

**PROCESS FOR THE MANUFACTURE OF A COMPOSITION
COMPRISING A VINYLAROMATIC POLYMER AND A RUBBER**

The present invention relates to a process
5 for the manufacture of a composition comprising a
vinylaromatic polymer and a rubber.

Compositions comprising a vinylaromatic
polymer and a rubber should exhibit properties such as
good impact resistance, a gloss suited to the desired
10 application and a melt index suited to the conversion
technique to be used for the composition. It is useful
to have available means of influencing these various
properties so as to control them better and to adapt
them according to the proposed use of the composition.

15 It is known that compositions comprising a
rubber in the form of nodules are generally more
resistant to impact when the distribution of the sizes
of the rubber nodules is broad, indeed bimodal. Various
processes have been proposed for producing this type of
20 material. European Patent EP 48389 teaches that a high-
impact polystyrene with a bimodal distribution of
nodules can be obtained by independent manufacture of
two compositions each containing a specific population
of nodules and then by mixing these two compositions.
25 European Patent Application EP 418042 teaches that such
a composition can be obtained using a single
polymerization reactor, using a polybutadiene

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☒	Claim(s)	: paged ¹¹ to paged ¹⁷
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exhibiting a bimodal molecular mass distribution.

International Patent Application WO 94/11412 teaches that polystyrene with a polydispersity of less than 2 and with a weight-average molecular mass of less than 80,000 can be obtained when the polymerization of styrene is carried out in the presence of a stable free radical and of a polymerization initiator and in the absence of rubber, the molar ratio of the stable free radical to the polymerization initiator being between 0.4 and 2.5, which corresponds to a concentration of stable free radical initiator which is markedly greater than 0.1 % by weight in the polymerization mixture and more generally in the region of 1 % by weight in the polymerization mixture.

The present invention provides a process for the manufacture of a composition comprising a vinylaromatic polymer and a rubber, which process comprises a polymerization stage in the presence of at least one vinylaromatic monomer and at least one rubber, there being a stable free radical present during the polymerization stage.

The presence of a stable free radical in the polymerization mixture, even in a very small amount, for example, of less than 0.1 % by weight, makes it possible markedly to influence the size of the rubber nodules in the final composition by generally increasing the mean size of the latter and by widening the size distribution of these nodules. Compositions

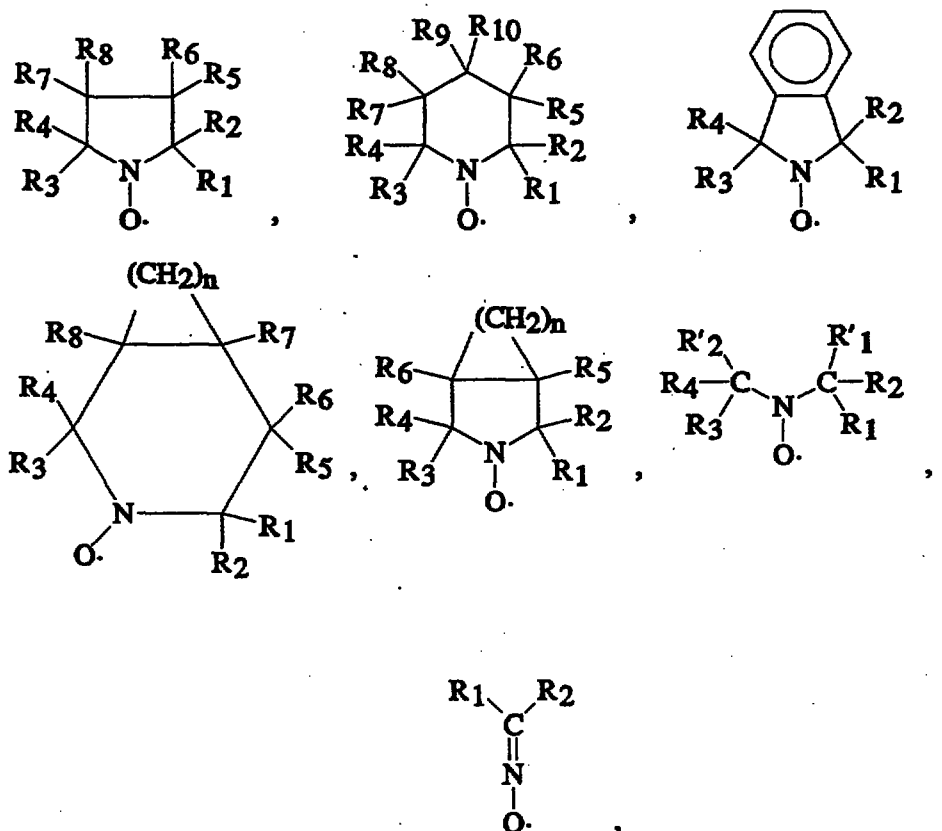


exhibiting markedly bimodal nodule size distributions can even be obtained.

A stable free radical is not to be confused with the free radicals whose lifetime is fleeting (a few milliseconds), such as free radicals resulting from usual polymerization initiators, such as peroxides, hydroperoxides and initiators of azo type. Free radicals which are polymerization initiators have a tendency to accelerate polymerization. By contrast, stable free radicals generally have a tendency to slow down polymerization. It may generally be said that a free radical is stable within the meaning of the present invention if it is not a polymerization initiator and if, under the conditions of use of the present invention, the mean lifetime of the radical is at least five minutes. During this mean lifetime, the stable free radical continually alternates between the radical state and the state of being a group bonded via a covalent bond to a polymer chain. It is preferable for the stable free radical to exhibit good stability throughout the duration of its use within the context of the present invention. Generally, a stable free radical can be isolated in the radical state at room temperature.

Stable free radicals include compounds which act as radical polymerization inhibitors, the stable nitroxide radicals, which comprise the $=N-O\cdot$ group,

such as the radicals represented by the following formulae:



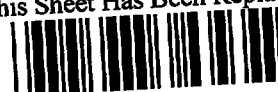
in which each of R_1 , R_2 , R_3 , R_4 , R'_1 and R'_2 , which can be identical or different, represents a halogen atom, such as chlorine, bromine or iodine, a saturated or unsaturated, linear, branched or cyclic hydrocarbon group, such as an alkyl or phenyl radical, or an ester group $-\text{COOR}$ or an alkoxy group $-\text{OR}$, or a phosphonate group $-\text{PO}(\text{OR})_2$, or a polymer chain which can be, for example, a poly(methyl methacrylate) chain, a polybutadiene chain, a polyolefin chain, such as a polyethylene or polypropylene chain, but which is preferably a polystyrene chain, and in which each of R_5 ,

R_6 , R_7 , R_8 , R_9 and R_{10} , which can be identical or different, can be chosen from the groups R_1 , R_2 , R_3 , R_4 , R'_1 and R'_2 above, or can represent a hydrogen atom, a hydroxyl group $-OH$ or an acid group such as $-COOH$ or $-PO(OH)_2$ or $-SO_3H$.

In particular, the stable free radical can be 2,2,5,5-tetramethyl-1-pyrrolidinyloxy, marketed under the tradename Proxyl, or 2,2,6,6-tetramethyl-1-piperidinyloxy, generally marketed under the name Tempo.

It would not be departing from the context of the present invention to introduce, in place of a stable free radical, an initiator or generator of a stable free radical under the conditions of polymerization, for example, a product which would not be a stable free radical at room temperature but which would be a source of a stable free radical as soon as the mixture intended to be polymerized was heated. Such compounds, containing $=N-O-X$ groups, have been described in US Patent 4,581,429. Such compounds generate, by heating at the usual polymerization temperatures, stable free radicals containing an $=N-O\cdot$ group.

The stable free radical is preferably present in the polymerization mixture in a proportion of from 1 to 1000 ppm and more preferably in a proportion of from 10 to 250 ppm, with respect to the total amount of vinylaromatic monomer. In the range of from 1 to 1000



ppm, when the concentration of stable free radical is increased, size distribution of the nodules tends to widen and to change from monomodal to bimodal, and the fraction, by volume, of rubbery phase in the final composition tends to increase. A distribution is said to be bimodal when a graph representing nodule amount as a function of nodule diameter exhibits two maxima. In the range of from 1 to 1000 ppm, when the concentration of stable free radical is increased, the impact strength of the material generally passes through a maximum and the melt index of the final composition tends to increase. This behaviour is noteworthy because, according to the prior art, these two properties, impact strength and fluidity, generally develop in opposite directions. This characteristic makes the composition obtained by the process according to the invention an ideal composition for injection moulding processes intended for the production of components which have to possess good impact strength.

The amount of stable free radical for which

- the distribution changes from monomodal to bimodal, or
- the impact strength of the material is maximum, or
- the best set of properties, impact strength and fluidity, taking into account the proposed use of the composition is obtained,



can depend on the nature and on the amount of the ingredients present in the polymerization and on the polymerization conditions. By virtue of the present invention, for given polymerization conditions, the
5 person skilled in the art can find, by routine tests, the concentration of stable free radical at which the distribution becomes bimodal and the concentration of stable free radical at which the impact strength of the material and its fluidity are optimised.

10 Except for the presence of the stable free radical, the other ingredients used, and the conditions of synthesis, may be those commonly used for the manufacture of compositions comprising a vinylaromatic polymer and a rubber.

15 The process according to the invention, which can operate continuously or in batch mode, involves a polymerization stage in which the mixture comprises at least one vinylaromatic monomer, at least one rubber, at least one stable free radical and, if appropriate,
20 at least one solvent.

By way of example, the mixture intended to be polymerized can comprise:

- from 2 to 35 parts by weight of rubber,
and
- 25 • from 0 to 15 parts by weight of solvent,
per 100 parts by weight of vinylaromatic monomer.

A vinylaromatic monomer is, for example, styrene, styrene substituted on the vinyl group by an alkyl group, such as alpha-methylstyrene or alpha-ethylstyrene, styrene substituted on the ring by an alkyl group, such as ortho-vinyltoluene, para-vinyltoluene, ortho-ethylstyrene or 2,4-dimethylstyrene, styrene substituted on the ring by a halogen, such as for example 2,4-dichlorostyrene, styrene substituted both by halogen and an alkyl group, such as 2-chloro-4-methylstyrene, and vinylanthracene. Styrene is a preferred vinylaromatic monomer.

The polymerization mixture can furthermore comprise at least one monomer which is copolymerizable with the vinylaromatic monomer(s), such as, for example, at least one acrylic or methacrylic monomer.

The rubber may be one commonly used to improve the impact properties of vinylaromatic polymers. They are usually conjugated polydienes such as polybutadiene or polyisoprene or styrene-butadiene copolymers of elastomer type also known as "SBR" ("styrene-butadiene rubber") rubber.

The polymerization mixture can also comprise at least one organic solvent. The latter is chosen so that it does not boil under the polymerization conditions and so that it is miscible with the vinylaromatic monomer and the vinylaromatic polymer which derives therefrom. Use may be made of alicyclic hydrocarbons such as cyclohexane or, preferably,

aromatic hydrocarbons such as toluene, benzene, ethylbenzene or xylene.

At least one polymerization adjuvant or initiator usual in this type of preparation can be added to the polymerization mixture, before or during polymerization. These adjuvants can be plasticizers, such as mineral oils, butyl stearate or dioctyl phthalate, or stabilizers, such as antioxidants which can be phenol substituted by an alkyl group, such as di-tert-butyl-para-cresol, or phosphites, such as trinonylphenyl phosphite.

A plasticizer can be introduced in an amount such that it is present in a proportion of from 0 to 6 % by weight in the composition finally synthesized.

A stabilizer can be introduced into the polymerization mixture in a proportion of from 0 to 3000 ppm.

The polymerization reaction can be thermally initiated, without either a polymerization initiator or a catalyst, or can be initiated by a polymerization initiator. If the polymerization is thermally initiated, it can be carried out at a temperature of from 100 to 200°C and preferably of from 110 to 160°C.

If the polymerization is initiated by a polymerization initiator, it can be carried out at a temperature of from 50 to 200°C and preferably of from 90 to 160°C. The polymerization initiator can be chosen from organic peroxides and hydroperoxides, such as

dibenzoyl peroxide, tert-butyl peroxybenzoate or 1,1-bis(tert-butylperoxy)cyclohexane, or azo compounds, such as azobisisobutyronitrile.

The polymerization initiator can be present
5 in a proportion of from 50 to 2000 ppm on the basis of the vinylaromatic monomer or monomers introduced.

During polymerization, the well-known
phenomenon of phase inversion takes place, resulting in the formation of rubber nodules dispersed in a matrix
10 of vinylaromatic polymer or copolymer. During polymerization, stirring must be sufficient for the dispersion of the rubber nodules to be uniform.

After polymerization, it is advisable to remove volatile species, such as unreacted monomers and
15 any organic solvent. This can be carried out by conventional techniques such as by a devolatilizer operating while hot and under vacuum.

The final rubber and vinylaromatic polymer or copolymer content of the composition according to the
20 invention depends on the degree of progression of the polymerization before removal of the volatile species. In fact, if the degree of progression of the polymerization is low, removal of the volatile species will result in the removal of a large amount of
25 vinylaromatic monomer and the final rubber content of the composition will be higher. To avoid excessively high crosslinking of the rubber, it is preferable not to continue the polymerization to 100 % of the



vinylaromatic monomers.

The progression of the polymerization can be monitored by withdrawing samples during the polymerization stage and by determining the level of solid in the samples. Level of solid means the percentage by weight of solid obtained after evaporation under a vacuum of 25 millibars for approximately 20 minutes at 200°C of the samples withdrawn with respect to the initial weight of the sample withdrawn. The polymerization can be continued, for example, until a level of solid of between 60 and 80 % by weight is obtained.

It is preferable to adjust the amounts of ingredients introduced and the manufacturing conditions so that the final composition contains from 2 to 25 % and more preferably from 4 to 15 % of rubber.

The invention is further illustrated, by way of example, in the following Examples.

In the Examples, the structure and properties of the compositions obtained were determined by the following techniques:

- Izod impact strength on an unnotched bar: 179/1D standard,
- molecular mass of the polystyrene: the polystyrene is extracted from the high-impact polystyrene with methyl ethyl ketone and its molecular mass is measured by gel permeation chromatography (GPC). In Table 1, Mw represents the weight-average

molecular mass of the polystyrene, M_n represents the number-average molecular mass of the polystyrene and M_w/M_n represents the ratio of the weight-average molecular mass to the number-average molecular mass of the polystyrene,

· level of polybutadiene in the compositions:
NF standard T 51-007, .

· melt index: ISO standard 1133,
· mean size of the rubber nodules and
10 distribution of the sizes of the nodules: sedimentary particle size determination (capa 700), after dissolving in methyl ethyl ketone.

In Table 1, "mono" means that the distribution of the sizes of the nodules is monomodal.
15 In Table 1, "bi" means that the distribution of the sizes of the nodules is bimodal.

Example 1 (comparative)

7360 g of styrene, 160 g of a plasticizing oil of Primol 352 trademark marketed by the company
20 Esso, 8 g of an antioxidant of Irganox 1076 trademark marketed by the company Ciba and 480 g of a polybutadiene of BR 1202 G trademark marketed by the company Shell, the last product exhibiting a weight-average molecular mass of 287,000 and a viscosity at
25 25°C at 5 % by weight in styrene of 160 centipoises, are introduced at room temperature into a 15-litre stainless steel reactor equipped with a stirrer system and a temperature control.

After the polybutadiene has completely dissolved, the solution is thermally polymerized, the temperature being raised to 130°C in 30 min, the reaction mixture then being left for 1 hour and
5 30 minutes at this temperature, the temperature then being raised from 130 to 150°C in 15 minutes and the reaction mixture being left for 55 minutes at 150°C. The contents of the reactor are then transferred into a devolatilizer at 210°C under a vacuum of 25 millibars
10 for approximately 10 minutes. The properties of the composition thus obtained are shown in Table 1. The distribution of the sizes of the nodules is represented in Figure 1, expressed as % by volume of nodules as a function of the diameter of these nodules.

15 Example 2

The procedure is as in Example 1, except that 0.8 g of 2,2,6,6-tetramethyl-1-piperidinyloxy (Tempo) is added just before heating. The properties of the composition thus obtained are shown in Table 1. The
20 distribution of the sizes of the nodules (% by volume) is represented in Figure 2.

Example 3

The procedure is as in Example 2, except that 2.4 g of Tempo are introduced in place of the 0.8 g.

25 The properties of the composition thus obtained are shown in Table 1. The distribution of the sizes of the nodules (% by volume) is represented in Figure 3.

Example 4 (Comparative)

The procedure is as in Example 1 but with the following amounts of the ingredients:

	• styrene:	7600 g
5	• Plasticizing oil Primol 352:	160 g
	• Antioxidant Irganox 1076:	8 g
	• Polybutadiene BR 1202 G	240 g

The properties of the composition thus obtained are shown in Table 1. The distribution of the sizes of the nodules (% by volume) is represented in Figure 4.

Example 5

The procedure is as in Example 4, except that 0.4 g of Tempo is introduced just before heating. The properties of the composition thus obtained are shown in Table 1. The distribution of the sizes of the nodules (% by volume) is represented in Figure 5.

Example 6

The procedure is as in Example 5, except that 0.8 g is introduced in place of the 0.4 g of Tempo. The properties of the composition thus obtained are shown in Table 1. The distribution of the sizes of the nodules (% by volume) is represented in Figure 6.

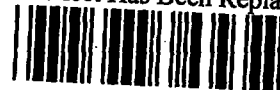
Example 7

The procedure is as in Example 5, except that 1.2 g are introduced in place of the 0.4 g of Tempo. The properties of the composition thus obtained are shown in Table 1. The distribution of the sizes of the nodules (% by volume) is represented in Figure 7.

TABLE 1

	UNIT	EXAMPLE 1 (comp.)	EXAMPLE 2	EXAMPLE 3	EXAMPLE 4 (comp.)	EXAMPLE 5	EXAMPLE 6	EXAMPLE 7
Amount of Tempo in the polymerization with respect to the amount of styrene charged	ppm	0	109	326	0	53	105	158
Level of polybutadiene	% by weight	7.3	7.6	7.7	4.3	4.3	4.1	4.3
Mean size of the nodules	μ m	1.07	1.46	3.8	0.84	1.07	1.27	1.37
Distribution of the sizes of the final nodules		Mono.	Bi.	Bi.	Mono.	Mono.	Mono.	Bi.
Mw		261,000	215,000	151,000	230,000	211,500	203,000	197,000
Mn		110,000	87,000	73,000	89,000	82,000	81,000	79,500
Mw/Mn		2.4	2.4	2.1	2.6	2.6	2.5	2.5
Melt index	g/ 10 min	3.5	7	40	4.5	7.5	8.5	10.5
Ixod impact strength	kJ/m ²	50	>70	<10	31	48	61	>70

Properties
of the
final
composition

CLAIMS

1. Process for the manufacture of a composition comprising a vinylaromatic polymer and a rubber, which process comprises a polymerization stage in the presence of at least one vinylaromatic monomer and at least one rubber, there being a stable free radical present during the polymerization stage.
2. Process according to Claim 1, wherein the stable free radical is present in the polymerization mixture in a proportion of from 1 to 1000 ppm with respect to the vinylaromatic monomer.
3. Process according to Claim 2, wherein the stable free radical is present in the polymerization mixture in a proportion of from 10 to 250 ppm with respect to the vinylaromatic monomer.
4. Process according to any one of Claims 1 to 3, wherein the stable free radical comprises an =N-O· group.
5. Process according to any one of Claims 1 to 4, wherein the mixture of the polymerization stage comprises:
from 2 to 35 parts by weight of rubber, and
from 0 to 15 parts by weight of solvent, per
100 parts by weight of vinylaromatic monomer.
6. Process according to Claim 5, wherein the solvent is ethylbenzene.
7. Process according to any one of Claims 1 to 6, wherein the mixture of the polymerization stage



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further comprises a polymerization initiator.

8. Process according to Claim 7, wherein the polymerization initiator is present in a proportion of from 50 to 2000 ppm with respect to the vinylaromatic monomer.

9. Process according to Claim 7 or 8, wherein the polymerization stage is carried out at a temperature of from 50 to 200°C.

10. Process according to claim 9, wherein the temperature is from 90 to 160°C.

11. Process according to any one of Claims 1 to 6, wherein the polymerization stage is carried out in the absence of polymerization initiator and at a temperature of from 100 to 200°C.

12. Process according to claim 11, wherein the temperature is from 110° to 160°C.

13. Process according to any one of Claims 1 to 12, wherein the rubber is a polybutadiene.

14. Process according to any one of Claims 1 to 14, wherein the vinylaromatic monomer is styrene.

15. Process according to any one of Claims 1 to 14, wherein the stable free radical is 2,2,6,6,-tetramethyl-1-piperidinyloxy.

16. Process according to Claim 1 substantially as described in any one of Examples 2, 3 and 5 to 7.

17. A polymer composition whenever prepared by a process as claimed in any one of Claims 1 to 16.

ABSTRACT

**PROCESS FOR THE MANUFACTURE OF A COMPOSITION
COMPRISING A VINYLAROMATIC POLYMER AND A RUBBER**

The present invention relates to a process
5 for the manufacture of a composition comprising a
vinylaromatic polymer and a rubber, which process
comprises a polymerization stage in the presence of at
least one vinylaromatic monomer and at least one
rubber, there being a stable free radical present
10 during the polymerization stage. The presence of a
stable free radical in the polymerization mixture makes
it possible to increase the melt index and to influence
the size of the rubber nodules in the final composition
by generally increasing the fraction, by volume, of
15 rubbery phase and by widening the distribution of the
size of these nodules. This is reflected by an
improvement both in the melt index and in the impact
strength of the final composition, which makes the
latter an ideal composition for injection moulding.

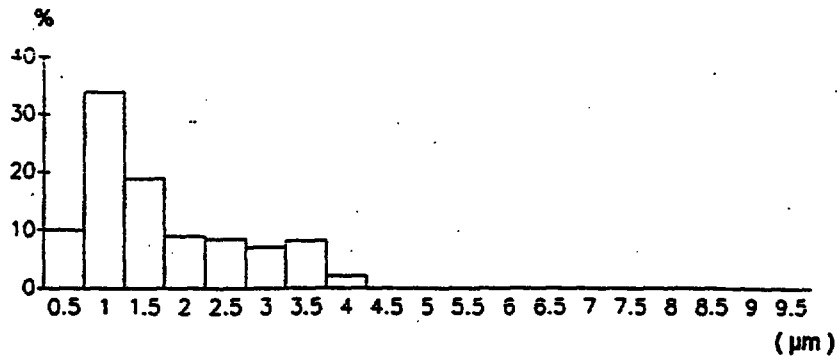


Figure 1

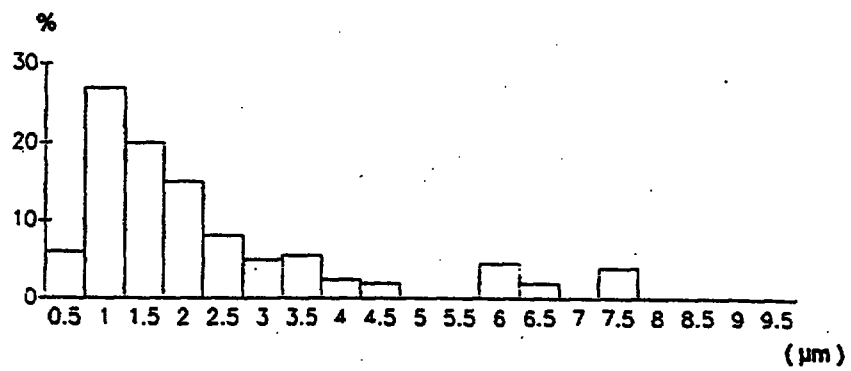


Figure 2

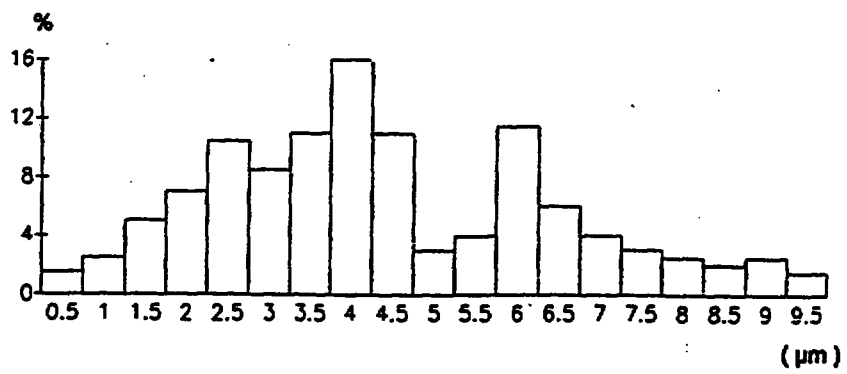


Figure 3

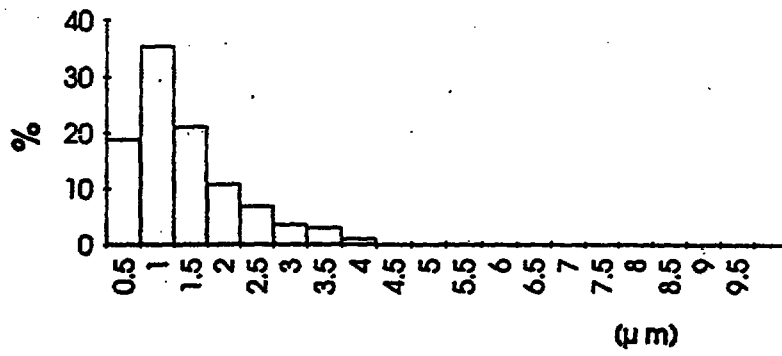


Figure 4

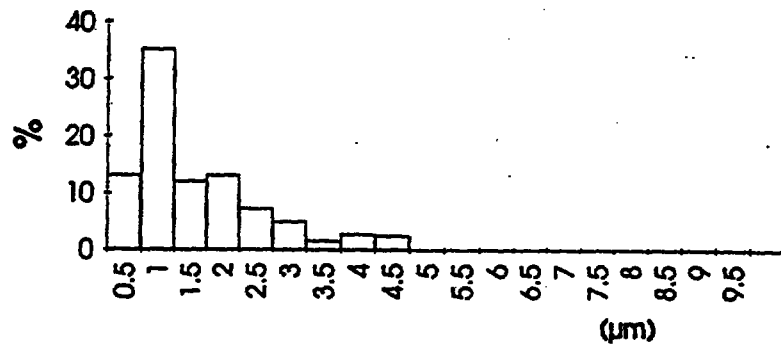


Figure 5

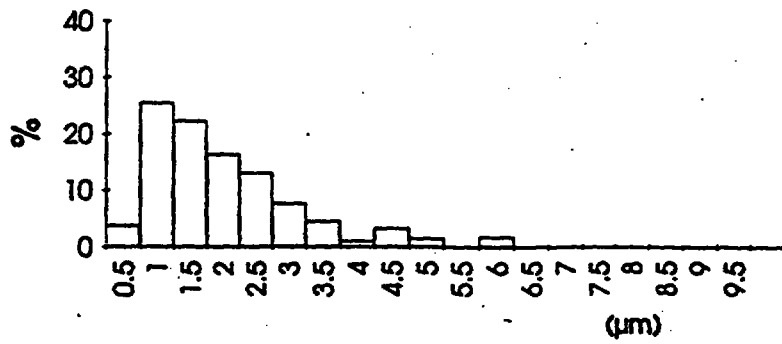


Figure 6

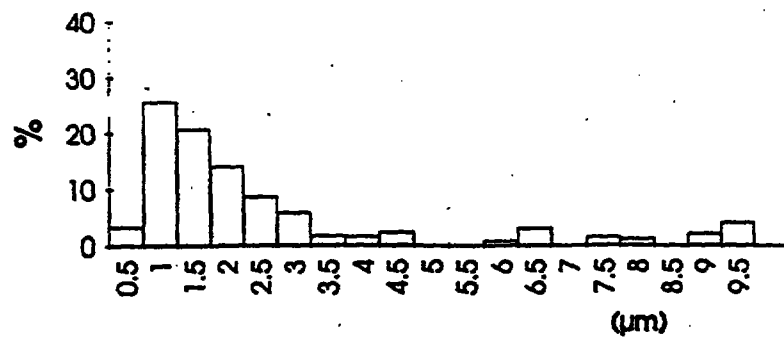


Figure 7

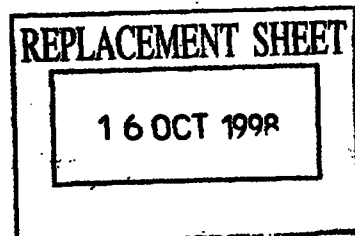
exhibiting a bimodal molecular mass distribution RECEIPT 11/10/98

International Patent Application WO 94/11412

teaches that polystyrene with a polydispersity of less than 2 and with a weight-average molecular mass of less than 80,000 can be obtained when the polymerization of styrene is carried out in the presence of a stable free radical and of a polymerization initiator and in the absence of rubber, the molar ratio of the stable free radical to the polymerization initiator being between 0.4 and 2.5, which corresponds to a concentration of stable free radical initiator which is markedly greater than 0.1% by weight in the polymerization mixture and more generally in the region of 1% by weight in the polymerization mixture.

The present invention provides a process for the manufacture of a composition comprising a vinylaromatic polymer or copolymer and a rubber, which process comprises a polymerization stage in the presence of at least one vinylaromatic monomer and at least one rubber, there being a stable free radical present during the polymerization stage in a proportion of at least 10ppm with respect to the vinylaromatic monomer.

The presence of a stable free radical in the polymerization mixture, even in a very small amount, for example, of less than 0.1% by weight, makes it possible markedly to influence the size of the rubber nodules in the final composition by generally increasing the mean size of the latter and by widening the size distribution of these nodules. Compositions

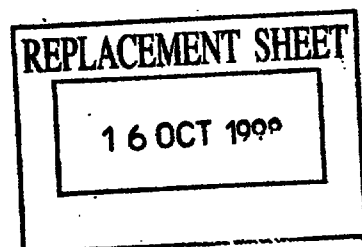


R₆, R₇, R₈, R₉ and R₁₀, which can be identical or different, can be chosen from the groups R₁, R₂, R₃, R₄, R'₁ and R'₂ above, or can represent a hydrogen atom, a hydroxyl group -OH or an acid group such as -COOH or -
5 PO(OH)₂ or -SO₃H.

In particular, the stable free radical can be 2,2,5,5-tetramethyl-1-pyrrolidinyloxy, marketed under the tradename Proxyl, or 2,2,6,6-tetramethyl-1-piperidinyloxy, generally marketed under the name Tempo.

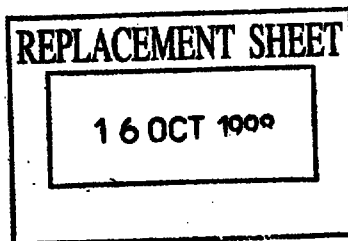
10 It would not be departing from the context of the present invention to introduce, in place of a stable free radical, an initiator or generator of a stable free radical under the conditions of polymerization, for example, a product which would not be a stable free
15 radical at room temperature but which would be a source of a stable free radical as soon as the mixture intended to be polymerized was heated. Such compounds, containing =N-O-X groups, have been described in US Patent 4,581,429. Such compounds generate, by heating at the
20 usual polymerization temperatures, stable free radicals containing an =N-O• group.

The stable free radical is preferably present in the polymerization mixture in a proportion of at most 1000 ppm and more preferably in a proportion of from 10
25 to 250 ppm, with respect to the total amount of vinylaromatic monomer. In the range of from 10 to 1000



ppm, when the concentration of stable free radical is increased, size distribution of the nodules tends to widen and to change from monomodal to bimodal, and the fraction, by volume, of rubbery phase in the final composition tends to increase. A distribution is said to be bimodal when a graph representing nodule amount as a function of nodule diameter exhibits two maxima. In the range of from 10 to 1000 ppm, when the concentration of stable free radical is increased, the impact strength of the material generally passes through a maximum and the melt index of the final composition tends to increase. This behaviour is noteworthy because, according to the prior art, these two properties, impact strength and fluidity, generally develop in opposite directions. This characteristic makes the composition obtained by the process according to the invention an ideal composition for injection moulding processes intended for the production of components which have to possess good impact strength. The amount of stable free radical for which

- the distribution changes from monomodal to bimodal, or
- the impact strength of the material is maximum, or
- the best set of properties, impact strength and fluidity, taking into account the proposed use of the composition is obtained,



CLAIMS



1. Process for the manufacture of a composition comprising a vinylaromatic polymer or copolymer and a rubber, which process comprises a polymerization stage in the presence of at least one vinylaromatic monomer and at least one rubber, there being a stable free radical present during the polymerization stage in a proportion of at least 10 ppm with respect to the vinylaromatic monomer.

2. Process according to Claim 1, wherein the stable free radical is present in the polymerization mixture in a proportion of at most 1000 ppm with respect to the vinylaromatic monomer.

3. Process according to Claim 1 or 2, wherein the stable free radical is present in the polymerization mixture in a proportion of from 10 to 250 ppm with respect to the vinylaromatic monomer.

4. Process according to any one of Claims 1 to 3, wherein the stable free radical comprises an =N-O• group.

5. Process according to any one of Claims 1 to 4, wherein the mixture of the polymerization stage comprises:

from 2 to 35 parts by weight of rubber, and from 0 to 15 parts by weight of solvent, per 100 parts by weight of vinylaromatic monomer.

6. Process according to Claim 5, wherein the solvent is ethylbenzene.

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7. Process according to any one of Claims 1 to 6, wherein the mixture of the polymerization stage further comprises a polymerization initiator.

8. Process according to Claim 7, wherein the polymerization initiator is present in the proportion of from 50 to 2000 ppm with respect to the vinylaromatic monomer.

9. Process according to Claim 7 or 8, wherein the polymerization stage is carried out at a temperature of from 50 to 200°C.

10. Process according to Claim 9, wherein the temperature is from 90 to 160°C.

11. Process according to any one of Claims 7 to 10, wherein the polymerization initiator is chosen from organic peroxides and hydroperoxides.

12. Process according to any one of Claims 7 to 11, wherein the initiator is tert-butyl peroxybenzoate or 1,1-bis (tert-butylperoxy) cyclohexane.

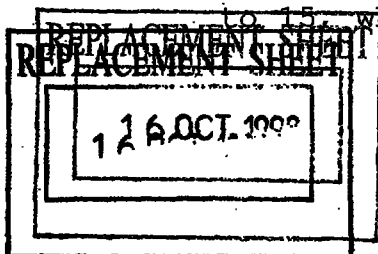
13. Process according to any one of Claims 1 to 6, wherein the polymerization stage is carried out in the absence of polymerization initiator and at a temperature of from 100 to 200°C.

14. Process according to Claim 13, wherein the temperature is from 110° to 160°C.

15. Process according to any one of Claims 1 to 14, wherein the rubber is a polybutadiene.

16. Process according to any one of Claims 1 to 15, wherein the vinylaromatic monomer is styrene.

17. Process according to any one of Claims 1





-18-

to 16, wherein the stable free radical is 2,2,6,6,-
tetramethyl-1-piperidinyloxy.

18. Process according to any one of the
preceding claims, wherein the composition comprises a
5 matrix of vinylaromatic polymer or copolymer in which
rubber nodules are dispersed, said nodules having a
widened size distribution in comparison with the
composition obtained with the same process carried out in
the absence of a stable free radical.

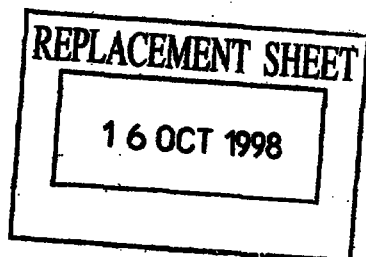
10 19. Process according to any one of the
preceding claims, wherein the rubber is in the form of
nodules whose size distribution is bimodal.

20. Process according to any one of the
preceding claims, wherein the composition comprises
15 between 2 and 25% by weight of rubber.

21. Process according to any one of the
preceding claims, wherein the composition comprises
between 4 and 15% by weight of rubber.

22. Process according to Claim 1 substantially
20 as described in any one of Examples 2, 3 and 5 to 7.

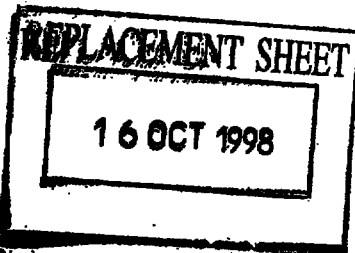
23. A polymer composition whenever prepared by
a process as claimed in any one of Claims 1 to 22.



ABSTRACT

**PROCESS FOR THE MANUFACTURE OF A COMPOSITION
COMPRISING A VINYLAROMATIC POLYMER AND A RUBBER**

The present invention relates to a process
5 for the manufacture of a composition comprising a
vinylaromatic polymer and a rubber, which process
comprises a polymerization stage in the presence of at
least one vinylaromatic monomer and at least one
rubber, there being a stable free radical present
10 during the polymerization stage. The presence of a
stable free radical in the polymerization mixture makes
it possible to increase the melt index and to influence
the size of the rubber nodules in the final composition
by generally increasing the fraction, by volume, of
15 rubbery phase and by widening the distribution of the
size of these nodules. This is reflected by an
improvement both in the melt index and in the impact
strength of the final composition, which makes the
latter an ideal composition for injection moulding.





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to 16, wherein the stable free radical is 2,2,6,6,-
tetramethyl-1-piperidinyloxy.

18. Process according to any one of the
preceding claims, wherein the composition comprises a
5 matrix of vinylaromatic polymer or copolymer in which
rubber nodules are dispersed, said nodules having a
widened size distribution in comparison with the
composition obtained with the same process carried out in
the absence of a stable free radical.

10 19. Process according to any one of the
preceding claims, wherein the rubber is in the form of
nodules whose size distribution is bimodal.

20. Process according to any one of the
preceding claims, wherein the composition comprises
15 between 2 and 25% by weight of rubber.

21. Process according to any one of the
preceding claims, wherein the composition comprises
between 4 and 15% by weight of rubber.

