing a highly intimate mixture of the two components very rapidly, and injecting the mixture produced into the mould. 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.

It is also possible to produce profile components
by coating, using, say, a "Pultrusion" technique, a glass fibre core which passes continuously through a die, called a crosshead, fed continuously with the liquid mixture of PPG and compound R, the said die having the cross-section of the profile which is to be produced.

These new polymers can also be used as binders in the manufacture of composite materials.

In addition to the two basic components it is also possible to use other compounds which can be added to the reaction mixture, such as dilution polymers, stabilizers against heat, light and oxidation, colourants, plasticizers and various reinforcing or non-reinforcing fillers.

It is also possible to prepare systems which are more complex than the simple two-component system: PPG/R by incorporating therein one or more components which react with PPG or R.

In any event, it is possible to produce finished articles by employing conventional conversion techniques for thermoplastics, such as extrusion, injection moulding, rotational moulding and thermoforming.

It is also possible to employ these polymeric compounds to coat metal articles and to protect them against corrosion in this way.

The following Examples further illustrate the present invention.
Example 1.

Maleic anhydride is grafted onto a propylene homo-polymer in the following manner:

- 5,500 g of monochlorobenzene
- 1,200 g of Lacqten 3050 FNI (polypropylene sold by ATOCHEM - ASTM D 1238-Flow Index at 230°C, 5 kg load, of 5),
- 200 g of maleic anhydride
- 36 g of benzoyl peroxide

are introduced into an autoclave. After maintaining at a temperature of 130°C for 3 hours, a 2.7% grafted PP is obtained, whose melt viscosity, measured at 200°C with the aid of a Rheomat 30 at a shear rate of 10 s⁻¹ is 10 Pa s, while that of Lacqten 3050 FNI was 1,300 Pa s under the same conditions.

The grafted PP obtained above is mixed, alone or with addition of 1,6-hexanediol, in a chamber of a Brabender blender at a temperature of 178°C.

In both cases the polymers are taken out after 10 minutes' blending and are compression-moulded in the press at 180°C into plaques 2 mm in thickness from which H₃-type tensile test specimens are cut out (French Standard NFT 51,034). The stress and the extension at break of these specimens are then measured by pulling at a rate of 1.42 mm/minute.

In addition, the melt viscosity of these polymers is measured.
Here are the results obtained:

<table>
<thead>
<tr>
<th>Weight of PPg in g</th>
<th>Weight of 1,6-hexanediol in g</th>
<th>[OH]</th>
<th>Break stress in MPa</th>
<th>Melt viscosity at 200°C in Pa s</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>45</td>
<td>0</td>
<td>brittle - unmeasurable</td>
<td>10</td>
</tr>
<tr>
<td>44.783</td>
<td>0.217</td>
<td>0.3</td>
<td>26</td>
<td>4,500</td>
</tr>
</tbody>
</table>

It can be seen that the break stress, which is practically zero for grafted PP, has increased to a value of 26 by the addition of hexanediol (its value for the same polypropylene, ungrafted, is 22 N/mm²).

Example 2.

By using an operating procedure similar to that of Example 1, 4.1% of maleic anhydride are grafted onto a propylene/ethylene block copolymer sold by ATOCHEM under the name Lacqten P 3050 MN4 (Flow Index of 5 at 230°C, 5 kg load).

This grafted copolymer, whose melt viscosity is 100 Pa s at 200°C at 10 s⁻¹ is then blended in the same Brabender blender as that in Example 1, still at a temperature of 178°C, alone or with various reactants: 1-dodecanol, polyoxymethylene glycol (PTMG), polyoxyethylene glycol (PEG), and alpha,omega-diamino polyamide 11 oligomer (di-NH₂ PA) of a molecular mass of 1,050, produced by polycondensation of 11-aminoundecanoic acid in the presence of hexamethylenediamine, according
to the operating procedure described in French Patent Application No. 84 13,244.

The resistance torque of the blender is recorded after 10 minutes' mixing at 178°C and, as in Example 1, the properties of plaques moulded from the polymers produced by the blending are measured.

The results entered in Table I show that, in the majority of cases, an increase in the physical properties is obtained relative to the copolymer 3050 MN4 (resistance torque : 1.35 kg/m; break stress: 22.5 N/mm², extension: 130%).

The addition of a monofunctional reactant such as 1-dodecanol produces no improvement.

<table>
<thead>
<tr>
<th>Weight of PPG in g</th>
<th>REACTANT</th>
<th>Weight in g</th>
<th>$\frac{D_{o}-D_{w}}{D_{o}}$</th>
<th>Resistance torque in kg m</th>
<th>MECHANICAL PROPERTIES</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0.17</td>
<td>not measurable</td>
</tr>
<tr>
<td>45.31</td>
<td>1-dodecanol</td>
<td>1.64</td>
<td>0.5</td>
<td>0.14</td>
<td>not measurable</td>
</tr>
<tr>
<td>45.75</td>
<td></td>
<td>3.23</td>
<td>1.0</td>
<td>0.74</td>
<td>not measurable</td>
</tr>
<tr>
<td>42.12</td>
<td>PEG Mn = 650</td>
<td>2.88</td>
<td>0.5</td>
<td>1.92</td>
<td>28</td>
</tr>
<tr>
<td>30.56</td>
<td></td>
<td>3.47</td>
<td>1.0</td>
<td>2.42</td>
<td>28</td>
</tr>
<tr>
<td>42.33</td>
<td>PEG Mn = 600</td>
<td>2.67</td>
<td>0.5</td>
<td>1.66</td>
<td>24</td>
</tr>
<tr>
<td>41.50</td>
<td>PEG Mn = 2,000</td>
<td>3.50</td>
<td>0.2</td>
<td>0.74</td>
<td>15</td>
</tr>
<tr>
<td>37.18</td>
<td></td>
<td>7.82</td>
<td>0.5</td>
<td>0.40</td>
<td>18</td>
</tr>
<tr>
<td>4.03</td>
<td>G=NH,PA Mn = 1,000</td>
<td>0.97</td>
<td>0.5</td>
<td>0.32</td>
<td>15</td>
</tr>
<tr>
<td>40.63</td>
<td></td>
<td>4.47</td>
<td>0.5</td>
<td>not measurable too high</td>
<td>20</td>
</tr>
</tbody>
</table>


Example 3.

As in Example 2, Lacqten P 3050 MN4 is modified by grafting, but in this case only 1.3% of maleic anhydride are grafted on; the PPG obtained has a flow index of 26.3 at 190°C, 2.16 kg load.

It is then blended for 10 minutes at 180°C with a hydrolysed ethylene/vinyl acetate copolymer (containing 28% of vinyl acetate) (EVA OH) whose molar equivalent of the hydroxyl group, measured by infrared analysis, is 100.2 mole OH/100 g of resin.

<table>
<thead>
<tr>
<th>Weight of PPG in g</th>
<th>Weight of EVA OH in g</th>
<th>MR = [OH] / [M]</th>
<th>Flow index at 190°C, 2.16 kg load</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.00</td>
<td>0</td>
<td>0</td>
<td>26.3</td>
</tr>
<tr>
<td>44.55</td>
<td>0.45</td>
<td>0.15</td>
<td>21.8</td>
</tr>
<tr>
<td>43.65</td>
<td>1.35</td>
<td>0.46</td>
<td>18.2</td>
</tr>
<tr>
<td>42.75</td>
<td>2.25</td>
<td>0.79</td>
<td>6.6</td>
</tr>
</tbody>
</table>

This example shows that, in the case of a polymeric reactant bearing secondary alcohol groups, the chain extension phenomenon occurs at molar ratios below unity.

Example 4.

As in Example 2, Lacqten P 3050 MN4 is modified by grafting, but 3.8% of maleic anhydride are grafted this time. The PPG produced has a melt viscosity of 100 Pa s measured at 200°C with a Rheomat 30.

It is then blended, alone or with the following reactants, at 180°C for 15 minutes in the Brabender blender.
epoxy resin DER 732, alpha,omega-diepoxo polypropylene glycol, marketed by the Dow Chemical Company, having the following properties:

- viscosity at 25°C: 55 to 100 cP;
- weight, in grammes, of resin containing 1 gramme equivalent of epoxy: 305-335;
- random ethylene/glycidyl methacrylate copolymer (E/GMA) with a content of 5% of GMA by weight.

The results obtained are listed in Table II.

Example 5.

Still in the same blender, the PPG of Example 4 is stirred alone or with 1,6-hexamethylene diisocyanate (HMDI) of $M_w = 168$.

<table>
<thead>
<tr>
<th>Weight of PPG in g</th>
<th>Weight of HMDI in g</th>
<th>[Isocyanate]</th>
<th>Resistance torque in kg m</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>0</td>
<td>0</td>
<td>0.12 measurable</td>
</tr>
<tr>
<td>43.58</td>
<td>1.42</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

The increase in torque clearly reflects the mutual reactivity of the two components, which produce a polymer in the form of powder.
Example 6

Maleic anhydride is grafted on a random copolymer of propylene and ethylene, in the following manner:

- 5,500 g of monochlorobenzene
- 1,200 g of Lacqten 3020 GN3 (copolymer containing 95 mol % of propylene and 5 mol % of ethylene, sold by Atochem - melt index ASTM D 1238 at 230°C, under 5 kg, equal to 2)
- 200 g of maleic anhydride
- 36 g of benzoyl peroxide

are introduced into an autoclave.

After being maintained for 3 hours at a temperature of 130°C, a 3.4% grafted polypropylene is obtained whose melt viscosity, measured at 200°C with the aid of a Rheomat 30 at a shear rate of 10 s⁻¹ is 9 Pa s, while that of the
Lacqene 3020 GN3 was 1,500 Pa s under the same conditions.

278.4 g of the grafted polypropylene obtained above are placed in a beaker at a temperature of 200°C.

In another beaker, 21.6 g of a polyoxyethylene glycol with a number average molecular mass of 600 are heated to 80-100°C. The molar ratio $\frac{[D]}{[MA]}$ is 0.75 under these conditions.

The PEG of Mn = 600 is poured into the beaker containing the grafted polypropylene. Mixing is carried out by hand with the aid of a glass stirrer for 90 seconds. During the mixing, the viscosity of the medium increases until a pale yellow homogeneous liquid is obtained; this liquid is cast in a steel mould 160 x 160 x 2 mm in size, which is maintained at 200°C for 15 minutes between the heating platens of a hydraulic press producing a pressure of 12 tonnes. After cooling and demoulding, a pale yellow plaque is obtained.

The mechanical properties of the material are given in Table III.

Example 7

The same operating procedure as in the preceding example is followed, but using, as reactant, a polyoxyethylene glycol of number average molecular mass of 2,000, with the following quantities:

- polypropylene grafted with 3.4% MA: 238.2 g
- PEG Mn = 2,000 : 61.8 g
MR = \frac{[\text{OH}]}{[\text{MA}]} = 0.75

The mechanical properties of the material are given in Table III.

Example 8

The same operating procedure as in the preceding example is followed, but using, as reactant, an alpha, omega-diamino polyamide 11 oligomer (di-\text{NH}_2 \text{PA}) of number average molecular mass 6,621, with the following quantities:
- polypropylene grafted with 3.4% of MA: 193.8 g
- di-\text{NH}_2 \text{PA}, Mn = 6,621: 106.2 g

MR = \frac{[\text{NH}_2]}{[\text{MA}]} = 0.5

In this case, the mixing time should not exceed 10 seconds; the homogeneous and viscous mixture obtained is poured into a mould. The total duration of the operations of mixing the components and filling the mould should not exceed 30 seconds.

The plaque obtained is homogeneous and translucent. The mechanical properties of the material are given in Table III.

Example 9

The same operating procedure as in the preceding example is followed, but using, as reactant, bisphenol A digly-cidyl ether (DGEBA: $M_w = 352$) sold by Dow Chemical under the reference DER 332, with the following quantities:
- polypropylene grafted with 3.4% of MA: 291 g
- DER 332: 9 g
The given quantity of DER 332 is poured into the bar containing the grafted polypropylene, previously heated to 200°C. Mixing is carried out manually for 90 seconds by means of a glass stirrer. During the mixing, the viscosity of the mixture increases until a homogeneous yellow liquid is obtained. This resin is poured into a steel mould which is maintained at 200°C for 15 minutes under a pressure of 12 tonnes. After cooling and demoulding, a yellow-coloured plaque is obtained.

The mechanical properties of the material are given in Table III.

| TABLE III |
|------------|-------------------|-----------------|
|            | BREAK STRESS IN   | ELONGATION AT   |
|            | Mpa               | BREAK, %         |
| EXAMPLE 6  | 18.5              | 250             |
| EXAMPLE 7  | 13.0              | 270             |
| EXAMPLE 8  | 20                | 0               |
| EXAMPLE 9  | 15                | 0               |
| CONTROL - pure Ppg | not measurable | 0               |

Example 10

A Martin Sweets reaction-injection-moulding
(RIM) machine, of the Flexamatic RHPI type, is employed to produce moulded plaques, by reaction of the PP grafted with maleic anhydride of Example 6 with a polyoxyethylene glycol of number average molecular weight 600.

The machine consists of the following components:

- a double-entry mixing head which, in an open position, ensures intimate mixing of the two reactants and their transfer towards the mould described below and, in a closed position, ensures recirculation, without mixing, of each of the reactants towards the lines A and B which are described below;
- a square mould 305 x 305 x 3 mm in size, supplied with the mixture produced in the mixing head;
- two lines A and B, connected to the mixing head, each comprising a storage volume for either of the reactants and a hydraulically-controlled metering unit. This metering unit permits either a closed-circuit recirculation between the storage volume and the mixing head in the closed position, of the reactant in the line, without mixing with the reactant in the other line, or the injection of the reactant into the mixing head in the open position, the delivery pressure simultaneously permitting intimate mixing with the reactant coming from the other line and flow of the mixture into the mould. A detailed description of the principle of the RIM machines is to be found in the work: Introduction to Reaction Injection Molding, Technomic Publ. Co. Inc. 1979 – pp. 77 to 126.
epoxycyclohexyl)-8,9-epoxy-2,4-dioxaspiro[5.5]undecane,
bis(2,3-epoxycyclopentyl) ether, bis(3,4-epoxy-6-methyl-
cyclohexyl) adipate and resorcinol diglycidyl ether.

All the machine components may be controlled up
to a temperature of 235\(^\circ\)C, and the operating temperature
of each component may be fixed independently of those of
the other components.

The molar ratio of the two reactants and the
homogeneity of the mixture are determined by modifying,
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.

10 The conditions of the tests carried out with the
RIM machine are collated in Table No. IV.

The mould is perfectly filled and the plaques
obtained have good surface appearance and excellent homo-
geneity. The properties of the material obtained are
given in Table No. V.
### TABLE IV

<table>
<thead>
<tr>
<th>LINE A</th>
<th>LINE B</th>
<th>MIXING</th>
<th>MOULD</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPg VISCOSITY 9 Pa s at 200°C</td>
<td>PEG Mn: 600</td>
<td>TEMPERATURE in °C</td>
<td>TEMPERATURE in °C</td>
</tr>
<tr>
<td>Flow rate g s⁻¹</td>
<td>Temperature °C</td>
<td>Flow rate g s⁻¹</td>
<td>Temperature °C</td>
</tr>
<tr>
<td>111</td>
<td>200</td>
<td>8.6</td>
<td>140</td>
</tr>
<tr>
<td>95.3</td>
<td>200</td>
<td>24.7</td>
<td>140</td>
</tr>
<tr>
<td>TABLE IV</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>LINE A</th>
<th>LINE B</th>
<th>MIXING</th>
<th>MOULD</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPG VISCOSITY 9 Pa S at 200°C</td>
<td>PEG Mn: 600</td>
<td>TEMPERATURE in °C</td>
<td>TEMPERATURE °C</td>
</tr>
<tr>
<td>Flow rate g s⁻¹</td>
<td>Temperature °C</td>
<td>Flow rate g s⁻¹</td>
<td>Temperature °C</td>
</tr>
<tr>
<td>111</td>
<td>200</td>
<td>8.6</td>
<td>140</td>
</tr>
<tr>
<td>95.3</td>
<td>200</td>
<td>24.7</td>
<td>140</td>
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PEG Mn: 2,000
<table>
<thead>
<tr>
<th>TERNATURE °C</th>
<th>FILLING TIME in s</th>
<th>HOLDING TIME in s</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>4</td>
<td>600</td>
</tr>
<tr>
<td>90</td>
<td>4</td>
<td>600</td>
</tr>
<tr>
<td>WEIGHT COMPOSITION (%)</td>
<td>MOLAR RATIO [OH] [MA]</td>
<td>TRACTION (ASTM D 638)</td>
</tr>
<tr>
<td>------------------------</td>
<td>------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>PP g PEG Mn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>92.8 7.2 0.75</td>
<td>18 250</td>
<td>9.6 26.8 650</td>
</tr>
<tr>
<td>PEG 600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>79.4 20.6 0.75</td>
<td>13 250</td>
<td>9.3 17.9 570</td>
</tr>
</tbody>
</table>
1,050, produced by polycondensation of 11-aminoundecanoic acid in the presence of hexamethylenediamine, according to

<table>
<thead>
<tr>
<th>WEIGHT COMPOSITION (%)</th>
<th>MOLAR RATIO [OH] [MA]</th>
<th>TRACTION (ASTM D 638)</th>
<th>FLEXURE (ASTM D 790)</th>
<th>SHORE D HARDNESS (ISO D 868)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>BREAK STRESS</td>
<td>MAX. STRESS UNDER LOAD</td>
<td>UNDER LOAD</td>
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<tr>
<td></td>
<td></td>
<td>MPa</td>
<td>MPa</td>
<td>mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EXTENSION AT BREAK</td>
<td>MAX. DEFLECTION UNDER LOAD</td>
<td>ELASTICITY MODULUS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>%</td>
<td>mm</td>
<td>MPa</td>
</tr>
<tr>
<td>PP 9 2000</td>
<td>PEG 600</td>
<td>600</td>
<td>92.8</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.2</td>
<td>0.75</td>
<td>26.8</td>
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<tr>
<td></td>
<td></td>
<td>18</td>
<td>250</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20.6</td>
<td>0.75</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td></td>
<td>79.4</td>
<td>13</td>
<td>9.3</td>
</tr>
<tr>
<td>Shore D</td>
<td>Elasticity Modulus (MPa)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>69</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>69</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Hardness obtained (ASTM D 790)
The PPG produced has a melt viscosity of 100 Pa s measured at 200°C with a Rheomat 30.

It is then blended, alone or with the following reactants, at 180°C for 15 minutes in the Brabender blender:

---

**Example 11 - Manufacture of a composite material**

The grafted PP of Example 2 is reduced to fine powder by grinding and the powder thus obtained is made into a paste with polyoxyethylene glycol of molecular mass 600, in a proportion of 6.3 g per 100 g of PPG, which corresponds to a molar ratio $\frac{[O]}{[M]}$ of 0.5.

The pasty powder is deposited by dusting on a made of long glass fibres of the Owens Corning Fiberglas 8610 type at 900 g/m$^2$.

This powder-impregnated mat is then placed between two pre-extruded sheets 1 mm in thickness, made of a standard polypropylene (Lacqtcne P 3030 FN1 - Atochem) of melt index 3, measured at 230°C under 2.16 kg in accordance with the ASTM standard 1238.

The above operation is repeated so as to obtain a stack of three mat layers impregnated with powders and four sheets of standard polypropylene 1 mm thick.

The whole is preheated to 200°C for 3 minutes between the platens of a press and then compressed at the same temperature under 25 bars for 1 minute. The whole is then cooled to 80°C under pressure. A 3.3 mm composite is obtained.

By way of comparison, a composite of identical structure is prepared under the same conditions, starting only with glass matting and standard polypropylene, the thickness of the polypropylene layers being corrected in order to obtain a composite identical in thickness and
glass content.

The results of the mechanical tests carried out on the products are given in the following table:

<table>
<thead>
<tr>
<th>COMPARATIVE TEST</th>
<th>Glass fibres, weight %</th>
<th>Traction</th>
<th>Flexure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>45</td>
<td>125</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td></td>
<td>87</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6,450</td>
<td>5,146</td>
</tr>
</tbody>
</table>

COATING OF METAL ARTICLES

In the coating field, the resins according to the invention may be subjected to the same techniques as those employed for polyamide powders but, in contrast to the latter, it is possible to obtain coatings having high adhesion to steel without the need for a preliminary treatment of the metal substrate with an undercoat intended to permit good bonding with the polyamide coating. Different techniques are possible for producing these coatings: it is possible to use a powder obtained by grinding the homogeneous prepolymer obtained by mixing in a suitable
compounding machine, in melt form, the Ppg oligomer and the reactant R, as defined earlier. It is also possible to employ a powder consisting of a mechanical mixture, produced cold, of, on the one hand, the Ppg oligomer and, on the other hand, the reactant R. Coating of the substrate using these powders may be carried out in accordance with the known coating techniques, for example by electrostatic spraying, followed by a cure for a few minutes at an elevated temperature of between 200 and 250°C, or by dipping the substrate, preheated to a high temperature, in a fluidised bed in which the powder is kept in suspension.

Example 12

Maleic anhydride is grafted onto a propylene/ethylene block copolymer in accordance with the operating procedure described in Example 2. The grafted PP obtained is reduced to a fine powder, of a particle size (measured in a Coulter counter) below 80 microns, by being passed through a grinder.

13 g of a polyoxyethylene glycol of number average molecular mass 600 are then dissolved separately in 34 g of 2-ethoxyethyl acetate. 100 g of grafted PP, such as described earlier, are added. The molar ratio $\frac{[\text{OH}]}{[\text{MA}]}$ is 1.

A dispersion is produced with a turbine over 5 to 10 minutes. This dispersion is applied with the aid of an 80 micron gauge to a degreased aluminium plate. The
plate coated in this way is placed in an oven at 200°C for 3 minutes and then cooled by immersion in water. A film 20 microns in thickness, with very good resistance to methyl ethyl ketone is obtained.

The film is transparent, semi-glossy and has excellent adhesion, together with excellent mechanical properties.

In a comparative test, the grafted PP is employed by itself without PEG. The film obtained is brittle and consequently unsuitable for producing a coating.

Example 13

10 g of DGEBA epoxide resin/-Epikote 828 from Shell, the epoxy equivalent weight of which (resin weight corresponding to 1 mol of epoxy) is 187, are dissolved in 15100 g of 2-butoxyethyl acetate (commercial butyl glycol acetate), and then 120 g of Ppg of Example 2 are dispersed in this solution with a turbine for 5 to 10 minutes.

The viscosity is then reduced by adding 200 g of butyl glycol acetate.

The molar ratio \( \frac{[\text{Epoxy}]}{[\text{MA}]} \) is 1.

The dispersion obtained is applied, using an 80 micron gauge, on a degreased aluminium plate. The plate coated in this way is stoved for 3 minutes at 200°C and then cooled by immersion in water. A film 20 microns in thickness, with good resistance to methyl ethyl ketone,
is obtained. This film is transparent, semi-glossy and has an excellent adhesion, together with very good mechanical properties.

Example 14

250 g of Ppg from Example 2 are mixed dry with 90 g of Epikote 3003 epoxide resin (epoxy equivalent weight 725-825) (Shell), previously ground, and 0.5 g of alumina. The powder obtained is applied with an electrostatic (+60 kV) spray gun onto a degreased smooth steel plate. The plate is stoved for 5 minutes at 200°C. A film 30/35 microns in thickness is obtained, which is transparent, semi-glossy and which covers the ridges well.

The methyl ethyl ketone resistance of this film, its adhesion to the steel plate and its mechanical properties are good.
| CONTROL - pure Ppg | not measurable | 0 |

**Example 10**

A Martin Sweets reaction-injection-moulding
The claims defining the invention are as follows:

1. A polymer obtained from the association of two reactive components having a low melt viscosity, one of the components being a grafted polypropylene (as hereinbefore defined) obtained using as grafting monomer an unsaturated compound bearing an acid anhydride group and the other component being a compound possessing at least two identical or different groups which react with such an anhydride group, the molar ratio of the components, defined as the ratio of the number of said reactive groups carried by the said compound to the number of anhydride groups carried by the grafted polypropylene, being from 0.01:1 to 2:1.

2. A polymer according to Claim 1 in which the said molar ratio is from 0.1:1 to 1:1.

3. A polymer according to Claim 1 or 2 in which the grafted polypropylene has a melt viscosity, measured at 200°C at a shear rate of 10 s⁻¹, not exceeding 500 Pa s.

4. A polymer according to any one of Claims 1 to 3, in which the polypropylene has been grafted with maleic anhydride.

5. A polymer according to any one of Claims 1 to 4, in which the said compound is a polyol, polyamine, polyepoxide or polyisocyanate and has a molecular weight not exceeding 50,000.

6. A polymer according to Claim 5 in which the said compound is 1,6-hexanediol.

7. A polymer according to Claim 5 in which the said
compound is a polyoxyethylene glycol or polyoxytetramethylene glycol.

8. A polymer according to Claim 5 in which the said compound is an alpha,omega-diamino polyamide 11 oligomer.

9. A polymer according to Claim 5 in which the said compound is a hydrolysed ethylene/vinyl acetate copolymer.

10. A polymer according to Claim 5 in which the said compound is an alpha,omega-diepoxy polypropylene glycol or an ethylene/glycidyl methacrylate copolymer.

11. A polymer according to Claim 1 substantially as described in any one of Examples 1 to 14.

12. Process for the manufacture of a polymer as claimed in any one of the preceding claims which comprises blending the two reactive components in the molten state.

13. Process according to Claim 12 substantially as described in any one of Examples 1 to 14.

14. An article obtained by molding by injection, compression or the reaction-injection molding technique, or obtained by extruding, a polymer as claimed in any one of Claims 1 to 11.

15. A composite article comprising long fibres connected by a polymer as claimed in any one of Claims 1 to 11.

16. A metal article coated with a polymer as claimed in any one of Claims 1 to 11.
Dated this twenty sixth day of september 1985

Atochem

patent attorneys for the applicant

Spruson & Ferguson