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(54) **Title:** RUBBER-REINFORCED VINYL AROMATIC (CO)POLYMER, HAVING AN OPTIMUM BALANCE OF PHYSICO-MECHANICAL PROPERTIES AND A HIGH GLOSS

(57) **Abstract:** Vinyl aromatic (co) polymer reinforced with a rubber selected from a linear diene rubber (i) with a solution viscosity lower than 70 cPs; a partially radial diene rubber (ii), with a solution viscosity lower than 70 cPs; a three-chain diene rubber (iii) with a solution viscosity lower than 70 cPs; a blend of linear diene rubbers (i) and radial diene rubbers (iv) in a maximum ratio between them (i)/(iv) of between 99.5/0.5 and 85/15.

RUBBER-REINFORCED VINYL AROMATIC (CO) POLYMER, HAVING AN
OPTIMUM BALANCE OF PHYSICO-MECHANICAL PROPERTIES AND A
HIGH GLOSS

5 The present invention relates to a rubber-reinforced vinyl aromatic (co)polymer having an optimum balance of physico-mechanical properties and a high gloss.

More specifically, the present invention relates to a vinyl aromatic (co)polymer reinforced with a diene rubber, having optimum physico-mechanical characteristics, such as impact resistance, tensile modulus, yield strength, ultimate tensile stress, combined with a high gloss.

In the present description and claims the terms rubber and elastomer should be considered synonyms. All the information contained herein should be considered preferred, even when not expressly specified.

Vinyl aromatic (co)polymers reinforced with rubber, in particular diene rubber, polybutadiene, for example, represent a well-known group of engineering polymers known on the market and widely described in literature. Specific examples of these (co)polymers are, for example, styrene/acrylonitrile co-polymers containing polybutadiene particles, dispersed in the polymeric matrix, generally known as ABS resins, and high impact polystyrene,

generally known as HIPS, comprising a continuous phase of polystyrene in which rubber particles are dispersed, for example polybutadiene particles.

It is known that the surface gloss of vinyl aromatic (co)polymers, reinforced with rubber particles, can be improved by reducing the rubber particle dimension to values lower than 1 μm . This condition can be obtained by increasing the shear during the polymerization reaction. Shear simply means the friction force imposed by the stirring of the mixture. The greater this force, the smaller the rubber particle diameter will be. As the shear is in relation to the revolution number of the stirrer of the polymerization reactor, this characteristic is an instrument on which it is possible to intervene within certain limits established by the motor power.

Another parameter which can be used for regulating the dimension of the rubber particles dispersed in the matrix is to reduce the viscosity in solution of the diene rubber used in the production of vinyl aromatic (co)polymers. As a diene rubber, however, such as polybutadiene, for example, in order to be handled and packed, must have a sufficient viscosity to avoid the "cold flow" phenomenon, it has so far been considered practically impossible to produce a reinforced vinyl aromatic (co)polymer, with a high surface gloss, using linear low-

viscosity polybutadiene homopolymer alone as rubber.

Examples are known in literature in which the production of ABS is described, having improved aesthetical properties (gloss), wherein diene rubbers are used, such 5 as polybutadiene, for example, which have been modified to reduce the viscosity in solution and which are suitable for producing ABS co-polymers with enhanced aesthetical properties. For example;

10 * US patent 4,421,895 describes the use of a diene rubber having a solution viscosity at 5% by weight of styrene at 25°C equal to or lower than 80 mPa*s, in the production of ABS. In particular, the diene rubber proposed in this patent is a linear styrene-butadiene block co-polymer. Using this type of rubber, rubber particles dispersed in the matrix are obtained, having dimensions smaller than 0.7 µm, and an ABS with high aesthetical properties (gloss) 15 is consequently obtained.

20 The improvement in the surface gloss obtained using styrene-butadiene linear block polymers, however, is achieved to the detriment of other physico-mechanical characteristics, in particular, the impact resistance. In order to improve this latter 25 property maintaining the surface gloss substantially unchanged, US patent 4,524,180 describes the

production of ABS with the use of a mixture of diene rubber (polybutadiene) and a styrene-butadiene linear block co-polymer having a low viscosity, when measured in solution at 5% by weight in styrene at 25°C;

- US 4,587,294 and 4,639,494 and European patent 277,687 describe the use of star-shaped or radial rubbers, with a low viscosity, when measured in solution at 5% by weight in styrene at 25°C, for producing ABS with an enhanced surface gloss. Radial or star-shaped rubbers are produced by means of well-known synthesis techniques, using lithium-alcohols as initiators of the anionic polymerization of butadiene, first producing the linear polymer with active chain-ends, carrying a negative charge and Li⁺ as counter-ion and subsequently adding a coupling agent, such as silicon tetrachloride, for example, capable of reacting with said chain-ends and binding various polymer chains to the silicon atom. Radial or star-shaped rubbers allow co-polymers to be obtained with an enhanced gloss, with respect to other known diene-based rubbers, having the same physico-mechanical characteristics, but they have the drawback of requiring a more complex process for their production.

The Applicant has now surprisingly found that it is possible to produce vinyl aromatic (co)polymers having an enhanced gloss, with the same the physico-mechanical characteristics, using a diene rubber as reinforcing 5 elastomer. By using linear diene rubbers having a viscosity (measured in solution at 5% by weight in styrene) equal to (or even higher than) that of block polybutadiene-polystyrene co-polymers or radial rubbers, i.e. diene rubbers structured as described hereunder, dispersed rubber particles are in fact obtained with smaller dimensions and therefore final polymers with enhanced aesthetical properties, having the same mechanical properties.

An object of the present invention therefore relates 15 to a rubber-reinforced vinyl aromatic (co)polymer comprising a polymeric matrix and a rubber phase consisting of a diene rubber dispersed and/or grafted to the polymeric matrix wherein said rubber phase is selected from at least one of the following:

20 (i) a linear diene rubber with a solution viscosity lower than 70 cPs, preferably between 40 and 60 cPs;

(ii) a partially radial diene rubber having a solution viscosity lower than 70 cPs, preferably between 40 and 60 cPs wherein up to 15% by weight, preferably from 25 1 to 12%, of the polymeric chains is terminated with a

quantity of tetra-functional coupling agent (non-limiting example, silicon tetrachloride) which is such as to generate a terminal radial structure of said chains of linear diene rubber;

5 (iii) a three-chain diene rubber, having a solution viscosity lower than 70 cPs, preferably between 40 and 60 cPs, i.e. a linear diene rubber coupled with a tri-functional agent (a non-limiting example is methyl trichlorosilane with a Si:Li ratio of 1:3);

10 (iv) a mixture of linear diene rubbers (i) and radial diene rubbers (v) in a maximum ratio between them (i)/(v) ranging from 99.5/0.5 to 85/15;

The radial diene rubbers (v) can be commercial radial polybutadiene rubbers.

15 The diene rubber (i), (ii), (iii) or (iv) used in the vinyl aromatic (co)polymer object of the present invention, can be either natural or synthetic. Suitable synthetic rubbers are those consisting of a polymer of a 1,3-conjugated diene containing from 4 to 6 carbon atoms, 20 and in particular polybutadiene, high and medium cis polybutadiene, polyisoprene.

Particularly preferred is polybutadiene having:

- a solution viscosity of 40 to 70 cPs, preferably between 40 and 60 cPs, measured in a solution thereof 25 at 5% by weight in styrene at 25°C;

- a 1,2 vinyl content ranging from 5 to 35%, preferably from 7 to 14% by weight;
- a 1,4-cis content of between 20 and 85%, preferably between 25 and 45% by weight; and
- 5 - a molecular structure among those described in (i), (ii), (iii) or (iv).

This type of polybutadiene is obtained by anionic polymerization of butadiene in a solution of aliphatic or cyclo-aliphatic solvents or a mixture thereof, with the 10 use of lithium-alkyl initiators. The polymerization can be carried out in batch reactors or continuous reactors; in batch reactors, the initiator, normally consisting of primary or secondary butyl lithium, is added to the reaction mixture consisting of the solvent and monomer 15 charged in such a quantity that the amount of total solids at the end of the polymerization is not higher than 20% by weight; it is known to experts in the field that said reaction can be carried out in the presence of Lewis bases in a higher or lower quantity depending on the content of vinyl or 1,2 units which are to be present in the 20 polymeric chain. Ethers are among the most widely-used Lewis bases, tetrahydrofuran in particular, which already in a quantity of 100 ppm with respect to the solvent is capable of considerably accelerating the reaction, 25 maintaining the content of vinyl unit at levels

< 12%; with higher quantities of THF, the microstructure is progressively modified up to vinyl unit contents higher than 40% for quantities of THF equal to 5,000 ppm. High vinyl unit quantities, however, are not necessary if 5 not harmful for the use of polybutadiene in the field of plastic material modification; it is preferable for the content of these units not to exceed the value of 15% even if, for a higher grafting efficiency, it is possible to use polybutadiene with a higher content of 1,2 units.

10 It is also known to experts in the art that reactions carried out in the absence of ethers or tertiary amines are sufficiently rapid to guarantee the complete polymerization of the monomer in times not longer than 1 hour, with final temperatures not higher than 120°C and, in any 15 case, controlled by the initial temperature of the reaction mixture which cannot be lower than 35-40°C to avoid an insufficiently rapid starting reaction and incompatible with normal production cycles. The reactor can be equipped with cooling jackets, however these are not particularly efficient as a result of the unfavourable surface/volume ratio typical of industrial reactors whose 20 volume is never smaller than 20 m³; a more efficient temperature control is obtained by means of a partial evaporation of the solvent which is condensed and subsequently 25 fed to the reaction reactor; this type of reactor, called

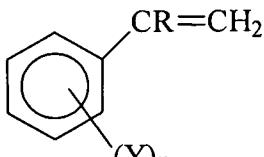
"boiling reactor" is quite efficient for the control of the reaction temperature and, in the state of the art, represents the best way for effectively limiting the natural increase in temperature due to the heat of the 5 butadiene polymerization. Carrying out the polymerization in batch reactors causes the formation of a polymer which, before a possible addition of a coupling agent, has a monomodal molecular weight distribution, wherein the ratio between the weight average molecular weight 10 (M_w) and the number average molecular weight (M_n) is very close to 1 and normally between 1 and 1.2. Carrying out the polymerization in a continuous reactor, of the CSTR type, or in various reactors in continuous of the CSTR type arranged in series, on the contrary, causes the formation 15 of a polymer with a monomodal molecular weight distribution in which the M_w/M_n ratio is between 1.8 and 2.5, the polymer, in both cases, at the end of the polymerization is linear and has chain-ends which are still active. These chain-ends consists of the species polybutadiene-lithium. The possible addition of a protogene 20 agent (an alcohol, for example) or a silicon halo-derivative wherein the ratio between the halogen and silicon is equal to 1 (a non-limiting example is trimethyl chlorosilane TMCS) causes the termination of 25 the butadiene-lithium chain-end and maintains the linear

macrostructure of the molecule. The addition of a poly-functional substance capable of reacting with the active chain ends, on the other hand, causes the formation of a branched macrostructure characterized in that it has a 5 node from which a number of branches depart having the same functionality as the polyfunctional substance used. As a non-limiting example, the use of silicon tetrachloride is known to experts in the field, which, when added to the reaction environment in a Si:Li ratio = 1:4, 10 causes the formation of a radial polymer which, if the polymer has been prepared in a batch reactor, has the four branches with the same lengths, whereas in the case of a polymer prepared in continuous, the four branches are different. If, on the other hand, the Si:Li ratio is 15 lower than 1:4, partially radial structures (ii) are obtained. If a trifunctional silicon compound is used as coupling agent (a non-limiting example is methyl trichloro-silane), tri-chain rubbers are obtained (iii). The normal production process of polybutadiene subsequently 20 comprises, after the addition of a pair of antioxidants consisting of a primary antioxidant of the phenolic type and a secondary antioxidant, typically an organic compound of trivalent phosphorous, the elimination of the solvent which is effected by means of the combined action 25 of water and vapour in stirred containers. This produces

a suspension of rubber granules in water from which, after draining on nets, the rubber is sent to a drying section consisting of two mechanical extruders. In the first extruder (expeller) a squeezing operation is carried out, 5 which eliminates most of the water which is drained through side slits of the extruder whereas the complete drying is effected in a second extruder (expander) in which the rubber subjected to mechanical action is heated to a temperature of 160-180°C. Part of the vapour is 10 eliminated from an aperture (vent) situated at the end of the extruder, whereas a part is eliminated at the outlet from the head. The rubber granules are then sent with belts or other conveying means to a packager where they are baled. The nature of polybutadiene (unsaturated rubber) requires a strict control of the finishing conditions, as experts in the field are aware of complications deriving from the formation of lumps of insoluble substances (gels) which are normally formed in the finishing area, in particular in the expander. These gels cause a 15 deterioration in the quality of the rubber destined for use in the field of the modification of plastic materials by the formation of substantial surface defects. A great deal of attention must therefore be paid in defining the finishing conditions of polybutadiene with the consequent 20 necessity of effecting numerous analyses for process and 25

product control.

The polymeric matrix of the rubber-reinforced (co)polymers of the present invention can be either a (co)polymer deriving from one or more vinyl aromatic monomers or a (co)polymer deriving from one or more vinyl aromatic monomers and one or more comonomers, for example 5 acrylic comonomers. The term vinyl aromatic monomer, as used in the present description and claims, comprises ethylenically unsaturated compounds having the general 10 formula



(I)

wherein R represents hydrogen or an alkyl radical having 15 from 1 to 4 carbon atoms, n is zero or an integer ranging from 1 to 5 and Y represents a halogen or an alkyl radical having from 1 to 4 carbon atoms. Examples of vinyl aromatic monomers having the above general formula are: styrene, α -methyl styrene, methyl styrene, ethyl styrene, 20 butyl styrene, dimethyl styrene, mono-, di-, tri-, tetra- and penta-chlorostyrene, bromo-styrene, methoxy-styrene, acetoxy-styrene, etc.. Preferred vinyl aromatic monomers are styrene and/or α -methyl styrene.

The vinyl aromatic monomers having general formula 25 (I) can be used alone or in a mixture of up to 50% by

weight with other co-polymerizable monomers. Examples of these monomers are (meth)acrylic acid, C₁-C₄ alkyl esters of (meth)acrylic acid such as methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, isopropyl acrylate, butyl acrylate, amides and nitriles of (meth)acrylic acid, such as acrylamide, methacrylamide, acrylonitrile, methacrylonitrile, butadiene, ethylene, divinyl benzene, maleic anhydride, etc.. Preferred co-polymerizable monomers are acrylic monomers such as 10 acrylonitrile and methyl methacrylate. The quantities of vinyl aromatic monomer and acrylic monomer used for the production of the copolymer vary in relation to the desired physico-mechanical properties in the vinyl aromatic copolymer reinforced with final rubber. The quantity of 15 acrylic monomer generally ranges from 5 to 45% by weight, preferably from 15 to 35% by weight and, correspondingly, the quantity of vinyl aromatic monomer ranges from 95 to 55% by weight, preferably from 85 to 65% by weight, based on the total weight of the vinyl aromatic monomer-acrylic 20 monomer copolymer. The quantity of diene rubber (i), (ii), (iii) or (iv) in the rubber-reinforced (co)polymer generally ranges from 4 to 30% by weight, preferably from 6 to 25% by weight, with respect to the weight of the (co)polymer.

25 The rubber-reinforced (co)polymer object of the pre-

sent invention can be prepared by means of any conventional technique used for producing crosslinked high impact co-polymers, such as mass polymerization, polymerization in solution, emulsion and mass-suspension. The 5 specimens obtained from the (co)polymer object of the present invention have a gloss at 60° higher than 85.

Some illustrative examples are provided for a better understanding of the present invention and for its embodiment, which should in no way be considered as being 10 of a limitative nature.

CHARACTERIZATION OF THE SYNTHESIZED POLYMERS

1. Determination of the viscosity in styrene solution

The method includes the preparation of a solution of polybutadiene in styrene at 5% by weight and the subsequent measurement of the viscosity at 25°C using a Cannon Fenske capillary tube whose dimension must be selected so as to avoid that the elution time through the capillary is neither too short nor too long. In the case of the polymers examined, the Model 300, valid within the range 20 of 50-250 cP, is used.

2. Determination of the average molecular weight of the SAN matrix.

The determination of the average molecular weight of the SAN matrix was effected on chromatographic equipment 25 consisting of: a degasser system, pump, injector: WATERS

Alliance 2695, set of Phenogel columns (300x7.6 mm) of 5 microns, porosity 106, 105, 104, 103 Angstrom, a Waters 410 differential refractive index detector, UV Waters 2487 detector, chromatographic analysis software: Millenium 32 version 3.2 (Waters).

3. Determination of the morphology of the rubber phase dispersed in ABS

The dimensions and morphology of the rubber phase dispersed in the SAN matrix were determined via T.E.M. (Transmission Electronic Microscopy), F. Lenz, A. Wiss - Mikroskopie 63, 1956, page 56. The morphology of the rubber particles was determined by visual inspection of the microographies and the characterization of the various structures was effected in accordance with the classification described in "Teilchenbildung bei der Herstellung von Kautschukmodifiziertem Polystyrol" of Adolf Echte 58/89 (1977), page 175-198, and in EP 716.664. For the calculation of the statistical parameter average volumetric Diameter of the particles DV the following formula was applied:

$$D_v = \frac{\sum_i N_i D_i^4}{\sum_i N_i D_i^3}$$

wherein D_i represents the diameter of the i -th particle whereas for the calculation of the percentage of parti-

cles of the "core shell" type or with a "mixed" structure (labyrinth or brain) the stereological method was used, described in C. Maestrini et al. Journal of Material Science, Vol. 27, 1992, page 5994. The T.E.M. analysis was 5 carried out on a transmission electron microscope Philips CM120.

4. Other characterizations

- * The concentration of the residual styrene monomer and acrylonitrile and other volatile organic substances was determined via gas-chromatography;
- * The concentration of polybutadiene in the ABS was determined by iodometric titration in accordance with the method of Wijs, Berichte, 1898, Vol. 31, page 750;
- 15 * The gel phase content (after thermal crosslinking of the rubber) and the swelling index (without thermal crosslinking of the rubber) were determined by means of the Ruffing test described in American patent US 4,214,056;
- 20 * The Melt Flow Index (MFI) was measured in accordance with the standard method ASTM D 1238 at 200°C under a weight of 5 kg;
- * The notched Izod value (on injection moulded specimens) was determined in accordance with the standard 25 method ISO 180/1A - ISO 179 (values expressed as

5 kJ/m²). Another parameter relating to the impact resistance of the materials is represented by the Ball Drop, determined in accordance with the standard method ISO 6603/2 on two different thicknesses specimens (2 mm and 3 mm).

10 * The tensile strength (yield strength, yield elongation, stress at break, elongation at break, tensile modulus) and the flexural strength properties (maximum stress, elastic modulus) were measured on injection moulded specimens in accordance with the standard methods ISO 527, ISO 178 and expressed as MPa, with the exception of the yield elongation and elongation at break which are expressed as percentages.

15 * The material gloss was determined in accordance with the standard method ASTM D 523 at two reading angles (20 and 60°C) using a Dr. Lange glossmeter. The measurement was effected on three steps specimens obtained by injection moulding with measurements of the reading area equal to: 95 mm x 75 mm x 3 mm. The moulding conditions of the test samples were the following: temperature of the melt 220°C and temperature of the mould 35°C.

Example 1

25 3.6 kg of linear polybutadiene (i), having a solution viscosity at 5% in styrene (SM) = 44 CPS, 20 g of

antioxidant ANOX PP 18 in 21.8 kg of styrene monomer and 7.6 kg of ethylbenzene, are dissolved in a 60-litre batch-type autoclave, equipped with a temperature regulator and stirring system, stirring for 5 hours at 85°C.

5 12.4 g of initiator 1,1-di(tertbutylperoxy)cyclohexane (Tx22E50) are then added.

The solution thus obtained is fed, after mixing under heat (at a temperature of 60°C) with a feed of acrylonitrile (weight ratio solution/acrylonitrile 10 82.5/17.5), into a first PFR reactor equipped with a stirrer and temperature regulation system, with a thermal profile of the reactor increasing from 112°C to 120°C, where the pre-polymerization is effected with grafting and phase inversion.

15 48 g of the transfer agent n-dodecylmercaptan (NDM) are added to the mixture leaving the first reactor which is then transferred to a second PFR reactor also equipped with a stirrer and temperature regulation system, with a thermal profile of the reactor increasing from 150°C to 20 165°C.

The mixture obtained is fed to a devolatilizer operating under vacuum at a temperature of 235°C in order to crosslink the rubber and remove the unreacted monomers and solvent from the polymer. The molten polymer thus obtained 25 is granulated so as to obtain the end-product

whose characteristics are indicated in Table 1.

Example 2

3.6 kg of partially radial polybutadiene (ii) (with a content of branched end groups of 10% by weight), having a solution viscosity at 5% in styrene (SM) = 45 CPs, 5 20 g of antioxidant ANOX PP 18 in 21.8 kg of styrene monomer and 7.6 kg of ethylbenzene, are dissolved in a 60-litre batch-type autoclave, equipped with a temperature regulator and stirring system, stirring for 5 hours 10 at 85°C. 12.4 g of initiator 1,1-di(tertbutylperoxy)cyclohexane (Tx22E50) are then added.

The solution thus obtained is fed, after mixing under heat (at a temperature of 60°C) with a feed of acrylonitrile (weight ratio solution/acrylonitrile 15 82.5/17.5), into a first PFR reactor equipped with a stirrer and temperature regulation system, with a thermal profile of the reactor increasing from 112°C to 120°C, where the pre-polymerization is effected with grafting and phase inversion.

20 48 g of the transfer agent n-dodecylmercaptan (NDM) are added to the mixture leaving the first reactor which is then transferred to a second PFR reactor also equipped with a stirrer and temperature regulation system, with a thermal profile of the reactor increasing from 150°C to 25 165°C.

The mixture obtained is fed to a devolatilizer operating under vacuum at a temperature of 235°C in order to crosslink the rubber and remove the unreacted monomers and solvent from the polymer. The molten polymer thus obtained is granulated so as to obtain the end-product whose characteristics are indicated in Table 1.

Example 3

3.6 kg of three-arm polybutadiene (iii), having a solution viscosity at 5% in styrene (SM) = 42 CPS, 20 g of antioxidant ANOX PP 18 in 21.8 kg of styrene monomer and 7.6 kg of ethylbenzene, are dissolved in a 60-litre batch-type autoclave, equipped with a temperature regulator and stirring system, stirring for 5 hours at 85°C. 12.4 g of initiator 1,1-di(tertbutylperoxy)cyclohexane (Tx22E50) are then added.

The solution thus obtained is fed, after mixing under heat (at a temperature of 60°C) with a feed of acrylonitrile (weight ratio solution/acrylonitrile 82.5/17.5), in a first PFR reactor equipped with a stirrer and temperature regulation system, with a thermal profile of the reactor increasing from 112°C to 120°C, where the pre-polymerization is effected with grafting and phase inversion.

48 g of the transfer agent n-dodecylmercaptan (NDM) are added to the mixture leaving the first reactor which

is then transferred to a second PFR reactor also equipped with a stirrer and temperature regulation system, with a thermal profile of the reactor increasing from 150°C to 165°C.

5 The mixture obtained is fed to a devolatilizer operating under vacuum at a temperature of 235°C in order to crosslink the rubber and remove the unreacted monomers and solvent from the polymer. The molten polymer thus obtained is granulated so as to obtain the end-product
10 whose characteristics are indicated in Table 1.

Example 4

3.4 kg of linear polybutadiene (i), having a solution viscosity at 5% in styrene (SM) = 44 CPs, 0.2 kg of radial polybutadiene, having a solution viscosity at 5% in styrene (SM) = 209 CPs, forming a mixture (iv), having a solution viscosity at 5% in styrene (SM) = 59 CPs, 20 g of antioxidant ANOX PP 18 in 21.8 kg of styrene monomer and 7.6 kg of ethylbenzene, are dissolved in a 60-litre batch-type autoclave, equipped with a temperature regulator and stirring system, stirring for 5 hours at 85°C.
20 12.4 g of initiator 1,1-di(tertbutylperoxy)cyclohexane (Tx22E50) are then added.

The solution thus obtained is fed, after mixing under heat (at a temperature of 60°C) with a feed of acrylonitrile
25 (weight ratio solution/acrylonitrile

82.5/17.5), in a first PFR reactor equipped with a stirrer and temperature regulation system, with a thermal profile of the reactor increasing from 112°C to 120°C, where the pre-polymerization is effected with grafting 5 and phase inversion.

48 g of the transfer agent n-dodecylmercaptan (NDM) are added to the mixture leaving the first reactor which is then transferred to a second PFR reactor also equipped with a stirrer and temperature regulation system, with a 10 thermal profile of the reactor increasing from 150°C to 165°C.

The mixture obtained is fed to a devolatilizer operating under vacuum at a temperature of 235°C in order to crosslink the rubber and remove the unreacted monomers 15 and solvent from the polymer. The molten polymer thus obtained is granulated so as to obtain the end-product whose characteristics are indicated in Table 1.

Example 5

3.2 kg of linear polybutadiene (i), having a solution viscosity at 5% in styrene (SM) = 44 CPS, 0.4 kg of 20 radial polybutadiene, having a solution viscosity at 5% in styrene (SM) = 209 CPS, forming a mixture (iv), having a solution viscosity at 5% in styrene (SM) = 65 CPS, 20 g of antioxidant ANOX PP 18 in 21.8 kg of styrene monomer 25 and 7.6 kg of ethylbenzene, are dissolved in a 60-litre

batch-type autoclave, equipped with a temperature regulator and stirring system, stirring for 5 hours at 85°C. 12.4 g of initiator 1,1-di(tertbutylperoxy)cyclohexane (Tx22E50) are then added.

5 The solution thus obtained is fed, after mixing under heat (at a temperature of 60°C) with a feed of acrylonitrile (weight ratio solution/acrylonitrile 82.5/17.5), in a first PFR reactor equipped with a stirrer and temperature regulation system, with a thermal 10 profile of the reactor increasing from 112°C to 120°C, where the pre-polymerization is effected with grafting and phase inversion.

48 g of the transfer agent n-dodecylmercaptan (NDM) are added to the mixture leaving the first reactor which 15 is then transferred to a second PFR reactor also equipped with a stirrer and temperature regulation system, with a thermal profile of the reactor increasing from 150°C to 165°C.

The mixture obtained is fed to a devolatilizer operating under vacuum at a temperature of 235°C in order to 20 crosslink the rubber and remove the unreacted monomers and solvent from the polymer. The molten polymer thus obtained is granulated so as to obtain the end-product whose characteristics are indicated in Table 1.

Reference example 6

3.6 kg of polybutadiene SOL B 183 (modified polybutadiene containing 10% by weight of styrene, produced by Polimeri Europa) (solution viscosity at 5% in styrene (SM) = 30 CPs), 20 g of antioxidant ANOX PP 18 in 21.8 kg of styrene monomer and 7.6 kg of ethylbenzene, are dissolved in a 60-litre batch-type autoclave, equipped with a temperature regulator and stirring system, stirring for 5 hours at 85°C. 12.4 g of initiator 1,1-di(tertbutylperoxy)cyclohexane (Tx22E50) are then added.

The solution thus obtained is fed, after mixing under heat (at a temperature of 60°C) with a feed of acrylonitrile (weight ratio solution/acrylonitrile 82.5/17.5), into a first PFR reactor equipped with a stirrer and temperature regulation system, with a thermal profile of the reactor increasing from 112°C to 120°C, where the pre-polymerization is effected with grafting and phase inversion.

48 g of the transfer agent n-dodecylmercaptan (NDM) are added to the mixture leaving the first reactor which is then transferred to a second PFR reactor also equipped with a stirrer and temperature regulation system, with a thermal profile of the reactor increasing from 150°C to 165°C.

The mixture obtained is fed to a devolatilizer oper-

ating under vacuum at a temperature of 235°C in order to crosslink the rubber and remove the unreacted monomers and solvent from the polymer. The molten polymer thus obtained is granulated so as to obtain the end-product 5 whose characteristics are indicated in Table 1.

Example 7 (comparative)

3.6 kg of polybutadiene INTENE P30 (four-arm star polybutadiene, produced by Polimeri Europa) (solution viscosity at 5% in styrene (SM) = 45 CPs), 20 g of anti-10 oxidant ANOX PP 18 in 21.8 kg of styrene monomer and 7.6 kg of ethylbenzene, are dissolved in a 60-litre batch-type autoclave, equipped with a temperature regulator and stirring system, stirring for 5 hours at 85°C. 12.4 g of initiator 1,1-di(terbutylperoxy)cyclohexane (Tx22E50) are 15 then added.

The solution thus obtained is fed, after mixing under heat (at a temperature of 60°C) with a feed of acrylonitrile (weight ratio solution/acrylonitrile 82.5/17.5), into a first PFR reactor equipped with a 20 stirrer and temperature regulation system, with a thermal profile of the reactor increasing from 112°C to 120°C, where the pre-polymerization is effected with grafting and phase inversion.

48 g of the transfer agent n-dodecylmercaptan (NDM) 25 are added to the mixture leaving the first reactor which

is then transferred to a second PFR reactor also equipped with a stirrer and temperature regulation system, with a thermal profile of the reactor increasing from 150°C to 165°C.

5 The mixture obtained is fed to a devolatilizer operating under vacuum at a temperature of 235°C in order to crosslink the rubber and remove the unreacted monomers and solvent from the polymer. The molten polymer thus obtained is granulated so as to obtain the end-product
10 whose characteristics are indicated in Table 1.

Example 8 (comparative)

3.6 kg of partially radial polybutadiene (II) (with a content of branched end groups of 25% by weight), having a solution viscosity at 5% in styrene (SM) = 65 CPS,
15 20 g of antioxidant ANOX PP 18 in 21.8 kg of styrene monomer and 7.6 kg of ethylbenzene, are dissolved in a 60-litre batch-type autoclave, equipped with a temperature regulator and stirring system, stirring for 5 hours at 85°C. 12.4 g of initiator 1,1-di(terbutylperoxy)cyclohexane (Tx22E50) are then added.
20

The solution thus obtained is fed, after mixing under heat (at a temperature of 60°C) with a feed of acrylonitrile (weight ratio solution/acrylonitrile 82.5/17.5), into a first PFR reactor equipped with a
25 stirrer and temperature regulation system, with a thermal

profile of the reactor increasing from 112°C to 120°C, where the pre-polymerization is effected with grafting and phase inversion.

48 g of the transfer agent n-dodecylmercaptan (NDM) 5 are added to the mixture leaving the first reactor which is then transferred to a second PFR reactor also equipped with a stirrer and temperature regulation system, with a thermal profile of the reactor increasing from 150°C to 165°C.

10 The mixture obtained is fed to a devolatilizer operating under vacuum at a temperature of 235°C in order to crosslink the rubber and remove the unreacted monomers and solvent from the polymer. The molten polymer thus obtained is granulated so as to obtain the end-product 15 whose characteristics are indicated in Table 1.

Example 9 (comparative)

2.7 kg of linear polybutadiene (i), having a solution viscosity at 5% in styrene (SM) = 44 CPS, 0.9 kg of radial polybutadiene, having a solution viscosity at 5% 20 in styrene (SM) = 209 CPS, forming a mixture (IV), having a solution viscosity at 5% in styrene (SM) = 85 CPS, 20 g of antioxidant ANOX PP 18 in 21.8 kg of styrene monomer and 7.6 kg of ethylbenzene, are dissolved in a 60-litre batch-type autoclave, equipped with a temperature regulator and stirring system, stirring for 5 hours at 85°C.

12.4 g of initiator 1,1-di(tertbutylperoxy)cyclohexane (Tx22E50) are then added.

The solution thus obtained is fed, after mixing under heat (at a temperature of 60°C) with a feed of acrylonitrile (weight ratio solution/acrylonitrile 5 82.5/17.5), in a first PFR reactor equipped with a stirrer and temperature regulation system, with a thermal profile of the reactor increasing from 112°C to 120°C, where the pre-polymerization is effected with grafting 10 and phase inversion.

48 g of the transfer agent n-dodecylmercaptan (NDM) are added to the mixture leaving the first reactor which is then transferred to a second PFR reactor also equipped with a stirrer and temperature regulation system, with a 15 thermal profile of the reactor increasing from 150°C to 165°C.

The mixture obtained is fed to a devolatilizer operating under vacuum at a temperature of 235°C in order to crosslink the rubber and remove the unreacted monomers 20 and solvent from the polymer. The molten polymer thus obtained is granulated so as to obtain the end-product whose characteristics are indicated in Table 1.

Example 10 (comparative)

3.6 kg of polybutadiene INTENE 40 (linear polybutadiene, produced by Polimeri Europa) (solution viscosity 25

at 5% in styrene (SM) = 95 CPs), 20 g of antioxidant ANOX PP 18 in 21.8 kg of styrene monomer and 7.6 kg of ethylbenzene, are dissolved in a 60-litre batch-type autoclave, equipped with a temperature regulator and stirring system, stirring for 5 hours at 85°C. 12.4 g of initiator 1,1-di(terbutylperoxy)cyclohexane (Tx22E50) are then added.

The solution thus obtained is fed, after mixing under heat (at a temperature of 60°C) with a feed of acrylonitrile (weight ratio solution/acrylonitrile 10 82.5/17.5), into a first PFR reactor equipped with a stirrer and temperature regulation system, with a thermal profile of the reactor increasing from 112°C to 120°C, where the pre-polymerization is effected with grafting 15 and phase inversion.

48 g of the transfer agent n-dodecylmercaptan (NDM) are added to the mixture leaving the first reactor which is then transferred to a second PFR reactor also equipped with a stirrer and temperature regulation system, with a 20 thermal profile of the reactor increasing from 150°C to 165°C.

The mixture obtained is fed to a devolatilizer operating under vacuum at a temperature of 235°C in order to crosslink the rubber and remove the unreacted monomers 25 and solvent from the polymer. The molten polymer thus ob-

tained is granulated so as to obtain the end-product whose characteristics are indicated in Table 1.

TABLE 1

	<i>Example 1</i>	<i>Example 2</i>	<i>Example 3</i>	<i>Example 4</i>	<i>Example 5</i>
PBDE characteristics					
ABS characteristics					
Rubber type	(i)	(ii)	(iii)	(iv)	(iv)
Rubber viscosity [cps]	44	45	42	59	65
Rubber in the final polymer [%]	11.9	12.1	11.8	11.9	12.1
Bound acrylonitrile [%]	19.0	19.1	19.2	19.1	19.1
GPC ABS (Dalton)	130,000	129,500	130,100	129,700	130,400
Mw/Mn	2.67	2.71	2.69	2.74	2.70
Swelling index	10.5	10.4	10.9	11.0	11.0
Crosslinked Gel [%]	21.9	22.1	22.0	22.1	22.5
Particle Num. Diam. D[4,3] [μm]	0.51	0.54	0.54	0.55	0.60
Gloss 20°	70	60	60	60	59
Gloss 60°	95	92	91	91	89
Melt Index [200 °C-5 Kg]	15.1	15.5	14.8	14.1	14.2
Vicat ISO 306 [5 Kg-50 °C/h]	103.0	103.2	102.9	103.1	103.1
Izod ISO 23 °C [kJ/m ²]	15.8	15.5	15.9	16.2	16.0
Charpy 23 °C [kJ/m ²]	15.5	15.1	15.7	15.5	15.3
Tensile ISO 527					
Stress at break [MPa]	46.9	47.5	47.0	46.8	46.5
Tensile Stress [MPa]	34.2	33.0	33.5	33.4	33.8
Elongation at break [%]	15.5	16.4	16.0	15.9	16.2
Tensile Modulus [MPa]	2360	2370	2310	2320	2290
Flexural properties ISO 178					
Maximum stress [MPa]	74.6	74.4	74.1	73.9	72.9
Tensile modulus [MPa]	2340	2250	2280	2210	2270
Falling weight					
2 mm test samples Total energy	18.6	19.1	20.1	19.8	20.2
3mm test samples Total energy	34.9	35.6	35.5	34.2	35.4

	<i>Example 6 (Reference)</i>	<i>Example 7 (Comparative)</i>	<i>Example 8 (Comparative)</i>	<i>Example 9 (Comparative)</i>	<i>Example 10 (Comparative)</i>
PBDE characteristics					
Rubber type	SOL B 183	INTENE P30	(II)	(IV)	INTENE 40
Rubber viscosity [cps]	30	45	65	85	95
Rubber in the final polymer [%]	12.6	12.5	12.1	12.7	11.8
Bound acrylonitrile [%]	19.2	19.0	19.3	19.2	19.1
GPC ABS (Dalton)	130600	129700	130800	130000	129800
Mw/Mn	2.78	2.81	2.68	2.65	2.71
Swelling index	10.9	10.5	11.1	10.8	10.4
Crosslinked Gel [%]	22.4	26.0	24.1	25.1	32.2
Particle Num. Diam. <i>D[4,3]</i> [μm]	0.6	0.95	0.84	0.90	1.8
Gloss 20°	59	30	41	37	25
Gloss 60°	89	68	80	75	51
Melt Index [200 °C-5 kg]	13.4	12.1	12.8	12.3	11.8
Vicat ISO 306 [5 kg-50 °C/h]	102.7	102.4	102.9	102.1	102.9
Izod ISO 23 °C [kJ/m ²]	16.1	18.0	17.0	16.4	12.1
Charpy 23 °C [kJ/m ²]	15.3	17.4	16.8	16.0	11.8
ABS characteristics					
Stress at break [MPa]	46.2	45.0	44.2	45.1	44.2
Tensile Stress [MPa]	33.9	32.2	31.8	32.0	31.0
Elongation at break [%]	16.1	33.0	34.1	32.5	32.1
Tensile Modulus [MPa]	2250	2180	2100	2100	2120
Tensile ISO 527					
Maximum stress [MPa]	72.5	71.2	70.5	73.0	71.1
Tensile modulus [MPa]	2190	2120	2100	2090	2110
Falling weight					
2 mm test samples Total energy [J]	20	32	30	31	31
3mm test samples Total energy [J]	35.1	67	64	69	65

CLAIMS

1. Rubber-reinforced vinyl aromatic (co)polymer comprising a polymeric matrix and a rubber phase of a diene rubber dispersed and/or grafted in the polymeric matrix wherein said rubber phase is selected between at least one of:
 - (i) a linear diene rubber having a solution viscosity lower than 70 cPs;
 - (ii) a partially radial diene rubber, having a solution viscosity lower than 70 cPs, wherein up to 15% by weight, preferably between 1 and 12%, of the polymeric chains end with a quantity of tetrafunctional coupling agent such as to generate a radial terminal structure of linear diene rubber chains;
 - (iii) a three-branches diene rubber, having a solution viscosity lower than 70 cPs, that is a linear diene rubber coupled with a trifunctional agent;
 - (iv) a mixture of linear diene rubbers (i) and radial diene rubbers (v) with a maximum ratio between one another (i)/(v) comprised between 99.5/0.5 and 85/15, having a solution viscosity lower than 70 cPs.
2. Vinyl aromatic (co)polymer according to claim 1, wherein the diene rubber is made up of a polymer of a 1,3-conjugated diene containing from 4 to 6 carbon atoms.

3. Vinyl aromatic (co)polymer according to claim 2, wherein the diene rubber is polybutadiene having:
a solution viscosity comprised between 40 and 70 cPs, preferably between 40 and 60 cPs, measured in a solution thereof at 5% by weight in styrene at 25°C;
a content of 1,2 vinyl comprised between 5 and 35, preferably between 7 and 14% by weight;
a content of 1,4-cis comprised between 20 and 85, preferably between 25 and 45% by weight; and
10 a molecular structure among those described in (i), (ii), (iii) or (iv).

4. Vinyl aromatic copolymer according to anyone of the previous claims, comprising a quantity of acrylic comonomer ranging from 5 to 45% by weight.
15 5. Vinyl aromatic (co)polymer according to any of the previous claims, wherein the amount of diene rubber (i), (ii), (iii) or (iv) is comprised from 4 to 30% by weight.

6. Process for the preparation of the rubber-reinforced vinyl aromatic (co)polymer according to anyone of claims from 1 to 5, comprising polymerising by means of bulk polymerisation, solution, emulsion and bulk suspension at least one vinyl aromatic monomer in the presence of at least one rubber chosen from the 25 group (i)-(iv).

7. Use of the rubber-reinforced vinyl aromatic (co)polymer according to anyone of claims from 1 to 5, for preparing bodies formed with a gloss at 60° higher than 85.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2009/008861

A. CLASSIFICATION OF SUBJECT MATTER					
INV.	C08F279/02	C08F279/04	C08L51/04	C08L55/02	C08F2/00

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)
C08F . C08L

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)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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

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"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	Date of mailing of the international search report
10 February 2010	16/02/2010
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Hammond, Andrew

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Information on patent family members

International application No

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