(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
13 September 2001 (13.09.2001)

PCT

(10) International Publication Number
WO 01/66632 A1

(51) International Patent Classification⁷: C08K 5/28, C08L 23/02, C08K 5/43, C08J 9/00

(21) International Application Number: PCT/EP00/01983

(22) International Filing Date: 7 March 2000 (07.03.2000)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant *(for all designated States except US)*: **BOREALIS TECHNOLOGIES OY** [FI/FI]; P.O. Box 330, FIN-06101 Porvoo (FI).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **BØRVE, Kjetil, Larsen** [NO/NO]; Kalliåsen 23, N-3280 Tjodalyng (NO). **REDFORD, Keith** [GB/NO]; Likollen 70, N-1481 Hagen (NO). **SKATTUM, Margrethe** [NO/NO]; Skolegt. 10D, N-2821 Gjøvik (NO). **THATCHER HAAVALDSEN, Jane** [GB/NO]; Hauanåsen 10, N-3213 Sandefjord (NO).

(74) Agents: **NOBBE, Matthias** et al.; Viering, Jentschura & Partner, Steinsdorfstrasse 6, D-80538 München (DE).

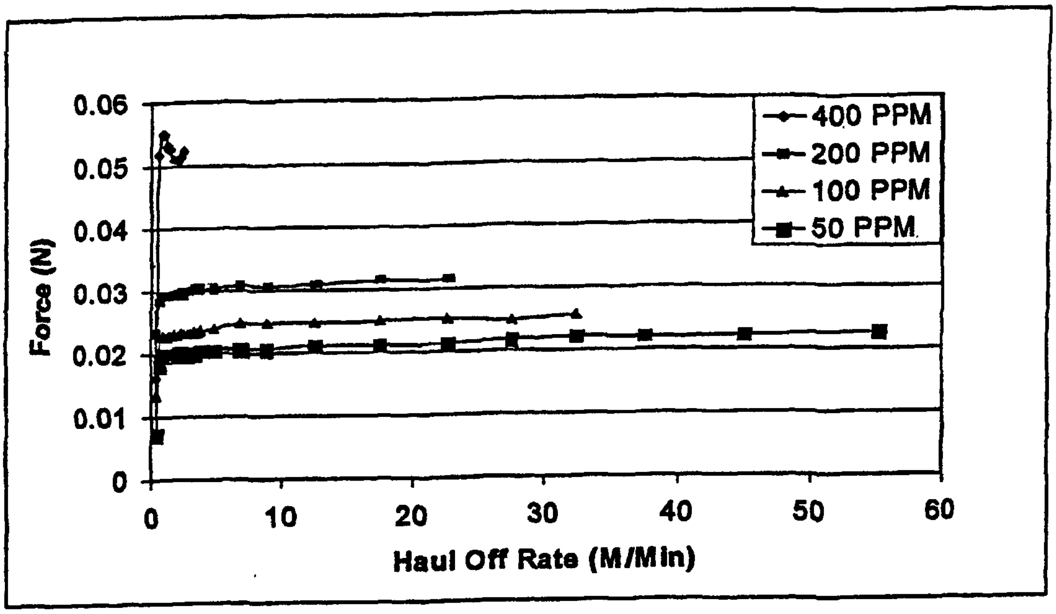
(81) Designated States *(national)*: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCESS FOR PREPARING CROSS-LINKED POLYOLEFINS



(57) **Abstract:** The present invention refers to a process for preparing cross-linked polyolefins, comprising the steps of adding a diazido compound of the formula (I): N=N=N-X-R-X-N=N=N wherein R represents an aryl, alkyl or aralkyl group having 3 to 20 carbon atoms and X stands for -CO-, -O-CO-, $-SO_2-$, $-PO_2-$, $-PO_3-$ or -Si(=O)-; to a polyolefin in a powder or pellet form; mixing the product to obtain a mixture; extruding the mixture in an extruder at a temperature above the decomposition temperature of the diazido compound of formula (I).

Process for preparing cross-linked polyolefins

The present invention relates to a process for preparing cross-linked polyolefins having an improved melt strength and for controlling the viscosity of polyolefins, in particular polypropylene, polyethylene, copolymers and mixtures thereof.

In the state of art, some processes for modifying the viscosity of polyolefins, in particular polypropylene, have been proposed. In said processes, use is mainly made of free radical chemistry. Using said free radical chemistry means that, by radiating polymers with high energy radiation, random scission of bonds has been caused by cleaving the C-H-bond on the main chain leading to reactive radicals. A similar process made use of inorganic or organic peroxides leading also to secondary or tertiary radicals. Both methods rely on the random combination of a so-called main chain radical to crosslink to yield long chain branching. Unfortunately, there is a competition between the desired branching, or grafting, reaction and the cleavage of the main chain by chain scission. It has been observed that at higher temperatures a chain scission was the main reaction leading to a number of byproducts including polymers having a shortened main chain. The use of peroxides for abstracting hydrogen from the main chain also leads to a number of undesired oxygen-containing byproducts.

As the viscosity modification of polyolefins by crosslinking reactions leads to modified olefines which are superior in their properties for blow-molding and foaming, there is a need for an improved process for preparing said cross-linked polymers by which the disadvantages mentioned above are avoided.

The inventors of the present invention surprisingly found that the use of aliphatic or aromatic diazido-compounds in the extrusion process of polyolefins leads to crosslinked polymers which exhibit superior viscosity properties.

There have been some proposals in the state of art to use diazido compounds in combination with polyolefins. For example, GB-1080619 refers to a process for producing several compositions from polymers and/or copolymers of aliphatic olefines which comprises incorporating into the polymer a hydrated salt of a group Ia or IIa metal and heating the resulting mixture to a temperature sufficient to release the hydrated water steam and to blow the polyolefins. According to said document, a chemical blowing agent is preferably incorporated into the polyolefin in order to further improve the foaming properties of the polyolefin foam. In addition to said blowing agents, the use of an azido crosslinking agent is described as a preferred measure for the production of cellular polyolefin compositions having a specific density as low as 20 lbs./cu.ft., as the use of said diazido compounds enables the production of a finer and more uniform cell structure and leads allegedly to a much higher percentage of closed cells. It is the object of said document to improve the properties of the steam blown foam.

A similar solution has been proposed in US-3298975, by the same applicant as GB-1080619. According to the disclosure thereof, a method for preparing shaped articles from expandable pellets is described, said pellets having a high impact strength and being free from weld seams between the particles and hence, free from fractures at the welds. The process comprises the steps of partially filling a mold for the desired shaped article with partially expanded pellets comprising a mixture of stereoregular polypropylene, a blowing agent and a poly(sulfonazide) as crosslinking agent, closing and heating said mold to a temperature above the softening temperature of said pellets, said temperature being sufficient to release the gas from the blowing agent to cause the pellets to expand and fill the mold, to complete the crosslinking reaction and to fuse the expanded pellets into an integral cellular structure. The poly(sulfonazide) compounds described in said document are largely the same as mentioned in the above GB-reference.

Furthermore, DE-OS-2118771 describes a process for preparing light-curable polymers containing curable groups in the side chains, said groups being bound by urethane linkages. These curable groups comprise carbonylazido or sulfonylazido functionalities which are decomposed under the influence of light and lead to a network-like polymer structure.

None of the above references however, discloses that organic diazido-compounds can be used for controlling the viscosity and melt strength of polyolefins, in particular polypropylene and polyethylene, by crosslinking the polymer chains.

According to the findings of the inventors, the bifunctional azido compound can be added to the polyolefin in such a way as to guarantee good dispersion, i.e., adding the bifunctional azido compound to the polyolefin followed by dry-mixing to obtain a uniform mixture. The polyolefin resins may be used in the form of pellets or as powder, preferably as a powder. The powder may be milled granules or corresponding material, or it may be the polymer substance as obtained from a polymerisation reactor, stabilised or not. Said mixture is then extruded or blow-molded at a temperature above the decomposition temperature of the bifunctional azido compound. Crosslinking of the polymer-chains can be observed as a result of the reaction of one end of the azido compound with one polymer chain and the other end with another polymer chain.

The inventors found out that the application of polyolefins being cross-linked according to invention to processes requiring enhanced melt strength is of much greater importance as the melt strength is the most important of the rheological characteristics for the purpose of further polymer processing. Such processing includes, for example, foaming, blow-molding, blow-film extrusion, thermo-forming and extrusion coating. In the former, an enhanced melt strength contributes not only to higher retention of gas bubbles in the resulting foamed polymer, but also to an improved morphology and regularity in the resulting cell structure. In the latter, an enhanced melt strength results in a uniform wall thickness in high volume structures, for example bottles for consumer products, manufactured by vacuum-stretching a molten polyolefin extrudate against the interior of a mold. A higher uniformity in wall thickness leads to reduction in the number of weak regions in the resulting product and, under conditions requiring high degrees of stretching, for example for very large wide containers, a reduction of the amount of polymer tearing during the molding process.

The present invention is therefore directed to a process for preparing cross-linked polyolefins having an improved melt strength, comprising the steps of:

a) adding a diazido compound of the formula (I)

$$N{=}N{=}N{-}X{-}R{-}X{-}N{=}N{=}N \quad (I),$$

wherein R represents an aryl, alkyl or aralkyl group having 3 to 20 carbon atoms and X stands for $-CO-$, SO_2-, $-PO_2-$, $-PO_3-$ or $-Si(=O)-$;

to a polyolefin in powder or pellet form;

b) mixing the components of step a) to obtain a mixture;

c) extruding the mixture of step b) in an extruder at a temperature above the decomposition temperature of the diazido compound of formula (I). Preferably, the mixture obtained in step b) is a homogeneous mixture.

The inventors surprisingly found that, by carrying out the process of the present invention, polyolefins can be obtained which show significant different properties with respect to melt rheology, when compared to the base polymer. In particular, increases in melt strength, elongational viscosity and die swell have been observed. Thereby, the increase in viscosity improves the properties of the polyolefins which are, for example, to be blow-molded.

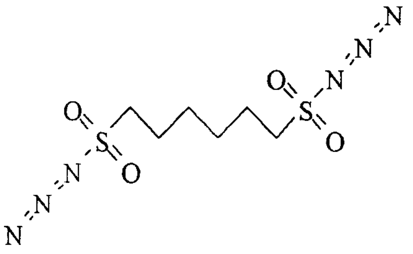
The inventors found that the diazido compound of the general formula I or mixtures thereof should be preferably limited to medium-sized diazido compounds. This might result from the fact that possible side reactions become a problem due the possibly reduced reactivity of the radical if the carbon backbone of the diazido compound is too large. Therefore, diazido compounds or mixtures thereof are preferred, wherein the diazido compound is of the formula (I):

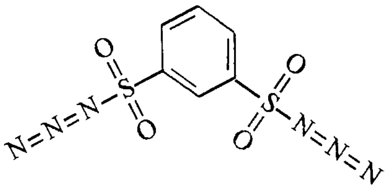
$$N{=}N{=}N{-}X{-}R{-}X{-}N{=}N{=}N \quad (I),$$

wherein R represents $-(CH_2)_n-R_1-(CH_2)_n-$ wherein R_1 represents an aryl or polyaryl, wherein aryl can also be substituted by branched or linear C1 to C6 alkyl, or an (CH2)w group, w being 3 to 6, n is 0, 1 or 2 and X stands for $-SO_2-$, -O-CO- or -CO-; and particularly preferred are diazido compounds of formula $N_3-SO_2-R_2-SO_2-N_3$ wherein R_2 represents an aryl or an alkyl group having 3 to 8 carbon atoms.

In the above formula, aryl group or polyaryl group, wherein aryl can also be substituted by branched or linear C1 to C6 alkyl, stands for an 1,3-benzo-, 1,3′-biphenyl-ring, 1,4-benzo-, 1,4′-biphenyl-ring, which may be substituted by branched or linear C1 to C6 alkyl.

Most preferred are the compounds 1,6-di(sulfonazido)-hexane and 1,3-di(sulfonazido)-benzene as represented below.





The diazido-compound is used preferably in powder form and usually in an amount of 5 to 25000 ppm, preferably 10 to 10000, more preferably 25 to 5000, even more preferably 50 to 800 and most preferably 50 to 400 ppm related to the amount of the polyolefin.

The polyolefin to be used in the inventive method is preferably a polypropylene, polyethylene, a copolymer or a mixture thereof, including all types of propylene and ethylene polymers such as propylene or ethylene homopolymers and copolymers, as well as blends and alloys containing polypropylene(s) or polyethylene(s) as the major part. The polyolefin is preferably used in the form of a powder or pellets, the powder being preferred in order to obtain a homogeneous mixture with the diazido compound.

Particularly preferred polyolefins are selected from the group comprising polypropylene and polyethylene homopolymers; copolymers of propylene with ethylene, containing from 0.1 to 50% by weight of ethylene; copolymers of ethylene with the monomers propylene, hexene, and/or octene, containing from 0.1 to 50% by weight of the mentioned monomers; blends of polypropylene with polyethylene such as high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE); blends of polyethylene with polyethylene such as high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE); ethylene propylene rubbers (EPDM or EPR); and alloys of polyethylene or polypropylene with another thermoplastic polymer selected from the group comprising polyamides (PA), polyesters (PET or PBT), polycarbonates (PC), and polystyrene (PS). Polypropylene or polyethylene blends may contain the second component in an amount from 0.1 to 50 % by weight based on the weight of the polymer composition. The polypropylene or polyethylene, or main polypropylene or main polyethylene component, should have a melt flow index from 0.01 to 5000 g/10, preferably 0.2 to 500 g/10 min (determined at the conditions 230°C/2.16 according to ASTM D 1238).

Although various polyolefins can be used in the process according to the present invention, the polyolefin is preferably polypropylene, polyethylene, a copolymer of propylene and ethylene, a copolymer of propylene and/or ethylene with at least one of methacrylate, methyl methacrylate, butyl methacrylate, vinylacetate, or a mixture thereof.

An extrudate obtained according to the process of the invention can be used for the preparation of shaped articles, in particular by blow-molding of large articles. Due to the increased viscosity and melt strength compared to the base polymers without crosslinking, the blow-molding forms can be uniformly filled and homogenous and uniform articles can be obtained.

The shaped or moulded articles prepared according to the inventive process can be used for preparing automotive parts such as dashboards, door panels, head liners, boot inlays etc. and for packaging purposes.

In addition, the inventors have also found that the principle of the process of the present invention can also be used for foaming polyolefins in the presence of an physical blowing agent, selected from nitrogen, carbon dioxide, an aliphatic organic solvent having 3 to 10, preferably 3 to 8 carbon atoms and other agents known in the art as blowing agents or mixtures thereof. The kind of the physical blowing agents is not decisive as far as the vapour pressure at the processing temperature is sufficient to blow the foam.

The aliphatic organic solvent having 3 to 10, preferably 3 to 8 carbon atoms or mixtures thereof are preferred as a physical blowing agent. N-Pentane, n-hexane, branched isomers or mixtures thereof are particularly preferred as physical blowing agents.

When using said lower alkanes as physical blowing agents, a uniform closed cell structure can be obtained wherein the cell gas is mainly comprised of said blowing agent and serves for good thermal insulation properties of the formed article.

The following examples illustrate the process of the present invention and provide data of the physical properties of the extrudates prepared according to the process of the invention.

Preparation Examples

In the extrusion tests following below, the compounds 1,3-di(sulfonazido)-benzene and 1,6-di(sulfonazido)-hexane have been tested in various concentrations relative to the polyolefin. Both compounds have been prepared by the following preparation methods.

Preparation of Hexane 1,6-disulfonyl azide

Hexane 1,6-disulfonic acid. 1,6-dibromohexane (25 mL, 0.16 mol) and sodium sulfite (45.5 g, 0.36 mol) in water (85 mL) were heated at reflux for 16 h. The mixture was then filtered whilst hot and the filtrate was concentrated under reduced pressure to yield the hexane 1,6-disulfonic acid (39.3 g, 0.16 mol) which was used without further purification. The diacid was ground into a fine powder and powdered phosphorus pentachloride (84 g, 0.4 mol) was added carefully. After an initial vigorous reaction, the mixture was heated with mechanical stirring at 110 °C for 90 min, yielding a mustard coloured solution. On cooling the mixture was cautiously triturated with ice/ water and the resultant solid filtered off. The solid was washed with water and dried under vacuum to afford the disulfonyl chloride hexane compound as a cream yellow solid (38.6 g, 96 %). This material was used without purification in the next step.

To sodium azide (20 g, 0.30 mol) in water (85 mL) was added dropwise a yellow solution of hexane 1,6-disulfonyl chloride (38.6 g, 0.15 mol) in acetone (255 mL) at 0°C. Upon addition of half of the solution a white precipitate was seen and upon complete addition a red coloured solution was afforded. After stirring for 1 h at < 5 °C the precipitate was filtered off and the solid washed with cold water to yield the diazide as fine white needles (25 g, 62 %) (NB azides can be destroyed in a careful manner by the addition of sodium thiosulfate and iodine). Thermal gravimetric analysis showed a sharp decomposition at 195 °C. 1H NMR (300 MHz, CDCl3) d 3.35 (m, 4H), 4.08 (m, 4H), 2.71 (m, 4H); nmax (KBr) 2941 (w), 2873 (w), 2153 (s).

<u>Preparation of Benzene 1,3-disulfonyl azide:</u>

1,3-Benzene disulfonyl azide was prepared in analogous manner as described before and yielded a white solid (20.5 g, 98 %). Thermal gravimetric analysis showed a sharp decomposition at 170 °C. 1H NMR (300 MHz, CDCl3) d 8.50 (s, 1H), 8.27 (dd, J = 7.6, 2.2 Hz, 2H), 7.90 (dd, J = 7.6, 1.0 Hz, 1H); nmax (KBr) 3101 (w), 2142 (s).

The other compounds used in the tests below have been prepared accordingly.

<u>Test experiments making use of the diazido compounds</u>

The diazido compounds including these compounds prepared above have been tested in extruder experiments at concentrations between 50 and 1600 ppm based on polypropylene (PP). All compounds resulted in significant changes in melt rheology of the modified polymers when compared to the base polymer. Increases in melt strength, elongational viscosity and die swell have been observed.

In the examples, the melt strength of the polymers can be measured by a so-called "haul-off" method. This method is a test method commonly used in the thermoplastic testing. In the following, the method to give a necessary understanding of its principles will be shortly explained. The polymer to be tested is extruded or pushed by a piston through a capillary die vertically downward. The formed strand is pulled downward by a force connected to a balance recording the pulling force. This method allows to measure the melt strength of the polymer strand in a molten stage just outside the capillary die. The extruded solidified strand is hauled off by the use of a pair of nip rollers. The measured melt strength will vary with the haul-off speed. Details are given in the examples. A high "haul-off" force indicates an improved melt strength. Increasing "haul-off" force by increasing haul-off speed indicates strain hardening.

Enclosed are experimental results from the characterisation of a polypropylene and a polyethylene each being compounded with a diazido compound described above. Extrusion was performed at 180°C - 200°C on a clextral BC21 extruder. Retention time in the extruder ranged from 1.5 to 5 minutes. The results are shown in Fig. 1 to 7.

The extrudates were characterized using a Rosand RH7-2 Capillary extrusion rheometer at 190°C, with a 1 mm ⌀ 16 mm long die and an inlet angle of 90°. The cross head speed was 1 mm/min (Ca. 0.177 cm^3/min).

As it can be taken from the results from haul-off tests shown in Fig. 1 - 7, a higher amount of azido compound added results in a greater force and a lower haul-off rate before fracture. As shown in some Examples, the samples containing 1600 ppm or more of the aromatic diazido compound could not be tested due to its high viscosity.

Experimental concerted crosslinking and foaming of PP

In the extrusion of polyolefin foam, for example, a polypropylene foam, the bi-functional azido compound will usually be added to the polypropylene melt along with the blowing agent (typically a low boiling point hydrocarbon, HCFC, nitrogen or carbon-di-oxide). The decomposition will in fact also yield an additional gas for blowing the foam. The build up in viscosity due to mild crosslinking will occur in the extruder from the point of injection to the die. Much smaller concentrations of the diazido compound are needed compared with the equivalent peroxide system.

In this example, 1,3 di-sulphonyl azido benzene (200mg) was dissolved in acetone (Ca. 10ml). This solution was added to unstabilised Polypropylene powder (500g Borealis HB120J). The powder was thoroughly mixed then the acetone permitted to evaporate. This was assumed to provide a Polypropylene with a reasonably well distributed 400ppm of diazido compound.

Extrusion conditions

A Clextral BC21 laboratory extruder was set-up with a temperature profile of 150-185°C. The throughput was 1 kg/h. Butane was introduced into the extruder at barrel segment 8, counted from the first feeding zone (of total 11).

Reference foam

A reference foam was produced using Borealis HB120J powder with no additives. The resultant string had a diameter of 3mm and an approximate density of 350 kg/m. The string collapsed very rapidly after the die and gas was seen to bubble from the string in the water cooling bath.

Modified foam

The Polypropylene with 400ppm diazido compound was extruded under identical conditions as the reference foam above. The resulting string had a diameter of 12mm and a density of 23 kg/m. There was no apparent collapse of the string after the extruder die and there was no leakage of gas from the string in the cooling bath.

Claims

1. Process for preparing cross-linked polyolefins having an improved melt strength, comprising the steps of:
   a) adding a diazido compound of the formula (I)

   $$N{=}N{=}N{-}X{-}R{-}X{-}N{=}N{=}N \quad \text{(I)},$$

   wherein R represents an aryl, alkyl or aralkyl group having 4 to 20 carbon atoms and X stands for -CO-, -O-CO- $-SO_2-$, $-PO_2-$, $-PO_3-$ or -Si(=O)-;
   to a polyolefin in powder or pellet form;
   b) mixing the components of step a) to obtain a mixture;
   c) extruding the mixture obtained in step b) in an extruder at a temperature above the decomposition temperature of the diazido compound of formula (I).

2. Process according to claim 1, wherein the mixture obtained in step b) is extruded in the presence of physical blowing agent, preferably an aliphatic organic solvent having 3 to 10, preferably 3 to 8 carbon atoms.

3. Process according to claim 1 or 2, wherein the homogenous mixture obtained in step b) is extruded in the presence of an aliphatic organic solvent selected from n-butane, n-pentane, n-hexane, branched isomers or mixtures thereof.

4. Process according to any of the foregoing claims, wherein the diazido compound is of the formula (I)

$$N{=}N{=}N{-}X{-}R{-}X{-}N{=}N{=}N \quad \text{(I)},$$

wherein R represents $-(CH_2)_n-R_1-(CH_2)_n-$ wherein R_1 represents an aryl or polyaryl, wherein aryl can also be substituted by branched or linear C1 to C6 alkyl, or an (CH2)w group, w being 4 to 6, n is 0, 1 or 2 and X stands for $-SO_2-$, -O-CO- or -CO-.

5. Process according to any of the foregoing claims, wherein, in formula (I), X stands for $-SO_2-$.

6. Process according to any of the foregoing claims, wherein the diazido compound is $N_3-SO_2-R_2-SO_2-N_3$ wherein R_2 represents an aryl group or an alkyl group having 4 to 8 carbon atoms.

7. Process according to any of the foregoing claims, wherein the diazido compound is 1,6-di(sulfonazido)-hexane or 1,3-di(sulfonazido)-benzene.

8. Process according to any of the foregoing claims, wherein the diazido compound is used in an amount of 5 to 25000 ppm, preferably 10 to 10000, more preferably 25 to 5000, even more preferably 50 to 800 and most preferably 100 to 400 ppm related to the amount of the polyolefin.

9. Process according to any of the foregoing claims, wherein the polyolefin is polypropylene, polyethylene, a copolymer or a mixture thereof.

10. Extrudate, obtainable according to process of any of the foregoing claims.

11. Use of the extrudate of claim 9 for the preparation of shaped or moulded articles.

12. Use according to claim 11, wherein the shaped or moulded articles are articles for automotive parts and packaging.

13. Use of a diazido compound of the formula (I)

$$N{=}N{=}N-X-R-X-N{=}N{=}N \quad (I),$$

wherein R represents a aryl, alkyl or aralkyl group having 3 to 20 carbon atoms and X stands for -CO-, SO_2, $-PO_2-$, $-PO_3-$ or -Si(=O)-, for modifying the melt strength of polymers, in particular polyolefins.

14. Use according to claim 13 wherein the polyolefin is polypropylene, polyethylene, a copolymer or a mixture thereof.

Fig 1 - Polyethylene PE8344 Melt Strength with Increasing Biphenyl 4,4 Disulfonyl azide Concentration.

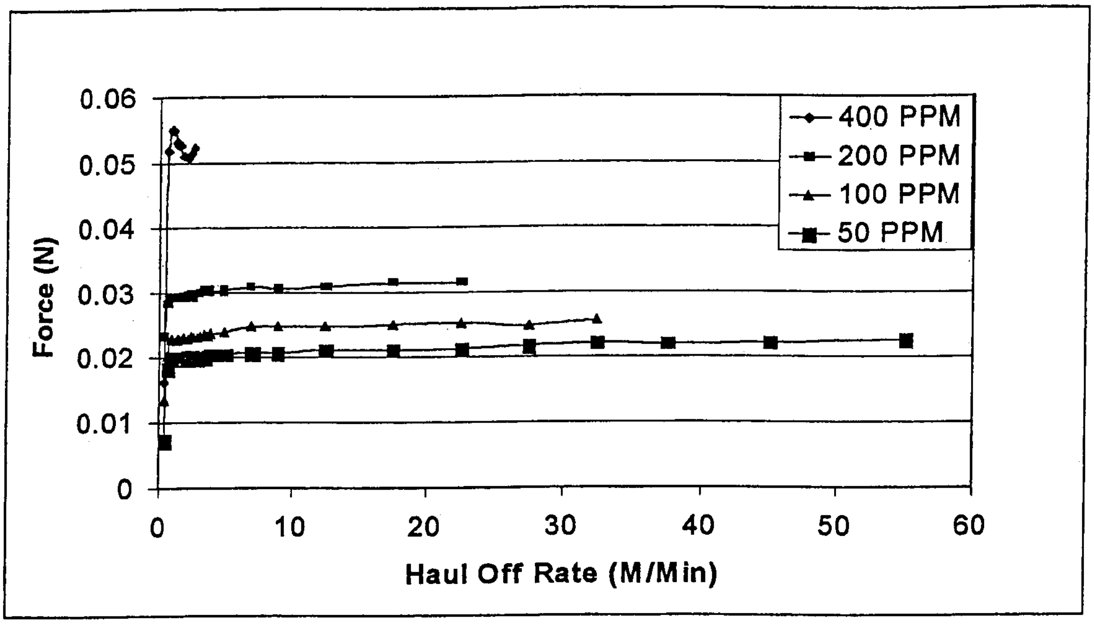


Fig. 2 – Polypropylene HB 120J with increasing Biphenyl 4,4-disulfonyl Azide concentration

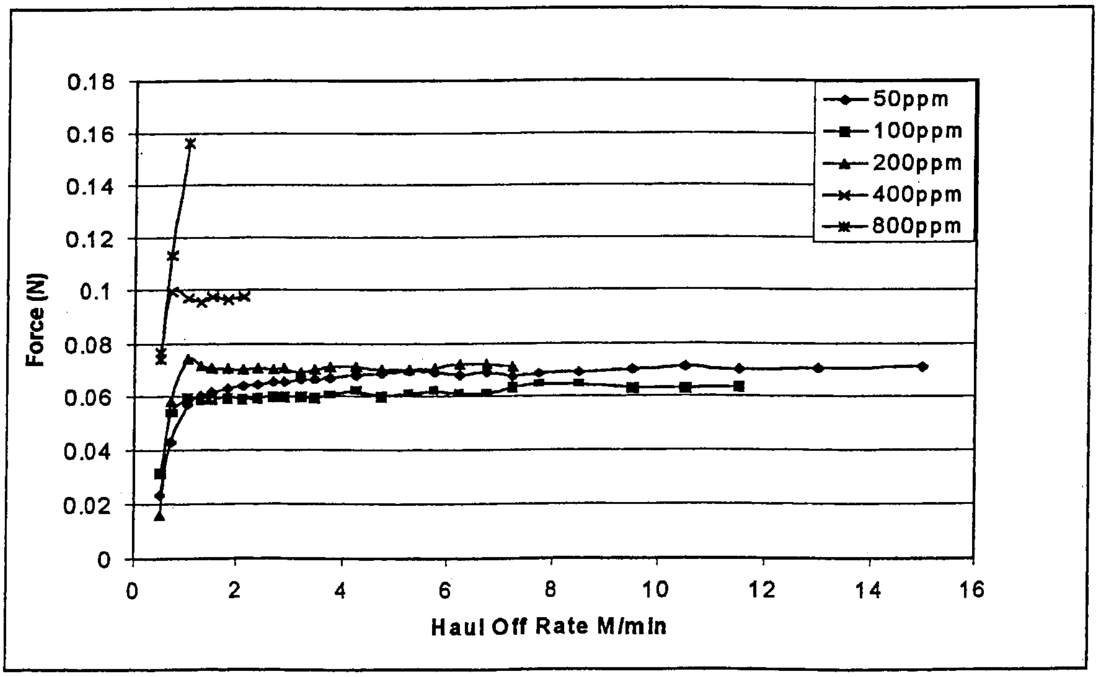


Fig. 3 - Polyethylene 6995 with Increasing Benzene 1,3 Disulfonyl Azide Concentration.

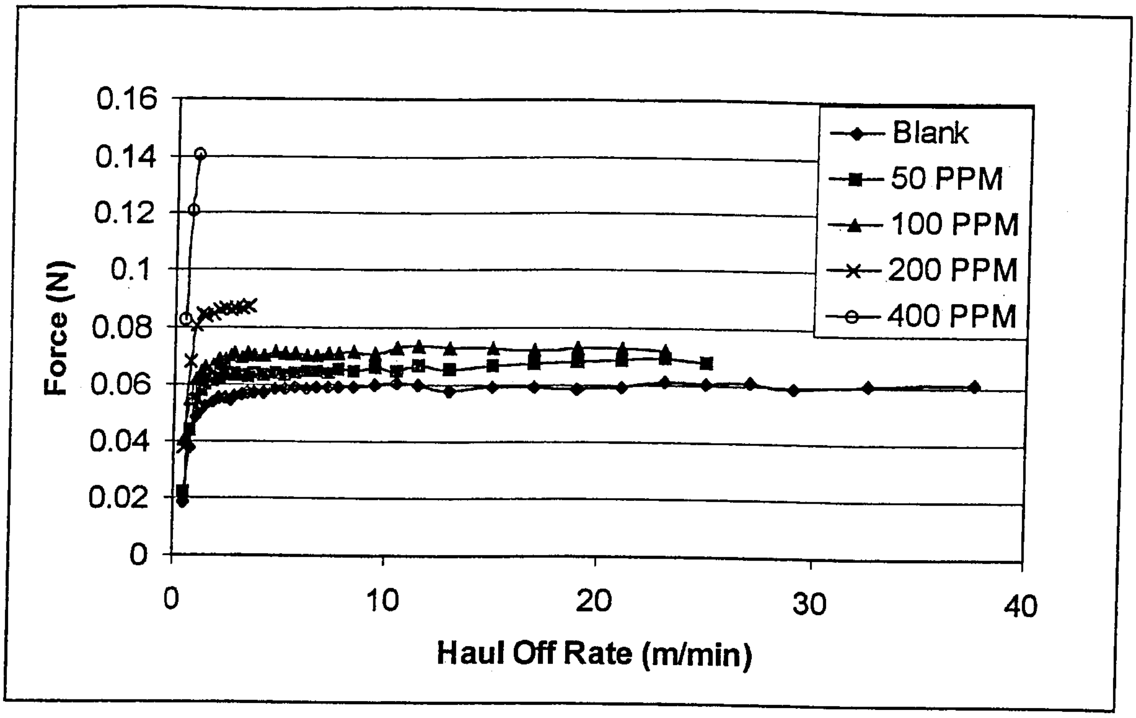


Fig 4 - Polyethylene 6995 with Increasing Hexane 1,6 Disulfonyl Azide Concentration

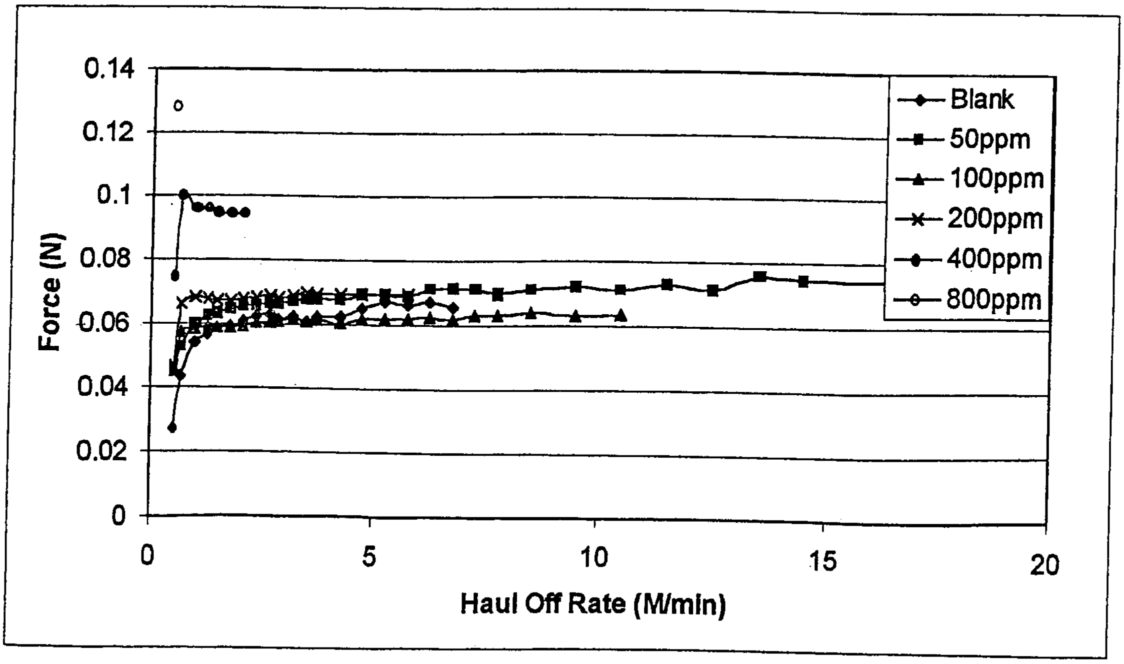


Fig 5 - Polypropylene HB 120J with increasing Hexane 1,6 DSA concentration

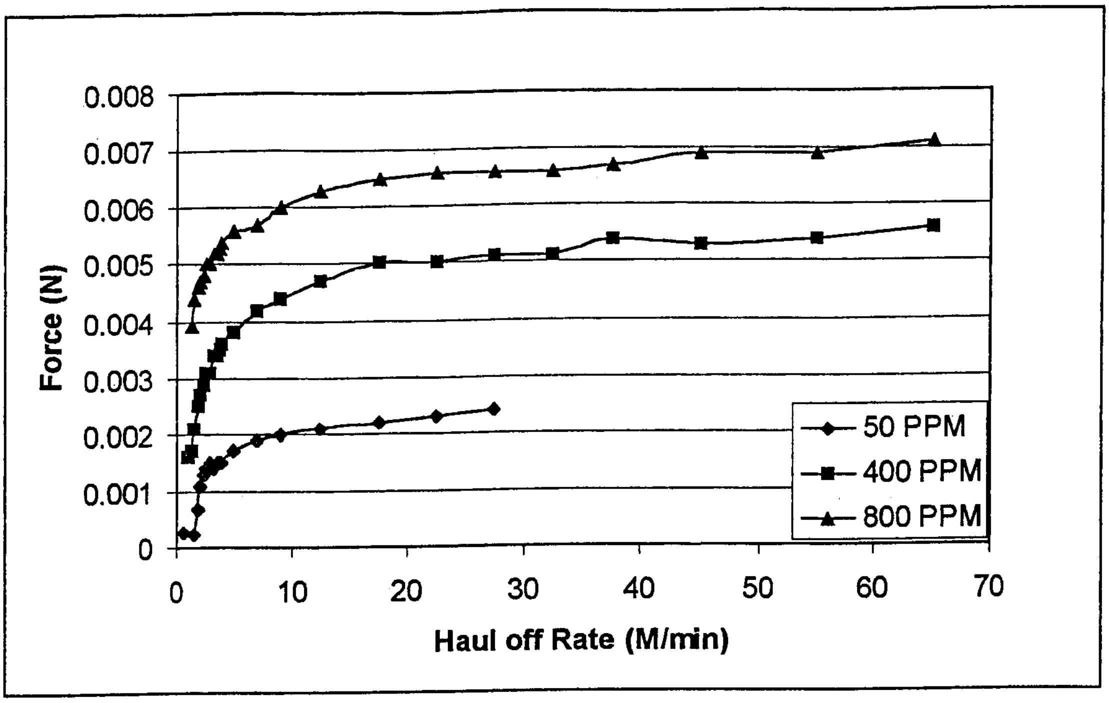
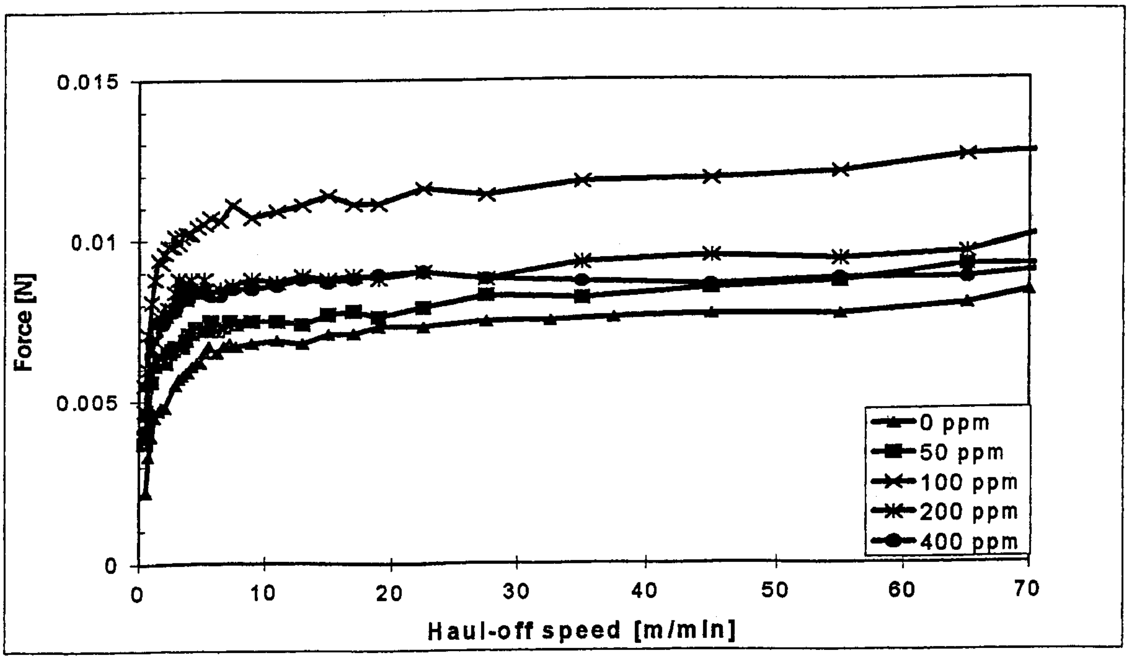


Fig. 6 - Polypropylene HB 120J with increasing benzene 1, 3 disulfonyl azide



INTERNATIONAL SEARCH REPORT

In ational Application No
PCT/EP 00/01983

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08K5/28 C08L23/02 C08K5/43 C08J9/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08K C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, CHEM ABS Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 261 818 A (MARCANTONIO) 19 July 1966 (1966-07-19) claims 1-4; examples ---	1,9
X	US 3 377 415 A (OPPENLANDER GEORGE C) 9 April 1968 (1968-04-09) column 2, line 55 -column 3, line 10; examples --- -/--	1,4,9,11

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search 1 November 2000	Date of mailing of the international search report 13/11/2000
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Engel, S

1

INTERNATIONAL SEARCH REPORT

Int tional Application No
PCT/EP 00/01983

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	LUIS GONZALEZ HERNANDEZ ET AL: "DIFFERENT CURING SYSTEMS FOR ETHYLENE-PROPYLENE ELASTOMERS" RUBBER CHEMISTRY AND TECHNOLOGY,US,RUBBER DIVISION ACS. AKRON, vol. 65, no. 5, 1 November 1992 (1992-11-01), pages 869-878, XP000335834 ISSN: 0035-9475 table II	1,4,9
X	US 5 977 271 A (TIMMERS FRANCIS J ET AL) 2 November 1999 (1999-11-02) column 14, paragraph 2 - paragraph 3; claims 1,8,17,22; examples	1,4,7,9, 11
A	EP 0 181 637 A (DOW CHEMICAL CO) 21 May 1986 (1986-05-21) page 4, paragraph 5 -page 5, paragraph 1; claims 1,3; table XIII	1,13

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

In :tional Application No
PCT/EP 00/01983

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3261818 A	19-07-1966	BE 645598 A	23-09-1964
		DE 1569006 A	26-06-1969
		FR 1401245 A	06-10-1965
		GB 996350 A	
		NL 6403104 A	30-09-1964
US 3377415 A	09-04-1968	GB 1087045 A	
US 5977271 A	02-11-1999	AU 8920998 A	16-03-1999
		EP 1007577 A	14-06-2000
		NO 20000963 A	26-04-2000
		WO 9910395 A	04-03-1999
		US 6111020 A	29-08-2000
		AT 185822 T	15-11-1999
		AU 700074 B	17-12-1998
		AU 3239095 A	27-03-1996
		BR 9509193 A	21-10-1997
		CA 2198136 A	14-03-1996
		CN 1159814 A	17-09-1997
		DE 69512926 D	25-11-1999
		DE 69512926 T	04-05-2000
		EP 0778852 A	18-06-1997
		ES 2139926 T	16-02-2000
		FI 970876 A	03-03-1997
		JP 10505621 T	02-06-1998
		NO 970942 A	28-04-1997
		WO 9607681 A	14-03-1996
		US 5869591 A	09-02-1999
EP 0181637 A	21-05-1986	US 4714716 A	22-12-1987
		AT 71640 T	15-02-1992
		BR 8505760 A	12-08-1986
		CA 1247816 A	03-01-1989
		DE 3585207 A	27-02-1992
		DK 526285 A	17-05-1986
		ES 548924 D	01-06-1987
		ES 8706176 A	16-08-1987
		FI 854509 A,B,	17-05-1986
		JP 63090544 A	21-04-1988
		JP 61126701 A	14-06-1986
		NO 854575 A,B,	20-05-1986
		US 4681715 A	21-07-1987