COMMONWEALTH OF AUSTRALIA
PATENTS ACT 1952
APPLICATION FOR A STANDARD PATENT

Atochem, a French Body Corporate, of La Defense 10, 4 & 8, Cours Michelet, 92800 Puteaux, FRANCE, hereby apply for the grant of a standard patent for an invention entitled:

New α-Mono-olefin Based Graft Copolymer

which is described in the accompanying complete specification.

Details of basic application(s):

Basic Applic. No: Country: Application Date:
8803877 FR 24 March 1988

The address for service is:

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

DATED this TWENTY SECOND day of MARCH 1989

Atochem

By: [Signature]

Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 90313
S&F CODE: 56550

REPRINT OF RECEIPT
S006350 23/03/89

5845/4
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 for an invention entitled:
New α-Mono-olefin Based Graft Copolymer

Michel ROCHE, care of: ATOCHEM, a French Body Corporate of:
La Defense 10, 4 & 8 Cours Michelet, 92800 PUTEAUX, France.

do solemnly and sincerely declare as follows:

- I(a) I am the applicant for the patent of addition for
or (b) I am authorized by

ATOCHEM, 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) MICHEL GLOTIN: ROLAND PARSY and PATRICK ABADIE, of: Domaine de Maubuisson, 27470 SERQUIGNY, France: Residence Helene BOUCHER - R 19, 25 rue Helene BOUCHER, 76600 LE HAVRE, France and 38, les Logis, Allee Fernand LEGER, 27300 BERNAY, France respectively.

are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follows:

"The applicant would, if a patent were granted upon an application made by the inventors, 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. 88.03877 on the 24th March, 1988 by ATOCHEM

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

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

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

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

Declared a day of

Michel ROCHE.
1. Graft copolymer of the formula:
   \[ A_{aM_b} X_{cP_d} \]
   in which:
   \( A_{aM_b} \) represents the (co)polymer backbone, and
   \( X_{cP_d} \) represents polymer grafted onto the (co)polymer backbone, and in which
   \( A \) is a unit derived from an \( \alpha \)-mono-olefin of 2 to 8 carbon atoms,
   \( M \) is a unit derived from either an \( \alpha \)-mono-olefin of 2 to 8 carbon atoms, or
two or more said \( \alpha \)-mono-olefins which have been randomly or block-copolymerized, or
a monomer which can be polymerized with a said \( \alpha \)-mono-olefin,
with the units \( A \) and \( M \) which form the said (co)polymer backbone being formed by random copolymerization or block copolymerization,
X is a unit derived from a monomer which can be grafted onto an ω-mono-olefin homo- or copolymer and contains a group which is capable of reacting with an amino-group,

P is derived from a polyamide oligomer of formula:

\[
H_2N-\left(\text{CH}_2\right)_f\text{C}^{\text{O}}-\text{NH}\left(\text{CH}_2\right)_g\text{C}^{\text{O}}-\text{R}_5,N\text{R}_6
\]

in which
- each \( f \) is a number from 3 to 11,
- \( g \) is a number from 5 to 80,
- \( R_5 \) is hydrogen or a linear or branched alkyl group containing up to 20 carbon atoms,
- \( R_6 \) is a linear or branched alkyl or alkenyl group containing up to 20 carbon atoms, a cycloaliphatic group, which may or may not be saturated, an aromatic group or a combination of the abovementioned.
- \( a \) is from 0 to 5,000,
- the sum \( a + b \) is from 350 to 45,000,
- \( c \) is a number such that the ratio by weight of the monomer X grafted onto the (co)polymer backbone to the copolymer grafted with X is from 500 ppm to 10%,
- and \( d \) is greater than zero and less than or equal to \( c \).

10. A mixture of two or more graft (co)polymers as claimed in any one of claims 1 to 9.
18. An alloy (as hereinbefore defined) of at least two incompatible thermoplastic polymers and a compound described in any one of claims 1 to 10.

19. An alloy according to claim 18, which comprises the graft copolymer according to any one of claims 1 to 10 and one of the following pairs of thermoplastic polymers: aliphatic (co)polyamide - (co)polymer or propylene and/or ethylene, semiaromatic (co)polyamide - (co)polymer of propylene and/or ethylene, block polyether amide - (co)polymer of propylene and/or ethylene, vinylphenolic polymer - (co)polymer of propylene and/or ethylene, hydrolysed (ethylene-vinyl acetate) copolymer - (co)polymer of propylene and/or ethylene.
FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

Class Int Class

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

Name and Address
of Applicant:
Atochem
La Defense 10, 4 & 8
Cours Michelet
92800 Puteaux
FRANCE

Address for Service:
Spruson & Ferguson, Patent Attorneys
Level 33 St Martins Tower, 31 Market Street
Sydney, New South Wales, 2000, Australia

Complete Specification for the invention entitled:

Newα-Mono-olefin Based Graft Copolymer

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

OX-MONO-OLEFIN BASED GRAFT COPOLYMER

The invention relates to a graft copolymer comprising at least one monoamino-substituted polyamide oligomer and an OX-mono-olefin polymer or copolymer grafted with a monomer which can react with the amine functional group of the oligomer. It is produced by free-radical grafting of the monomer and then by addition of the oligomer. The invention also relates to the use of this graft copolymer as a compatibility agent for at least two mutually incompatible thermoplastic polymers for the production of alloys.
The present invention relates to an α-mono-olefin based graft copolymer, a process for its production and its use as an agent enabling at least two incompatible thermoplastic polymers to be made compatible.

It is known how to make two incompatible polymers compatible, in certain specific mixtures, by combining them with a third polymer, which is partially compatible with both of the polymers.

Thus, for example, various third polymers have been proposed for a polypropylene/polyamide mixture:

In Japanese Patent No. 70-030943, a composition comprising polypropylene, polyamide and polypropylene grafted with maleic anhydride is disclosed.

In Japanese Patent No. 59-149940 a composition containing polypropylene, polyamide and an ethylene-propylene copolymer grafted with maleic anhydride is disclosed.

In French Patent No. FR 2,107,538, a composition made from polypropylene and glass fibre-reinforced polyamide, which was rendered compatible by adding a copolymer of
propylene and α-olefin grafted by polyamide chains is disclosed. This graft copolymer is obtained by polycondensation of an amino-acid in the presence of a propylene copolymer previously grafted with maleic anhydride.

In Japanese Patent No. 60-233131, the production of a graft copolymer, making a mixture of polypropylene and polyvinyl chloride compatible is disclosed. This graft copolymer is obtained by reacting a polypropylene modified with 2 to 20% by weight of maleic anhydride with a polymethyl methacrylate having a terminal hydroxyl group.

The present invention relates to novel graft copolymers comprising at least one monoamino-substituted polyamide oligomer and an α-mono-olefin polymer (or copolymer) grafted with a monomer which can react with an amine functional group of the monoamino-substituted polyamide oligomer.

The invention also relates to the process for the production of this graft polymer. It can be produced by free-radical grafting onto a polymer chain containing units derived from α-mono-olefin, of a monomer which can react with an amine functional group, and then by additional of the monoamino-substituted polyamide oligomer onto the graft copolymer.
The invention additionally relates to the use of this graft copolymer with at least two mutually incompatible thermoplastic polymers of which at least one is compatible with the polyamide oligomer and at least one is compatible with the α-mono-olefin polymer or copolymer.

The copolymer according to the invention comprises a graft copolymer represented by the expression $A_a M_b X_c P_d$ in which:

- $A_a M_b$ corresponds to the (co)polymer backbone,
- $X_c P_d$ corresponds to the polymers grafted onto the (co)polymer backbone,
- $A$ is a unit derived from an α-mono-olefin containing from 2 to 8 carbon atoms, and is preferably a unit derived from propylene,
- $M$ is selected from the group comprising:
  - units derived from an α-mono-olefin containing from 2 to 8 carbon atoms, and preferably derived from ethylene,
  - units derived from several α-mono-olefins as previously defined, which may be merely mixed together or may be randomly copolymerized or block-copolymerized, and one of these α-mono-olefins is preferably ethylene,
  - units derived from a monomer which can be polymerized with one of the α-mono-olefins as previously defined, for example an alkyl acrylate,
the units A and M which form the said (co)polymer backbone are randomly copolymerized or block-copolymerized or are simply mixtures,

X is a unit derived from a monomer which can be grafted by a free-radical mechanism onto an \( \alpha \)-mono-olefin homo- or copolymer and containing a functional group which can react with an amino-substituted unit,

P is derived from a polyamide oligomer of the formula:

\[
\begin{align*}
\text{R}_2\text{N} & - \left(\text{CH}_2\right)_f \text{C} \left[ \begin{array}{c}
\text{NH} \\
\left(\text{CH}_2\right)_g \text{C}
\end{array} \right] \text{N} \\
\text{R}^5 & \text{N}
\end{align*}
\]

in which

\( f \) is a number from 3 to 11,

\( g \) is a number from 5 to 80 and preferably from 15 to 55,

\( R_5 \) is hydrogen or a linear or branched alkyl group containing up to 20 carbon atoms,

\( R_6 \) is a linear or branched alkyl or alkenyl group containing up to 20 carbon atoms, a cycloaliphatic radical, which may or may not be saturated, an aromatic radical or a combination of the abovementioned,

\( a, b, c \) and \( d \) are numbers which correspond to the following definitions:

\( a \) is from 0 to 5,000 and preferably from 350 to 2,000.
The sum \( a + b \) is from 350 to 45,000 and preferably from 500 to 10,000.

\( c \) is selected in such a way that the ratio by weight of the monomer \( X \) grafted onto the (co)polymer backbone to the copolymer grafted with \( X \) is from 500 ppm to 10%, preferably less than 2%, and most preferably from 5,000 ppm to 1.5%.

\( d \) is above zero and less than or equal to \( c \), and preferably at least equal to 0.3 \( c \).

A (Co)polymer backbone of the formula:

\[
A_a M_b
\]

in which \( a \), \( b \), \( A \) and \( M \) are as previously defined, means any polymer composed of \( A \) and \( M \) units derived from monomers which have been randomly polymerized or block-polymerized, or as the case may be any mixture of polymers obtained by separate polymerizations of monomers from which the \( A \) and \( M \) units are derived.

This copolymerization or this mixing may be carried out in accordance with known processes.

For example, propylene and an \( \alpha \)-olefin may be copolymerized in the presence of a Ziegler catalyst or a coordination catalyst.

The graft copolymer according to the invention can be obtained by free-radical grafting onto the (co)polymer backbone of a monomer which can react with an amine functional group and then by addition of the oligomer onto the previously grafted (co)polymer.
The monomer X which can be grafted by a free-radical mechanism onto the (co)polymer backbone and which has a functional group which can react with an amine functional group typically corresponds to one of the following formulae:

\[
\begin{align*}
R_1 & - C \equiv C - R_2 \\
R_3 & - C = C - R_4
\end{align*}
\]

in which:
- \(R_1\) and \(R_2\) are either hydrogen, or a linear or branched alkyl chain containing up to 8 carbon atoms, with at least one of these symbols representing hydrogen,
- \(R_3\) is hydrogen or a linear or branched alkyl group containing 1 to 10 carbon atoms,
- \(R_4\) is a linear or branched alkenyl group containing 2 to 12 carbon atoms.

The preferred monomers X are citraconic anhydride, fumaric acid, mesaconic acid, the anhydride of 3-allylsuccinic acid and, most preferably maleic anhydride.

The grafting of the monomer X onto the (co)polymer backbone carried out by a free-radical mechanism, takes place in the presence of a free-radical initiator which may be dicumyl peroxide, benzoyl peroxide or 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane.
Normally the initiator is used in a proportion of 2.5 \times 10^{-4} to 4 \times 10^{-2} in relation to the weight of the (co)polymer.

The free-radical grafting of the monomer X onto the (co)polymer backbone may be carried out in the molten state or in solution in a solvent for the (co)polymer backbone. Examples of solvents of this type include toluene, xylene and chlorobenzene.

The solution grafting technique is particularly recommended when a degree of grafting greater than 1.5\% is desired. (Ratio by weight of the grafted monomer X to the (co)polymer backbone grafted with X).

The (co)polymer backbone, the monomer X and the free-radical polymerization initiator are mixed with solvent for the (co)polymer. The mixture is brought to a temperature such that thermal decomposition of the free-radical initiator takes place so that the grafting reaction occurs. Generally, the duration of this reaction is from 0.5 to 10 times, and preferably from 1 to 4 times, the duration of the half-life of the free-radical initiator at the reaction temperature.

Generally the temperature of thermal decomposition of the free-radical initiator is from 90 to 200\degree C, and preferably from 110 to 140\degree C.

The technique of free-radical grafting of the monomer X onto the (co)polymer backbone in the molten state is particularly useful when a degree of
grafting of from 500 ppm to 1.5% is required.

Free-radical grafting in the molten state consists in mixing the (co)polymer backbone with the required quantities of monomer X and free-radical initiator, for example in an extruder. The mixture is brought to a temperature which is generally from 170 to 250°C, and preferably from 180 to 200°C.

The average residence time of the molten material in the extruder is normally selected from 15 seconds to 3 minutes, and preferably from 40 to 80 seconds.

The degree of grafting of the monomer X onto the (co)polymer backbone can be measured by analysis of the anhydride functional groups by infrared spectrophotometry.

The monoamino-substituted polyamide oligomer, P, of formula:

\[
\begin{array}{c}
\text{H}_2\text{N}-(\text{CH}_2)_f-\text{C}-\text{NH}-(\text{CH}_2)_g-\text{C}^\text{O} \quad \text{R}_5 \\
\end{array}
\]

in which \( f, \ g, \ R_5, \) and \( R_6 \) are as previously defined, is subsequently added to the graft (co)polymer.

This monoamino-substituted polyamide oligomer can be obtained by polycondensation of an amino acid of the formula:

\[
\begin{array}{c}
\text{H}_2\text{N}-(\text{CH}_2)_f-\text{C}^\text{O} \quad \text{OH} \\
\end{array}
\]
or by polyaddition of a lactam of formula:

\[
\left(\text{CH}_2\right)_f\quad N-C\quad H O
\]

in which \( f \) has the meaning previously given,
in the presence of a monofunctional polymerization regulator of the formula:

\[
R_5\quad \text{NH}\quad R_6
\]

in which \( R_5 \) and \( R_6 \) have the meaning previously given.

The amino acid or lactam monomers preferred for the synthesis of the monoamino-substituted oligomer of the invention are caprolactum, 11-aminoundecanoic acid and dodecalactam.

The preferred monofunctional polymerization regulators are laurylamine and oleylamine.

The polycondensation defined above can be carried out in accordance with conventionally known processes, for example at a temperature generally of from 200 to 300°C, under vacuum or in an inert atmosphere, with stirring of the reaction mixture.

The average chain length of the oligomer is determined by the initial molar ratio between the polycondensable monomer or the lactam and the monofunctional polymerization regulator.
To calculate the average chain length, one molecule of chain regulator is normally counted for each oligomer chain.

The addition of the monoamino-substituted polyamine oligomer onto the (co)polymer backbone grafted with a monomer $X$ is carried out by reacting an amine functional group of the oligomer with at least one anhydride or acid functional group of the graft (co)polymer. Amide or imide linkages are thus created.

The addition of the oligomer $P$ onto the graft (co)polymer backbone is preferably carried out in the molten state. Thus, it is possible to knead the oligomer and the (co)polymer at a temperature generally of from 230 to 250°C in an extruder. The average residence time of the molten material in the extruder may be from 15 seconds to 5 minutes, and preferably from 1 to 3 minutes.

The addition of the oligomer onto the graft (co)polymer backbone is evaluated by selective extraction of the free polyamide oligomers, that is to say those which have not reacted to form the final graft copolymer.

The α-mono-olefin graft copolymers according to the invention have the following advantages over the third polymers referred to in the prior art.

- It is possible to control the degree of grafting of the polyamide oligomer onto the graft (co)polymer and thus to have more complete control of the structure
of the graft copolymer.

- It is possible to adjust and control the average molecular mass of the monoamino-substituted polyamide oligomer. Indeed, the average molecular mass of the polyamide oligomer is a determining factor for the action and the effectiveness of the graft copolymer according to the invention as a compatibility agent for alloys of incompatible polymers.

- The graft copolymers according to the invention do not have any chain ends which are reactive in the context of polycondensation, and during the kneading of the components of the alloy with the graft copolymer according to the invention, the said chain ends will not react in an uncontrolled manner.

The graft copolymer according to the invention particularly enables at least two mutually incompatible thermoplastic polymers, one of which, however, is compatible with the polyamide oligomer component of the said copolymer and the other of which is compatible with the (co)polymer backbone, to be combined homogeneously.

The graft copolymer may be incorporated in the usual manner into a mixture of thermoplastic resins, in the molten state, in a kneading device. The quantity of copolymer introduced is typically from 0.1 to 30% and preferably from 5 to 15% by weight in relation to the weight of the mixture of thermoplastic resins.
Examples of polymers or thermoplastic resins which are compatible with the polyamide oligomers forming part of the composition of the graft copolymer, include:

- aliphatic polyamides such as polyamides 6, 11 or 12,
- semiaromatic polyamides, for example those defined in French Patents FR 1,588,130, 2,324,672 and 2,575,756, in European Patent EP 53,876, and in Japanese Patents 60,217,237 and 59,015,447.
- block-copolymerized polyetheresteramides or block-copolymerized polyetheramides, for example the products described in US Patents 4,332,920 and 4,331,786.
- hydrolysed ethylene-vinyl acetate copolymers,
- resins comprising phenolic units such as poly-para-vinylphenol.

It is to be understood that the term "polymers" also includes copolymers to the extent that the content of compatible units of the copolymer is adequate to maintain compatibility.

It is also appropriate to use the term "polymers" to include the mixture of polymers, or copolymers, with various additives, for example impact modifiers, inorganic fillers, glass fibres, and pigments.

Examples of thermoplastic polymers which are compatible with the (co)polymer backbone, include polypropylene, polylethylene or
ethylene-propylene copolymers.

By virtue of the compatibility agent according to the invention, it is possible to produce improved alloys such as:

- Polyamide 6 - polypropylene
- Polyamide 6 - polyethylene
- Polyamide 6 - ethylene/propylene copolymer
- Polyamide 11 or 12 - polypropylene or polyethylene or ethylene/propylene copolymer
- Hydrolysed ethylene-vinyl acetate copolymer - polypropylene or polyethylene or ethylene/propylene copolymer
- Polypara-vinylphenol - polypropylene or polyethylene or ethylene/propylene copolymer
- Block polyetheramide - polypropylene or polyethylene or ethylene/propylene copolymer
- Semiaromatic polyamide - polypropylene or polyethylene or ethylene/propylene copolymer

The compatibility caused by the graft copolymer according to the invention is demonstrated by electron microscopy and by the mechanical properties of the product resulting from the mixture of the incompatible thermo-
plastic polymers.

The morphology of a mixture of thermoplastic polymers without the graft copolymer according to the invention, examined by electron microscopy, is generally seen in the form of large nodules of one polymer surrounded by the matrix formed by the other polymer, the adhesion between the nodules and the matrix being substantially non-existent. The addition of the graft copolymer causes a significant diminution in the size of the nodules. A strong adhesion between the visible phases is also observed as the nodules being coated by the matrix. Under these conditions, there is formed what may be called an alloy, by analogy with metallurgical structures, as distinct from simple mixtures.

The mechanical properties of thermoplastic alloys of this kind are at least equal to those of the components, weighted by the volume fraction of each component, and in certain cases greater than those of the two components, for example in impact strength.

In contrast with these alloys according to the invention, simple mixtures of the same mutually incompatible polymers, without the effect of the graft copolymer according to the invention, have mechanical properties which are generally close to those of the component having the lowest performance.

The following examples further illustrate the invention.
EXAMPLE 1:

A. - Synthesis of the graft copolymer backbone X

Into a WERNER extruder, a mixture is continuously
introduced which comprises by weight 100 parts of propyl-
ene-ethylene block copolymer (containing 12% by weight of
ethylene, of melt index = 5, of melting point = 163°C),
1.6 parts of maleic anhydride and 1.7 parts of 2,5-
dimethyl-2,5-di(tert-butylperoxy)hexane dissolved in one
part of chlorobenzene.

The mixture is brought to 200°C and the rotational
speed of the screw is 100 revolutions/minute.

Devolatilization of the mixture is then carried
out before the die entry in order to remove chlorobenzene
and the maleic anhydride which has not reacted.

At the die exit, a sample of the graft polymer is
taken, which is dissolved in xylene and then precipitated
in acetone in order to be purified.

By analysis of the anhydride functions by infra-
red spectrophotometry, 1.16% by weight of grafted an-
hydride is determined.

By gel permeation chromatography, it is deter-
mined that the number-average molecular mass is equal to
32,000.

B - Synthesis of the polyamide oligomer (P)

Into a 100-litre stainless steel reactor, are
introduced 31 kg of caprolactam, 0.91 kg of laurylamine
and 3.5 litres of water.
Having purged the reactor with nitrogen, it is heated in the closed state for 2 hours at 250°C, while stirring at 35 revolutions/minute. The pressure of the atmosphere in the reactor is subsequently reduced over 1 hour.

After the reactor has been swept with nitrogen for 15 minutes, the oligomer is poured into water, centrifuged, washed with water at 80°C then dried for 16 hours in a vacuum oven at 80°C.

In this way, a polyamide oligomer is obtained whose number average molecular mass is 5,700, determined by potentiometric analysis of the terminal amine functional groups.

C - Preparation of the graft copolymer

A mixture comprising by weight 59.8 parts of the graft copolymer backbone described under A and 40.2 parts of the oligomer described under B in a WERNER ZSK30 extruder, is kneaded in the molten state.

The mixture is brought to 240°C.

The average residence time of the mixture in the extruder is about 3 minutes.

At the outlet from the extruder, a sample of material is taken which is introduced to an extractor of the KUMAGAWA type.

In this way the polyamide oligomers which have not reacted with the anhydride functional groups of the maleinated copolymer are selectively extracted with
formic acid. By this method, a degree of condensation of the polyamide oligomer onto the graft (co)polymer of 65% is determined.

The graft copolymer obtained in this way can be represented by the expression:

$$A_{663}M_{138}X_{3.78}P_{2.45}$$

in which
- A is a unit derived from propylene
- M is a unit derived from ethylene
- X is a unit derived from maleic anhydride
- P is an oligomer of caprolactam for which $$\overline{Mn} = 5700$$

EXAMPLE 2:

Into a WERNER extruder is continuously introduced a mixture comprising by weight 33 parts of polypropylene, 57 parts of polyamide 6 and 10 parts of the maleinated copolymer backbone described in Example 1.A (SAMPLE 1).

The material temperature along the barrel is between 255 and 270°C. The rotational speed of the screw is 150 revolutions/minute and the output of material is 20 kg/hour.

Under the same conditions a mixture is extruded containing by weight 33 parts of polypropylene, 57 parts of polyamide 6 and 10 parts of the graft copolymer described in Example 1.C (SAMPLE 2).

Also under the same conditions, a reference mixture is produced containing (by weight) 36.7 parts of polypropylene and 63.3 parts of polyamide 6 (SAMPLE 3).
In the case of the SAMPLES 1, 2 and 3, the polypropylene used is a propylene homopolymer having a melt index = 3 and a melting point = 166°C, and the polyamide 6 used is a homopolymer of caprolactam having a melting point = 218°C.

Samples 1, 2 and 3 are injection-moulded in the form of plaques of dimensions 100 X 100 X 3 mm from which are cut the half size ISO test pieces conforming to the standard NFT 51034.

Some test pieces are cut in the direction of injection flow (TEST PIECES A); others are cut perpendicularly to the direction of injection flow (TEST PIECES B).

Some test pieces are also moulded from the samples in accordance with the standard defined by the Institut Français du Caoutchouc (TEST PIECES C).

The test pieces A, B and C are evaluated by tensile elongation in accordance with the standard NFT 51034.

The test pieces from SAMPLE 3 (reference) are extremely brittle: they break at 5 to 6% elongation; this indicates a coarse and inhomogeneous morphology as well as a lack of adhesion between the two components of REFERENCE SAMPLE 3.

The test pieces A, B and C from SAMPLE 1 behave differently: the test pieces A and B have a more brittle behaviour than test piece C; this corresponds to an
inhomogeneity of the sample as well as a susceptibility to orientation.

In the case of the three types of test pieces from SAMPLE 2, a homogeneous ductile behaviour is observed: this indicates a good homogeneity in SAMPLE 2 as well as a low susceptibility to transformation and orientation.

SAMPLES 1 and 2 are also tested for CHARPY impact strength at ambient temperature, after having been injection-moulded into test pieces.

In the case of SAMPLE 1, a breakage rate of 60% is observed.

In the case of SAMPLE 2, none of the test pieces broke under test.

EXAMPLE 3:

A. Into a WERNER ZSK30 extruder, a mixture is continuously introduced containing by weight 100 parts of an ethylene-propylene block copolymer (containing 12% by weight of ethylene, having a melt index = 5, and a melting point = 163°C), 1.5 parts of maleic anhydride and 1.7 parts of 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane dissolved in one part of chlorobenzene.

The extrusion conditions and purification conditions are identical with those described in Example 1.A.

The analysis of the anhydride functional groups by infrared spectrophotometry of a sample of graft copolymer shows that 1.02% by weight of anhydride has
been grafted.

The number-average molecular mass $M_n$ determined by gel permeation chromatography is 19,700.

B. A monoamino-substituted polyamide oligomer is produced under the same conditions as those described in Example 1.B with a ratio by weight of caprolactam to laurylamine equal to 15.7. The number-average molecular mass $M_n$ of the oligomer is 2,800.

C. In a WERNER ZSK30 extruder, there is kneaded in the molten state, under the same conditions as those described in Example 1.C, a mixture comprising by weight 77 parts of the graft copolymer described above and 23 parts of the polyamide oligomer such as previously described.

After the extrusion, the degree of condensation of the oligomer onto the graft copolymer backbone is measured under the same conditions as those described in Example 1.C, this being 65.8%.

The graft copolymer obtained in this way can be represented by the expression:

$$A_{109}M_{64}X_{2.03}P_{1.33}$$

in which $A$ represents a unit derived from propylene
$M$ represents a unit derived from ethylene
$X$ represents a unit derived from maleic anhydride and
$P$ represents a unit derived from an oligomer of caprolactam having $M_n = 2,800$. 
EXAMPLE 4:

A mixture comprising by weight 50 parts of polypropylene and 50 parts of hydrolysed ethylene-vinyl acetate copolymer (EVOH) is brought to 220°C and kneaded in the chamber of a BRABENDER plastograph for 30 minutes with a mixing speed of 50 revolutions/minute (SAMPLE 4).

A mixture comprising by weight 49 parts of polypropylene, 49 parts of EVOH and 2 parts of the maleinated ethylene-propylene copolymer backbone described in Example 3.A, is kneaded under the same conditions as above (SAMPLE 5).

A mixture is also produced under the same conditions, containing by weight 49 parts of polypropylene, 49 parts of EVOH and 2 parts of the graft copolymer described in Example 3.C (SAMPLE 6).

In the case of SAMPLES 4, 5 and 6, the polypropylene used has a melt index equal to 5 and a melting point equal to 166°C and the EVOH used is such that its ethylene content is 38% (by moles).

SAMPLES 4, 5 and 6 are subsequently examined by scanning electron microscopy (magnification: 2,500 X).

Examination of SAMPLE 4 shows that the two polymers have very little compatibility: very disparate nodules of EVOH are distinguished, the diameter of which varies from 11 to 27 µm in the polypropylene matrix; moreover it is observed that the adhesion between these nodules of EVOH and the polypropylene matrix is very
Examination of SAMPLE 5 shows a morphology which is quite coarse; nodules of EVOH are distinguished having a diameter between 5.7 and 7 μm, whose adhesion to the polypropylene matrix is poor.

Examination of SAMPLE 6 shows a fine morphology typified by nodules having a diameter of between 1.7 and 2.8 μm and whose adhesion to the polypropylene matrix is very good.

**EXAMPLE 5**

A mixture comprising by weight 50 parts of polypropylene and 50 parts of polypara-vinylphenol (PPVP) is brought to 200°C and kneaded in the chamber of a BRABENDER plastograph for 15 minutes with a mixing speed of 50 revolutions/minute (SAMPLE 7).

A mixture comprising by weight 49 parts of propylene, 49 parts of polypara-vinylphenol and 2 parts of the maleinated ethylene-propylene copolymer described in Example 3.A, is kneaded under the same conditions as above (SAMPLE 8).

A mixture is also prepared under the same conditions comprising by weight 49 parts of polypropylene, 49 parts of polypara-vinylphenol and 2 parts of the graft copolymer described in example 3.C (SAMPLE 9).

In the case of SAMPLES 7, 8 and 9, the polypropylene used has a melt index equal to 5 and a melting point equal to 166°C and the polypara-vinylphenol is an oligomer.
whose weight-average molecular mass is 4,000 and whose melting point ranges between 160 and 200°C.

SAMPLES 7, 8 and 9 are subsequently examined by scanning electron microscopy (magnification: 2,500 X).

Examination of SAMPLE 7 shows a coarse morphology in which localized cocontinuous phases are found or ovoid nodules of PPVP having an average diameter equal to 30 μm, dispersed in a matrix of PP. The total incompatibility of the two polymers is shown by observing fracture surfaces.

Examination of SAMPLE 8 shows an improved dispersion of the polypara-vinylphenol (PPVP) in the polypropylene. The average size of the nodules of PPVP dispersed in the PP matrix is about 10 μm. The adhesion between the phases is unimproved in relation to SAMPLE 7.

Examination of SAMPLE 9 shows a fine morphology, typified by nodules of PPVP having an average diameter equal to 2 μm, dispersed in the matrix of PP and whose adhesion to this matrix is greatly improved in relation to that of SAMPLES 7 and 8.

EXAMPLE 6

A mixture comprising by weight 50 parts of polypropylene and 50 parts of polyetheresteramide is brought to 200°C and kneaded in the chamber of a BRABENDER plastograph for 15 minutes with a stirring speed of 50 revolutions/minute (SAMPLE 10).
A mixture comprising by weight 49 parts of propylene, 49 parts of polyetheresteramide and 2 parts of the maleinated ethylene-propylene copolymer described in Example 3.A, is kneaded under the same conditions as above (SAMPLE 11).

A mixture is also produced under the same conditions comprising by weight 49 parts of polypropylene, 49 parts of polyetheresteramide and 2 parts of the graft copolymer described in example 3.C (SAMPLE 12).

In the case of SAMPLES 10, 11 and 12, the polypropylene used has a melt index equal to 5 and a melting point equal to 166°C and the polyetheresteramide is obtained by copolycondensation of α,ω-dicarboxyl-substituted polyamide 12 blocks having $\bar{M}_n = 600$, and α,ω-dihydroxyl-substituted polytetramethylene glycol blocks having $\bar{M}_n = 2,000$.

SAMPLES 10, 11 and 12 are subsequently examined by scanning electron microscopy (magnification: 2,500 X). Examination of SAMPLE 10 shows a particularly coarse morphology typified by a three-dimensional network.

Examination of SAMPLE 11 does not show any improvement in adhesion, nor any reduction in the size of the three-dimensional network in relation to the examination of SAMPLE 10.

When SAMPLE 12 is examined, a less coarse morphology is observed than that of SAMPLES 10 and 11. The
morphology of SAMPLE 12 is no longer typified by a three-dimensional network but by the dispersion of nodules of polyetheresteramide in a matrix of polypropylene.

**EXAMPLE 7**

A mixture comprising by weight 50 parts of polypropylene and 50 parts of amorphous semiaromatic polyamide is brought to 220°C and kneaded in the chamber of a BRABENDER plastograph for 30 minutes at a mixing speed of 50 revolutions/minute (SAMPLE 13).

A mixture comprising by weight 49 parts of polypropylene, 49 parts of amorphous semiaromatic polyamide and 2 parts of the maleinated ethylene-propylene copolymer described in Example 3.A, is kneaded under the same conditions as above (SAMPLE 14).

A mixture is also produced under the same conditions containing by weight 49 parts of polypropylene, 49 parts of amorphous semiaromatic polyamide and 2 parts of the graft copolymer described in Example 3.C (SAMPLE 15).

In the case of SAMPLES 13, 14 and 15 the polypropylene used has a melt index equal to 5 and a melting point equal to 166°C and the amorphous semiaromatic polyamide used is based on terephthalic acid and 2,2,4-trimethyl-1,6-diaminohexane and 2,4,4-trimethyl-1,6-diaminohexane.

SAMPLES 13, 14 and 15 are subsequently examined by scanning electron microscopy (magnification: X 2,500).
Examination of SAMPLE 133 shows an incompatibility between the 2 polymers: nodules of amorphous semiaromatic polyamide are distinguished whose average diameter is 30 µm, dispersed in the matrix of polypropylene. Moreover, adhesion between the nodules of amorphous semiaromatic polyamide and the matrix of PP is non-existent.

SAMPLE 14 has quite a coarse morphology; nodules of amorphous semiaromatic polyamide having an average diameter equal to 5 µm, are dispersed in the matrix of polypropylene; there is moderate adhesion of the nodules to the matrix.

Examination of SAMPLE 15 shows a quite fine morphology characterized by nodules of amorphous semiaromatic polyamide having an average diameter equal to 3.3 µm and whose adhesion to the matrix of PP is good.

EXAMPLE 8

A mixture comprising by weight 50 parts of polypropylene and 50 parts of amorphous semiaromatic polyamide is brought to 280°C and kneaded in the chamber of a HAAKE plastograph for 20 minutes with a mixing speed of 50 revolutions/minute (SAMPLE 16).

A mixture comprising by weight 49 parts of polypropylene, 49 parts of amorphous semiaromatic polyamide and 2 parts of the maleinated ethylene-propylene copolymer described in example 3.A, is kneaded under the same conditions as above (SAMPLE 17).
A mixture is also produced under the same conditions containing by weight 49 parts of polypropylene, 49 parts of amorphous semiaromatic polyamide and 2 parts of the graft copolymer described in example 3.C (SAMPLE 18).

In the case of SAMPLES 16, 17 and 18 the polypropylene used has a melt index equal to 5 and a melting point equal to 166°C; the amorphous semiaromatic polyamide used is based on isophthalic acid, 4,4’-diamino-3,3’-dimethylidicyclohexylmethane and lauryllactam.

SAMPLES 16, 17 and 18 are subsequently examined by scanning electron microscopy (magnification: X 2,500).

Examination of SAMPLE 16 shows an incompatibility between the 2 polymers: nodules of amorphous semiaromatic polyamide are distinguished whose average diameter is 20 μm dispersed in the matrix of polypropylene. Moreover, adhesion between the nodules of amorphous semiaromatic polyamide and the matrix of PP is nonexistant.

Examination of SAMPLE 17 shows a quite coarse morphology: nodules of amorphous semiaromatic polyamide having an average diameter equal to 10 μm are dispersed in the matrix of polypropylene; there is moderate adhesion of the nodules to the matrix.

Examination of SAMPLE 18 shows a quite fine morphology characterized by nodules of amorphous semiaromatic polyamide having an average diameter equal to 3.5 μm and whose adhesion to the matrix of polypropylene is good.
EXAMPLE 9:

Into a WERNER extruder, a mixture is continuously introduced comprising by weight 26 parts of polypropylene, 67 parts of polyamide 6 and 7 parts of the maleinated ethylene-propylene copolymer described in example 3-A (SAMPLE 19).

The temperature of the material along the barrel is between 260°C and 290°C. The rotational speed of the screw is 150 revolutions/minute and the output of material is 20 kg/hour.

A mixture is extruded under the same conditions comprising by weight 26 parts of polypropylene, 67 parts of polyamide 6 and 7 parts of the graft copolymer described in Example 1.C (SAMPLE 20).

A reference mixture is produced, also under the same conditions, containing (by weight) 32.7% of polypropylene and 67.3% of polyamide 6.

In the case of SAMPLES 19, 20 and 21, the polypropylene used is a polypropylene homopolymer having a melt index of 12 and a melting point of 166°C, and the polyamide 6 is a homopolymer of caprolactam having a melting point of 218°C.

Samples 19, 20 and 21 are injection-moulded in the form of test pieces having dimensions 127 X 12.7 X 6.4 mm and their IZOD impact strength is evaluated in accordance with ISO standard at 23°C and at 40°C. The results of this evaluation are presented in the table.
below.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>IZOD IMPACT STRENGTH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>23°C</td>
</tr>
<tr>
<td>19</td>
<td>6</td>
</tr>
<tr>
<td>20</td>
<td>10.5</td>
</tr>
<tr>
<td>21</td>
<td>2</td>
</tr>
</tbody>
</table>
CLAIMS
The claims defining the invention are as follows:

1. Graft copolymer of the formula:

\[ \text{A}_a \text{M}_b \text{X}_c \text{P}_d \]

in which:

- \( \text{A}_a \text{M}_b \) represents the (co)polymer backbone, and
- \( \text{X}_c \text{P}_d \) represents polymer grafted onto the (co)polymer backbone, and in which
  - \( A \) is a unit derived from an \( \alpha \)-mono-olefin of 2 to 8 carbon atoms,
  - \( M \) is a unit derived from either an \( \alpha \)-mono-olefin of 2 to 8 carbon atoms, or two or more said mono-olefins which have been randomly or block-copolymerized, or a monomer which can be polymerized with a said \( \alpha \)-mono-olefin,
  - with the units \( A \) and \( M \) which form the said (co)polymer backbone being formed by random copolymerization or block copolymerization,
  - \( X \) is a unit derived from a monomer which can be grafted onto an \( \alpha \)-mono-olefin homo- or copolymer and contains a group which is capable of reacting with an amino group,
  - \( P \) is derived from a polyamide oligomer of formula:
in which

\[
\begin{align*}
\text{each } f & \text{ is a number from 3 to 11,} \\
g & \text{ is a number from 5 to 80,} \\
R_5 & \text{ is hydrogen or a linear or branched alkyl group containing up to 20 carbon atoms,} \\
R_6 & \text{ is a linear or branched alkyl or alkenyl group containing up to 20 carbon atoms, a cycloaliphatic group, which may or may not be saturated, an aromatic group or a combination of the abovementioned.} \\
a & \text{ is from 0 to 5,000,} \\
\text{the sum } a + b & \text{ is from 350 to 45,000,} \\
c & \text{ is a number such that the ratio by weight of the monomer } X \text{ grafted onto the (co)polymer backbone to the copolymer grafted with } X \text{ is from 500 ppm to 10\%,} \\
\text{and } d & \text{ is greater than zero and less than or equal to } c.
\end{align*}
\]

2. Graft copolymer according to claim 1, in which A is a unit derived from propylene.

3. Graft copolymer according to claims 1 or 2, in which M is a unit derived from ethylene.

4. Graft copolymer according to any one of claims 1 to 3, in which g is a number from 15 to 55.

5. Graft copolymer according to any one of claims 1 to 4, in which a is from 350 to 2000.

6. Graft copolymer according to any one of claims 1 to 5, in which the sum of a + b is from 500 to
10,000.

7. Graft copolymer according to any one of claims 1 to 6, in which c is a number such that the ratio by weight of the monomer X grafted onto the (co)polymer backbone to the copolymer grafted with X is from 5000 ppm to 2%.

8. Graft copolymer according to any one of claims 1 to 7, in which d is equal to at least 0.3c.

9. Graft copolymer according to any one of claims 1 to 8, in which the monomer from which X is derived has the formula:

\[
\begin{align*}
\text{R}_1 & \quad \text{C} \quad \text{C} \quad \text{O} \\
\text{R}_2 & \quad \text{C} \quad \text{C} \quad \text{O} \\
\end{align*}
\]

in which:

- \( \text{R}_1 \) and \( \text{R}_2 \) are independently hydrogen, or a linear or branched alkyl chain containing up to 8 carbon atoms, at least one of these being hydrogen,
- \( \text{R}_3 \) is hydrogen or a linear or branched alkyl group containing up to 10 carbon atoms, and
- \( \text{R}_4 \) is a linear or branched alkenyl group containing up to 12 carbon atoms.

10. A mixture of two or more graft (co)polymers as claimed in any one of claims 1 to 9.
11. Process for producing a graft copolymer as claimed in any one of claims 1 to 10, which comprises:

grafting a monomer which can react with an amine functional group onto a (co)polymer $A_{a}M_{b}$ backbone, and

adding a polyamide oligomer onto the previously grafted copolymer.

12. Process according to claim 11, in which the monomer which reacts with an amine functional group is citraconic anhydride, fumaric acid, mesaconic acid, the anhydride of 3-allyl-succinic acid or maleic anhydride.

13. Process according to claims 11 or 12, in which the polyamide oligomer of formula:

\[
H_{2}N-(CH_{2})_{\varepsilon}-C[\text{NH}(CH_{2})_{\gamma}-C(\text{NH})(CH_{2})_{\gamma}-C]\overset{\gamma}{\underset{\delta}{\text{N}}} R_{5} \quad R_{6}
\]

in which $\varepsilon$, $\gamma$, $R_{5}$ and $R_{6}$ are as defined in claims 1 or 4, is obtained by polycondensation of an amino acid of the formula:

\[
H_{2}N-(CH_{2})_{\varepsilon}-C=O
\]

or by polyaddition of a lactam of formula

\[
(SH_{2})_{\varepsilon}\quad N-C(\overset{\gamma}{\underset{\delta}{\text{N}}})\quad R \quad O
\]
with \( f \) as defined above, in the presence of a monofunctional polymerization regulator of the formula:

\[
\begin{array}{c}
\text{R} \\
\text{R}^6
\end{array}
\]

\[
\text{NH}
\]

in which \( R_5 \) and \( R_6 \) are as defined in claim 1.

14. Process according to claim 13, in which the monomer for the synthesis of the polyamide oligomer is caprolactam, 11-aminoundecanoic acid or dodecalactam.

15. Process according to any one of claims 13 or 14, in which the monofunctional polymerization regulator is either laurylamine or oleylamine.

16. Graft copolymer according to any one of claims 1 to 10 produced by the process of any of claims 11 to 15.

17. Graft copolymer according to claim 1 substantially as described in any of the Examples 1 to 9.

18. An alloy (as hereinbefore defined) of at least two incompatible thermoplastic polymers and a compound described in any one of claims 1 to 10.

19. An alloy according to claim 18, which comprises the graft copolymer according to any one of claims 1 to 10 and one of the following pairs of thermoplastic polymers: aliphatic (co)polyamide - (co)polymer or propylene and/or ethylene, semiaromatic (co)polyamide - (co)polymer of propylene and/or ethylene, block polyether amide - (co)polymer of propylene and/or ethylene, vinylphenolic
polymer - (co)polymer of propylene and/or ethylene,
hydrolysed (ethylene-vinyl acetate) copolymer - (co)polymer
of propylene and/or ethylene.

20. An alloy according to claim 19 selected from
5 pairs:
Polyamide 6 - polypropylene
Polyamide 6 - polyethylene
Polyamide 6 - ethylene/propylene copolymer
Polyamide 11 or 12 - polypropylene or polyethylene
or ethylene/propylene copolymer
Hydrolysed ethylene-vinyl acetate copolymer
- polypropylene or polyethylene
or ethylene/propylene copolymer
Block polyether amide - polypropylene or polyethylene
or ethylene/propylene copolymer
Polyparavinylphenol - polypropylene or polyethylene
or ethylene/propylene copolymer
Semi-aromatic polyamide - polypropylene or polyethylene
or ethylene/propylene copolymer

21. An alloy according to any one of claims 18 to 20 which contains from 0.1 to 30% by weight of the graft copolymer as defined in claims 1 to 10 in relation to the weight of the mixture of thermoplastic resins.

22. An alloy according to claim 21, in which the weight of the graft copolymer is from 5 to 15%.
DATED this TWENTY SECOND day of MARCH 1989

Atochem

Patent Attorneys for the Applicant
SPRUSON & FERGUSON