

POLYESTER-POLYCARBONATE COMPOSITION WITH IMPROVED HOT-PLATE WELDABILITY

BACKGROUND OF THE INVENTION

The present invention relates to a polyester resin composition that contains a polycarbonate resin, and more specifically relates to a resin composition that is optimal for use in the manufacture of automobile lamps, etc., by a hot-plate welding process.

BRIEF DESCRIPTION OF THE RELATED ART

Thermoplastic resins are widely used as automotive materials because of their advantages in terms of light weight, workability and economy, etc.

When automobile rear combination housings, electrical circuit boxes and batteries, etc., are manufactured from thermoplastic resins, it is necessary to weld the resins. Three main types of methods are used for such welding. Specifically, these are methods that use an adhesive agent, methods that depend on the heat of friction (vibration welding methods) and methods that use heating (hot-plate welding methods). Among these methods, methods that use an adhesive agent use solvents, and are therefore undesirable from an environmental standpoint; furthermore, such methods suffer from the drawback of a long cycle time. In the case of vibration welding methods, particles of the powdered resin are scattered, so that the working environment is poor; moreover, there are restrictions in terms of design, and problems such as contamination of the welded parts, etc. Accordingly, such methods are used only in limited applications. Hot-plate welding methods are most widely used; however, such methods suffer from the following drawbacks: first of all, when the resin is caused to contact the hot plate, a portion of the material remains on the hot plate, and the carbonized material thus produced lowers the strength of the weld, so that the product yield drops. As a result, an operation to remove the resin debris must be performed

periodically. Secondly, when the resin is drawn from the hot plate, strings are drawn from the resin so that fine filament-form matter remains on the molded product. In particular, such problems are fatal in the case of optical products such as lamp lenses, etc.

- 5 In order to solve the abovementioned problems, methods in which a special sheet is used in the hot-plate welding machine, or in which welding is performed without contact with the welding machine, have been employed. However, such methods require a considerable expenditure on equipment, and do not provide an essential solution to the abovementioned problems.

10 **PROBLEMS TO BE SOLVED BY THE INVENTION**

- Accordingly, the object of the present invention is to solve the abovementioned problems by improving the composition; more concretely, the object of the present invention is to provide a resin composition with improved hot-plate weldability in which no carbonized resin remains on the
15 hot plate, and in which no fine filaments of the resin are drawn out.

 Specifically, the present invention comprises the following resin composition:

 A resin composition which contains

- (A) a polyester resin at the rate of 98 to 1 wt %,
- 20 (B) a polycarbonate resin at the rate of 1 to 98 wt %,
- (C) a core-shell copolymer at the rate of 0.5 to 18 wt %, and
- (D) a polytetrafluoroethylene with a number average molecular weight of 30,000 or greater at the rate of 0.01 to 4 wt % (with the total of A through D being 100 wt %).

Furthermore, the present invention also comprises a resin composition which is characterized by the fact that the abovementioned core-shell polymer (C) is formed by polymerizing at least one type of shell-forming monomer selected from a set consisting of vinyl aromatic compounds, vinyl cyanide, alkyl acrylates, alkyl methacrylates, acrylic acid and methacrylic acid with a core consisting of an acrylate rubber or butadiene rubber.

A universally known resin can be used as the polyester resin (A) in the present invention. Examples of such resins include polycondensed polyesters obtained by a reaction between a dicarboxylic acid or derivative and a diol; polycondensed polyesters obtained by a reaction between a dicarboxylic acid or derivative and a cyclic ether compound; polycondensed polyesters obtained by a reaction between a metal salt of a dicarboxylic acid and a dihalogen compound; and polycondensed polyesters obtained by the ring-opening polymerization reaction of a cyclic ester compound.

Either aliphatic dicarboxylic acids or aromatic dicarboxylic acids may be used as the abovementioned dicarboxylic acid. Examples of aliphatic dicarboxylic acids include aliphatic acids such as oxalic acid, succinic acid and adipic acid, etc. Furthermore, alicyclic dicarboxylic acids such as cyclohexanedicarboxylic acid, etc., may also be cited as examples. Examples of aromatic dicarboxylic acids which can be used include terephthalic acid, isophthalic acid, phthalic acid and chlorophthalic acid, etc. These acids may be used singly, or may be used in combinations consisting of two or more acids. Furthermore, examples of dicarboxylic acid derivatives that can be used include anhydrides, ester compounds, hydrochlorides and salts with alkali metals such as potassium and sodium, etc.

Diols that can be used include both aliphatic diols and aromatic diols. Examples of aliphatic diols include dihydric alcohols such as ethylene glycol, propylene glycol, butane-1,4-diol and hexamethylene glycol, etc.; ethylene

glycol and butane-1,4-diol are especially desirable. Furthermore, examples of aromatic diols that can be used include bisphenol A and resorcinol, etc. These diols may be used singly, or may be used in combinations consisting of two or more diols.

5 Examples of cyclic ether compounds that can be used include ethylene oxide and propylene oxide, etc. Examples of dihalogen compounds that can be used include compounds obtained by substituting the two hydroxy groups of the abovementioned diols with halogen atoms, e. g., chlorine or bromine. Cyclic ester compounds that can be used include ϵ -caprolactone, etc.

10 Polyester resins (A) that are especially desirable for use in the present invention are polyethylene terephthalate resins obtained from aromatic dicarboxylic acids, especially terephthalic acid, isophthalic acid or orthophthalic acid, and ethylene glycol or butylene glycol, and polybutylene terephthalates obtained from the aforementioned terephthalic acid, etc., and
15 1,4-butanediol. The amount of this polyester resin (A) that is contained in the composition is 98 to 1 wt % of the resin composition; this content is preferably 80 to 5 wt %, and is even more preferably 60 to 15 wt %. If the aforementioned upper-limit value is exceeded, the impact resistance deteriorates; on the other hand, if the content is less than the aforementioned lower-limit value, the
20 chemical resistance of the composition deteriorates.

 Aromatic polycarbonates obtained by the universally known phosgene process or fusion process (for example, see Japanese Patent Application Kokai No. Sho 63-215763 and Japanese Patent Application Kokai No. Hei 2-124934) can be used is the abovementioned polycarbonate resin (B) in the present
25 invention. Polycarbonate resins consist of a carbonate component and a diphenol component. Examples of precursor substances that can be used to derive the carbonate component include phosgene and diphenyl carbonate, etc. Furthermore, examples of diphenol components that can be used include

2,2-bis(4-hydroxyphenyl)propane (so-called bisphenol A), 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane, 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)cyclohexane, 1,1-bis(3,5-dimethyl-4-hydroxyphenyl)cyclohexane, 1,1-bis(4-hydroxyphenyl)decane,
5 1,4bis(4-hydroxyphenyl)propane, 1,1-bis(4-hydroxyphenyl)cyclododecane, 1,1-bis(3,5-dimethyl-4-hydroxyphenyl)cyclododecane, 4,4-dihydroxydiphenyl ether, 4,4-oxyphenol, 4,4-dihydroxy-3,3-dichlorodiphenyl ether and 4,4-dihydroxy-2,5-dihydroxydiphenyl ether, etc. These diphenol components may be used singly or in combination. In addition, compounds that have
10 three or more phenolic hydroxy groups may also be used.

Polycarbonate resins (B) that are desirable for use in the present invention include (for example) LEXAN (registered trademark) 101 and LEXAN (registered trademark) 121, etc., which are bisphenol A polycarbonate resins commercially marketed by General Electric Co. The content of the
15 polycarbonate resin (B) in the resin composition is 1 to 98 wt %, preferably 15 to 90 wt %, and even more preferably 30 to 80 wt %.

Alternatively, component (B) may be an aromatic copolyester carbonate. In addition to carbonate units originating in a universally known aromatic diol, such a component also has ester units originating in an
20 aromatic diol and an aliphatic dicarboxylic acid with 6 to 18 carbon atoms. The phosgene method or fusion method, which are already universally known as methods for manufacturing aromatic polycarbonates, can be used to manufacture such aromatic copolyester carbonates. (See U.S. Patent No. 4,238,596, U.S. Patent No. 4,238,597 and U.S. Patent No. 3,169,121.)

25 The core-shell copolymer constituting component (C) of the present invention is a copolymer formed by graft-polymerizing one or more shell-forming monomers on a rubber-form core. Examples of such copolymers include copolymers formed by grafting a polystyrene or polymethacrylate,

etc., as a shell on a core consisting of an acrylate type rubber, butadiene type rubber, polyorganosiloxane or compound rubber consisting of these rubbers. Core-shell copolymers, methods for manufacturing such copolymers, and the use of core-shell copolymers in combination with polycarbonate resins and polyester resins as impact resistance improving agents, are described in (for example) U.S. Patent No. 3864428, U.S. Patent No. 4180434, U.S. Patent No. 4257937 and U.S. Patent No. 4264487. Furthermore, a thermoplastic composition which is superior in terms of weather resistance, and which is formed by mixing a polycarbonate resin and/or polyester resin, a polyolefin rubber graft copolymer and a core-shell copolymer is disclosed in Japanese Patent Application Kokai No. Hei 9-302206. However, these references do not mention the thermal fusibility of the resin compositions; furthermore, there is no suggestion of the mixing of core-shell copolymers and polytetrafluoroethylenes.

15 In core-shell copolymers that are desirable for use in the present invention, the core consists of an acrylate rubber or a butadiene rubber. Acrylate rubbers are rubbers derived from acrylic acid esters such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, isopropyl methacrylate and butyl methacrylate, etc. Preferably, such rubbers are
20 obtained from methyl methacrylate, ethyl methacrylate, propyl methacrylate or mixtures of these. Desirable monomers for forming the shell by graft polymerization onto such a core consist of at least one monomer selected from a set consisting of vinyl aromatic compounds, vinyl cyanide, alkyl acrylates, alkyl methacrylates, acrylic acid and methacrylic acid. It is desirable that the
25 monomers forming the aforementioned core and/or shell contain multifunctional compounds which can act as cross-linking agents and/or grafting agents, such as butylene diacrylate or divinylbenzene. Especially desirable for use in the present invention is a methyl methacrylate-butadiene-styrene polymer (MBS) obtained by polymerizing methyl methacrylate and

styrene with a butadiene rubber. The amount of this core-shell copolymer (C) that is contained in the resin composition is 0.5 to 18 wt %, preferably 1 to 15 wt %, and even more preferably 3 to 13 wt %. If the content is less than the aforementioned lower-limit value, the effect in improving the hot-plate weldability is insufficient; on the other hand, if the content exceeds the aforementioned upper-limit value, the moldability and mechanical strength of the composition may drop.

The polytetrafluoroethylene constituting component (D) of the present invention is in itself universally known. Furthermore, a composition including a polyester carbonate resin, a polycarbonate resin, a phosphoric acid ester and a polytetrafluoroethylene is disclosed in Japanese Patent Application Kokai No. Hei 9-183893; here, the polytetrafluoroethylene is added together with the phosphoric acid ester in order to improve the flame retarding properties. There is no mention of thermal weldability in this reference, and there is no suggestion of the mixing of a core-shell copolymer and polytetrafluoroethylene.

The polytetrafluoroethylene constituting component (D) used in the present invention can be manufactured by any universally known manufacturing method. Preferably, this polytetrafluoroethylene is obtained by a suspension polymerization process or emulsion polymerization process.

It is necessary that the polytetrafluoroethylene used in the present invention have a number average molecular weight of 30,000 or greater. In cases where the molecular weight is less than this value, the effect in improving the hot-plate weldability is insufficient. The inferred reason for this will be described below without limiting the present invention. During hot-plate welding, the resin in the vicinity of the hot plate is melted, but the portions of the resin that are distant from the hot plate are not melted. A polytetrafluoroethylene with long molecular chains extends across the molten

portions and non-molten portions of the resin, so that portions of the molecular chains are fixed in the non-molten portions, while other portions extend into the molten portions of the resin. When the resin is pulled away from the hot plate, the molten resin entangled with the

5 polytetrafluoroethylene chains extending into the molten portions of the resin is pulled by the non-molten portions so that this molten resin is carried away from the hot plate. However, if a polytetrafluoroethylene with short molecular chains is used, it is hardly possible for this polytetrafluoroethylene to extend across the molten portions and non-molten portions of the resin. As
10 a result, when the resin is pulled away from the hot plate, the polytetrafluoroethylene remains on the hot plate together with the molten resin. Accordingly, in order to improve the hot-plate weldability, it appears that it is necessary to use a polytetrafluoroethylene whose molecular weight exceeds a certain value.

15 The content of this polytetrafluoroethylene (D) in the resin composition is 0.01 to 4 wt %, preferably 0.1 to 2 wt %, and even more preferably 0.1 to 1 wt %. If this content is less than the abovementioned lower-limit value, the effect in improving the hot-plate weldability is insufficient. On the other
20 hand, if this content exceeds the abovementioned upper-limit value, die wells are formed, so that there is a drop in productivity when the resin is extruded.

In the composition of the present invention, hot-plate weldability is conspicuously improved as a result of the combined use of the abovementioned core-shell copolymer (C) and polytetrafluoroethylene (D). The effect of the present invention may be inferred as follows without limiting
25 the present invention: specifically, as was described above, the polytetrafluoroethylene constituting component (D) carries the molten thermoplastic resin away from the hot plate; furthermore, the core-shell copolymer constituting component (C) strengthens the melt tension of the resin composition so that the resin that is carried away is prevented from

being pulled into fine filaments. Furthermore, the core-shell copolymer (C) also acts to increase the viscosity of the resin composition, and it appears that this also inhibits the pulling of the resin into filaments. Thus, the hot-plate weldability is conspicuously improved by the addition of components (C) and
5 (D).

Customary additives such as coloring agents (pigments or dyes), thermal stabilizers, anti-oxidants, weather resistance improving agents, slip agents, mold release agents, crystal nucleus forming agents, plasticizers, flame retarding agents, fluidity improving agents, impact resistance improving
10 agents, anti-static agents and ester interchange preventing agents, etc., may be appropriately added to the resin composition of the present invention during mixing or molding of the resin, as long as there is no loss of the object of the present invention.

There are no particular restrictions on the method used to manufacture
15 the resin composition of the present invention; ordinary methods can be satisfactorily used. Preferably, a molten mixing method is used. Small amounts of solvents may also be used, but are ordinarily unnecessary. Examples of apparatus that can be used include extruders, Banbury mixers, rollers and kneaders, etc. Such apparatus may be operated in a batch
20 operation or continuously.

There are no particular restrictions on the molding method used, either; various types of methods may be used. Examples include injection molding, gas-assisted molding, cold-hot cycle molding, blow molding, extrusion molding, and thermo-forming molding, etc. Injection molding is
25 especially desirable for use.

EXAMPLES

Below, the present invention will be described in greater detail in terms of working examples. However, the present invention is not limited to these examples.

I) Resins Used

- 5 The resins used in the working examples and comparative examples were as shown below.

Resins Used in Working Examples

(A) Polyester Resin

PET: MA-580, manufactured by Mitsubishi Rayon K.K.

10 (B) Polycarbonate Resin

PC: LEXAN 125 (trademark: manufactured by Nippon GE Plastics K.K.)

(C) Core-Shell Copolymer

MBS: KANEACE B-56 (trademark), manufactured by Kanegafuchi Kagaku Kogyo K.K.

15 (D) Polytetrafluoroethylene

TEFN-1: Freon CD-1 (trademark), number average molecular weight (Mn) = 99,000, manufactured by Asahi ICI Fluoropolymers K.K.

Other Resins Used in Comparative Examples

SEBS: KRATON G1651, manufactured by Shell Kagaku K.K.

20 SEP: Septone-1001, manufactured by Kurare K.K.

TEFN-2: Lupron L-5 (trademark), number average molecular weight (Mn) = 25,000, manufactured by Daikin Kogyo K.K.

Furthermore, the molecular weights of polytetrafluoroethylenes were measured using the method indicated by T. Suwa, M. Takehisa and S. Machi in "Melting and Crystallization Behavior of Poly(tetrafluoroethylene). New Method for Molecular Weight Measurement of Poly(tetrafluoroethylene) Using a Differential Scanning Calorimeter", Jr. Appl. Polym. Science, Vol. 17, pp. 3253-3257 (1973).

II) Evaluation Methods

In the present invention, the hot-plate weldability was evaluated in terms of the level of filament drawing and the amount of resin adhering to the plate (hot plate) as shown below. Details of the evaluation methods are shown below along with details of other evaluation methods used.

(1) IZOD Impact Strength

This was measured according to ASTM D256.

(2) Heat Deformation Temperature

This was measured according to ASTM D648 at a load of 4.6 kg.

(3) Melt Flow Index (MI)

This was measured according to ASTM D1238 at a temperature of 266°C and a load of 2.16 kg.

(4) Level of Filament Drawing

A Teflon sheet was placed on a hot plate heated to 300°C or 370°C, and a sample piece was light pressed against this. The sample piece used in each case was $\frac{1}{4}$ bar, and a $\frac{1}{4} \times \frac{1}{2}$ inch cross section was subjected to testing. After heating for 15 seconds, the sample piece was pulled away, and the cross section was examined. The length of the filament-form resin that was

extended when the pressed cross section was stripped away was measured. This test was performed three times, and the maximum value obtained was recorded.

(5) Amount of Resin Adhering to Plate

- 5 A Teflon sheet was placed on a hot plate heated to 300°C or 370°C, and a sample piece was light pressed against this. The sample piece used in each case was $\frac{1}{4}$ bar, and a $\frac{1}{4} \times \frac{1}{2}$ inch cross section was subjected to testing. After heating for 15 seconds, the sample piece was pulled away, and the extent of filament drawing was observed. The weight of the sample piece was
- 10 measured before and after this welding test, and the difference between the two values obtained was taken as the amount of resin adhering to the plate. This test was performed three times, and the mean value obtained was recorded.

Working Examples 1 Through 4 and Comparative Examples 1 Through 9

- 15 The respective components used were mixed in the proportions shown in Table 1, and pellets were manufactured by extruding the respective mixtures at a set temperature of 280 to 300°C and an rpm of 300 to 400 rpm using a two-shaft extruding machine. Various evaluation sample pieces (described below) were injection-molded from these pellets, and were used in
- 20 testing. The evaluation results are shown in Table 1.

TABLE 1

	Working Example				Comparative Example								
	1	2	3	4	1	2	3	4	5	6	7	8	9
Component (parts by weight)													
(A) PET													
(B) PC	38	53.7	37.5	17.9	42	40	40	40	38	33	18	38	37.5
(C) MBS	51.5	35.8	51.5	71.6	58	55	55	55	52	47	72	51.5	52
SEBS	10	10	10	10	-	5	-	-	10	20	10	10	
SEP					-	-	5	-	-	-	-	-	10
(D) TEFN-1					-	-	-	5	-	-	-	-	
TEFN-2	0.5	0.5	1	0.5	-	-	-	-	-	-	-	-	0.5
	-		-	-	-	-	-	-	-	-	-	0.5	
Evaluation test													
IZOD (kgfcm/cm)	57	45	55	72	9	42	24	11	64	45	15	52	45
HDT (°C)	127	125	127	127	135	132	134	135	125	123	132	130	126
MI (g/10 min)	8	12	7	6	22	18	17	17	19	11	20	17	8
Filament drawing test													
- Level of filament drawing ¹⁾ (mm)	1	<1	<1	<1	20<	5	20<	20<	1	<1	1	5	15
- Amount of resin adhering to plate ¹⁾ (mg)	4	2	2	2	10	10	11	10	9	6	9	9	4
- Level of filament drawing ²⁾ (mm)	1	2	1	1	20<	20	20<	20<	20<	2	20<	20<	20<
- Amount of resin adhering to plate ²⁾ (mg)	2	2	2	2	13(9)	7	13	15	8	7	13	6	2

1) Hot-plate welding test performed at 370°C

2) Hot-plate welding test performed at 300°C

It is seen that when a specified amount of a core-shell copolymer (MBS) (Comparative Example 2) is added to a composition containing a polyester resin and a polycarbonate resin (Comparative Example 1), the level of
5 filament drawing is conspicuously reduced. The rubbers used in Comparative Examples 3 and 4 are not core-shell copolymers, and have no strengthening effect on the melt tension of the resin composition; accordingly, compared to a core-shell copolymer, these rubbers have little effect in reducing the level of filament drawing.

10 Furthermore, the level of filament drawing is reduced as the amount of core-shell copolymer increases, in the order of Comparative Example 1 (containing no MBS), Comparative Example 2 (5 wt % MBS), Comparative Example 5 (10 wt % MBS) and Comparative Example 6 (20 wt %). However, as is seen from a comparison of Comparative Examples 5 and 6, the heat
15 resistance (HDT) of the resin composition drops, and problems appear in the mechanical strength (IZOD), when the MBS content exceeds a certain level.

It is seen from a comparison of Working Examples 1 through 4 with Comparative Examples 5 and 7 that the amount of resin adhering to the hot plate and the level of filament drawing at a high temperature (370°C) are
20 further ameliorated by the addition of component (D), i. e., a polytetrafluoroethylene, along with the core-shell copolymer. When a rubber (SEBS) other than the abovementioned core-shell copolymer is added along with the polytetrafluoroethylene (D) (Comparative Example 9), some amelioration of the amount of adhering resin is seen; however, the
25 improvement in terms of level of filament drawing is small compared to that seen in Working Examples 1 through 4.

Furthermore, in cases where the molecular weight of the polytetrafluoroethylene is less than 30,000, almost no improvement is seen in

terms of the level of filament drawing or amount of resin adhering to the plate (Comparative Example 8).

Thus, in the thermoplastic resin composition of the present invention, the hot-plate weldability is conspicuously improved as a result of the
5 presence of a core-shell copolymer (C) and polytetrafluoroethylene (D) with a specified molecular weight in the composition.

**CLAIMS**

1. A resin composition which contains
 - (A) a polyester resin at the rate of 98 to 1 wt %,
 - (B) a polycarbonate resin at the rate of 1 to 98 wt %,
 - 5 (C) a core-shell copolymer at the rate of 0.5 to 18 wt %, and
 - (D) a polytetrafluoroethylene with a number average molecular weight of 30,000 or greater at the rate of 0.01 to 4 wt % (with the total of A through D being 100 wt %).



2. The resin composition claimed in Claim 1, which is characterized by the fact that the core-shell polymer (C) is formed by polymerizing at least one type of shell-forming monomer selected from a set consisting of vinyl aromatic compounds, vinyl cyanide, alkyl acrylates, alkyl methacrylates,
- 5 acrylic acid and methacrylic acid with a core consisting of an acrylate rubber or butadiene rubber.