Impact-strength-modified polymethacrylate molding compound with improved melt volume-flow rate

The invention relates to impact-strength-modified polymethacrylate molding compounds with improved melt volume-flow rate.

Prior Art

Impact-strength modifiers for polymethacrylate plastics have been known for many years. The manufacture and structure of impact-strength-modified polymethacrylate molding compounds are described in, for example, European Patent Applications EP A 0113924, EP A 0522351, EP A 0465049 and EP A 0683028.

EP A 469521 relates to improvement of flow in the processing of PVC blends to be impact-strength-modified, for example during injection molding. In this process, polymers based on alkyl methacrylate, comprising at least 50 wt% of methyl methacrylate as well as 2 to 50 wt% of C2 to C8 alkyl methacrylates and having molecular weights (Mw) in the range of 2,000 to 20,000 g/mol are added to PVC-ABS polymer mixtures.

Object and Achievement

The object was considered to be to provide an impact-strength-modified polymethacrylate molding compound which has improved melt volume-flow rate at high temperatures, such as are used in the injection-molding process, and which at the same time has high dimensional stability at high temperature and high notched impact strength.

The object is achieved by an

impact-strength-modified polymethacrylate molding compound, characterized by

a Vicat softening temperature per ISO 306 (B 50) of at least 90°C,

a notched impact strength (Charpy) per ISO 179/1eA of at least 3.0 kJ/m^2 at 23°C,

and

a melt volume-flow rate MVR (230°C/3.8 kg) per ISO 1133 of at least 11 $cm^3/10$ min

obtainable by mixing, in the melt,

a) 80 to 98 wt% of an impact-strength-modified polymethacrylate molding compound with

b) 20 to 2 wt% of a low molecular weight polymethacrylate molding compound

the impact-resistant molding compound comprising 70 to 99 wt% of a matrix of 80 to 100 wt% of radical-polymerized methyl methacrylate units and if necessary 0 to 20 wt% of further comonomers that can undergo radical polymerization, and containing 1 to 30 wt% of an impact-strength modifier,

and the low molecular weight polymethacrylate molding compound comprising 80 to 100 wt% of radical-polymerized methyl methacrylate units and 0 to 20 wt% of further comonomers that can undergo radical polymerization, and having a viscosity number ($\eta_{sp/c}$) of 25 to 35 ml/g as measured in chloroform per ISO 1628 Part 6.

It was not foreseeable that the desired characteristics could be achieved by addition of a low molecular weight polymethacrylate molding compound. The new impact-strength-modified molding compound is suitable in particular for use in the injection-molding process, where good melt volume-flow rate is required in order to ensure short cycle times and good filling of the molds. In the process, the other characteristics of the obtained injection-molded articles are not impaired, especially the dimensional stability at high temperature and the notched impact strength.

Description of the Invention

Polymethacrylate matrix

The impact-resistant molding compound comprises 70 to 99 wt% of a matrix of 80 to 100, preferably 90 to 98 wt% of radical-polymerized methyl methacrylate units and if necessary 0 to 20, preferably 2 to 10 wt% of further comonomers that can undergo radical polymerization, such as C1 to C4 alkyl (meth)acrylates, especially methyl acrylate, ethyl acrylate or butyl methacrylate. Preferably the average molecular weight Mw of the matrix ranges from 90,000 g/mol to 200,000 g/mol, especially 100,000 g/mol to 150,000 g/mol.

Impact-strength modifier

The polymethacrylate matrix contains 1 to 30, preferably 2 to 20, particularly preferably 3 to 15, especially 5 to 12 wt% of an impact-strength modifier, which is an elastomer phase of cross-linked polymer particles. The impact-strength modifier is incorporated in a manner known in itself by bead polymerization or by emulsion polymerization.

The simplest case is one in which the cross-linked particles obtainable by means of bead polymerization have a mean particle size ranging from 50 to 500 μm, preferably 80 to 120 μm. They usually comprise at least 40, preferably 50 to 70 wt% of methyl methacrylate, 20 to 40, preferably 25 to 35 wt% of butyl acrylate as well as 0.1 to 2, preferably 0.5 to 1 wt% of a cross-linking monomer, for example a multifunctional (meth)acrylate such as allyl methacrylate and if necessary further monomers such as 0 to 10, preferably 0.5 to 5 wt% of C1 to C4 alkyl methacrylates, such as ethyl acrylate or

butyl methacrylate, preferably methyl acrylate, or other monomers that can undergo vinyl polymerization, such as styrene.

Preferred impact-strength modifiers are polymer particles which have a two-layer, particularly preferably a three-layer core-shell structure and which can be obtained by emulsion polymerization (see, for example, EP A 0113924, EP A 0522351, EP A 0465049 and EP A 0683028). Typical particle sizes of these emulsion polymers range from 100 to 500 nm, preferably 200 to 400 nm.

A three-layer or three-phase structure with a core and two shells can be obtained as follows. An innermost (hard) shell can, for example, comprise substantially methyl methacrylate, small proportions of comonomers such as ethyl acrylate, and a proportion of cross-linking agent, such as allyl methacrylate. The middle (soft) shell can, for example, be formed from butyl acrylate and if necessary styrene, whereas the outermost (hard) shell usually corresponds substantially to the matrix polymer, whereby compatibility with the matrix and good bonding thereto are achieved. The polybutyl acrylate proportion in the impact-strength modifier is decisive for the impact-strength effect, and preferably ranges from 20 to 40 wt%, particularly preferably from 25 to 35 wt%.

Impact-strength-modified polymethacrylate molding compounds

In the extruder, the impact-strength modifier and matrix polymer can be intermixed in the melt to obtain impact-strength-modified polymethacrylate molding compounds. The discharged material is usually chopped up into the form of granules at first. These can be further processed by means of extrusion or injection molding to obtain molded articles, such as plates or injection-molded parts.

Notched impact strengths and melt volume-flow rate of the prior art

Molded articles of commercial impact-strength-modified polymethacrylate molding compounds have Charpy notched impact strengths per ISO 179/1eA ranging from 3.0 kJ/m^2 to 5.0 kJ/m^2.

Commercial impact-strength-modified polymethacrylate molding compounds have flow-rates MVR (230°C/3.8 kg) ranging from 0.4 to 8.1 cm^3/10 min per ISO 1133. The melt volume-flow rate of impact-strength-modified polymethacrylate molding compounds must be as high as possible, especially for processing by injection molding. Impact-strength-modified polymethacrylate molding compounds optimized for melt volume-flow rate reach MVR values (230°C/3.8 kg, ISO 1133) in the range of about 10.0 cm^3/10 min at the most.

Low molecular weight polymethacrylate molding compound

The melt volume-flow rate of impact-strength-modified polymethacrylate molding compounds can be increased while maintaining notched impact strength by addition of a low molecular weight polymethacrylate molding compound.

The proportion of low molecular weight polymethacrylate molding compound in the impact-strength-modified polymethacrylate molding compound ranges between 2 and 20, preferably between 3 and 15 wt%.

The low molecular weight polymethacrylate molding compound comprises 80 to 100 wt% of radical-polymerized methyl methacrylate units and 0 to 20 wt% of further comonomers that can undergo radical polymerization, for example C1 to C4 alkyl (meth)acrylates, especially methyl acrylate, ethyl acrylate or butyl methacrylate. The low molecular weight polymethacrylate molding compound has a

viscosity number ($\eta_{sp/c}$) ranging from 25 to 35 ml/g, preferably 27 to 33 ml/g as measured in chloroform per ISO 1628 Part 6, corresponding to an average molecular weight Mw (weight average) of 30,000 to 70,000, especially 40,000 to 60,000.

The molecular weight can be determined by methods such as differential scanning chromatography (DSC) or by gel chromatography on the basis of polymethyl methacrylate calibration standards or calibration lines correlated with the viscosity number.

Addition/use of the low molecular weight polymethacrylate molding compound

The low molecular weight polymethacrylate molding compound can be added as granules during melt processing of impact-strength modifier and polymethacrylate matrix in the extruder. In this way the low molecular weight polymethacrylate molding compound is worked into or intermixed with the melt and is then a constituent of the impact-strength-modified molding compound discharged from the extruder. This compound either can be processed directly to molded articles by extrusion or injection molding or can be pellerized first of all to transform it to salable granules.

The low molecular weight polymethacrylate molding compound can also be mixed in the form of granules together with granules comprising impact-strength modifier and polymethacrylate matrix already mixed in the melt (granule mixture) and then processed in the melt.

Characteristics of the new polymethacrylate molding compound

The polymethacrylate molding compound obtained by mixing the low molecular weight polymethacrylate molding compound and the impact-strength-modified polymethacrylate molding compound in the melt is characterized by a Vicat softening temperature per ISO 306 (B 50) of at least 90°C, a notched impact strength (Charpy) per ISO 179/1eA of at least 3.0 kJ/m^2 at 23°C and a melt volume-flow rate MVR (230°C/3.8 kg) per ISO 1133 of at least 11 $cm^3/10$ min.

EXAMPLES

An impact-strength-modified molding compound with a content of 7.5 wt% of impact-strength modifier (base emulsion polymer) was homogeneously mixed at 220°C in the melt with 5 and 10 wt% of a low molecular weight molding compound in a twin-screw extruder (ZSK 25 of W&P). The strands drawn from the extruder were cooled and chopped up to obtain granules. Specimens were made from the resulting granules by means of an injection-molding machine. Various characteristics were measured on the obtained specimens.

Impact-strength-modified molding compound:

comprising 92.5 wt% of matrix polymer and 7.5 wt% of impact-strength modifier

Matrix polymer:

91 wt% of methyl methacrylate and 9 wt% of methyl acrylate.

Impact-strength modifier:

A commercial three-phase (core and two shells) emulsion polymer with a particle size ranging from 300 to 500 nm and a core/shell 1/shell 2 ratio of 1:1:1 with a butyl acrylate proportion of 27 wt% relative to the impact-strength modifier.

Core:

95.5 wt% of methyl methacrylate, 4 wt% of ethyl acrylate and 0.5 wt% of 0.5 wt% of allyl methacrylate.

Shell 1:

81.2 wt% of butyl acrylate, 17.5 wt% of styrene, 1.3 wt% of allyl methacrylate.

Shell 2:

96 wt% of methyl methacrylate, 4 wt% of ethyl acrylate.

Low molecular weight molding compound:

comprising 85 wt% of methyl methacrylate and 15 wt% of methyl acrylate units with a viscosity number ($\eta_{sp/c}$) in the range of 30 ml/g as measured in chloroform per ISO 1628 Part 6, corresponding to an Mw of about 50,000 g/mol.

The results are summarized in the following table. The addition of 5 or 10 wt% of the low molecular weight molding compound leads to a distinct increase of melt volume-flow rate MVR, whereas the dimensional stability at high temperature (VST) and the notched impact strength remain practically unchanged compared with the example without addition of low molecular weight molding compound.

Proportion of low molecular weight molding compound				
	Standard	0 wt%	5 wt%	10 wt%
MVR (230°C/3.8 kg) in cm^3/10 min	ISO 1133	8.9	11.1	13.0
VST (B 50) in °C	ISO 306	94.6	94.8	94.2
Notched impact strength (Charpy/23°C) in kJ/m^2	ISO 179/1eA	3.4	3.4	3.4

CLAIMS

1. An impact-strength-modified polymethacrylate molding compound, characterized by

a Vicat softening temperature per ISO 306 (B 50) of at least 90°C,

a notched impact strength (Charpy) per ISO 179/1eA of at least 3.0 kJ/m^2 at 23°C,

and

a melt volume-flow rate MVR (230°C/3.8 kg) per ISO 1133 of at least 11 $cm^3/10$ min,

obtainable by mixing, in the melt,

a) 80 to 98 wt% of an impact-strength-modified polymethacrylate molding compound with

b) 20 to 2 wt% of a low molecular weight polymethacrylate molding compound

the impact-resistant molding compound comprising 70 to 99 wt% of a matrix of 80 to 100 wt% of radical-polymerized methyl methacrylate units and if necessary 0 to 20 wt% of further comonomers that can undergo radical polymerization, and containing 1 to 30 wt% of an impact-strength modifier,

and the low molecular weight polymethacrylate molding compound comprising 80 to 100 wt% of radical-polymerized methyl methacrylate units and 0 to 20 wt% of further comonomers that can undergo radical polymerization, and having a viscosity number ($\eta_{sp/c}$) of 25 to 35 ml/g as measured in chloroform per ISO 1628 Part 6.

2. A molding compound according to claim 1, characterized in that the matrix polymer has a molecular weight Mw of 90,000 g/mol to 200,000 g/mol.

3. A molding compound according to claim 1, characterized in that it contains an impact-strength modifier with a polybutyl acrylate proportion of 20 to 40 wt%.

4. The use of a molding compound according to one or more of claims 1 to 3 for making molded articles in the injection-molding process.

5. The use according to claim 4, wherein the low molecular weight polymethacrylate molding compound is used as a granule mixture together with the impact-strength-modified polymethacrylate molding compound.