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(54) POLYAMIDE BLENDS

(71) We, BAYER AKTIENGESSELLSCHAFT a body corporate organised under the laws of the Federal Republic of Germany of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention relates to a thermoplastic moulding composition based on polyamide-6 which combines high toughness with excellent homogeneity.

The mechanical properties of polymers usually depend upon their pre treatment. Thus, for example, the impact strength of mouldings of polyamide plastics is governed to a large extent by the water content of the mouldings.

In particular, mouldings produced from free-flowing, preferably high crystalline polyamides of average molecular weight are relatively sensitive in anhydrous form to impact stressing. Accordingly, there is a need for rapidly processible, free-flowing polyamide plastics from which it is possible to produce, in particular, mouldings which show increased impact strength in their dry state. Polyamides of particular interest are those which combine the characteristics of high tensile strength, high thermal stability under load, high resistance to solvents and ready processibility with high impact strength and flexibility.

There are already various methods of increasing the toughness and flexibility of polyamides. According to one known method, for example, low molecular weight plasticizers are mixed into polyamides. But most of the plasticisers suitable for plastics are not sufficiently compatible with polyamides and they separate out during processing or tend to exude. However, compatible plasticisers which form true solutions with polyamides generally have an adverse effect upon the favourable mechanical properties of the polyamides. Although strongly polar substances of low molecular weight, such as water or dimethyl formamide, have a strong plasticising effect, they can only be worked into the polyamide mouldings after the mouldings have actually been produced because otherwise bubble-containing mouldings would be formed during processing of the pretreated polyamide granulate on account of the relatively low boiling points of these plasticisers.

In addition, this process is generally time consuming and expensive. Furthermore, it is unsuitable for the production of thick-walled mouldings on account of the irregular distribution of the plasticiser in the moulding. Moreover, these plasticisers partially escape from the polyamide again on account of their relatively high vapour pressure.

In particular these measures have proved to be unsuitable for processing the thus pretreated polyamide granulate into high-quality films.

Attempts have also been made to improve the impact strength of polyamides by the incorporation of polymeric substances, such as polyethylene and copolymers of vinylacetate and ethylene (German Auslegeschrift No. 1,138,922 = British Patent 919098. Although the production of such mixtures necessitates extremely intensive kneading, disintegration occurs during further processing, for example, by injection moulding and, particularly, in the manufacture of films.

Accordingly, mouldings produced therefrom show a tendency towards white fracture. In

the manufacture of films, rapid disintegration occurs immediately after emergence from the die, even in cases where high working pressures are applied.

5 The flexibility of polyamides can also be increased by mixing them with polyethylenes containing acidic groups, for example copolymers of ethylene and unsaturated acids or polyethylene grafted with unsaturated acids. Although such mixtures are more finely 5 disperse and, under stressing, show a much lower tendency towards white fracture than the mixtures described above, their somewhat improved toughness and flexibility is offset by considerably poorer mechanical properties such as, E-modulus, tensile strength, hardness and rigidity, than that of polyamides.

10 Copolymers of ethylene and acrylic or methacrylic acid have also been used in attempts to increase the flexibility of polyamides in their freshly injection-moulded state. 10

Thus, according to the teaching of US Patent No. 3,472,916 and German Patent No. 1,669,702, a certain improvement is obtained by using copolymers of ethylene and acrylic or methacrylic acid esters. But their notched impact strength immediately after injection- 15 moulding is still unsatisfactory, as well as their significant tendency towards disintegration. These disadvantages also show the blends known from US Patent No. 3,845,163 and French Patent No. 1,504,113. Additionally on account of the methacrylic acid being partly present in salt form, the tracking resistance is known to deteriorate to such a considerable extent that the products cannot be effectively used in the electrical field. In addition, most of the 20 metal ions used for neutralisation, for example Zn^{2+} , Ba^{2+} , Cd^{2+} and Hg^{2+} , are physiologically incompatible. Thus, such products cannot be used either in the food-packaging field or in children's toys. 20

Finally, copolymers of ethylene, acrylic or methacrylic acid and acrylates or methacrylates have also been added as elasticising component to polyamides (DAS No. 1,241,606 = 25 British Patent 998439) whereby an improvement in impact strength is obtained. However, products of sufficient high impact strength are not described there either. 25

However, polyamide blends showing sufficient high impact strength in freshly injection-moulded form, coupled with extremely high homogeneity and the absence of any tendency towards disintegration, are surprisingly obtained by using polyamide-6 with a certain 30 minimum relative viscosity and ternary copolymers of ethylene, acrylic or methacrylic acid and a derivative of acrylic or methacrylic acid having a certain melt index. 30

Accordingly, the present invention provides thermoplastic moulding compositions of high impact strength comprising

1. 70 to 96% by weight, preferably 80 to 92% by weight of a polyamide-6 having a 35 relative viscosity of at least 3.5, preferably 3.7 to 4.5, as measured on a 1% solution (as hereinafter defined), in *m*-cresol at 25°C; 35

2. 4 to 30% by weight, preferably 8 to 20% by weight, of an at least ternary copolymer comprising:

a) 50 to 95% by weight, preferably 80 to 95% by weight of ethylene; 40
b) 1 to 20% by weight, preferably 1 to 10% by weight of acrylic or methacrylic acid which may be completely or partly present in the form of a salt thereof; 40

c) 1 to 30% by weight, preferably 1 to 20% by weight, of at least one ester of acrylic or methacrylic acid with C_1 - C_9 alcohols and having a melt index (MI), as determined according to DIN 53735, of 2 to 15 g/10 min., preferably 5 to 10 g/10 min., the sum total of 45 components 1 + 2 and a + b + c amount to 100% by weight. 45

The relative viscosity of the polyamide-6 used is measured on a 1% solution, that is, 1g of the polyamide is present in 100 ml of solution, in *m*-cresol at 25°C. Na-, K-, Zn- or Ca-salts can be used as the salts of acrylic or methacrylic acid. Esters with C_1 - C_9 - alcohols 50 preferably C_2 - C_6 alcohols may be used as the esters of acrylic or methacrylic acid. Most preferably acrylic or methacrylic acid ethyl, tert.-butyl or n-butyl ester is used. 50

Surprisingly the compatibility of the composition according to the invention blends is so high that they can be processed by standard methods into homogeneous films which are even transparent in the most common layer thicknesses of from 10 μm to 70 μm .

Polyamide-6 is advantageously used without any additives, for example lubricants, such as calcium stearate or ethoxylated long-chain amines and/or crystallisation promoters, for 55 example talcum. The polymer components are mixed preferably above the melting point of the polyamide used, advantageously at temperatures in the range from 200°C to 320°C and, more especially, at temperatures of from 260°C to 290°C. 55

60 Machines in which the moulding compositions according to the invention may be produced are standard screw machines. It is possible to use both machines comprising a single screw and also machines comprising double screws. Twin-screw extruders are preferably used. 60

However, it is also possible to use other mixing machines which are suitable for plasticising plastics.

65 In addition, stabilisers, mould-release agents, lubricants, crystallisation accelerators, plasticisers, pigments, dyes or fillers, such as glass fibres or asbestos, may also be 65

incorporated in the highly elastic blends in case they are used as thermoplastic moulding compositions. Monofils and other shaped articles produced of the inventive blends do not show any white fracture at breaks and cuts, nor any signs of disintegration. In addition, they also show surfaces of extremely good quality in comparison with shaped articles of known polyamide/polyolefin mixtures. They also have a reduced water absorption capacity and solubility or swellability in conventional solvents and show greatly increased notched impact strength in their dry state in comparison with shaped articles of polyamides alone. The compositions are suitable for extrusion and injection moulding for the production of shaped articles such as housings, sheets, filaments, tapes, tubes and, in particular, homogeneous, transparent films and foils.

The invention is illustrated by the following Examples.

Example 1

90 parts by weight of a polyamide-6 having a relative viscosity of 3.9, as measured on a 1% solution in *m*-cresol at 25°C in an Ubbelohde viscosimeter, and a notched impact strength according to DIN 53453 of 4 kJ/m², and 10 parts by weight of a copolymer of ethylene, acrylic acid and ethylacrylate (ratio by weight 84:4:12) having a melt index, as determined according to DIN 53735, of 7 g/10 min., were mixed for 5 minutes in a mixer. The mixture thus prepared was kneaded and extruded in a twin-screw extruder of the ZSK 53 type at 90 rpm/270°C, the melt was spun off into a water bath, granulated and then dried *in vacuo* at 80°C to a water content of less than 0.05% by weight.

Freshly injected test specimens are found to show good homogeneity by alternating bending tests and have a notched impact strength according to DIN 53453 of 22 kJ/m².

Examples 2 to 3

Further tests carried out in the same way as Example 1 are summarised in Table 1 below. The quantity in which the ethylene/acrylic acid/acrylic ester terpolymer described in Example 1 was used amounted to 10 parts by weight in each case. The measured notched impact strength values according to DIN 53453 are set out in Table 1.

Examples 4 to 6

Following the procedure of Example 1, the quantities indicated in Table 2 of a polyamide-6 having a relative viscosity of 3.9, as measured on a 1% solution in *m*-cresol at 25°C, were mixed with various quantities of the terpolymer described in Example 1. The notched impact strength and the homogeneity were determined as described in Example 1.

Examples 7 to 10

The quantities indicated in Table 3 of a polyamide-6 having a relative viscosity of 3.94, as measured on a 1% solution in *m*-cresol at 25°C, and a notched impact strength of 3.8 kg/m² (DIN 53 453) were mixed and kneaded with various quantities of a copolymer of ethylene, acrylic acid and tert.-butyl acrylate (ratio by weight 89 : 4 : 12) having a melt index of 6.5 g/10 min. in a twin-screw extruder of the ZSK 53 type at 120 rpm at 270°C. The mixtures were worked up as described in Example 1. The notched impact strength and the homogeneity of the test samples are set forth in Table 3.

Example No.	PA-6 % by weight	(η_{rel})	Terpolymer % by weight	Notched impact strength [kJ/m ²]	Homogeneity
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TABLE 1

2	90	(3.5)	10	17.3	very good
3	90	(4.4)	10	26.0	very good

Example No.	PA-6 % by weight	(η_{rel})	Terpolymer % by weight	Notched impact strength [kJ/m ²]	Homogeneity	
5					5	
TABLE 2						
4	94	(3.9)	6	17.8	very good	
10	5	(3.9)	15	38.3	very good	10
	6	(3.9)	20	55.7	very good	
15					15	
TABLE 3						
7	95	(3.94)	5	12.7	very good	
8	90	(3.94)	10	23	very good	
20	9	(3.94)	15	40.5	very good	20
	10	(3.94)	20	59.2	very good	
25	U.K. Patent Application No. 49405/77 (Serial No. 1,575,339) describes and claims: Moulding compositions consisting essentially of:					25
	(1) from 65 to 99.4% by weight of a polyamide;					
	(2) from 0.1 to 25% by weight of a copolymer consisting of					
30	(a) from 99.8 to 40 mole % of ethylene; (b) from 0.1 to 30 mole 1) of (meth)acrylic acid which may be partly or completely present in salt form; and					30
	(c) from 0.1 to 30 mole % of at least one ester, amide or nitrile of (meth)acrylic acid; the sum of components (a) to (c) being 100 mole %, and					
35	(3) from 0.5 to 25% by weight of polyethylene and/or ethylene-vinyl acetate copolymer, the vinyl acetate content of the copolymer being from 0.1 to 30 mole %, the sum of components (1) to (3) being 100% by weight.					35
	We make no claim herein to that invention.					
	U.K. Patent No. 1,491,433 describes and claims a moulding composition comprising (A) 50 to 95 parts by weight of a polyamide and (B) 50 to 5 parts by weight of an ethylenic copolymer of ethylene, (a) an alkyl ester of a C ₃ - C ₈ unsaturated carboxylic acid, (b) 1 C ₃ - C ₈ unsaturated carboxylic acid, and (c) a metal salt of a C ₃ - C ₈ unsaturated carboxylic acid, the proportion of ethylene in the copolymer being from 90% to 98% by mole and the monomeric units (a), (b) and (c) having the following relationship in terms of the number of moles a, b and c, respectively:					40
45	$a/(a + b + c) \times 100 = 5-50\%, \text{ and}$ $c/(a + b + c) \times 100 = 5-90\%.$					45
50	We make no claim herein to that invention subject to the foregoing disclaimers. WHAT WE CLAIM IS:					50
	1. A thermoplastic moulding composition with high notched impact strength comprising:					
55	1) 70 to 96% by weight of a polyamide-6 having a relative viscosity of at last 3.5 as measured on 1% solution (as hereinbefore defined) in <i>m</i> -cresol at 25°C; and					55
	2) 4 to 30% by weight of an at least ternary copolymer comprising:					
	a) 50 to 95% by weight of ethylene;					
60	b) a to 20% by weight of acrylic or methacrylic acid which may be completely or partly present in the form of a salt thereof; and					60
	c) 1 to 30% by weight of at least one ester of acrylic or methacrylic acid with C ₁ -C ₉ alcohols					
	and having a melt index determined according to DIN 53 735, of 2 to 15 g/10 minute. the sum total of components 1 + 2 and a+b+c amounting to 100% by weight.					
65	2. A thermoplastic moulding composition as claimed in claim 1 wherein the component					65

1) has a relative viscosity of from 3.7 to 4.5, as measured on a 1% solution (as hereinbefore defined) in *m*-cresol at 25°C.

3. A thermoplastic moulding composition as claimed in claim 1 or 2 which consists of from 80 to 92% by weight of component 1).

5 4. A thermoplastic moulding composition as claimed in any of claims 1 to 3, which consists of from 8 to 20% by weight of the copolymer 2). 5

5. A thermoplastic moulding composition as claimed in any of claims 1 to 4, wherein component 2 consists of from 80 to 95% by weight of component 2a), from 1 to 10% by weight of component 2b), and 10 from 1 to 20% by weight of component 2c). 10

6. A thermoplastic moulding composition as claimed in any of claims 1 to 5, wherein component 2 has a melt index, as determined according to DIN 53 735 of 5 to 10 g/10 min.

7. A thermoplastic moulding composition as claimed in any of claims 1 to 6, wherein the alcoholic component of the acrylic or methacrylic acid ester consists of 2 to 6 carbon atoms. 15

8. A thermoplastic moulding composition as claimed in claim 7, wherein the ester is an ethyl, *n*-butyl or tert.-butyl acrylate. 15

9. A thermoplastic moulding composition substantially as herein described with reference to any of the specific Examples.

10. A shaped article produced from a thermoplastic moulding composition as claimed in any of claims 1 to 9. 20

11. A film produced from a thermoplastic moulding composition as claimed in any of claims 1 to 9.

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