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(54) REINFORCED VINYL CHLORIDE POLYMER COMPOSITIONS

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of 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 thermoplastic compositions based on vinyl chloride polymers which contain a reinforcing agent.

In the manufacture of injection moldings from fiber-reinforced thermoplastics, a lubricant or slip agent is added to the plastics material to achieve good flow of the polymer melt during processing. The lubricant may also serve as a mold release agent, so as to achieve short cycle times. In addition, good lubricants result in moldings of reinforced thermoplastics having a smooth surface.

The lubricants conventionally used for processing reinforced thermoplastics by injection molding are metal salts, esters or amides of fatty acids. It is true that these additives improve the melt flow, the ease of mold release and, in many cases, also the surface quality of the moldings, but as a rule they worsen the mechanical properties, such as tensile strength and impact strength, since they detract from the adhesion between the reinforcing agent and the plastic matrix.

In the processing of fiber-reinforced polyvinyl chloride, to produce injection molding compositions and sheeting, as described, for example, in German Laid-Open Application DOS 2,312,816, achieving adequate flow of the material, required to give products having good properties, again presents a problem; this cannot be solved by means of the lubricants and processing assistants conventionally used for injection molding of reinforced thermoplastics and polyvinyl chloride.

The present invention seeks to provide processing assistants for reinforced vinyl chloride polymers, especially for injection molding, which improve the flow of the polymer melt, the ease of mold release and the surface quality of the moldings, without adversely affecting the level of mechanical properties of the reinforced vinyl chloride polymers, and which in particular give products of high rigidity.

The present invention provides reinforced vinyl chloride polymer composition which comprise

A) from 99 to 50 parts by weight of a homopolymer of vinyl chloride or a copolymer of vinyl chloride with up to 30 per cent by weight of one or more copolymerizable monomers,

B) from 1 to 50 parts by weight of a linear polyester which is solid at room temperature, compatible with the vinyl chloride polymer and based on terephthalic acid and neopentylglycol, the sum of A and B being 100,

C) from 10 to 50 percent by weight, based on the sum of A and B, of a reinforcing agent and

D) from 0 to 90 per cent by weight, based on the sum of A and B, of one or more other fillers.

It is true that the use of polyesters as plasticizers and processing assistants for vinyl chloride polymers has already been disclosed and is described, for example, in German Laid-Open Application DOS 2,017,398 and DOS 2,252,104. However, the addition of polyesters to vinyl chloride polymers which do not contain any reinforcing agents give products which have a low rigidity and low Vicat heat distortion point; even the addition of reinforcing agents cannot offset this deterioration. It was therefore surprising and unforseeable that, by adding specific linear polyesters which are solid at room temperature to reinforced vinyl chloride polymers, molding compositions can be obtained which not only have good flow and good processability, especially by extrusion and

injection molding, but in addition have mechanical properties of a good level, in particular high rigidity and a high heat distortion point.

The component A of the compositions according to the invention may be a conventional vinyl chloride homopolymer or copolymer. The vinyl chloride homopolymers and copolymers preferably have a K-value, measured by the Fikentscher method (DIN 53,726) of from 55 to 80, particularly preferably from 58 to 70. The vinyl chloride copolymers contain up to 30 per cent by weight, preferably up to 15 per cent by weight, based on the vinyl chloride polymer, of one or more other monomers copolymerizable with vinyl chloride, e.g. vinylidene chloride, a vinyl ester, an acylic ester, acrylonitrile or an olefin. The homopolymers and copolymers of vinyl chloride may be manufactured by any conventional or customary polymerization process, which may entail polymerizing the monomers in mass, in solution, in aqueous suspension or in aqueous emulsion. The use of vinyl chloride homopolymers, especially of those which have been manufactured by aqueous suspension polymerization, is preferred. If a suspension polyvinyl chloride is employed, the mean particle size of the polymer is in general less than 300 μm. The polyvinyl chloride preferably has a Vicat softening point of from 70 to 85°C (measured according to DIN 53,460, method B).

The component B of the compositions according to the invention is a linear polyester based on terephthalic acid and neopentylglycol which is solid at room temperature (preferably one which has a melting point of from 100°C to 200°C) and is compatible with the vinyl chloride polymer. The polyester employed should advantageously have a high molecular weight, preferably a weight-average molecular weight of from 5,000 to 50,000.

The polyester may be manufactured by a conventional or customary process, for example by esterifying terephthalic acid with a 1.2-molar to 2-molar excess of neopentylglycol, if necessary under superatmospheric pressure, at from 150 to 220°C, and then condensing the low molecular weight ester thus obtained under reduced pressure, down to 1 mm Hg, at up to 250°C using a conventional condensing catalyst, to give a high molecular weight polyester. In an alternative method, a lower alkyl ester, preferably the dimethyl ester, of terephthalic acid is employed and is reacted with a 1.2-molar to 2-molar excess of neopentylglycol in the presence of a trans-esterifying catalyst, e.g. tetrabutyl orthotitanate. The polycondensation of the trans-esterification product is then again carried out under reduced pressure, down to 1 mm Hg, at up to 250°C, in the presence of a conventional condensing catalyst.

The compositions according to the invention contain from 99 to 50 parts by weight, preferably from 90 to 70 parts by weight, of the vinyl chloride polymer (component A) and from 1 to 50 parts by weight, preferably from 10 to 30 parts by weight of the polyester (component B), with the proviso that the sum of the components A+B is 100.

In the main, glass fibers are used as the reinforcing agent (component C). However, glass beads, carbon fibers and mineral reinforcing agents, e.g. talc, asbestos or gypsum fibers, may also be used. The use of low-alkali E-glass fibers is preferred. The glass fibers in general have a diameter of from 5 to 20μ, preferably from 8 to 10 μ, and a mean length of from 0.05 to 1 mm, preferably from 0.1 to 0.5 mm. They may be finished, in the conventional manner, with a conventional size or adhesion promoter, e.g. those based on organosilanes. The glass fibers are particularly suitable reinforcing agents if the compositions according to the invention are to be injection-molded; for such cases, the fibers may be used as glass fiber rovings or as chopped strands. If a composition within the invention are to be processed to give sheeting, the reinforcing agents are preferably employed as textile sheet-like materials, in the form of mats, webs, felts or woven fabrics produced from the fibrous reinforcing agents, especially from glass fibers. The compositions according to the invention contain from 10 to 50 per cent by weight, preferably from 20 to 30 percent by weight of the reinforcing agents, based on the sum of the components A and B.

In addition to the reinforcing agents, the compositions according to the invention may contain, as component D, other fillers in amounts of up to 90 per cent by weight, based on the sum of the components A and B. Examples of such fillers are metal powders of particle size from 1 to 150 μ, pulverulent carbon, preferably graphite powder, with particle sizes of from 0.1 to 1,000 μ, and mineral fillers, e.g. chalk. The proportion of the fillers in a composition within the invention is preferably from 10 to 90 per cent by weight, especially from 30 to 50 per cent by weight, based on the sum of the components A and B.

The advantages achieved by compositions within the invention are that the use of the polyester(s) as processing assistant(s) gives reinforced vinyl chloride polymers which generally have better flow than is achievable with conventional lubricants, and which generally are easily processable, especially by injection molding. Moldings

manufactured from the compositions generally exhibit improved surface quality and have a good level of mechanical properties, in particular high rigidity and a high heat distortion point.

The reinforced molding compositions may contain conventional additives, e.g. stabilizers, antioxidants, dyes and pigments and, where necessary, also conventional lubricants.

The conventional processes for reinforced thermoplastics may be used to manufacture molding compositions within the invention. For example, they can be manufactured in any suitable kneader in which case the vinyl chloride polymer and the polyester are melted and mixed with the reinforcing agent and the other additives. If the reinforcing agents are used as textile sheet-like structures, the compositions can also be manufactured by impregnating the said structures with a melt of the vinyl chloride polymer and the polyester. The compositions according to the invention may in particular be used for the manufacture of injection moldings or of sheeting.

In the Examples which follow, parts and percentages are by weight, unless stated otherwise.

The tensile strength and flexural strength of the reinforced vinyl chloride polymer compositions in the Examples were determined as described in DIN 53,455. The impact strength a_n was measured as described in DIN 53,453; the heat distortion point was determined as described in DIN 53,460, method B.

EXAMPLE 1

70 parts of a polyvinyl chloride manufactured by suspension polymerization and 30 parts of polyneopentyl terephthalate (PNT) were processed with 24.8 parts by weight, based on the sum of polyvinyl chloride and PNT, of short glass fibers. The polyvinyl chloride had a K value of 61 and a Vicat softening point of 83°C. The amorphous PNT, manufactured from terephthalic acid and neopentylglycol, had a K value of 58 and a glass transition temperature of 80°C.

The individual components were mixed in a suitable twinscrew extruder without exceeding 190°C. After extruding strands of the mixture and chopping these, the product is obtained in a granular form. These granules are processed on commercial injection moulding machines at up to 230°C. The mechanical properties of the mixture are summarized in the Table below.

EXAMPLE 2

Using the method described in Example 1, 80 parts of polyvinyl chloride and 20 parts of PNT were processed with 23.3 per cent by weight, based on the sum of polyvinyl chloride and PNT, of short glass fibers. The mechanical properties of the mixture are shown in the Table.

EXAMPLE 3

A mixture of 70 parts of polyvinyl chloride and 30 parts of PNT was processed together with 2 glass mats of continuous filaments of E-glass, weighing 600 g/m² (glass content: 23.7%, based on the sum of polyvinyl chloride and PNT). A flat sheet was produced; its mechanical properties are shown in the Table.

EXAMPLE 4

Example 1 was repeated but in this case 21.4%, based on the sum of polyvinyl chloride and PNT, of talc of particle size less than 10 μ were also incorporated into the mixture. The product obtained had the mechanical properties shown in the Table.

TABLE

Example	Tensile strength (N/mm²)	Flexural strength (N/mm²)	Impact strength a_n (kJ/m²)	Vicat temperature (°C)
1	61	95	12.5	73
2	61	94	12.3	72
3	63.2	105	43	78
4	57	95	10.2	76

WHAT WE CLAIM IS:—

1. A reinforced vinyl chloride polymer composition comprising

A) from 99 to 50 parts by weight of a homopolymer of vinyl chloride or a copolymer of vinyl chloride with up to 30 per cent by weight of one or more copolymerizable monomers,

B) from 1 to 50 parts by weight of a linear polyester which is solid at room temperature, compatible with the vinyl chloride polymer, and based on terephthalic acid and neopentylglycol with the proviso that the sum of A and B is 100,

C) from 10 to 50 per cent by weight, based on the sum of A and B, of a reinforcing agent and

D) from 0 to 90 per cent by weight, based on the sum of A and B, of one or more other fillers.

2. A reinforced vinyl chloride polymer composition as claimed in Claim 1, wherein

the polyester employed as component B has a melting point of 100 to 200°C and a weight-average molecular weight of 5,000 to 50,000.

3. A reinforced vinyl chloride polymer composition as claimed in Claim 1 or Claim 2 containing from 10 to 30 per cent by weight of component B based on the sum of A and B.

4. A reinforced vinyl chloride polymer composition as claimed in any of Claims 1 to 3, wherein the reinforcing agent is glass fibres.

5. A reinforced vinyl chloride polymer composition as claimed in any of Claims 1 to 4, wherein the component A is a vinyl chloride polymer having a K value of from 55 to 80 and contains at most 15 per cent by weight of copolymerizable monomers.

6. A reinforced vinyl chloride polymer composition as claimed in any of Claims 1 to 5, wherein component D is present in an amount of from 10 to 90 per cent by weight and is selected from metal powders of particle size 1 to 150 μ, pulverulent carbon of particle size from 0.1 to 1,000 μ and mineral fillers.

7. A reinforced vinyl chloride polymer composition containing a linear polyester and substantially as described in any of the foregoing Examples.

8. A molding process in which a composition as claimed in any of Claims 1 to 7 is injection moulded.

9. Moldings made from reinforced vinyl chloride polymer compositions as claimed in any of Claims 1 to 7.

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