

19



Europäisches Patentamt
European Patent Office
Office européen des brevets

11 Publication number:

**0 000 429
B1**

12

EUROPEAN PATENT SPECIFICATION

45 Date of publication of patent specification: **28.10.81**

51 Int. Cl.³: **C 08 L 25/12**

21 Application number: **78300104.3**

22 Date of filing: **29.06.78**

54 **Thermoplastic moulding materials based on a styrene-acrylonitrile copolymer, an elastomer and a polyimide.**

30 Priority: **06.07.77 GB 2826077**

43 Date of publication of application:
24.01.79 Bulletin 79/2

45 Publication of the grant of the European patent:
28.10.81 Bulletin 81/43

84 Designated Contracting States:
BE DE FR GB NL SE

56 References cited:
None

73 Proprietor: **TBA Industrial Products Limited
20, St. Mary's Parsonage
Manchester M3 2NL (GB)**

72 Inventor: **Davis, John Idwal
26 Rose Avenue
Littleborough Lancashire (GB)**

74 Representative: **Wetters, Basil David Peter et al,
20 St. Mary's Parsonage
Manchester M3 2NL (GB)**

EP 0 000 429 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Thermoplastic moulding materials based on a styrene-acrylonitrile copolymer, an elastomer and a polyimide

The invention is concerned with plastics molding materials, and particularly moulding materials based on thermoplastics.

Certain thermoplastics materials such as polystyrene and styrene-acrylonitrile copolymer (SAN) have excellent moulding properties but are brittle so that the impact resistance of articles moulded from
5 them is not good.

It is well known that brittle thermoplastics polymers such as polystyrene and SAN can be rendered less brittle by incorporation therein of rubber. This so called "toughening" can increase the impact strength over untreated polymer by a factor of from 2 to 6. However, it has been found that when the impact strength is increased in this way there is an accompanying undesirable decrease in
10 strengths and moduli, which may be up to 50% lower than those of the unmodified polymer.

BACKGROUND ART

In German Offenlegungsschriften Nos. 2,633,501 and 2,744,593 we described moulding compositions comprising thermoplastics materials, a reinforcing filler which is either glass fibres or
15 mica, and a minor proportion of a polyimide prepolymer, which is capable of thermosetting. The polyimide prepolymers concerned are addition polymers and their preparation is described in UK Patent Nos. 1,190,718; 1,355,401; 1,355,402; 1,355,403; 1,355,405; 1,355,406 and 1,355,407.

The effect of the polyimide prepolymers in these compositions is to increase strength and impact resistance of mouldings produced therefrom.

US Patent No. 3,717,615 discloses polymer compositions based on a mixture of a mono-imide of specified general formula and a bis-imide of specified general formula. It also discloses that the mono- and bis-imides can be co-reacted with various thermoplastics during copolymerisation of the imides and that the resulting compositions may be compounded with fillers including glass fibres, and with
20 synthetic rubbers. The polyimides prepared in this specification are, however, the basis of the compositions described, and the final product in each case is a thermoset material. Where thermoplastics materials are used, their proportion is less than that of the mixture of imides and they are co-reacted in the polymerisation of the imides.

US Patent No. 3,678,075 discloses reacting an organic diamine with an aliphatically unsaturated dicarbonyl reagent in a solvent system to produce a polyimide by a condensation reaction. The
30 polyimide is said to be able to be employed in combination with various thermoplastics polymers and can be compounded with fillers including glass fibre. The compositions disclosed are thermosetting, and the polyimide is not an addition polymer, nor is the inclusion of rubbery polymers in the compositions disclosed.

35 DESCRIPTION OF THE INVENTION

According to the invention there is provided a thermoplastic moulding material comprising a styrene-acrylonitrile copolymer containing a ratio of styrene to acrylonitrile in the range 85:15 to 60:40 by weight, and having a melt flow index (MFI) of 2 to 25 g/10 mins at 230°C under a 5 Kg load, an elastomeric material having an elongation at break greater than the styrene-acrylonitrile copolymer, in
40 an amount of 1 to 50% by weight of the moulding material, and a reinforcing filler comprising glass fibres or mica characterised in that the material also comprises a poly-imide pre-polymer being the reaction product of a polyamine and a bis-imide of an unsaturated carboxylic acid and being capable of reacting further to give a thermoset resin.

The test used for melt flow index of the styrene-acrylonitrile polymer as quoted above is
45 BS2782—105C. Styrene-acrylonitrile copolymers of the description in the preceding paragraph are widely commercially available.

We have found that when an elastomeric material is incorporated into a reinforced styrene/acrylonitrile copolymer as toughening agent together with a polyimide prepolymer the impact strength of the composition is increased with less reduction of the strengths or moduli than would be
50 expected in view of prior art methods of increasing the impact strength.

As previously stated the toughening agent is an elastomeric material having an elongation at break greater than the styrene/acrylonitrile copolymer. It is preferred that the elongation at break should be significantly greater than that of the styrene-acrylonitrile copolymer, for example at least 10 times as great. We have found that both sulphur vulcanisable rubbers and thermoplastic rubbers can be used,
55 vulcanisable rubbers preferably being used in a substantially uncured or partially cured state. The toughening agent is included in an amount of from 1 to 50% by weight (based on the weight of the total composition) preferably from 1 to 30% and more preferably from 5 to 20%. The toughening agent preferably has a glass transition temperature below 20°C.

Preferred sulphur vulcanisable elastomeric materials are rubbers such as nitrile rubbers, poly-
60 acrylate rubbers and polyurethanes.

Preferred thermoplastic rubbers are block copolymers containing styrene e.g. block copolymers of styrene and butadiene, which have been found particularly useful in the compositions of this invention

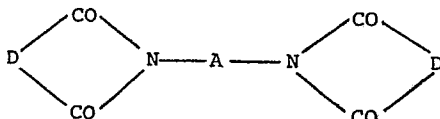
although other thermoplastic rubbers such as polybutylene have also been found effective.

The elastomeric material used must be compatible with the styrene/acrylonitrile copolymer i.e. able to be compounded with the SAN in a satisfactory manner, and should be an elastomer which improves the impact resistance of the copolymer when so compounded, in the absence of other materials.

The polyimide prepolymer is preferably incorporated in an amount of from 0.1 to 10% by weight (based on the weight of the total composition) more preferably 0.5% to 5.0% by weight. Polyimides which can be used are described, inter alia, in British Patent Specifications Nos. 1,190,718; 1,355,401; 1,355,402; 1,355,403; 1,355,405; 1,355,406 and 1,355,407, and are believed to be formed by an addition reaction between the polyamine and the unsaturated bis-imide, rather than by a condensation reaction, the latter being the case with other polyimides.

It is preferred that the polyimide prepolymer is the reaction product of a primary diamine containing not more than 30 carbon atoms and an N,N¹ bis imide of general formula

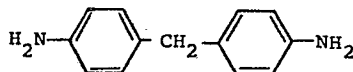
15



in which D represents a divalent radical containing a carbon-carbon double bond, and A is a divalent radical containing at least two carbon atoms.

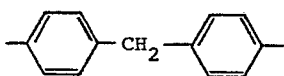
Preferably the primary diamine is an aromatic compound, e.g. containing at least one phenylene group. A preferred compound is the compound of formula

25



Preferably the radical D in the N,N¹ bis imide is derived from an $\alpha\beta$ unsaturated dicarboxylic acid such as maleic acid. The radical A is preferably an aromatic radical containing at least one phenylene group such as

35



The number average molecular weight of the prepolymer is preferably not more than 5000. In the polyimide the molar ratio of bis-imide to polyamine is preferably in the range 1.2 to 1 up to 50 to 1, more preferably in the range 1.2 to 1 up to 2.9 to 1.

The amount of filler present preferably does not exceed 50% by weight of the total composition and preferably is not less than 15 per cent. The particularly preferred range is 20 to 40 per cent by weight of the total composition.

The composition may optionally also include one or more other additives such as antioxidants, flame retardants, blowing agents, antistatic agents and pigments.

These should not be added in such quantities, however, that the proportion by weight of styrene/acrylonitrile copolymer in the total moulding material falls too low for the composition to have satisfactory thermoplastic flow properties. Preferably the composition contains at least 30% by weight of styrene/acrylonitrile copolymer.

The composition can be prepared by any suitable method such as by milling, extrusion, injection moulding all of which are known per se. The order in which the components of the composition are compounded together is not important. For example the polyimide prepolymer can be added to the base polymer and the resultant mixture combined with the toughening agent. Alternatively the polyimide prepolymer can be added to the toughening agent and the resultant mixture combined with the base polymer. When a filler is present the polyimide prepolymer can be applied as a dressing to the filler prior to incorporation of the filler into the composition i.e. when glass fibre is used the polyimide prepolymer may be used in a dressing for the glass fibres.

EMBODIMENTS OF THE INVENTION

The following series of comparative Examples further illustrate the invention. In the Examples all percentages are by weight of total composition unless otherwise stated, and the words "Kerimid", "Krynac", "Flammex", "Perbunan", "Hycar", "Chemigum", "Paracril", "Elastothane", "Cariflex", "Solprene" and "Hytrel" used therein are Registered Trade Marks in the United Kingdom.

Example 1

A composition consisting of styrene/acrylonitrile copolymer marketed by Monsanto as "QE 1044", 30% (based on the total composition) of glass fibre marketed by TBA Industrial Products, as

0 000 429

"ECR 1346", 2% of a polyimide prepolymer derived from an aromatic diamine and a bis-maleimide marketed by Rhone Poulenc SA as "Kerimid 601" and 5% nitrile rubber marketed by Polysar as "Krynac 802" was produced by compounding the constituents in a twin screw extruder. The nitrile rubber has an acrylonitrile content of 28% and was added as uncured crumb.

5 The materials were compounded on a twin-screw extruder at barrel temperatures of 200°C, 125°C, 125°C and 190°C (die) and the extruded composition was chopped into pellets.

The resultant material was formed into test bars by injection moulding using conventional moulding conditions for reinforced styrene/acrylonitrile copolymer (220/250°C barrel temperatures). The test bars were tested for tensile strength, tensile modulus, flexural strength, flexural modulus and
10 impact strength. The results are shown in the following Table 1.

Examples 2 and 3

The same procedure was followed as in Example 1 save that the amount of nitrile rubber was increased to 10% (Example 2) and 15% (Example 3). The products were tested and the results are set
15 out in the Table 1.

Table 1			
Example No.	1	2	3
	30% glass 2% polyimide 5% rubber	30% glass 2% polyimide 10% rubber	30% glass 2% polyimide 15% rubber
20			
Tensile Strength 25 MPa	130	121	102
Tensile Modulus GPa	11.4	10.1	9.7
30			
Flexural Strength MPa	181	163	155
Flexural Modulus GPa	9.7	8.7	8.3
35			
Notched Izod Impact J/m	73	83	99
40			
Notched Charpy Impact KJ/m ²	7.1	7.9	9.2
Unnotched Charpy Impact KJ/m ²	19	22	24

45

Comparison Example 4

A composition was made in the same manner as in Example 1 except that both "Kerimid 601" and the nitrile rubber "Krynac 802" were omitted. Test bars formed from the composition by injection moulding were tested for the same properties as in Example 1. The results are set out in Table 2.

50

Comparison Example 5

A composition was made in the same manner as in Example 1 except that the nitrile rubber "Krynac 802" was omitted.

Test bars formed from the composition by injection moulding were tested. The results are shown
55 in Table 2.

Comparison Example 6

A composition was made in the same way as in Example 1 but "Kerimid 601" was omitted. The results of tests made on test bars formed from the composition are shown in the Table 2.

60

65

Table 2

Example No.	4	5	6	
	30% glass	30% glass 2% polyimide	30% glass 5% rubber	
5				
10				
15				
20				
25				
30				
35				
40				
45				
50				
55				
60				
65				
	Tensile Strength MPa	110	127	73
	Tensile Modulus GPa	10.7	11.9	9.3
	Flexural Strength MPa	150	172	101
	Flexural Modulus GPa	8.7	9.7	7.9
	Notched Izod Impact J/m	44	60	57
	Notched Charpy Impact KJ/m ²	4.0	5.3	6.3
	Unnotched Charpy Impact KJ/m ²	10.0	13.2	14.9

Examples 7 to 22

A series of compositions of increasing glass fibre content were prepared each containing the styrene/acrylonitrile copolymer of Example 1. For comparison, compositions of corresponding glass content were prepared in which 2 parts SAN by weight per 100 of composition were replaced by the polyimide prepolymer KERIMID 601; further compositions of corresponding glass content were prepared in which 15 parts of SAN per 100 of composition were replaced by the nitrile rubber KRYNAC 802; and further compositions of corresponding glass content were prepared in which 17 parts of SAN by weight per 100 of composition were replaced by 2 parts by weight of the polyimide prepolymer KERIMID 601 and 15 parts by weight of the nitrile rubber KRYNAC 802.

Compounding was carried out as in Example 1 and then test samples were injection moulded and tested as before.

The physical properties of the samples so obtained are tabulated in Tables 3, 4, 5 and 6 each Table representing comparative results at a particular glass content. In these Tables, for brevity, the polyimide prepolymer is represented by "PI" and the nitrile rubber by "R".

It will be noted that at each glass content the addition of the polyimide prepolymer alone gives some improvement in tensile, flexural and impact strengths. The addition of the nitrile rubber alone has a beneficial effect on impact strength but is detrimental to flexural strength in particular. The addition of both the polyimide prepolymer and the nitrile rubber gives a massive improvement in impact strength but also has very little effect on tensile or flexural strength despite the massive loss of flexural strength caused by addition of rubber alone (see particularly Tables 5 and 6).

0 000 429

Table 3

(SAN filled with 15% by weight of glass fibre)

Example No.	7	8	9	10
	SAN + 15% glass	+ 2% PI	+ 15% R	+ 2% PI + 15% R
Tensile Strength MPa	87	96		62
Flexural Strength MPa	109	120	81	100
Flexural Modulus GPa	5.0	5.4	3.4	4.2
Notched Izod Impact J/m	31	36.1	63	76
Notched Charpy Impact kJ/m ²	3.4	4.7	6.1	8.3
Unnotched Charpy Impact kJ/m ²	9.7	13.7	17.1	22
DTUL (0.46 MPa) °C	103			100
Specific Gravity	1.18	1.18	1.14	1.16

Table 4

(SAN filled with 25% by weight of glass fibre)

Example No.	11	12	13	14
	SAN + 15% glass	+ 2% PI	+ 15% R	+ 2% PI + 15% R
Tensile Strength MPa	96	121		84
Flexural Strength MPa	139	152	75	135
Flexural Modulus GPa	6.9	7.6	4.5	6.4
Notched Izod Impact J/m	39	62.0	69	97
Notched Charpy Impact kJ/m ²	3.8	7.0	7.0	9.1
Unnotched Charpy Impact kJ/m ²	9.4	19.8	16.6	25
DTUL (0.46 MPa) °C	104			103
Specific Gravity	1.26	1.26	1.23	1.24

0 000 429

Table 5

(SAN filled with 35% of weight of glass fibre)

5	Example No.	15	16	17	18
		SAN + 35% glass	+ 2% PI	+ 15% R	+ 2% PI + 15% R
10	Tensile Strength MPa	99	127		92
	Flexural Strength MPa	161	175	62	153
15	Flexural Modulus GPa	9.4	9.8	5.6	8.2
20	Notched Izod Impact J/m	44	62.8	69	113
	Notched Charpy Impact kJ/m ²	4.0	7.3	6.4	10.0
25	Unnotched Charpy Impact kJ/m ²	9.0	19.4	16.5	27
	Specific Gravity	1.35	1.36	1.31	1.33

Table 6

(SAN filled with 45% by weight of glass fibre)

35	Example No.	19	20	21	22
		SAN + 45% glass	+ 2% PI	+ 15% R	+ 2% PI + 15% R
40	Tensile Strength MPa	100	126		90
	Flexural Strength MPa	170	193	47	162
45	Flexural Modulus GPa	12.3	12.1	6.9	9.4
50	Notched Izod Impact J/m	45	60.2	67	164
	Notched Charpy Impact kJ/m ²	4.0	6.7	6.3	10.2
55	Unnotched Charpy Impact kJ/m ²	8.6	13.0	16.2	25.5
	DTUL (0.46 MPa) °C	105			105
60	Specific Gravity	1.46	1.46	1.40	1.40

Examples 23 to 26

These examples show that the invention can be used in a composition in which another filler and flame retardants are present in addition to glass fibres.

A composition was prepared by compounding together the following ingredients in a twin-screw extruder in the same manner as described in Example 1. The ingredients were 60 parts by weight of

styrene/acrylonitrile copolymer (Monsanto QE 1044 as in Example 1), 15 parts by weight of glass fibres, (ECR 1346 as in Example 1) 15 parts by weight of talc and 10 parts by weight of fire retardants. The fire retardants consisted of a 3:1 w/w mixture of decabromobiphenyl (Flammex B10 commercially available from Berk Ltd.) and Antimony Trioxide.

5 Three comparable compositions were prepared by respectively replacing (i) 2 parts of the styrene/acrylonitrile copolymer (SAN) by 2 parts of the polyimide prepolymer KERIMID 601, (ii) 15 parts of the SAN by 15 parts of PERBUNAN N2810 (a nitrile rubber containing 28% by weight of acrylonitrile and commercially available from Farbenfabriken Bayer AG) and (iii) 7 parts of SAN by 2 parts of the KERIMID 601 and 5 parts of the PERBUNAN N2810.

10 Test mouldings were made from these compositions as before and the results of physical testing and fire testing of the mouldings are given below in Table 7. In this table the polyimide prepolymer is referred to as "PI" and the nitrile rubber as "R".

Table 7

15 Example No.	23	24	25	26
	No Impact Modifier	2% PI	5% R	2% PI + 5% R
20 Tensile Strength MPa	85	88	59	84
25 Tensile Modulus GPa	10.4	9.7	6.6	8.0
Flexural Strength MPa	108	115	81	113
30 Flexural Modulus GPa	7.4	8.1	6.4	7.1
Notched Izod Impact J/m	24	35	39	49
35 Notched Charpy Impact kJ/m ²	2.9	4.2	4.1	5.0
40 Unnotched Charpy Impact kJ/m ²	13.6	11.4	12.1	12.5
DTUL (0.46 MPa) °C	103	104	101	104
45 Specific Gravity	1.43	1.40	1.39	1.41
Flammability Rating (to Lloyd's Underwriter's) test UL94	V—0	V—0	V—0	V—0

Examples 27 to 30

50 These examples investigate the effect of curing the rubber before it is compounded into the composition.

Four compositions were prepared using SAN and glass fibre as used in Example 1. Each composition contained 30% by weight of glass fibre.

55 Two compositions contained 5% by weight of a nitrile rubber (KRYNAC 802) one having uncured rubber incorporated into it and the other having cured rubber incorporated into it. The other two compositions also contained 5% of uncured and cured rubber respectively but additionally contained 2% by weight of the polyimide prepolymer KERIMID 601. In each case SAN made up the whole of the balance of the composition.

60 The compounding was carried out in a twin screw extruder under the same conditions as in Example 1, and test mouldings were injection moulded from each of the four compositions.

The cured rubber was a compounded rubber in which the following formulation was compounded on a mill and press cured for 10 minutes at 150°C in sheets 1.5 mm thick. Under these conditions the rubber was substantially fully vulcanised i.e. 95% of available cross linking sites used up.

65

0 000 429

The rubber formulation was:—

	KRYNAC 802	100	parts	by	weight
5	Zinc Oxide	5	"	"	"
	Stearic Acid	1	"	"	"
10	TMT	3	"	"	"
	Sulphur	1	"	"	"

(TMT is tetramethyl thiuram disulphide)

15 The physical properties of the mouldings from the four different compositions are given below in Table 8 in which cured rubber is signified by "CR", uncured rubber by "UR" and the polyimide prepolymer by "PI".

Table 8

20	Example No.	27	28	29	30
		5% UR	5% CR	5% UR 2% PI	5% CR 2% PI
25	Tensile Strength MPa	73	80	130	118
30	Tensile Modulus GPa	9.3	11.8	11.4	10.8
	Flexural Strength MPa	101	103	181	160
35	Flexural Modulus GPa	7.9	8.7	9.7	8.3
	Notched Izod Impact J/m	57	33	73	65
40	Notched Charpy Impact kJ/m ²	6.3	3.7	7.1	6.2
45	Unnotched Charpy Impact kJ/m ²	14.9	7.3	19.0	15.8
	DTUL (0.46 MPa) °C	103	103	105	104
50	Specific Gravity	1.32	1.34	1.34	1.34

55 These results show that the same sort of advantage is obtained when the polyimide prepolymer and cured rubber are used as when the polyimide prepolymer and uncured rubber are used. However, the cured rubber is less effective than the uncured rubber in improving the impact strength of the glass filled SAN. (These Examples may be compared directly with Example 4 (Table 2) which gives the properties of the glass/SAN without additives).

Examples 31 to 42

60 The following examples illustrate the use of the invention with various kinds of commercially available synthetic rubbers. In every case the composition was compounded as in Example 1, using the same type of SAN, glass fibre and polyimide prepolymer as in Example 1, to the following formulation: Glass fibre 30 parts by weight, polyimide prepolymer 2 pbw, Rubber 5 pbw and SAN 63 pbw.

Test mouldings were made as before by injection moulding, and the properties of the mouldings were measured.

65

0 000 429

The rubbers used in the various examples were as follows:—

- Example 31 — "HYCAR 1411", a nitrile rubber containing 41% by weight of acrylonitrile, the remainder being butadiene, commercially available from B.F. Goodrich. Used uncured.
- Example 32 — "HYCAR 1422", another nitrile rubber, containing 33% by weight acrylonitrile, available from B.F. Goodrich and used uncured.
- Example 33 — "CHEMIGUM N8B" a nitrile rubber containing 32% by weight acrylonitrile, available from Goodyear, and used uncured.
- Example 34 — "PARACRIL D" a nitrile rubber containing 45% by weight acrylonitrile, available from Uniroyal and used uncured.
- Example 35 — "ELASTOTHANE 640" a polyurethane rubber, sulphur vulcanizable available from Thiokol Chemical Corporation. Used uncured.
- Example 36 — "CARIFLEX TR1102" a thermoplastic rubber available from Shell. This is an S—B—S block copolymer of polystyrene and polybutadiene.
- Examples 37 and 38 — "SOLPRENE 415" and "SOLPRENE 416", both thermoplastic rubbers available from Philips Petroleum. Both are block copolymers of styrene and butadiene containing respectively 40% styrene and 60% butadiene and 30% styrene and 70% butadiene.
- Examples 39 and 40 — "Polybutylene Grade 20" and "Polybutylene Grade 0.5", both thermoplastic rubbery polybutylenes available from CdF Chemie.
- Example 41 — "HYTREL 6345" a thermoplastic polyester elastomer available from Du Pont de Nemours.
- Example 42 — "CYANACRYL R" a sulphur vulcanizable polyacrylate elastomer available from American Cyanamid Company.

The physical test results obtained on the mouldings from the various compositions are given below in Tables 9 and 10.

Table 9

Example No.	31	32	33	34	35	36
Tensile Strength MPa	125	125	118	118	116	117
Tensile Modulus GPa	10.6	10.2	9.7	9.5	11.2	10.4
Flexural Strength MPa	174	172	175	172	172	177
Flexural Modulus GPa	9.3	9.3	8.4	7.9	9.2	9.2
Notched Izod Impact J/m	67	64	71	78	71	66
Notched Charpy Impact kJ/m ²	6.9	6.5	7.0	7.4	3.7	7.4
Unnotched Charpy Impact kJ/m ²	18.0	15.9	20.0	21.0	19.0	15.0
DTUL (0.46 MPa) °C	104	107	104	105	94	103
Specific Gravity	1.33	1.33	1.30	1.28	1.34	1.31

Table 10

Example No.	37	38	39	40	41	42
5 Tensile Strength MPa	123	122	112	122	105	119
Tensile Modulus GPa	10.4	10.5	9.9	10.9	10.8	9.6
10 Flexural Strength MPa	192	190	176	188	144	157
Flexural Modulus GPa	9.4	9.5	9.3	10.0	9.8	8.1
15 Notched Izod Impact J/m	76	72	74	71	70	68
20 Notched Charpy Impact kJ/m ²	7.9	7.7	7.9	7.4	6.6	7.1
Unnotched Charpy Impact kJ/m ²	19.0	14.0	16.0	13.0	17.0	17.0
25 DTUL (0.46 MPa) °C	101	103	104	104	101	
30 Specific Gravity	1.32	1.32	1.32	1.32	1.34	1.30

As can be seen from these results, both the sulphur vulcanizable rubbers and the thermoplastic rubbers gave results showing improvement in impact strength without the accompanying loss of flexural strength which results from use of rubbers alone.

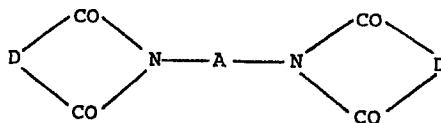
This series of Examples is comparable with Examples 4 and 5 (Table 2) which show the properties of the glass/SAN alone and with 2% of the polyimide prepolymer.

Claims

1. A thermoplastic moulding material comprising a styrene-acrylonitrile copolymer containing a ratio of styrene to acrylonitrile in the range 85:15 to 60:40 by weight, and having a melt flow index (MFI) of 2 to 25 g/10 mins at 230°C under a 5 Kg load, an elastomeric material having an elongation at break greater than the styrene-acrylonitrile copolymer, in an amount of 1 to 50% by weight of the moulding material and a reinforcing filler comprising glass fibres or mica characterised in that the material also comprises a poly-imide pre-polymer being the reaction product of a polyamine and a bis-imide of an unsaturated carboxylic acid and being capable of reacting further to give a thermoset resin.
2. A moulding material according to Claim 1 in which the elastomeric material has an elongation at break at least 10 times as great as the styrene-acrylonitrile co-polymer.
3. A material according to Claim 1 or 2 in which the elastomeric material is included in an amount of from 1 to 30% by weight of the moulding material.
4. A material according to Claim 3 in which the elastomeric material is included in an amount of from 5 to 20% by weight of the moulding material.
5. A material according to any one of the preceding claims in which the elastomeric material is an sulphur vulcanisable rubber.
6. A material according to Claim 5 in which the rubber is substantially uncured.
7. A material according to Claim 5 or 6 in which the elastomeric material is a nitrile rubber, a polyacrylate rubber or a polyurethane.
8. A material according to any one of Claims 1 to 4 in which the elastomeric material is a thermoplastic rubber.
9. A material according to Claim 8 in which said thermoplastic rubber is a polybutylene, or a block copolymer of styrene and butadiene.
10. A material according to any one of the preceding claims in which the polyimide prepolymer is included in an amount of from 0.1 to 10% by weight based on the weight of the moulding material.
11. A material according to Claim 10 in which the amount of polyimide prepolymer is in the range 0.5 to 5.0% by weight of the moulding material.

12. A material according to any one of the preceding claims in which the polyimide prepolymer comprises the reaction product of a primary diamine containing not more than 30 carbon atoms and an N,N¹ bis-imide of general formula

5



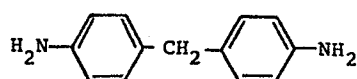
10 in which D represents a divalent radical containing a carbon-carbon double bond and A is a divalent radical containing at least two carbon atoms.

13. A moulding material according to Claim 12 in which the primary diamine is an aromatic compound.

14. A moulding material according to Claim 13 in which the primary diamine contains at least one phenylene group.

15. A moulding material according to Claim 14 in which the primary diamine is the compound of formula

20



16. A moulding material according to any one of Claims 12 to 15 in which the radical D in the N,N¹ bis-imide is derived from an $\alpha\beta$ unsaturated dicarboxylic acid.

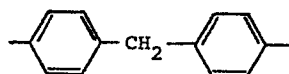
17. A moulding material according to Claim 16 in which the radical D is derived from maleic acid.

18. A moulding material according to any one of Claims 12 to 17 in which the radical A in the N,N¹ bis-imide is an aromatic radical.

19. A moulding material according to Claim 18 in which the aromatic radical contains at least one phenylene group.

20. A moulding material according to Claim 19 in which the radical has the formula

30



21. A moulding material according to any one of claims 12 to 20 in which the molar ratio of bis-imide to polyamine is in the range 1.2 to 1 up to 50 to 1.

22. A moulding material according to Claim 21 in which the molar ratio of bis-imide to polyamine is in the range 1.2 to 1 up to 2.9 to 1.

23. A moulding material according to any one of the preceding Claims in which the amount of said reinforcing filler is not more than 50% by weight of the moulding material.

24. A moulding material according to Claim 23 in which the amount of said reinforcing filler is at least 15% by weight of the moulding material.

25. A moulding material according to Claim 24 in which the amount of said reinforcing filler is in the range 20% to 40% by weight.

26. A moulding material according to any one of the preceding claims which also includes a filler other than glass fibres or mica.

27. A moulding material according to any one of the preceding claims in which the proportion of thermoplastic styrene-acrylonitrile copolymer is not less than 30% by weight of the moulding material.

50 Revendications

1. Matière à mouler thermoplastique, constituée d'un copolymère de styrène-acrylonitrile présentant un rapport pondéral du styrène à l'acrylonitrile compris entre 85/15 et 60/40 et ayant un indice de fluidité de 2 à 25 g/10 min à 230°C sous une charge de 5 kg, d'une matière élastomère ayant un allongement à la rupture supérieur à celui du copolymère de styrène-acrylonitrile, à raison de 1 à 50% en poids de la matière à mouler, et d'une charge de renforcement constituée de fibres de verre ou de mica, caractérisée en ce qu'elle contient également un prépolymère de type polyimide qui est le produit de la réaction d'une polyamine et d'un bis-imide dérivant d'un acide carboxylique insaturé et capable de réagir encore pour former une résine thermodurcie.

2. Matière à mouler selon la revendication 1, caractérisée en ce que la matière élastomère a un allongement à la rupture au moins dix fois supérieur à celui du copolymère de styrène-acrylonitrile.

3. Matière selon l'une des revendications 1 ou 2, caractérisée en ce que la matière élastomère est incorporée à raison de 1 à 30% du poids de la matière à mouler.

4. Matière selon la revendication 3, caractérisée en ce que la matière élastomère est incorporée à raison de 5 à 20% du poids de la matière à mouler.

5. Matière selon l'une quelconque des revendications précédentes, caractérisée en ce que la matière élastomère est un caoutchouc vulcanisable au soufre.

6. Matière selon la revendication 5, caractérisée en ce que le caoutchouc est pratiquement non durci.

5 7. Matière selon l'une des revendications 5 ou 6, caractérisée en ce que la matière élastomère est un nitrile caoutchouc, un caoutchouc de polyacrylate ou un polyuréthane.

8. Matière selon l'une quelconque des revendications 1 à 4, caractérisée en ce que la matière élastomère est un caoutchouc thermoplastique.

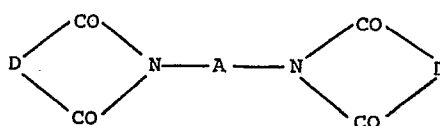
9. Matière selon la revendication 8, caractérisée en ce que le caoutchouc thermoplastique est un 10 polybutylène ou un copolymère séquencé de styrène et de butadiène.

10. Matière selon l'une quelconque des revendications précédentes caractérisée en ce que le prépolymère de type polyimide est incorporé à raison de 0,1 à 10% en poids par rapport au poids de la matière à mouler.

11. Matière selon la revendication 10, caractérisée en ce que la quantité de prépolymère de type 15 polyimide est comprise entre 0,5 et 5,0% du poids de la matière à mouler.

12. Matière selon l'une quelconque des revendications précédentes, caractérisée en ce que le prépolymère de type polyimide est le produit de la réaction d'une diamine primaire ne contenant pas plus de 30 atomes de carbone et d'un N,N'-bis-imide de formule générale:

20



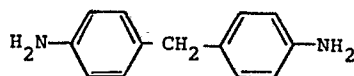
25 où D représente un radical divalent contenant une double liaison carbone-carbone et A est un radical divalent contenant au moins deux atomes de carbone.

13. Matière à mouler selon la revendication 12, caractérisée en ce que la diamine primaire est un composé aromatique.

14. Matière à mouler selon la revendication 13, caractérisée en ce que la diamine primaire 30 contient au moins un radical phénylène.

15. Matière à mouler selon la revendication 14, caractérisée en ce que la diamine primaire est le composé de formule:

35



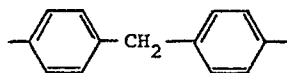
16. Matière à mouler selon l'une quelconque des revendications 12 à 15, caractérisée en ce que le radical D du N,N'-bis-imide dérive d'un acide dicarboxylique α,β -insaturé.

17. Matière à mouler selon la revendication 16, caractérisée en ce que le radical D dérive de 40 l'acide maléique.

18. Matière à mouler selon l'une quelconque des revendications 12 à 17, caractérisée en ce que le radical A du N,N'-bis-imide est un radical aromatique.

19. Matière à mouler selon la revendication 18, caractérisée en ce que le radical aromatique contient au moins un radical phénylène.

45 20. Matière à mouler selon la revendication 19, caractérisée en ce que le radical a pour formule:



50

21. Matière à mouler selon l'une quelconque des revendications 12 à 20, caractérisée en ce que le rapport molaire du bis-imide à la polyamine est compris entre 1,2/1 et 50/1.

22. Matière à mouler selon la revendication 21, caractérisée en ce que le rapport molaire du bis-imide à la polyamine est compris entre 1,2/1 et 2,9/1.

55 23. Matière à mouler selon l'une quelconque des revendications précédentes caractérisée en ce que la quantité de la charge de renforcement ne dépasse pas 50% du poids de la matière à mouler.

24. Matière à mouler selon la revendication 23, caractérisée en ce que la quantité de la charge de renforcement est au moins égale à 15% du poids de la matière à mouler.

60 25. Matière à mouler selon la revendication 24, caractérisée en ce que la quantité de la charge de renforcement est comprise entre 20 et 40% en poids.

26. Matière à mouler selon l'une quelconque des revendications précédentes caractérisée en ce qu'elle contient également une charge autre que des fibres de verre ou du mica.

65 27. Matière à mouler selon l'une quelconque des revendications précédentes caractérisée en ce que la proportion du copolymère thermoplastique de styrène-acrylonitrile n'est pas inférieure à 30% du poids de la matière à mouler.

Patentansprüche

1. Thermoplastische Formmasse enthaltend ein Styrol-Acrylnitrilcopolymerisat mit einem Gewichtsverhältnis von Styrol zu Acrylnitril im Bereich von 85:15 bis 60:40 und einem Schmelzflußindex (MFI) von 2 bis 25 g/10 min bei 230°C unter einer Belastung von 5 kg, ein elastomeres Material mit einer Bruchdehnung von mehr als der des Styrol-Acrylnitrilcopolymerisats, in einer Menge von 1 bis 50 Gew.-% der Formmasse, und einen Verstärkungsfüllstoff enthaltend Glasfasern oder Glimmer, dadurch gekennzeichnet, daß die Masse auch ein Polyimidvorpolymerisat enthält, welches das Umsetzungsprodukt eines Polyamins und eines Bis-imids einer ungesättigten Carbonsäure ist und zur weiteren Umsetzung unter Bildung eines hitzehärtenden Harzes befähigt ist.

2. Formmasse nach Anspruch 1, dadurch gekennzeichnet, daß die Bruchdehnung des elastomeren Materials wenigstens zehnmal so hoch ist wie die des Styrol-Acrylnitrilcopolymerisats.

3. Masse nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das elastomere Material in einer Menge von 1 bis 30 Gew.-% der Formmasse enthalten ist.

4. Masse nach Anspruch 3, dadurch gekennzeichnet, daß das elastomere Material in einer Menge von 5 bis 20 Gew.-% der Formmasse enthalten ist.

5. Masse nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das elastomere Material ein mit Schwefel vulkanisierbarer Kautschuk ist.

6. Masse nach Anspruch 5, dadurch gekennzeichnet, daß der Kautschuk im wesentlichen unvulkanisiert ist.

7. Masse nach Anspruch 5 oder 6, dadurch gekennzeichnet, daß das elastomere Material ein Nitrilkautschuk, ein Polyacrylatkautschuk oder ein Polyurethan ist.

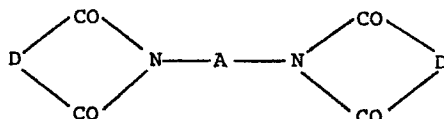
8. Masse nach irgendeinem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das elastomere Material ein thermoplastischer Kautschuk ist.

9. Masse nach Anspruch 8, dadurch gekennzeichnet, daß der thermoplastische Kautschuk ein Polybutylen oder ein Blockcopolymerisat von Styrol und Butadien ist.

10. Masse nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Polyimidvorpolymerisat in einer Menge von 0,1 bis 10 Gew.-%, bezogen auf das Gewicht der Formmasse, vorliegt.

11. Masse nach Anspruch 10, dadurch gekennzeichnet, daß die Menge an Polyimidvorpolymerisat im Bereich von 0,5 bis 5,0 Gew.-% der Formmasse liegt.

12. Masse nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Polyimidvorpolymerisat das Umsetzungsprodukt eines primären Diamins mit nicht mehr als 30 Kohlenstoffatomen und eines N,N'-Bis-imids der allgemeinen Formel

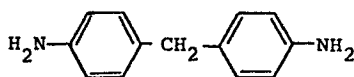


enthält, worin D einen zweiwertigen Rest mit einer Kohlenstoff-Kohlenstoff-Doppelbindung und A einen zweiwertigen Rest mit wenigstens zwei Kohlenstoffatomen bedeuten.

13. Formmasse nach Anspruch 12, dadurch gekennzeichnet, daß das primäre Diamin eine aromatische Verbindung ist.

14. Formmasse nach Anspruch 13, dadurch gekennzeichnet, daß das primäre Diamin wenigstens eine Phenylengruppe aufweist.

15. Formmasse nach Anspruch 14, dadurch gekennzeichnet, daß das primäre Diamin eine Verbindung der Formel



ist.

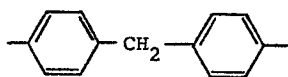
16. Formmasse nach irgendeinem der Ansprüche 12 bis 15, dadurch gekennzeichnet, daß der Rest D in dem N,N'-Bis-imid von einer α,β -ungesättigten Dicarbonsäure abgeleitet ist.

17. Formmasse nach Anspruch 16, dadurch gekennzeichnet, daß der Rest D von Maleinsäure abgeleitet ist.

18. Formmasse nach irgendeinem der Ansprüche 12 bis 17, dadurch gekennzeichnet, daß der Rest A in dem N,N'-Bis-imid ein aromatischer Rest ist.

19. Formmasse nach Anspruch 18, dadurch gekennzeichnet, daß der aromatische Rest wenigstens eine Phenylengruppe enthält.

20. Formmasse nach Anspruch 19, dadurch gekennzeichnet, daß der Rest die Formel



aufweist.

0 000 429

21. Formmasse nach irgendeinem der Ansprüche 12 bis 20, dadurch gekennzeichnet, daß das molare Verhältnis von Bis-imid zu Polyamin im Bereich von 1,2 zu 1 bis zu 50 zu 1 liegt.

22. Formmasse nach Anspruch 21, dadurch gekennzeichnet, daß das molare Verhältnis von Bis-imid zu Polyamin im Bereich von 1,2 zu 1 bis zu 2,9 zu 1 liegt.

5 23. Formmasse nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Menge an Verstärkungsfüllstoff nicht mehr als 50 Gew.-% der Formmasse beträgt.

24. Formmasse nach Anspruch 23, dadurch gekennzeichnet, daß die Menge an Verstärkungsfüllstoff wenigstens 15 Gew.-% der Formmasse beträgt.

10 25. Formmasse nach Anspruch 24, dadurch gekennzeichnet, daß die Menge an Verstärkungsfüllstoff im Bereich von 20 bis 40 Gew.-% liegt.

26. Formmasse nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß sie auch einen anderen Füllstoff als Glasfasern oder Glimmer enthält.

15 27. Formmasse nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Anteil an thermoplastischem Styrol-Acrylnitrilcopolymerisat nicht weniger als 30 Gew.-% der Formmasse beträgt.

20

25

30

35

40

45

50

55

60

65