(12) PATENT ABRIDGMENT **(11)** Document No. **AU-B-25893/88**
(19) AUSTRALIAN PATENT OFFICE **(10)** Acceptance No. **609216**

(54) Title
PROCESS FOR THE PREPARATION OF CARBOXYLATED PROPYLENE POLYMERS

International Patent Classification(s)
(51)[4] C08F 008/34 C08F 008/44 C08L 023/26 C08L 077/02
C08L 077/04

(21) Application No. : 25893/88 (22) Application Date : 24.11.88

(30) Priority Data

(31) Number	(32) Date	(33) Country
8727775	27.11.87	GB UNITED KINGDOM

(43) Publication Date : 01.06.89

(44) Publication Date of Accepted Application : 26.04.91

(71) Applicant(s)
SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.

(72) Inventor(s)
ANNE CATHARINUS UDDING

(74) Attorney or Agent
SPRUSON & FERGUSON, GPO Box 3898, SYDNEY NSW 2001

(56) Prior Art Documents
US 4548993
US 3220985
US 4555566

(57) The invention provides a process for the preparation of carboxylated propylene homo- and copolymers which comprises the reaction of a thermoplastic propylene homo- or copolymer with an azidosulfonylbenzoic acid by mechanically mixing said polymer and said acid at a temperature of at least 180 °C in the ~~substantial~~ absence of a free-radical initiator.

CLAIM

1. A process for the preparation of carboxylated propylene homo- and copolymers which comprises the reaction of a thermoplastic propylene homo- or copolymer with an azidosulfonylbenzoic acid by mechanically mixing said polymer and said acid at a temperature of at least 180 °C in the ~~substantial~~ absence of a free-radical initiator.

609216

S & F Ref: 77396

FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

This document contains the amendments made under Section 49 and is correct for printing

FOR OFFICE USE:

Class Int Class

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

Name and Address of Applicant: Shell Internationale Research Maatschappij B.V.
Carel van Bylandtlaan 30
2596 HR
The Hague
THE NETHERLANDS

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:

Process for the Preparation of Carboxylated Propylene Polymers

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

S003831 24/11/88
5845/3

PROCESS FOR THE PREPARATION OF CARBOXYLATED PROPYLENE POLYMERS

The invention relates to a process for the preparation of carboxylated propylene polymers, to the carboxylated propylene polymers prepared and to their use.

It is known that by carboxylation of polypropylene it is possible to improve e.g. its dyeability and its adhesion to polar surfaces. The method commonly used to prepare such carboxylated polypropylene is grafting maleic anhydride onto commercially available polypropylene. This method however, requires a free-radical generating catalyst such as a peroxide. The presence of such compounds is known to lead to a reduction of the polymer molecular weight.

In EP 0086159 a process for crosslinking polymers and copolymers of alpha-olefins is described, suitable for improving the mechanical resistance characteristics of said polymers under heat. Said process which can be accomplished within a relatively short time, consists of grafting a carboxylic acid onto the polymeric chain through mechanical mixing thereof at a temperature of at least 170 °C, possibly in the presence of a generator of radicals, and the subsequent salification of the free carboxylic groups with metal compounds of a basic character. However, this document does not teach how to avoid severe polymer degradation during carboxylation of the polymer.

It has now been found that the solution to the problem for providing carboxylated polymers in a fast reaction without undesirable reduction of molecular weight can be found in a proper selection of the carboxylic acid used for carboxylation of the polymer, in combination with proper process conditions.

The invention provides a process for the preparation of carboxylated propylene homo- and copolymers which comprises the reaction of a thermoplastic propylene homo- or copolymer with an azidosulfonylbenzoic acid by mechanically mixing said polymer and said acid at a temperature of at least 180 °C in the ~~substantial~~ absence of a free-radical initiator.

The azidosulfonylbenzoic acids which may be used in the process of the present invention include 3-azidosulfonylbenzoic acid, 4-azidosulfonyl-phthalic acid and 4-azidosulfonyl-phenoxyacetic acid as well as such acids having further substituents attached to the aromatic nucleus such as 2-chloro-5-azidosulfonylbenzoic acid, 4-neopentyl-5-azidosulfonylbenzoic acid, 4-ethyl-5-azidosulfonylbenzoic acid and 2-hydroxy-5-azidosulfonylbenzoic acid. 3-Azidosulfonylbenzoic acid is a preferred azidosulfonylbenzoic acid.

The preferred thermoplastic propylene homo- and copolymers which may be employed in the process of the present invention are essentially saturated polymers. Most preferred are crystalline propylene homopolymers. The propylene copolymers are preferably block copolymers of propylene with ethylene.

The mechanical mixing at a temperature of at least 180 °C required for the process of the present invention, can conveniently be achieved by conducting the reaction of the propylene homo- or copolymer and the mono- or dicarboxylic acid as hereinbefore described in, for example an internal mixer (batch process) or an extruder (continuous process).

In order to obtain a carboxylated propylene polymer wherein the carboxyl groups are distributed homogeneously along the polymers chains, it is preferred to blend the polymer and the carboxylic acid as hereinbefore described at a temperature which is high enough for the polymer to melt and low enough to avoid a significant degree of reaction between the carboxylic acids and the polymer, i.e. a temperature below 180 °C, preferably at a temperature in the range from 160 - 170 °C. Subsequently the temperature of the blend may be raised to >180 °C and preferably to a value in the range of from 200 - 220 °C for the reaction between polymer and carboxylic acid.

In view of the preferred and specific temperature requirements of the blending step and the subsequent reaction stage in combination with the time constraints it is preferred to conduct the process of the present invention in an extruder type of reactor. Such an apparatus is generally equipped to have a controlled temperature profile along its barrel, i.e. the barrel is divided into zones wherein the temperature can be regulated independently. When employing an extruder type of reactor in the process of the present invention it would in principle be sufficient to have next to a feeding zone a blending zone wherein the temperature is <180 °C, followed by a reaction zone wherein the temperature is preferably in the range of from 200 - 220 °C. It will be understood by those skilled in the art that the number of temperature zones can be extended to accommodate the process requirements such as with a devolatilizing step or a step wherein further components are added to the reaction mixture.

The amount of mono- or dicarboxylic acid having a monosulfonylazide-substituted aromatic nucleus which may be employed in the process of the present invention is preferably at least 0.05 % m, calculated on the weight of polymer to be carboxylated. Optimum results are obtained when the amount of acid is in the range of from 0.1 to 6 % m on polymer. The polymer and the acid may conveniently be fed into the reactor as a preblended powder.

The time required for the process of the present invention will be determined by the amount of acid to be reacted, the temperature at which the carboxylation is to be conducted as well as by the equipment used. Preferred are reaction periods of up to 30 minutes, for example 10 to 15 minutes.

Although the carboxylated propylene polymers made according to the process of the present invention will show considerably less reduction in molecular weight, when compared to such polymers prepared in the presence of a radical generator, a slight degree of reduction in molecular weight will generally be observed. Without wishing to be bound by any theory it is believed that said reduction in molecular weight observed can be ascribed to the presence of radicals generated during the carboxylation reaction which in combination with high shear and high temperatures may result in a certain degree of polymer degradation. In addition, degradation may also occur due to the presence of oxygen, especially when conducting the process of the invention in an internal mixer, wherein the polymer melt is more or less continuously in contact with air. In such a solution it may be beneficial to conduct the reaction between polymer and carboxylic acid in the presence of a blanket of an inert gas, such as nitrogen.

An alternative and preferred method for carrying out the carboxylation of the propylene polymers is in the presence of a radical scavenger, which compound may be added to the reactor, e.g. the extruder, together with the sulfonylazide compound and the propylene polymer.

Suitable radical scavengers are compounds containing one or more sterically hindered phenol or phenoxy groups and include: 4-methyl-2,6-di-tertiarybutylphenol, 4,4'-methylene-bis-2,6-di-tertiary butylphenol, 1,3,5-trimethyl-2,4,6-tris (3,5-di-tertiarybutyl-4-hydroxybenzyl) benzene, 2-hydroxy-5-methoxy-tertiarybutylbenzene, n-octadecyl 3,5-di-tertiarybutyl-4-hydroxyphenyl-proprionate and pentaerythrityl tetrakis (3,5-di-tertiarybutyl-4-hydroxyphenylproprionate).

1,3,5-trimethyl-2,4,6-tris(3,5-di-tertiarybutyl-4-hydroxyphenyl) benzene is a preferred radical scavenger.

The radical scavengers may be used in the process of the present invention in an amount of from 0.1 to 2.0 % m on total polymer, which amount may be fed into the internal mixer or extruder together with the other reactants.

Carboxylated propylene polymers, such as those prepared according to the process of the present invention, differ from the corresponding non-modified polymers in that they have improved adhesion to polar surfaces as well as improved dyeability, and can thus be employed in applications wherein such properties are important. An important outlet for carboxylated propylene polymers will be in polymer blends, e.g. blends with polar polymers. Such blends are generally prepared to upgrade the performance of one of the blend components or alternatively to prepare polymer compositions having properties which would not be obtainable with the individual polymers. Well-known blends of carboxylated polymers and polar polymers are blends of carboxylated polypropylene and polyamides. The carboxylated polypropylenes used therein however, are generally relatively low molecular weight polymers, as they derive their carboxyl functionality via a reaction in the presence of a free-radical generator. It can be expected that when these relatively low molecular weight carboxylated polymers are replaced with carboxylated propylene polymers which derive their carboxyl functionality from a reaction with an azidosulfonylbenzoic acid, such as those prepared according to the process of the present invention, will provide blends having improved performance characteristics. These blends are novel.

Therefore the invention also provides carboxylated propylene polymer-polyamide blends comprising:

a) 0.5-99.5 % m of a carboxylated propylene polymer prepared as disclosed herein, and

b) 99.5-0.5 % m of a polyamide polymer.

The polyamide polymers which may be employed in the blend compositions of the present invention are commercially available water-insoluble polymers having recurring amide groups. A preferred class of such polyamide polymers are the nylon-type of polyamides.

The carboxylated propylene polymers which may be employed in the blend compositions hereinbefore described are preferably made according to the process of the present invention.

The polyamide-carboxylated propylene polymer blends can be obtained by conventional melt blending procedures such as e.g. on hot roll mills, in internal mixers and extruders and at a temperature in the range of from 150 to 280 °C.

The blends of this invention may also contain one or more additives such as stabilizers, processing aids, dyes, pigments, reinforcing fillers, and the like. These additives can conveniently be added during the mixing step.

A further outlet for the carboxylated polymers prepared according to the process of the present invention is in ionomers, i.e crosslinked polymers, wherein the crosslinking between the molecules is accomplished by ionic bonds rather than by covalent bonds. At normal temperatures ionomers behave as conventionally crosslinked polymers, whereas at elevated temperatures they become thermoplastic and can be deformed. The ionomers can be obtained by treating the carboxylated polymers with metal compounds of basic character based on mono-, di or trivalent metals. Suitable such metal compounds include oxides, salts and alcoholates. Said metal compounds are generally added, depending on the carboxylic acid content of the polymer, in stoichiometric or more than stoichiometric amounts with respect to the carboxyl groups, although less than stoichiometric amounts are not excluded. Zinc oxide is a preferred such metal compound and is preferably used in an amount which is at least 200% of the stoichiometric amount.

Preferred such ionomers are those based on carboxylated propylene polymers which derive their carboxyl functionality from the reaction with an azidosulfonylbenzoic acid and which carboxylated propylene polymers have been prepared in the presence of a radical scavenger as hereinbefore mentioned. These ionomers are novel.

The preparation of the ionomers can be effected in the melt, e.g. subsequently to the preparation of the carboxylated polymers. An alternative method for the preparation of the ionomers is dissolving the carboxylated propylene polymer in a suitable solvent medium, e.g. a boiling hydrocarbon solvent such as a mixture of xylene isomers, followed by the addition of the appropriate amount metal compound. The thus obtained ionomer solutions are very suitable for use in the preparation of glass mat prepregs and adhesive tapes.

The ionomers based on the carboxylated propylene polymers as hereinbefore described can be used as such as thermoplastic polymers or e.g. in blends with other polymers such as in blends with polyamide polymers.

The invention will be further illustrated with the following examples for which the following information is provided.

Materials used:

Polypropylene: grade KY 6100 (ex Shell Ned. Chemie), a stabilized polypropylene having a melt index (M.I.) 3.1 g/10 min.

Toughened polypropylene: grade KMT 6100 (ex Shell Ned. Chemie), having a M.I. 4.0 g/10 min.

AKULON Polyamide 6: a Nylon-6 type polyamide (ex AKZO Plastics).

Ionox-330: 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert.-butyl-4 hydroxybenzyl) benzene, antioxydant (ex Shell Ned. Chemie).

Carboxylic acid: 3-azidosulfonylbenzoic acid (ASB).

Methods for product characterization:

Melt index (MI) was determined according to ASTM D 1238-L at 230 ^{o}C using a load of 2.16 kg.

Tensile Yield Stress was determined according to ISO R 527.

E-Modulus was determined from stress-strain curves obtained according to ISO R 527.

Notched Charpy Impact was determined according to ISO 179.

Examples I-IV

Preparation of carboxylated polypropylene in an internal mixer.

A blend comprising 50 g powdered polypropylene, varying amounts of 3-azidosulfonylbenzoic acid (ASB) and optionally Ionox-330, was fed into an internal mixer (Brabender Plastograph. 50 ml) equipped with kneading screws and having a temperature of 170 °C. The mixer was operated at a speed of 30 revolutions per minute (rpm). The total mixing time was 5 minutes while the final temperature was 210 °C (external heating). After removal from the mixer the mixture was allowed to cool to 20 °C. Analysis of the product with infrared spectroscopy showed that the conversion of ASB was essentially complete (no azide absorption left at about 2150 cm^{-1}). Elemental analysis for nitrogen and sulphur applied to the polymer after two extractions with 2/1 v/v blend of xylene and 2-butanone showed that between 65 and 70 % of the ASB had become attached to the polymer.

The carboxylated propylene polymers were further characterized by measuring the melt index (MI), a measure for molecular weight and melt viscosity. An increase in MI corresponds with a decrease in molecular weight.

The amount of each of the reactants used together with the corresponding product data are given in Table 1.

Examples V-X

Preparation of carboxylated propylene polymer in an extruder.

The preparation of carboxylated propylene polymer following the procedure of examples I-IV was repeted but employing a co-rotating twin-screw extruder (Werner/Pfleiderer) having twin 28 mm diameter bores and a length/diameter ratio of 27.6. The feed section of the extruder was held at a temperature of approximately 30 °C, while the temperature of the five subsequent sections of the extruder was set a 170 °C, 210 °C, 210 °C, 205 °C (devolatilizing section) and 210 °C respectively. The extruder was operated at 30 or 100 rpm while the residence time was 2-4 minutes. In two of the examples polypropylene was replaced with toughened polypropylene.

The amounts of each of the reactants and expressed as parts by weight (pbw) used have been collected in Table I together with the corresponding product data.

Comparative Experiment A.

Preparation of carboxylated polypropylene using maleic anhydride and a peroxide.

Following the procedure of examples V-X a blend of 100 parts by weight (pbw) of polypropylene, 0.9 pbw of maleic anhydride and 0.1 pbw of dicumyl peroxide (a free-radical initiator) was fed into the extruder which was operated at a speed of 30 rpm. The corresponding product characteristics data has been incorporated in Table 1.

Table 1

Example*	Poly-propylene	Ionox 330	ASB	Reactor type**	Reactor Speed rpm	MJ g/10 min	Polymer bound ASB %
I	50	-	0.5	B	30	16.0	70
II	50	-	1	B	30	14.0	70
III	50	-	2	B	30	13.1	66
IV	50	0.15	2	B	30	9.0	66
V	100	-	1	W.P	30	9.0	75
VI	100	-	4	"	30	8.1	68
VII	100	1	4	"	30	4.0	68
VIII	100	1	4	"	100	5.8	68
IX	100***	1	2	"	100	6.0	75
X	100***	1	4	"	100	5.3	70
Comp. Exp.A	100	-	0.9[1]	"	100	80	-

* Examples I-IV quantities in g, Example V-X and comparative experiment A quantities in pbw.

** B: Brabender Plastograph, W.P: Werner-Pfleiderer extruder.

*** Polypropylene copolymer.

[1] Maleic anhydride.

From the Examples I-X and the comparative experiment A it can be seen that carboxylated propylene polymers obtained via a reaction with ASB, both in an internal mixer and an extruder, have a considerably lower MI compared to that of the carboxylated polypropylene obtained via the maleic anhydride modification.

Furthermore for the ASB modified polymers the use of an extruder gives lower MI values, i.e. less polymer break down than when using an internal mixer. Finally the beneficial influence of a radical scavenger on the MI of the carboxylated propylene polymers is clearly demonstrated, both in the internal mixer and the extruder.

Examples XI and XII

Mechanical performance properties of carboxylated propylene polymers prepared via reaction with ASB.

Carboxylated polypropylene and carboxylated polypropylene copolymer as prepared in Examples VII and X respectively were compression moulded into sheets at 210 °C for testing selected mechanical performance properties. The data obtained is given in Table 2, together with similar data of the corresponding non-modified propylene polymers.

Table 2

Example	Carboxylated Polymer	Tensile Yield Stress MPa	E-Modulus MPa	Charpy Impact Strength (notched) KJ/m^2
XI	ex Example VII	34.8	1465	2.1
	non-carboxyl. polypropylene	33.6	1410	2.0
XII	ex Example X	27.7	1260	9.1
	non-carboxyl. polypropylene copolymer	25.3	1240	4.9

Examples XIII and XIV

Blends of carboxylated propylene polymers, prepared via reaction with ABS, and Nylon-6.

Carboxylated propylene polymers as prepared in Examples VII and X respectively were blended with Nylon-6 in an 80/20 and 20/80 m/m ratio employing the Werner-Pfleiderer twin-screw extruder mentioned hereinbefore at a temperature of 240°C ± 5°C. Prior to use the polymers were dried very thoroughly.

The blends thus obtained showed a high degree of dispersion, were very stable and did not delaminate upon bending or during compression moulding at 260 °C, as opposed to the blends of Nylon-6 and the corresponding non-carboxylated propylene polymers prepared by the same procedure. The tensile yield stress data of these blends have been collected in Table 3 together with the data obtained with corresponding blends of Nylon-6 with the maleic anhydride modified polypropylene as prepared in comparative experiment A.

Table 3

Example	Propylene polymer ex Example	Blend with Nylon-6 in m/m ratio	Tensile Yield stress MPa
XIII	VII	80/20	41.4
		20/80	59.4
XIV	X	80/20	31.7
		20/80	56.0
Comparative Experiment B	Comp. Exp. A	80/20	32.1
		20/80	38.1

Examples XV and XVI

Ionomers based on blends of ZnO and carboxylated polypropylene.

Carboxylated polypropylene as prepared in Example II and having a MI 14.0 g/10 min and carboxylated polypropylene prepared according to Example II but in the presence of 0.5 g Ionox-330 and having a MI 6.1 g/10 min were blended respectively with varying amounts of zinc oxide in the Brabender Plastograph during 5 minutes at a temperature in the range of from 200-215 °C. The amounts of ZnO employed in the blends corresponded respectively with 100, 200 and 300 % of the theoretical amount required for complete neutralisation of the amount of ASB used in the preparation of the carboxylated polypropylenes. The MI data of the ionomers thus prepared is given in Table 4. These results clearly illustrate the advantage of using at least stoichiometric amounts of ZnO in the preparation of these ionomers and especially of using at least 200 % of the stiochiometric amounts of ZnO, as well as the beneficial influence of using a carboxylated polypropylene which has been prepared in the presence of a radical scavenger.

Table 4

Example	Carboxylated Polypropylene	Degree of neutralisation with ZnO %	MI of Ionomers g/10 min
XV	ex Example II (MI:14.0 g/10 min)	100	8.1
		200	3.2
		300	1.1
XVI	as prepared in Example II + 0.5 g Ionox-330 (MI:6.1 g/10 min)	100	5.1
		200	1.6
		300	0.1

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the preparation of carboxylated propylene homo- and copolymers which comprises the reaction of a thermoplastic propylene homo- or copolymer with an azidosulfonylbenzoic acid by mechanically mixing said polymer and said acid at a temperature of at least 180 °C in the ~~substantial~~ absence of a free-radical initiator.

2. A process as claimed in claim 1, wherein the reaction is conducted at a temperature in the range of from 200-220 °C for a period of not more than 30 minutes.

3. A process as claimed in claim 1 or 2, wherein the azidosulfonylbenzoic acid is 3-azidosulfonylbenzoic acid.

4. A process as claimed in any one of claims 1-3, wherein the reaction is carried out in the presence of a radical scavenger.

5. A process as claimed in any one of claims 1-4, wherein the reaction between the propylene homo- or copolymer and the azidosulfonylbenzoic acid is conducted in an extruder type reactor.

6. Blends of carboxylated propylene polymers with polyamide polymers comprising:

0.5-99.5 % m of a carboxylated propylene homo- or copolymer prepared in accordance with a process as claimed in any one of claims 1 to 5, and
99.5-0.5 % m of a polyamide polymer.

7. Ionomers being reaction products of carboxylated propylene homo- or copolymers prepared according to a process as claimed in any one of claims 1 to 5 and a

metal compound of basic character based on a mono-, di- or trivalent metal.

8. Ionomers as claimed in claim 7, wherein the metal compound is zinc oxide.

9. Ionomers as claimed in claim 8, wherein the amount of zinc oxide is at least 200 % of the stoichiometric amount.

10. A process for the preparation of carboxylated propylene homo- and copolymers substantially as hereinbefore described with reference to any one of the Examples.

DATED this ELEVENTH day of NOVEMBER 1988

Shell Internationale Research Maatschappij B.V.

Patent Attorneys for the Applicant

SPRUSON & FERGUSON