

60210/000.332

5 The invention relates to impact-modified thermoplastic moulding compounds consisting of an aromatic polycarbonate and a 2-phase copolymer as an impact modifier.

10 Among the materials used for preparing moulded plastics parts, thermoplastic materials are of particular significance, especially those thermoplastics which have heat-resistance values of clearly more than 100°C. The thermoplastics with relatively high heat-resistance values include polycarbonates which are usually polycondensates based on bisphenol A. The polycarbonate based on tetramethylbisphenol A which, 15 itself, is a condensation product of 2,6-dimethylphenol and acetone differs from the "normal" bisphenol A-polycarbonate by a freezing temperature which is about 50°C higher. Its Vicat B-softening point is about 198°C and it may still be processed thermoplastically.

20 For many desirable applications of plastics e.g. in automobile and vehicle construction, however, the properties of the plastics have to be further improved. The resistance to impact is an important characteristic of plastics which are increasingly used nowadays as 25 construction materials. A measure of the resistance of a plastics material is the notch impact strength which may be determined by experiment according to DIN 53 453 and which explains how suddenly received mechanical stresses are absorbed and converted by a polymer 30 material.

For a long time technology has been faced with the task of converting relatively brittle plastics materials into technically usable products with an improved impact strength. One method of improving the resistance of 35 thermoplastic materials, even of polycarbonate, is the rubber-elastication thereof, as disclosed by D. Neuray and K.H. Ott in Angew, Makromol. Chem. 98, 213 - 224

(1981). In this document, it is also emphasised that the rubber segments must be anchored in or "coupled to" the thermoplastic matrix as otherwise no improvement of the resistance is achieved even if the elastomer content increases. The anchoring of the elastomers is achieved, for example, by grafting the rubbers with polymers consisting of monomers which cannot be polymerised on their own to form thermoplastic materials.

The impact-resistance improvement of polycarbonate by adding graft elastomers has been disclosed frequently. Thus, DE-OS 26 53 143 to DE-OS 26 53 145 recommend the use of graft polymers consisting of styrene and/or methylemethacrylate and/or (meth)acrylonitrile on diene or EPDM-rubber in order to prepare thermoplastic moulding compounds using polycarbonate. DE-OS 32 45 292 discloses a thermoplastic moulding compound of polycarbonate and a copolymer consisting of a polymer composed of many layers, the core being an acrylic rubber, onto which a shell consisting, in particular, of (α -methyl)styrene/acrylonitrile/methylemethacrylate and a further hard component separately prepared from the monomers styrene, α -methyl styrene, acrylonitrile, methylemethacrylate, maleic acid anhydride and/or acrylic acid is grafted.

European Patent Application 0 036 127 discloses polycarbonates with an improved impact-resistance in the form of a mixture of a polycarbonate resin and an acrylic rubber-interpolymer compound containing diallylmalate as a grafting monomer and methylemethacrylate as a monomer of the second polymer phase. A polymer blend consisting of polycarbonate and an EPDM-g-methylemethacrylate/N-maleic imide graft polymer is disclosed in European Patent Application 0 144 213.

European Patent Application 260 558 also discloses thermoplastic compounds consisting of polycarbonates and thermoplastic graft polymers on silicone rubbers with a

high viscosity, the silicone rubbers being provided with an intermediate shell of cross-linked acrylic rubber in order to improve grafting with the resin-forming monomers.

5 DE-OS 31 18 526 discloses thermoplastic moulding compounds consisting of polyalkylene terephthalate, polycarbonate and a graft polymer. Here, the graft polymer may also be an acrylic rubber core, synthesized with aromatic esters such as benzylacrylate and
10 phenylacrylate.

Compatible polymer mixtures of polycarbonate and thermoplastically deformable methylmethacrylate copolymers are known. The compatibility of the polymethylmethacrylate is produced in accordance with
15 German Patent Application P 36 32 946.0 using N-cyclically substituted (meth)acrylamides, or in accordance with German Patent Application 37 09 562.5, using N-cyclohexyl- or N-phenyl-substituted maleic imides, or in accordance with German Application P 37 19
20 239.6 using cycloaliphatic or aromatic (meth)acrylic esters as comonomers.

Object and Solution

25 The invention has the object of providing polycarbonates with an improved impact strength or notch-impact strength. Here, because of polycarbonate blends with a modified impact strength being used e.g. as vehicle parts, improved notch impact strength is
30 especially important for lower temperatures, i.e. for the temperature range from 0° to about -50°C, and the improvement should be possible without a significant impairment of the other properties.

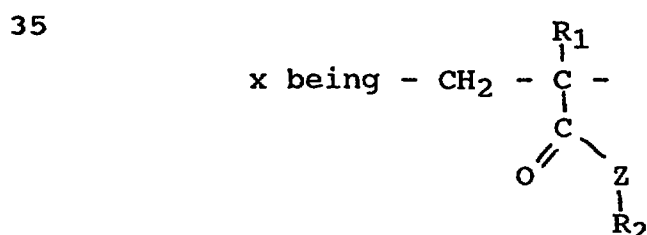
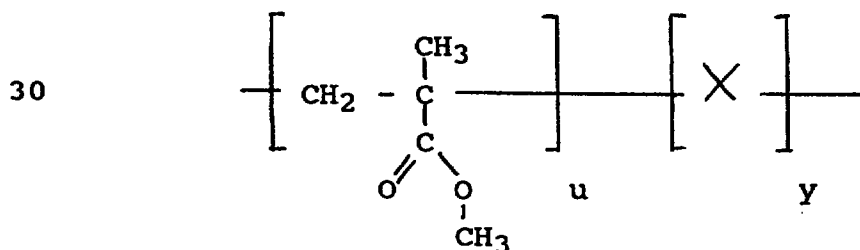
This object is achieved by the invention.
35 Surprisingly, it has been found that the methylmethacrylate copolymers known from prior art and highly compatible with polycarbonate are eminently

suitable as impact modifiers for polycarbonate, when the hard phase is combined with a rubber (elastomer) phase and is polymerised onto this phase. Thus, impact modifiers have been found by means of which the viscous phase (elastomer phase) is anchored in the polycarbonate by copolymers which, themselves, are highly compatible with the coherent phase. The methymethacrylate copolymers responsible for the anchorage may be provided on the viscous phase as graft branches or as shells.

The invention relates to thermoplastic moulding compounds and moulded articles synthesized from 95 to 30 wt.% of polycarbonates of divalent phenols, more particularly based on bisphenol-A, and 5 to 70 wt.% of a copolymer having at least two phases as an impact modifier consisting of

A) more than 20 to 90 wt.% of an optionally cross-linked polymer P having a glass transition temperature $T_g \leq 10^\circ\text{C}$, preferably $\leq -10^\circ\text{C}$, and

B) less than 80 to 10 wt.% of a methymethacrylate copolymer at least partly covalently bonded with A), the methymethacrylate copolymer, itself, being compatible with polycarbonate and having a glass transition temperature $T_g > 30^\circ\text{C}$ of the statistical composition:



wherein Z is -O- and/or-NH-

R₁ is -H and/or -CH₃

R₂ is -(CH₂)_n-W with n being 0 to 5,

wherein, if Z is -O-, W is an optionally alkyl substituted aryl group having 6 to 12 C-atoms and, if Z is -NH-, W is an optionally substituted aryl group having 6 to 12 C-atoms or an optionally substituted cycloalkyl group having 5 to 9 C-atoms, wherein

u is between 10 to 98 wt.% (preferably 50-95 wt.%) and

y is between 2 to 90 wt.% (preferably 5-50 wt.%),

u+y being 100 wt.%

and which may also contain further comonomers in an amount of from 0 to 15 wt.%.

By means of the methylmethacrylate copolymers described under B) and the at least partly covalently bonded copolymer branches or copolymer shells, the viscous phase A) is molecularly anchored in the polycarbonate matrix thereby forming a polymer mixture (blend) which has outstanding mechanical properties.

In order to prepare the impact modifiers, polymers P having a glass transition temperature $T_g \leq 10^\circ\text{C}$, preferably $\leq -10^\circ\text{C}$ are used as the viscous phase. These include polymers which are normally listed under the heading of rubber. The polymers of Component A) are optionally cross-linked. Their glass transition temperatures T_g may be determined in accordance with Edith. A. TURI "Thermal Characterization of Polymeric Materials" p. 169 ff, Academic Press, New York 1981. The polymers P for the viscous phase A) are preferably chosen from the group consisting of polyolefins, polydienes, ethylene-vinylacetate copolymers, polyacrylates, polysiloxanes (cf. Ullmanns Encyklopädie

der technischen Chemie, 4th ed. vol. 13, pp. 595 to 635, Verlag Chemie 1977).

5 The above reference lists methods for preparing these rubbers as well as their properties such as their solubilities and viscosities as well as their molecular weights Mw.

10 Preferably, tert. polymers consisting of ethylene, propylene and a diene, the so called EPDM types and acrylate rubbers are used as viscous phases A). These polyacrylates are preferably prepared by polymerisation in aqueous emulsion, partly also in suspension using conventionally known methods. (Ullmanns Encyklopädie der technischen Chemie, 4th ed. vol. 19, pp. 125 to 137, Verlag Chemie 1980).

15 In order to prepare the methylmethacrylate copolymer B) bonded with A), compounds X are known to be incorporated into the polymer component. They are also disclosed as comonomers for methylmethacrylate by the above German Patent Applications P 36 32 946.0, 37 09
20 562.5 and 37 19 239.6. In a preferred embodiment, R_1 is CH_3 i.e. the Compounds X preferably derive from methacrylic acid. X includes e.g. phenylmethacrylate, benzylmethacrylate, phenylethylmethacrylate, phenylethylacrylate, N-phenylmethacrylamide, N-
25 cylcohexylacrylamide, N-2-methylcyclohexylmethacrylamide and, optionally, also N-cyclohexylmaleic imide, N-4-methylcyclohexylmaleic imide.

The amounts of methylmethacrylate and X in B), i.e. the amounts u and y lie, in the case of u, between
30 10 and 98 wt.%, preferably between 50 and 95 wt.%, and in the case of y between 2 and 90 wt.%, preferably between 5 and 50 wt.%, u and y being 100 wt.%.

The methylmethacrylate copolymers B), themselves, are polymers with glass transition temperatures $T_g \geq$
35 30°C.

The copolymer B) may also contain, in amounts of 0 to 15 wt.%, more particularly in amounts of 0.5 to 5

wt.%, based on B), further homopolymerised α , β -unsaturated compounds such as styrene, α -methylstyrene, acrylic acid, methacrylic acid C_1 to C_6 - ester of acrylic acid such as methylacrylate and further esters (C_2 to C_6) of methacrylic acid such as ethylmethacrylate. The addition of compounds with several polymerisable double bonds i.e. of cross-linking agents is also possible and optionally advantageous.

The preparation of the impact modifiers may be carried out in accordance with known methods as follows: As a rule, the polymer P is introduced to the phase A), preferably in the form of a solution in a solvent suitable for further processing such as a solvent suitable for the radical polymerisation of monomers B) (H. Rauch-Puntigam, Th. Völker, Acryl- and Methacrylverbindungen, Springer-Verlag, Heidelberg 1967; J. Brandrup, E.H. Immergut, Polymer Handbook, III-144 to III-148, John Wiley 1975). Here, the tendency of the solvents to carry out transfer reactions must be taken into account.

Mention must be made of e.g. esters such as butylacetate, ethylacetate, hydrocarbons such as toluene, ketones such as acetone. Generally, solutions with a content of about 15 to 50 wt.% of the polymer P are used to which the monomers and polymerisation excipients are added, for example, dropwise. The polymerisation is normally carried out at elevated temperature, for example, within the range of 80 to 140°C. The initiators used include conventional ones, such as peroxides or azo compounds ((H. Rauch-Puntigam, Th. Völker, Acryl- and Methacrylverbindungen loc.cit). With solvents boiling at a lower temperature dibenzoylperoxide may be used, whereas with solvents boiling at a higher temperature, it may be of advantage to use e.g. tert.-butyl compounds such as tert. butylperoctoate.

In the case of an EPDM grafting, the polymerisation of the monomers to form Component B) may, for example, be carried out with butylacetate as solvent, initially at about 120°C, and then at about 80°C with further addition of methylmethacrylate, cross-linking agents and initiator. Advantageously, the polymerisation may be carried out in the presence of regulators such as mercaptans.

The impact modifier is advantageously produced by precipitation from the solution, for example using methanol as precipitating agent. If the modifier is prepared by emulsion polymerisation, it is preferably produced by squeezing out the emulsion polymer using an extruder.

Polycarbonate Impact Modification

The plastics to be modified are polycarbonates, above all thermoplastically deformable aromatic polycarbonates i.e. those polycarbonates prepared by means of bisphenols such as 2,2-Bis-(3,5-dimethyl-4-hydroxyphenyl)-propane, but especially 2,2-Bis-(4-hydroxyphenyl)-propane, i.e. the compound known as Bisphenol A. Polycarbonates of Bisphenol A are for example the commercially available Makrolon® products. The thermoplastic, aromatic polycarbonates have average molecular weights of at least about 10,000, preferably between about 20,000 and about 200,000. This corresponds to a relative viscosity range of 1.1 to 1.5, measured on a 0.5 wt.% solution in methylene chloride at 25°C.

The polycarbonates to be modified may be mixed with the impact modifiers, in a manner known per se, by mechanical mixing such as on roller kneaders or in the extruder (cf. Ullmanns Encyklopädie der technischen Chemie, 4th ed. vol. 15, pp. 281 - 285). Generally, the impact modifier added to the thermoplastic aromatic

polycarbonate to be modified is about 5 to 70 wt.%, preferably 5 to 50 wt.%, particularly preferred 10 to 40 wt.%, based on the impact-modified thermoplastic moulding compound. In so doing, the object always is to achieve a total characteristics profile as favourable as possible.

The impact modifiers are clearly superior to conventional agents which are largely combinations of styrene-methylmethacrylate-acrylonitrile copolymers and a viscous phase. This is achieved by the greater compatibility of the B) phase of the new modifiers with the polycarbonate and thus a better anchorage in the total system, in the case of energetic stresses, more particularly low temperature stresses.

The excellent suitability of the impact modifier is demonstrated by the following Examples. The impact strength (SZ) and the notch impact strength (KSZ) are determined according to DIN 53 453. The determination of the VICAT-softening temperature takes place according to DIN 53 460 (VST/B).

EXAMPLES

Example 1

- 5 Preparing the impact modifier for polycarbonate with EPDM as viscous phase.

10 Whilst stirring, 200 g of EPDM (EPSYN ® 55) is dissolved in butylacetate within 75 minutes to form a 30% solution. Then, during another 2 hours at 120°C, whilst stirring, a mixture consisting of:

- 356 g of methylmethacrylate
40 g of phenylmethacrylate
4 g of methylacrylate
15 6 g of tert-butylperoctoate
600 g of butylacetate

is added. After cooling for about 30 minutes to 80°C, whilst stirring, a mixture of 10 g of triallylcyanurate, 10 g of methylmethacrylate and 4 g of tert-
20 butylperoctoate is added, and stirred for 2 hours at 80°C and then for 2 hours at 90°C.

After cooling, the graft copolymer is precipitated in methanol.

The SZ-modifier has the following composition:

- 25 67 wt.% of copolymer consisting of
methylmethacrylate-phenyl-
methacrylate in a weight ratio
of 89 - 10 -1
and 33 wt.% of EPDM

30

Example 2

Preparing the SZ-modified PC

- 35 15 wt.% of the SZ-modifier described in Example 1 is mixed with 85 wt.% of Makrolon ® 3100 and injection moulded. A shiny, opaque polymer mixture with excellent

SZ, KSZ and heat dimensional stability is obtained (Diagram 1 and Table 1).

Example 3

5

Preparing an impact modifier with a core-shell structure for PC

10 Into a Wittschen pot equipped with heater and stirrer, 1,270 g of water (dist.), 0.5 g of acetic acid, 0.5 g of iron-(II)-sulphate and 125 g of a monomer emulsion A, consisting of 1,460 g of water (dist.), 4 g of C15-paraffinsulphonate, 1,115 g of butylacrylate and 23 g of allylmethacrylate are introduced and the
15 polymerisation is started at ambient temperature with 0.15 g of diisopropylbenzolmonohydroperoxide and 1.3 g of sodium hydroxy methylsulphinate. After reaching the maximum temperature, a further 2,478 g of the monomer emulsion A are added and polymerised with 1.26 g of
20 diisopropylbenzolmonohydroperoxide and 0.3 g of sodium hydroxy methyl sulphinate (core polymer).

When the reaction has finished, the resultant dispersion is heated to 90°C. At this temperature, over 2 hours, a monomer emulsion B consisting of 1,460 g of
25 water, 4 g of C15-paraffinsulphonate, 570 g of methylmethacrylate, 560 g of phenylmethacrylate, 12 g of methylmethacrylate and 6 g of 2-ethylhexylthioglycolate is added by metering and polymerised in the presence of 2 g of potassium peroxydisulphate (shell polymer).

30

Example 4

12 wt.% (corresponding to an amount of 6 wt.% of butylacrylate) of the SZ-modifier described in Example 3
35 is mixed with 88 wt.% of Makrolon ® 3,100 and injection moulded (the butylacrylate-amount corresponds approximately to the EPDM-amount of Example 2). A

shiny, opaque polymer mixture with an improved low temperature-notch impact strength and an excellent heat dimensional stability results (Table 2).

5 Example 5

12 wt.% (corresponding to an amount of 6 wt.% of butylacrylate) of the SZ modifier described in Example 3 is mixed with 88 wt.% of Makrolon ® 1189 ("low molecular" polycarbonate) and injection moulded (the butylacrylate amount corresponds approximately to the EPDM amount of Example 2). The resultant polymer mixture is opaque and has a satisfactory surface sheen. While maintaining the excellent Makrolon ® heat dimensional stability, the notch impact strength of the Makrolon ® 1189 is improved by 50% at ambient temperature (Table 2).

TABLE 1
20 Characteristics Profile of the Mixture according to Example 2

		Blend	Makrolon ® 3100 Comparison
25	SZ (NKS)	23 degrees C	without breakage
	(KJm ⁻²)		without breakage
	KSZ (NKS)		
30	(KJm ⁻²)	23 degrees C	55 (hinge breakage) 48
		0 degrees C	45 (hinge breakage) 25
		-20 degrees C	23 8.5
		-40 degrees C	13 8.5
	VST/B	(degrees C)	131 148
35			

TABLE 2
Characteristics of the blends

		Blend mixed	Blend mixed	Comparison
		Example 4	Example 5	Example
				Makrolon ® 1189
5	SZ (23°C) without breakage (KJm ⁻²)		without breakage	without breakage
10	KSZ (23°C)	40.3	19.7	13
	(hinge breakage)			
	0°C	31.5	11.7	
	(hinge breakage)			
15	-20°C	12.5	7.9	
	-40°C	9.1	6.5	
	VST/B	142	136	138
	(°C)			

Claims

1. Thermoplastic moulding compounds and moulded articles synthesized from
 - 95 to 30 wt.% of aromatic polycarbonates, in particular based on bisphenol A, and
 - 5 to 70 wt.% of a copolymer having at least two phases as an impact modifier

consisting of

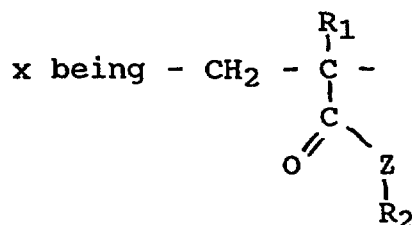
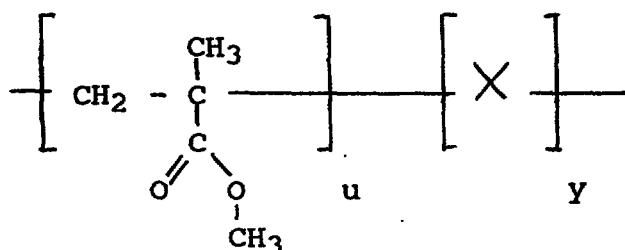
10

- A) more than 20 to 90 wt.% of an optionally crosslinked polymer P having a glass transition temperature $T_g \leq 10^\circ\text{C}$, preferably $\leq -10^\circ\text{C}$, and

15

- B) less than 80 to 10 wt.% of a methyl methacrylate copolymer at least partly covalently bonded with A), the methyl methacrylate copolymer, itself, being compatible with polycarbonate and having a glass transition temperature $T_g > 30^\circ\text{C}$ and a statistical composition:

20



wherein Z is -O- and/or-NH-

R₁ is -H and/or -CH₃

R₂ is -(CH₂)_n-W with n being 0 to 5,

wherein, if Z is -O-, W is an optionally substituted aryl group having 6 to 12 C-atoms and, if Z is -NH-, W is an

optionally substituted aryl group having 6 to 12 C-atoms or an optionally substituted cycloalkyl group having 5 to 9 C-atoms,

wherein

u is between 10 to 98 wt.% and

y is between 2 to 90 wt.%,

u+y being 100 wt.%

and which may also contain further comonomers in an amount of from 0 to 15 wt.%.

2. Thermoplastic moulding compounds and moulded articles according to claim 1, characterized in that the amount of polycarbonate is between 95 and 50 wt%, preferably between 90 and 60 wt.% and the amount of copolymer is between 5 and 50 wt.%, preferably between 10 and 40 wt.%.

3. Thermoplastic moulding compounds and moulded articles according to claims 1 and 2, characterized in that in the copolymer in B) u is between 50 to 95 wt.% and y is between 5 to 50 wt.%, wherein u+y = 100 wt.% in B).

4. Thermoplastic moulding compounds and moulded articles according to claims 1 to 3, characterized in that in the copolymer A) more than 5 wt.% is covalently bonded with B).

