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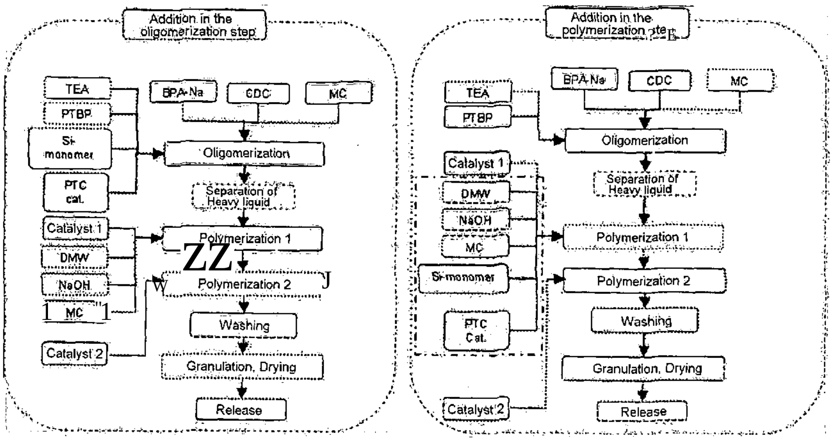
(54) Title: METHOD OF PREPARING POLYSILOXANE-POLYCARBONATE COPOLYMER



(57) **Abstract:** The present invention relates to a method of preparing polysiloxane-polycarbonate copolymer. More specifically, the present invention relates to a method of preparing polysiloxane-polycarbonate copolymer which can improve a silicon monomer reaction ratio and secure superior low-temperature impact resistance and ductility ratio by controlling the addition time of silicon monomer depending on the molecular weight of oligomeric polycarbonate in the synthesis of the polysiloxane-polycarbonate copolymer.

WO 2013/100494 A1

Description

Title of Invention: METHOD OF PREPARING POLYSILOXANE-POLYCARBONATE COPOLYMER

Technical Field

[1] The present invention relates to a method of preparing polysiloxane-polycarbonate copolymer. More specifically, the present invention relates to a method of preparing polysiloxane-polycarbonate copolymer which can improve a silicon monomer reaction ratio and secure superior low-temperature impact resistance and ductility ratio by controlling the addition time of silicon monomer depending on the molecular weight of oligomeric polycarbonate in the synthesis of the polysiloxane-polycarbonate copolymer.

Background Art

[2] Polycarbonate has good mechanical properties such as tensile strength, impact resistance, etc. and also has good dimensional stability, heat resistance and optical transparency. Thus, it has been extensively used in many industries. However, although polycarbonate has good impact resistance at room temperature, its impact resistance is rapidly deteriorated at low temperature.

[3] To improve such a disadvantage, various copolymers have been researched and it has been known that polysiloxane-polycarbonate copolymer, of which skeleton has polydimethylsiloxane (PDMS), shows relatively good impact resistance at low temperature.

[4] Generally, the synthesis of polysiloxane-polycarbonate copolymer consists of a beginning step, an oligomerization step, a first polymerization step and second polymerization step. A silicon monomer is added at the oligomerization step, and an intermediate is formed via a reaction with an oligomeric polycarbonate. Such synthesis of polysiloxane-polycarbonate copolymer is through an interfacial reaction which occurs at the interface between a heavy liquid of methylene chloride (MC) layer and a light liquid of water layer. In addition, in order to narrow the molecular weight distribution of final products, the synthesis of polysiloxane-polycarbonate copolymer requires a process to decrease the reaction rate by lowering pH and increasing a water phase ratio in the beginning step and oligomerization step. That is why the molecular weight distribution of the oligomers broadens, and accordingly the molecular weight distribution of final products also widens when high pH and low water phase ratio are maintained in the initial stage.

[5] In addition, when a silicon monomer having a higher molecular weight (number average molecular weight, Mn) is used, the low-temperature impact strength and ductility ratio is more improved in the same amount but the reactivity becomes worse,

accordingly silicon monomers which fail to bind to polycarbonate oligomer in the low pH-oligomerization step (e.g., in the pH range of 6 to 8) stay at the interface of heavy/light liquid layers and are omitted from the reaction solution during transferring the heavy liquid into the next step. Such missing of the silicon monomers results in a decrease of the silicon content in final products and leads to deterioration in the physical properties. Furthermore, the silicon monomers omitted are accumulated in the middle layer part during the oligomerization step as the processes go through and then irregularly introduced into the first polymerization step during transferring the heavy/light liquid, which causes differences between LOTs of the final product and occurrence of defective products and also contaminates the process line. On the other hand, if more excessive amount of silicon monomers is used in view of the silicon monomers to be omitted, the increase of production cost is inevitable.

[6] Hence, there is a need to develop an effective and economical method for preparing polysiloxane-polycarbonate copolymer, which can impart excellent low-temperature impact resistance and ductility ratio to the final products by innovatively improving a silicon monomer reaction ratio.

[7]

[8] [Prior Art Document]

[9] <Patent Document>

[10] US 2003/0105226 A

[11]

Disclosure of Invention

Technical Problem

[12] The present invention is intended to solve the problems involved in the prior arts as stated above. The technical purpose of the present invention is to provide a method of preparing polysiloxane-polycarbonate copolymer, which can improve a silicon monomer reaction ratio and secure superior low-temperature impact resistance and ductility ratio.

Solution to Problem

[13] The present invention provides a method for preparing the polysiloxane-polycarbonate copolymer comprising: a) a step of preparing an oligomeric polycarbonate having a viscosity average molecular weight of 3,000 to 20,000; b) a step of admixing a hydroxy-terminated siloxane to the prepared oligomeric polycarbonate; and c) a step of reacting the oligomeric polycarbonate and the hydroxy-terminated siloxane under an interfacial reaction condition to polymerize.

[14] In other aspect, the present invention also provides a polysiloxane-polycarbonate copolymer prepared according to said method.

[15] In another aspect, the present invention also provides a thermoplastic resin composition comprising a polysiloxane-polycarbonate copolymer prepared according to said method and an additive.

[16] In another aspect, the present invention also provides a molded article prepared from said thermoplastic resin composition.

Advantageous Effects of Invention

[17] By using the method for preparing a polysiloxane-polycarbonate copolymer of the present invention, a silicon monomer reaction ratio is significantly improved; desired physical properties such as low-temperature impact resistance, ductility ratio, etc. can be secured even when a viscosity average molecular weight of the copolymer is maintained low; and a polysiloxane-polycarbonate copolymer can be economically synthesized without the need for an additional process or manufacture of a reactor.

Brief Description of Drawings

[18] Figure 1 is a flow chart illustrating the process of adding a silicon monomer in the polymerization step of the present invention, comparing with a conventional process of adding a silicon monomer in the oligomerization step.

Best Mode for Carrying out the Invention

[19] Hereinafter, the present invention will be described more specifically. The purpose, features and advantages of the present invention will be easily understood through the following embodiments. The present invention is not limited to the embodiments as explained herein and may be reduced to practice in other forms. The embodiments introduced herein are provided in order to make the disclosed matters thorough and complete, and to sufficiently communicate the concept of the present invention to a person skilled in the art. Thus, the present invention is not limited to the following exemplified description and embodiments.

[20] The term "reaction product" as used herein means a substance that is formed by reacting two or more reactants.

[21] In addition, although the terms "first," "second" and the like are used herein for the description of polymerization catalysts, the polymerization catalysts are not limited by these terms. These terms are just used to distinguish the polymerization catalysts from each other. For example, a first polymerization catalyst and a second polymerization catalyst may be of the same kind of catalyst or different kinds of catalyst.

[22] Furthermore, in the chemical formulas described herein, although the English character "R" used for representing hydrogen, halogen atom and/or hydrocarbon group, etc. has a numerical subscript, "R" is not limited by such a subscript. "R" independently represents hydrogen, halogen atom and/or hydrocarbon group, etc. For example, even if two or more "R"s have the same numerical subscript, such "R"s may

represent the same hydrocarbon group or different hydrocarbon groups. Also, even if two or more "R"s have different numerical subscripts, such "R"s may represent the same hydrocarbon group or different hydrocarbon groups.

[23] The method for preparing a polysiloxane-polycarbonate copolymer according to the present invention comprises a) a step of preparing an oligomeric polycarbonate having a viscosity average molecular weight of 3,000 to 20,000; b) a step of admixing a hydroxy-terminated siloxane to the prepared oligomeric polycarbonate; and c) a step of reacting the oligomeric polycarbonate and the hydroxy-terminated siloxane under an interfacial reaction condition to polymerize.

[24]

[25] **a) Oligomerization step**

[26] This step is for preparing an oligomeric polycarbonate to be used in the formation of polysiloxane-polycarbonate copolymer (Si-PC) by polymerization with silicon monomers. Silicon monomers are not added in this step and a viscosity average molecular weight (M_v) of the oligomeric polycarbonate is adjusted to 3,000 to 20,000, and preferably 4,000 to 15,000. If the polymerization with silicon monomers is conducted when a viscosity average molecular weight of the oligomeric polycarbonate is less than 3,000, the molecular weight distribution may broaden and the physical properties may be deteriorated. If the polymerization with silicon monomers is conducted when a viscosity average molecular weight of the oligomeric polycarbonate is greater than 20,000, the reactivity may be severely deteriorated.

[27] In one embodiment, the oligomeric polycarbonate may be prepared by adding a dihydric phenol compound to an aqueous alkaline solution to make it in a phenol salt form, and then adding the phenol compound in a salt form to methylene chloride (MC) or dichloromethane containing injected phosgene gas for reaction. To prepare the oligomer, it is preferable to maintain the molar ratio of phosgene to bisphenol within a range of about 1 : 1 to 1.5 : 1, and more preferably about 1 : 1 to 1.2 : 1. If the molar ratio of phosgene to bisphenol is less than 1, the reactivity may be lowered. If the molar ratio of phosgene to bisphenol is greater than 1.5, the molecular weight increases excessively to deteriorate the processability.

[28] Triethylamine (TEA) may be used as a catalyst for forming the oligomers of this step, but it is not limited thereto.

[29] In addition, as the molecular weight regulator, a monofunctional compound similar to a monomer used in preparation of polycarbonate may be used. The monofunctional compound may be, for example, a derivative based on phenol such as p-isopropylphenol, p-ieri-butylphenol (PTBP), p-cumylphenol, p-isooctylphenol and p-isononylphenol, or an aliphatic alcohol. Preferably, p-ieri-butylphenol (PTBP) may be used.

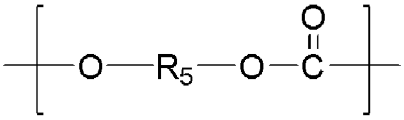
[30] The above reaction may suitably be conducted under a pH range of 6 to 8 and a temperature range of 15 to 40°C, and alkali metal hydroxide (for example, sodium hydroxide) may be used to adjust pH of the reaction mixture. If pH of the reaction mixture is less than 6, the reactivity may be deteriorated to decline the increase of molecular weight or to extend the reaction time. If pH of the reaction mixture is higher than 8, the molecular weight distribution of the oligomers may broaden, which causes the problem of widening the molecular weight distribution of final products.

[31] In a preferred embodiment, the polysiloxane-polycarbonate copolymer prepared according to the present invention comprises, as a repeating unit, a polycarbonate block of the following chemical formula 4:

[32]

[33] [Chemical formula 4]

[34]



$$\left[-O-R_5-O-\overset{O}{\overset{\|}{C}}- \right]$$

[35]

[36] in the above chemical formula 4,

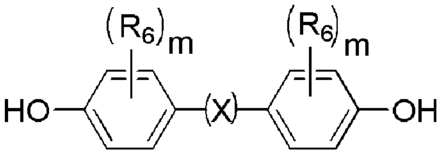
[37] R_5 represents aromatic hydrocarbon group having 6 to 30 carbon atoms that is unsubstituted or substituted with alkyl group having 1 to 20 carbon atoms (for example, alkyl group having 1 to 13 carbon atoms), cycloalkyl group (for example, cycloalkyl group having 3 to 6 carbon atoms), alkenyl group (for example, alkenyl group having 2 to 13 carbon atoms), alkoxy group (for example, alkoxy group having 1 to 13 carbon atoms), halogen atom or nitro.

[38] The aromatic hydrocarbon group may be derived from a compound of the following chemical formula 4a.

[39]

[40] [Chemical formula 4a]

[41]



[42]

[43] in the above chemical formula 4a,

[44] X represents alkylene group; linear, branched or cyclic alkylene group having no functional group; or linear, branched or cyclic alkylene group comprising a functional group such as sulfide, ether, sulfoxide, sulfone, ketone, naphthyl, isobutylphenyl. Preferably, X may be linear or branched alkylene group having 1 to 10 carbon atoms, or cyclic alkylene group having 3 to 6 carbon atoms.

[45] R_6 independently represents hydrogen atom, halogen atom or alkyl group— for example, linear or branched alkyl group having 1 to 20 carbon atoms, or cyclic alkyl group having 3 to 20 (preferably, 3 to 6) carbon atoms.

[46] The subscripts "n" and "m" independently represent an integer of 0 to 4.

[47] The compound of the above chemical formula 4a may be, for example, bis(4-hydroxyphenyl)methane, bis(4-hydroxyphenyl)phenylmethane, bis(4-hydroxyphenyl)naphthylmethane, bis(4-hydroxyphenyl)-(4-isobutylphenyl)methane, 1,1-bis(4-hydroxyphenyl)ethane, 1-ethyl-1,1-bis(4-hydroxyphenyl)propane, 1-phenyl-1,1-bis(4-hydroxyphenyl)ethane, 1-naphthyl-1,1-bis(4-hydroxyphenyl)ethane, 1,2-bis(4-hydroxyphenyl)ethane, 1,10-bis(4-hydroxyphenyl)decane, 2-methyl-1,l-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)butane, 2,2-bis(4-hydroxyphenyl)pentane, 2,2-bis(4-hydroxyphenyl)hexane, 2,2-bis(4-hydroxyphenyl)nonane, 2,2-bis(3-methyl-4-hydroxyphenyl)propane, 2,2-bis(3-fluoro-4-hydroxyphenyl)propane, 4-methyl-2,2-bis(4-hydroxyphenyl)pentane, 4,4-bis(4-hydroxyphenyl)heptane, diphenyl-bis(4-hydroxyphenyl)methane, resorcinol, hydroquinone, 4,4'-dihydroxyphenyl ether[bis(4-hydroxyphenyl)ether], 4,4'-dihydroxy-2,5-dihydroxydiphenyl ether, 4,4'-dihydroxy-3,3'-dichlorodiphenyl ether, bis(3,5-dimethyl-4-hydroxyphenyl)ether, bis(3,5-dichloro-4-hydroxyphenyl)ether, l,4-dihydroxy-2,5-dichlorobenzene, 1,4-dihydroxy-3-methylbenzene, 4,4'-dihydroxydiphenol[p,p'-dihydroxyphenyl], 3,3'-dichloro-4,4'-dihydroxyphenyl, l,l-bis(4-hydroxyphenyl)cyclohexane, l,l-bis(3,5-dimethyl-4-hydroxyphenyl)cyclohexane, l,l-bis(3,5-dichloro-4-hydroxyphenyl)cyclohexane, l,l-bis(3,5-dimethyl-4-hydroxyphenyl)cyclododecane, 1,1-bis(4-hydroxyphenyl)cyclododecane, 1,1-bis(4-hydroxyphenyl)butane, 1.1-bis(4-hydroxyphenyl)decane, l,4-bis(4-hydroxyphenyl)propane, 1,4-bis(4-hydroxyphenyl)butane, 1,4-bis(4-hydroxyphenyl)isobutane, 2.2-bis(4-hydroxyphenyl)butane, 2,2-bis(3-chloro-4-hydroxyphenyl)propane, bis(3,5-dimethyl-4-hydroxyphenyl)methane, bis(3,5-dichloro-4-hydroxyphenyl)methane, 2,2-bis(3,5-dimethyl-4-hydroxyphenyl)propane, 2,2-bis(3,5-dibromo-4-hydroxyphenyl)propane, 2,2-bis(3,5-dichloro-4-hydroxyphenyl)propane, 2,4-bis(4-hydroxyphenyl)-2-methyl-butane, 4,4'-thiodiphenol[bis(4-hydroxyphenyl)sulfone], bis(3,5-dimethyl-4-hydroxyphenyl)sulfone, bis(3-chloro-4-hydroxyphenyl)sulfone,

bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)sulfoxide, bis(3-methyl-4-hydroxyphenyl)sulfide, bis(3,5-dimethyl-4-hydroxyphenyl)sulfide, bis(3,5-dibromo-4-hydroxyphenyl)sulfoxide, 4,4'-dihydroxybenzophenone, 3,3',5,5'-tetramethyl-4,4'-dihydroxybenzophenone, 4,4'-dihydroxy diphenyl, methylhydroquinone, 1,5-dihydroxynaphthalene, or 2,6-dihydroxynaphthalene, but it is not limited thereto. Among them, the representative one is 2,2-bis(4-hydroxyphenyl)propane (bisphenol A). For other functional dihydric phenols, US Patent Nos. 2,999,835; 3,028,365; 3,153,008 and 3,334,154 may be referred to. The above dihydric phenol may be used alone or in combination of two or more of them.

[48] In case of carbonate precursor, for example, carbonyl chloride (phosgene), carbonyl bromide, bis halo formate, diphenylcarbonate, dimethylcarbonate, etc. may be used as another monomer of the polycarbonate resin.

[49] In one embodiment, the heavy liquid comprising the oligomeric polycarbonate prepared in this step is extracted and separated from the reaction mixture, and then used in the next polymerization step.

[50]

[51] **b) and c): Silicon monomer addition step and Polymerization step**

[52] This step is for forming the polysiloxane-polycarbonate copolymer by admixing the hydroxy-terminated siloxane as a silicon monomer to the oligomeric polycarbonate prepared in the a) step; and reacting them under an interfacial reaction condition consisting of an aqueous alkaline solution and an organic phase to polymerize. The present invention is characterized in that the addition of silicon monomer for forming the copolymer is carried out after the oligomeric polycarbonate of which viscosity average molecular weight is adjusted to a certain high level is firstly prepared, unlike the conventional method where the silicon monomer is added in an oligomerization step.

[53] The mixture of oligomeric polycarbonate and hydroxy-terminated siloxane may further comprise a molecular weight regulator, a first polymerization catalyst, a phase transfer catalyst, a pH adjusting agent (for example, NaOH) and methylene chloride (MC), etc. Concretely, the polysiloxane-polycarbonate copolymer may be prepared by adding the hydroxy-terminated siloxane to an organic phase-aqueous phase mixture comprising the oligomeric polycarbonate, and subsequently adding a molecular weight regulator, a catalyst, etc. in the order.

[54] As the molecular weight regulator, a monofunctional compound similar to a monomer used in preparation of polycarbonate as stated above may be used.

[55] As the catalyst, a polymerization catalyst and/or a phase transfer catalyst may be used. The polymerization catalyst may be, for example, triethylamine (TEA), and the

phase transfer catalyst may be a compound of the following chemical formula 5.

[56]

[57] [Chemical formula 5]

[58] $(R_7)_4Q^+X^-$

[59]

[60] in the above chemical formula 5,

[61] R_7 represents alkyl group having 1 to 10 carbon atoms; Q represents nitrogen or phosphorus; and X represents halogen atom or $-OR_8$ wherein R_8 represents hydrogen atom, alkyl group having 1 to 18 carbon atoms or aryl group having 6 to 18 carbon atoms.

[62] Concretely, the phase transfer catalyst may be, for example, $[CH_3(CH_2)_3]_4NX$, $[CH_3(CH_2)_3]_4PX$, $[CH_3(CH_2)_5]_4NX$, $[CH_3(CH_2)_6]_4NX$, $[CH_3(CH_2)_4]_4NX$, $CH_3[CH_3(CH_2)_3]_3NX$ or $CH_3[CH_3(CH_2)_2]_3NX$, wherein X represents Cl, Br or $-OR_8$ where R_8 represents hydrogen atom, alkyl group having 1 to 18 carbon atoms or aryl group having 6 to 18 carbon atoms.

[63] The amount of the phase transfer catalyst is preferably about 0.01 to 10% by weight, and more preferably 0.1 to 10% by weight based on total weight of the hydroxy-terminated siloxane and the oligomeric polycarbonate. If the amount of the phase transfer catalyst is less than 0.01% by weight, the reactivity may be lowered. If the amount of the phase transfer catalyst is greater than 10% by weight, precipitation may happen or the transparency may be deteriorated.

[64] Preferably, the hydroxy-terminated siloxane that is fed in this step has a molecular weight (number average molecular weight, M_n) of 2,500 to 15,000, more preferably 3,000 to 8,000. If the molecular weight of hydroxy-terminated siloxane is less than 2,500, the low-temperature impact resistance and ductility ratio may be deteriorated. If the molecular weight is greater than 15,000, the reactivity may be lowered and thus there may be a problem in synthesizing the polysiloxane-polycarbonate copolymer with a desired molecular weight.

[65] The weight ratio of oligomeric polycarbonate : hydroxy-terminated siloxane is preferably 80 : 20 to 99 : 1, more preferably 85 : 15 to 97 : 3, in this step. In other words, the feed amount of hydroxy-terminated siloxane in the preparation of the polysiloxane-polycarbonate copolymer according to the present invention is preferably 1 to 20% by weight, more preferably 3 to 15% by weight, based on the total reactants. If the feed amount of hydroxy-terminated siloxane is less than 1% by weight, the low-temperature impact resistance may be deteriorated. If the feed amount is greater than 20% by weight, physical properties such as flowability, heat resistance, transparency, etc. may be deteriorated, and the manufacturing cost may be increased to be economically infeasible. In the present invention, excellent low-temperature impact re-

sistance can be achieved even in a relatively low amount of siloxane—i.e., a level of 1 to 20% by weight—by maximizing the reaction ratio through controlling the addition time of a hydroxy-terminated siloxane.

[66] Preferably, the addition of hydroxy-terminated siloxane and polymerization in this step is conducted at a high pH range (for example, a pH range of 9 to 14). If pH is lower than 9, the reactivity may be lowered, and thus unreacted silicon may remain or the polysiloxane-polycarbonate copolymer may not reach the desired molecular weight. If pH is higher than 14, a molecular weight distribution may broaden due to a drastic reaction or a large amount of acid should be introduced in the washing process after the reaction for neutralization, and thus extra costs may occur. Therefore, the method of the present invention can effectively complete the reaction without unreacted silicon monomer by adding the silicon monomer in the polymerization step whose pH is high due to the addition of significant amount of NaOH after undergoing an oligomerization step for homogenizing the oligomeric polycarbonate.

[67] In a preferred embodiment, the polymerization of oligomeric polycarbonate and hydroxy-terminated siloxane is successively performed through first and second steps of polymerization. Specifically, after conducting the first polymerization from the mixture in which a hydroxy-terminated siloxane, a first polymerization catalyst, a phase transfer catalyst, a molecular weight regulator, a pH adjusting agent (for example, NaOH), methylene chloride (MC), etc. are added to the oligomeric polycarbonate, the second polymerization is successively conducted by adding a second polymerization catalyst. The second polymerization step may be performed by providing a second polymerization catalyst to the resulting mixture after completion of the first polymerization step.

[68] Preferably, a viscosity average molecular weight of the polysiloxane-polycarbonate copolymer prepared according to the present invention is from 15,000 to 30,000, and more preferably from 17,000 to 22,000. If the viscosity average molecular weight of the copolymer is less than 15,000, the mechanical properties may significantly be deteriorated. If the viscosity average molecular weight is greater than 30,000, the melt viscosity increases and thus there may be a problem in resin processing. In the present invention, formability can be enhanced under the same processing condition since good low-temperature impact resistance and ductility ratio can be secured even when the viscosity average molecular weight of the copolymer is lowered to a level of 30,000 or less by maximizing the reaction ratio through controlling the addition time of hydroxy-terminated siloxane. Accordingly, molding can be effectively performed even when the processing temperature for extrusion/injection is lowered compared to when the viscosity average molecular weight is 30,000, and thus a production increase in continuous injection may be expected by decreasing energy cost required for raising

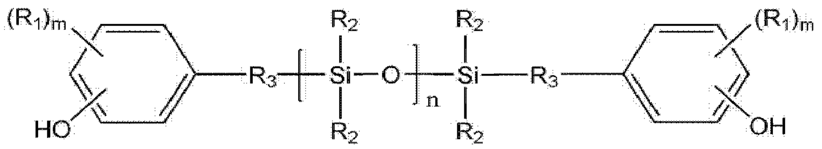
temperature and shortening cooling time. In addition, a kneading with other resins of poor heat-stability becomes available, which facilitates developments for more various uses.

[69] In a preferred embodiment, the polysiloxane-polycarbonate copolymer prepared according to the present invention comprises, as repeating units, a hydroxy-terminated siloxane of the following chemical formula 1a or chemical formula 1; and a polycarbonate block of the above chemical formula 4:

[70]

[71] [Chemical formula 1a]

[72]



[73]

[74] in the above chemical formula 1a,

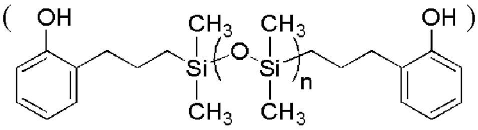
[75] R_1 independently represents hydrogen atom, halogen atom, hydroxy group, or alkyl group, alkoxy group or aryl group having 1 to 20 carbon atoms. For example, the halogen atom may be Cl or Br, and the alkyl group may be an alkyl group having 1 to 13 carbon atoms such as methyl, ethyl or propyl. In addition, the alkoxy group may be an alkoxy group having 1 to 13 carbon atoms such as methoxy, ethoxy or propoxy, and the aryl group may be an aryl group having 6 to 10 carbon atoms such as phenyl, chlorophenyl or tolyl.

[76] R_2 independently represents substituted or unsubstituted aryl group having 6 to 30 carbon atoms, hydrocarbon group having 1 to 13 carbon atoms or hydroxy group. For example, R_2 may be alkyl or alkoxy group having 1 to 13 carbon atoms, alkenyl or alkenyloxy group having 2 to 13 carbon atoms, cycloalkyl or cycloalkoxy group having 3 to 6 carbon atoms, aryl or aryloxy group having 6 to 10 carbon atoms, aralkyl or aralkoxy group having 7 to 13 carbon atoms, or alkaryl or alkaryloxy group having 7 to 13 carbon atoms.

[77] R_3 independently represents alkylene group having 2 to 8 carbon atoms.

[78] The subscript "m" independently represents an integer of 0 to 4.

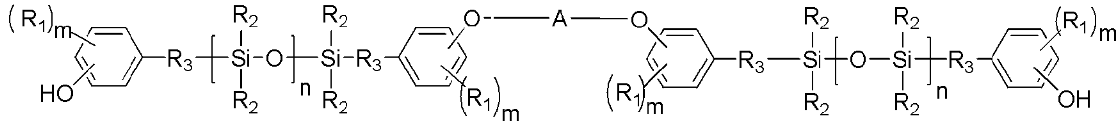
[79] The subscript "n" independently represents an integer of 30 to 200, preferably 40 to 170, and more preferably 50 to 120.

[80] In one embodiment, as a hydroxy-terminated siloxane of chemical formula 1a, a silicon monomer available from Dow Corning () may be used, but it is not limited thereto.

[81]

[82] [Chemical formula 1]

[83]



[84]

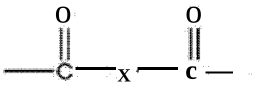
[85] in the above chemical formula 1, R_1, R_2, R_3 and m are the same as defined in chemical formula 1a above, and n independently represents an integer of 15 to 100, preferably 20 to 80, and more preferably 25 to 60.

[86] "A" represents a structure of the following chemical formula 2 or 3.

[87]

[88] [Chemical formula 2]

[89]



$$-\overset{\displaystyle O}{\overset{\|}{C}}-X-\overset{\displaystyle O}{\overset{\|}{C}}-$$

[90]

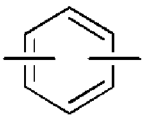
[91] in the above chemical formula 2,

[92] X represents Y or NH-Y-NH, wherein Y represents linear or branched aliphatic group having 1 to 20 carbon atoms, cycloalkylene group (for example, cycloalkylene group having 3 to 6 carbon atoms), or mono- or polycyclic arylene group having 6 to 30 carbon atoms and being unsubstituted or substituted with halogen atom, alkyl group, alkoxy group, aryl group or carboxyl group. For example, Y may be an aliphatic group that is unsubstituted or substituted with halogen atom, an aliphatic group that contains oxygen, nitrogen or sulfur atom in its main chain, or an arylene group that can be derived from bisphenol A, resorcinol, hydroquinone or diphenylphenol. Y can be represented, for example, by one of the following chemical formulas 2a to 2h.

[93]

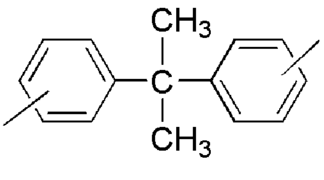
[94] [Chemical formula 2a]

[95]

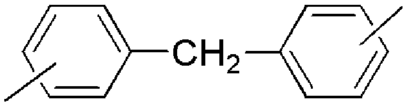


[96] [Chemical formula 2b]

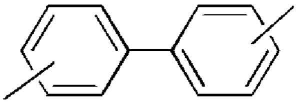
[97]



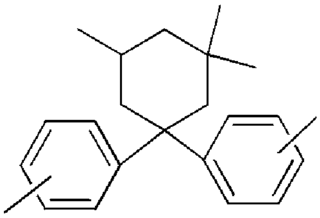
[98] [Chemical formula 2c]

[99] 

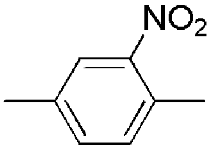
[100] [Chemical formula 2d]

[101] 

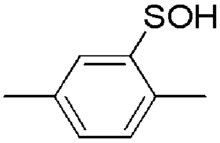
[102] [Chemical formula 2e]

[103] 

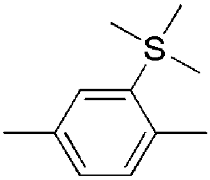
[104] [Chemical formula 2f]

[105] 

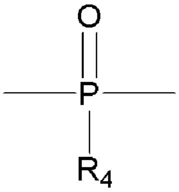
[106] [Chemical formula 2g]

[107] 

[108] [Chemical formula 2h]

[109] 

[110] [Chemical formula 3]

[111] 

[112]

[113] in the above chemical formula 3,

[114] R_4 represents an aromatic hydrocarbon group or aromatic/aliphatic mixed-type hydrocarbon group having 6 to 30 carbon atoms, or an aliphatic hydrocarbon group having 1 to 20 carbon atoms. R_4 may have a structure containing halogen, oxygen,

nitrogen or sulfur as well as carbon atom(s). For example, R_4 may be phenyl, chlorophenyl or tolyl (preferably, phenyl).

[115] In one embodiment, the hydroxy-terminated siloxane of chemical formula 1 may be a reaction product of a hydroxy-terminated siloxane of the above chemical formula 1a (provided that n is an integer of 15 to 100) and an acyl compound.

[116] The acyl compound may have, for example, an aromatic structure, an aliphatic structure, or a mixed type structure comprising both aromatic and aliphatic forms. When the acyl compound is of an aromatic structure or a mixed type structure, it can have 6 to 30 carbon atoms, and when the acyl compound is of an aliphatic structure, it can have 1 to 20 carbon atoms. The acyl compound may further comprise halogen, oxygen, nitrogen or sulfur atom.

[117] In another embodiment, the hydroxy-terminated siloxane of the above chemical formula 1 may be a reaction product of a hydroxy-terminated siloxane of the above chemical formula 1a (provided that n is an integer of 15 to 100) and a diisocyanate compound.

[118] The diisocyanate compound may be, for example, 1,4-phenylenediisocyanate, 1,3-phenylenediisocyanate or 4,4'-methylenediphenyl diisocyanate.

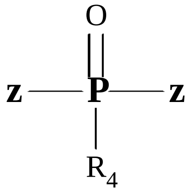
[119] In another embodiment, the hydroxy-terminated siloxane of the above chemical formula 1 may be a reaction product of a hydroxy-terminated siloxane of the above chemical formula 1a (provided that n is an integer of 15 to 100) and a phosphorous-containing compound (an aromatic or an aliphatic phosphate compound).

[120] The phosphorous-containing compound may have a structure of the following chemical formula 1b.

[121]

[122] [Chemical formula 1b]

[123]



$$Z-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle R_4}{|}}{P}}-Z$$

[124]

[125] In the above chemical formula 1b, R_4 is the same as defined in chemical formula 3 above, and Z independently represents phosphorus, halogen atom, hydroxyl group, carboxyl group, or alkyl group, alkoxy group or aryl group (having 1 to 20 carbon atoms).

[126] In one embodiment, after the polysiloxane-polycarbonate copolymer is prepared according to the present invention, the organic phase dispersed in methylene chloride is washed with alkali and then separated. Subsequently, the organic phase is washed

with 0.1 N solution of hydrochloric acid and then rinsed with distilled water 2 or 3 times. After rinsing is completed, the concentration of the organic phase dispersed in methylene chloride is adjusted constantly and granulation is conducted by using a certain amount of demineralized water at 30 to 100°C, preferably 60 to 80°C. If the temperature of the demineralized water is lower than 30°C, the granulation rate is low and thus the granulation time may be too long. If the temperature of the demineralized water is higher than 100°C, it may be difficult to obtain the polycarbonate in uniformly sized morphology. After granulation is completed, it is preferable to dry the product at 100 to 120°C for 5 to 10 hours. More preferably, the product is dried at 100 to 110°C for 5 to 10 hours first, and then at 110 to 120°C for 5 to 10 hours.

[127] In addition, according to another aspect of the present invention, the polysiloxane-polycarbonate copolymer prepared according to the methods of the present invention is provided. The polysiloxane-polycarbonate copolymer of the present invention has various applications since it has good processability and formabiltity as well as superior low-temperature impact resistance and ductility ratio due to its low viscosity average molecular weight.

[128] Thus, according to another aspect of the present invention, there is provided a thermoplastic resin composition comprising the polysiloxane-polycarbonate copolymer prepared according to the methods of the present invention and an additive. As the additive, those typically added to the thermoplastic resin composition (for example, heat stabilizer, antioxidant, UV stabilizer, flame retardant, release agent, etc.) may be used.

[129] In addition, according to another aspect of the present invention, there is provided a molded article prepared from the thermoplastic resin composition above. For processing the molded article, methods typically used for processing thermoplastic resin compositions, for example, extrusion, thermoforming, injection, etc. may be used.

[130]

[131] **Examples and Comparative Examples**

[132]

[133] Example _1

[134] <Preparation of hydroxy-terminated siloxane>

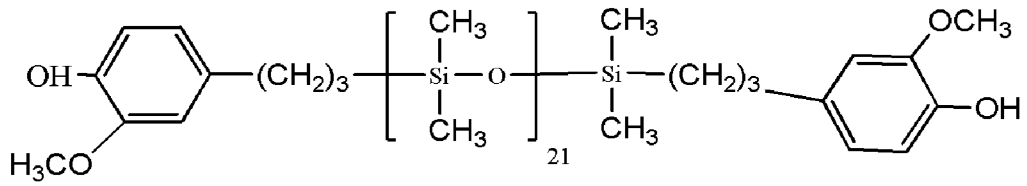
[135] In a lOOmL three-necked flask equipped with a condenser, 0.03 mol of eugenol and 0.015 mol of polydimethylsiloxane were dissolved in 50mL of chlorobenzene under nitrogen atmosphere. After the dissolution was completed, 0.00364 mmol of platinum catalyst (platinum(0)-l,3-divinyl-l,l,3,3-tetramethyldisiloxane complex) was added thereto and the mixture was refluxed for 24 hours. After the solvent was removed from the reaction solution, washing was conducted with distilled water. By drying for 24

hours in a vacuum oven, the hydroxy-terminated siloxane of the following chemical formula 6 was prepared.

[136]

[137] [Chemical formula 6]

[138]



[139]

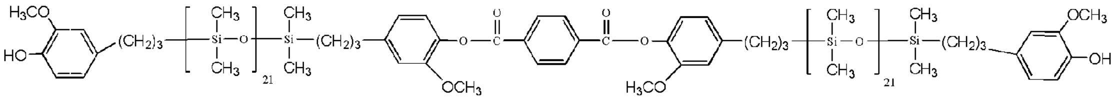
[140] <Preparation of hydroxy-terminated siloxane having ester linkage>

[141] 0.4 mol of hydroxy-terminated siloxane having the linkage of chemical formula 6 was dissolved in 300mL of chloroform, and then 67mL of triethylamine (TEA) catalyst was added thereto under nitrogen atmosphere. Under refluxing the resulting solution, 0.2 mol of terephthaloylchloride (TCL) dissolved in 1,000mL of chloroform was slowly added thereto for 1 hour, and the resulting solution was refluxed for 12 hours. After the reaction was completed, the solvent was removed from the solution, and the product was dissolved in acetone and washed with hot distilled water. By drying for 24 hours in a vacuum oven, the hydroxy-terminated siloxane having ester linkage of the following chemical formula 7 (number average molecular weight: 4,000) was prepared. The synthesis was confirmed by H-NMR analysis wherein the peak of methylene group of the polysiloxane was observed at 2.6ppm, the peak of hydrogen of benzene ring of TCL was observed at 8.35ppm and the peak of hydrogen of benzene ring of the polysiloxane was observed at 6.75-7.35ppm.

[142]

[143] [Chemical formula 7]

[144]



[145] <Preparation of polysiloxane-polycarbonate copolymer>

[146] An interfacial reaction of bisphenol A in an aqueous solution phase of sodium hydroxide and phosgene gas was conducted in the presence of methylene chloride to prepare an oligomeric polycarbonate mixture having a viscosity average molecular weight of about 1,000. To the obtained oligomeric polycarbonate mixture, 2.6g of p-ieri-butylphenol (PTBP) and 275μl of triethylamine (TEA, 15 wt% aqueous solution) were admixed and reacted for 30 minutes to prepare 400mL of an oligomeric polycarbonate mixture having a viscosity average molecular weight of 3,000 to 6,000. To the obtained oligomeric polycarbonate mixture, 4.5% by weight of the hydroxy-terminated siloxane having ester linkage of chemical formula 7 dissolved in methylene

chloride, 0.8mL of tetrabutylammonium chloride (TBAC1, 43 wt% aqueous solution), 160g of an aqueous solution of sodium hydroxide, 300g of methylene chloride and 25μï of triethylamine (15 wt% aqueous solution) were admixed and reacted for 1 hour for the first step of polymerization. After 260 μï of triethylamine (TEA, 15 wt% aqueous solution) was admixed, the reaction was conducted for 30 minutes. After phase separation, the viscosity-increased organic phase was washed with alkali and separated. Next, the resulting organic phase was washed with 0.1N hydrochloric acid solution and then rinsed with distilled water 2 to 3 times. After rinsing was completed, the organic phase was granulated at 76°C using a certain amount of demineralized water. After granulation was completed, the product was dried first at 110°C for 8 hours, and second at 120°C for 10 hours. The synthesis of the copolymer was confirmed by H-NMR analysis wherein the peaks of methylene group of the polysiloxane were observed at 2.6ppm and 2.65ppm, the peak of hydrogen of benzene ring of TCL was observed at 8.35ppm, and the peak of hydrogen of benzene ring of the polysiloxane was observed at 6.95 to 7.5ppm. The physical properties of the prepared polysiloxane-polycarbonate copolymer were measured, and the results are shown in Table 1 below.

[147]

[148] Example 2

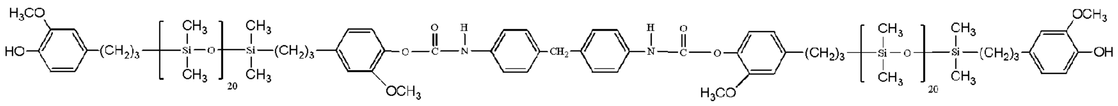
[149] <Preparation of hydroxy-terminated siloxane>

[150] 0.0666 mol of hydroxy-terminated siloxane having the linkage of chemical formula 6 was dissolved in lOOmL of benzene under nitrogen condition, and 6.66 mmol of l,4-diazabicyclo[2,2,2] -octane was added thereto. Under refluxing of the resulting solution, 0.0333 mol of 4,4-methylene bis(phenyl isocyanate) dissolved in 200mL of benzene was slowly added thereto for 1 hour. The resulting solution was refluxed for 12 hours. After the reaction was completed, the solvent was removed from the solution, and the resulting product was dissolved in acetone, washed with hot distilled water, and dried for 24 hours in a vacuum oven to prepare hydroxy-terminated siloxane having urethane linkage of the following chemical formula 8 (molecular weight: 4,000). The synthesis was confirmed by H-NMR analysis wherein the peak of hydrogen atom that is combined with the first carbon atom of the aliphatic chain adjacent to the terminal phenyl group in the following chemical formula 8 was observed at 2.75ppm.

[151]

[152] [Chemical formula 8]

[153]



[154] <Preparation of polysiloxane-polycarbonate copolymer>

[155] An interfacial reaction of bisphenol A in an aqueous solution phase of sodium hydroxide and phosgene gas was conducted in the presence of methylene chloride to prepare an oligomeric polycarbonate mixture having a viscosity average molecular weight of about 1,000. To the obtained oligomeric polycarbonate mixture, 2.6g of p-ieri-butylphenol (PTBP) and 275µ1of triethylamine (TEA, 15 wt% aqueous solution) were admixed and reacted for 30 minutes to prepare 400mL of an oligomeric polycarbonate mixture having a viscosity average molecular weight of 3,000 to 6,000. To the obtained oligomeric polycarbonate mixture, 4.5% by weight of the hydroxy-terminated siloxane having urethane linkage of chemical formula 8 dissolved in methylene chloride, 0.8mL of tetrabutylammonium chloride (TBAC1, 43 wt% aqueous solution), 160g of an aqueous solution of sodium hydroxide, 300g of methylene chloride and 25µï of triethylamine (15 wt% aqueous solution) were admixed and reacted for 1 hour for the first step of polymerization. After 260 µï of triethylamine (TEA, 15 wt% aqueous solution) was admixed, the reaction was conducted for 30 minutes. After phase separation, the viscosity-increased organic phase was washed with alkali and separated. Next, the resulting organic phase was washed with 0.1N hydrochloric acid solution and then rinsed with distilled water 2 to 3 times. After rinsing was completed, the organic phase was granulated at 76°C by using a certain amount of demineralized water. After granulation was completed, the product was dried first at 110°C for 8 hours, and second at 120°C for 10 hours. The synthesis of the copolymer was confirmed by H-NMR analysis wherein the peak of methylene group of the polysiloxane was observed at 2.65ppm, the peak of methoxy group was observed at 3.85ppm, and the peak of hydrogen of benzene ring was observed at 7.1 to 7.5ppm. The physical properties of the prepared polysiloxane-polycarbonate copolymer were measured, and the results are shown in Table 1 below.

[156]

[157] <u>Example 3</u>

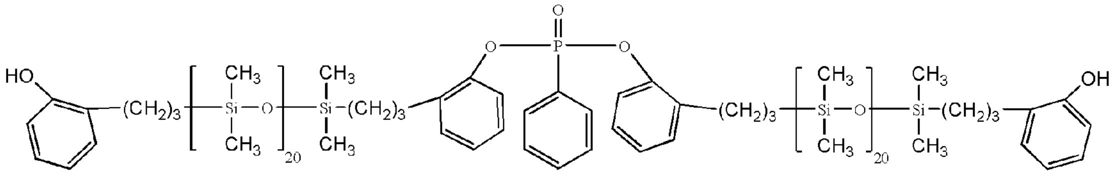
[158] <Preparation of hydroxy-terminated siloxane>

[159] In a 500mL three-necked flask equipped with a condenser, 0.01 mol of PMS-25 (available from Damipolychem Corporation) was dissolved in lOOmL of toluene under nitrogen atmosphere, and then 0.01 mol of triethylamine (TEA) catalyst was added thereto. Under refluxing of the resulting solution, 0.005 mol of phenyl phosphonic dichloride was slowly added thereto for 1 hour, and the resulting solution was refluxed for 5 hours. After the reaction was completed, the toluene solvent was removed from the solution, and the product was dried for 24 hours in a vacuum oven to prepare a phosphate-containing hydroxy-terminated siloxane of the following chemical formula 9 (molecular weight: 4,000).

[160]

[161] [Chemical formula 9]

[162]



[163]

[164] <Preparation of polysiloxane-polycarbonate copolymer>

[165] An interfacial reaction of bisphenol A in an aqueous solution phase of sodium hydroxide and phosgene gas was conducted in the presence of methylene chloride to prepare an oligomeric polycarbonate mixture having a viscosity average molecular weight of about 1,000. To the obtained oligomeric polycarbonate mixture, 2.6g of p-ieri-butylphenol (PTBP) and 275µ1of triethylamine (TEA, 15 wt% aqueous solution) were admixed and reacted for 30 minutes to prepare 400mL of an oligomeric polycarbonate mixture having a viscosity average molecular weight of 3,000 to 6,000. To the obtained oligomeric polycarbonate mixture, 4.5% by weight of the phosphate-containing hydroxy-terminated siloxane of the above chemical formula 9, 0.8mL of tetrabutylammonmm chloride (TBACl, 43 wt% aqueous solution), 160g of an aqueous solution of sodium hydroxide, 300g of methylene chloride and 25µï of triethylamine (15 wt% aqueous solution) were admixed and reacted for 1 hour for the first step of polymerization. After 260 µï of triethylamine (TEA, 15 wt% aqueous solution) was admixed, the reaction was conducted for 30 minutes. After phase separation, the viscosity-increased organic phase was washed with alkali and separated. Next, the resulting organic phase was washed with 0.1N hydrochloric acid solution and then rinsed with distilled water 2 to 3 times. After rinsing was completed, the organic phase was granulated at 76°C by using a certain amount of demineralized water. After granulation was completed, the product was dried first at 110°C for 8 hours, and second at 120°C for 10 hours. The physical properties of the prepared polysiloxane-polycarbonate copolymer were measured, and the results are shown in Table 1 below.

[166]

[167] Example 4

[168] A polysiloxane-polycarbonate copolymer was prepared by the same method as described in Example 1, except that the polysiloxane-polycarbonate copolymer was prepared by using 4.5% by weight of hydroxy-terminated siloxane BY16-752 (molecular weight: 3,000, Dow Corning). The physical properties of the prepared polysiloxane-polycarbonate copolymer were measured, and the results are shown in Table 1 below.

[169]

[170] Example 5

[171] <Preparation of hydroxy-terminated siloxane>

[172] The hydroxy-terminated siloxane having ester linkage of the above chemical formula 7 (number average molecular weight: 4,000) was prepared by the same method as described in Example 1.

[173]

[174] <Preparation of polysiloxane-polycarbonate copolymer>

[175] An interfacial reaction of bisphenol A in an aqueous solution phase of sodium hydroxide and phosgene gas was conducted in the presence of methylene chloride to prepare an oligomeric polycarbonate mixture having a viscosity average molecular weight of about 1,000. To the obtained oligomeric polycarbonate mixture, 2.8g of p-ieri-butylphenol (PTBP) and 275µ1of triethylamine (TEA, 15 wt% aqueous solution) were admixed and reacted for 30 minutes. To the obtained oligomeric polycarbonate mixture, 160g of an aqueous solution of sodium hydroxide, 300g of methylene chloride and 25µï of triethylamine (15 wt% aqueous solution) were admixed and reacted for 1 hour for the first step of polymerization to prepare an oligomeric polycarbonate mixture having a viscosity average molecular weight of 8,000 to 12,000. Thereafter, 4.5% by weight of the hydroxy-terminated siloxane having ester linkage of the above chemical formula 7 dissolved in methylene chloride, 0.8mL of tetrabutylammonium chloride (TBAC1, 43 wt% aqueous solution) and 260µ1of triethylamine (TEA, 15 wt% aqueous solution) were admixed and reacted for 30 minutes. After phase separation, the viscosity-increased organic phase was washed with alkali and separated. Next, the resulting organic phase was washed with 0.1N hydrochloric acid solution and then rinsed with distilled water 2 to 3 times. After rinsing was completed, the organic phase was granulated at 76°C by using a certain amount of demineralized water. After granulation was completed, the product was dried first at 110°C for 8 hours, and second at 120°C for 10 hours. The synthesis of the copolymer was confirmed by H-NMR analysis wherein the peaks of methylene group of the polysiloxane were observed at 2.6ppm and 2.65ppm, the peak of hydrogen of benzene ring of TCL was observed at 8.35ppm, and the peak of hydrogen of benzene ring of the polysiloxane was observed at 6.95 to 7.5ppm. The physical properties of the prepared polysiloxane-polycarbonate copolymer were measured, and the results are shown in Table 1 below.

[176]

[177] Comparative Example 1

[178] The physical properties of a linear polycarbonate 3022PJ (M_v: 21,000, Samyang Corporation) were measured, and the results are shown in Table 1 below.

[179]

[180] Comparative Example 2

[181] The physical properties of a linear polycarbonate 3030PJ (M_v: 31,200, Samyang Corporation) were measured, and the results are shown in Table 1 below.

[182]

[183] Comparative Example 3

[184] The physical properties of a linear polycarbonate synthesized to have a viscosity average molecular weight of 70,800 were measured, and the results are shown in Table 1 below.

[185]

[186] Comparative Example 4

[187] <Preparation of hydroxy-terminated siloxane>

[188] The hydroxy-terminated siloxane having ester linkage of the above chemical formula 7 (number average molecular weight: 4,000) was prepared by the same method as described in Example 1.

[189]

[190] <Preparation of polysiloxane-polycarbonate copolymer>

[191] An interfacial reaction of bisphenol A in an aqueous solution phase and phosgene gas was conducted in the presence of methylene chloride to prepare 400mL of an oligomeric polycarbonate mixture having a viscosity average molecular weight of 1,000 to 2,000. To the obtained oligomeric polycarbonate mixture, 4.5% by weight of the hydroxy-terminated siloxane having ester linkage of the above chemical formula 7 dissolved in methylene chloride, 0.8mL of tetrabutylammonium chloride (TBAC1), 2.6g of p-ieri-butylphenol (PTBP) and 275µ1of triethylamine (TEA, 15 wt% aqueous solution) were admixed and reacted for 30 minutes. The reacted oligomeric polycarbonate mixture was kept for phase separation. After the phases were separated, only the organic phase was collected and thereto 160g of an aqueous solution of sodium hydroxide, 300g of methylene chloride and 25µï of triethylamine (TEA, 15 wt% aqueous solution) were admixed and reacted for 1 hour. Then, 260µ1of triethylamine (TEA, 15 wt% aqueous solution) were admixed and reacted for 30 minutes. After phase separation, the viscosity-increased organic phase was washed with alkali and separated. Next, the resulting organic phase was washed with 0.1N hydrochloric acid solution and then rinsed with distilled water 2 to 3 times. After rinsing was completed, the organic phase was granulated by using a certain amount of demineralized water at 76°C. After the granulation was completed, the product was dried first at 110°C for 8 hours and second at 120°C for 10 hours. The synthesis of the copolymer was confirmed by H-NMR analysis wherein the peaks of methylene group of the polysiloxane were observed at 2.6ppm and 2.65ppm, the peak of hydrogen of benzene ring of TCL was observed at 8.35ppm, and the peak of hydrogen of benzene ring of the

polysiloxane was observed at 6.95 to 7.5ppm. The physical properties of the prepared polysiloxane-polycarbonate copolymer were measured, and the results are shown in Table 1 below.

[192]

[193] Comparative Example 5

[194] A polysiloxane-polycarbonate copolymer was prepared by the same method as described in Comparative Example 4, except that the polysiloxane-polycarbonate copolymer was prepared by using hydroxy-terminated siloxane having urethane linkage of the above chemical formula 7 (molecular weight: 4,000). The physical properties of the prepared polysiloxane-polycarbonate copolymer were measured, and the results are shown in Table 1 below.

[195]

[196] Comparative Example 6

[197] A polysiloxane-polycarbonate copolymer was prepared by the same method as described in Comparative Example 4, except that the polysiloxane-polycarbonate copolymer was prepared by using phosphate-containing hydroxy-terminated siloxane of the above chemical formula 9 (molecular weight: 4,000). The physical properties of the prepared polysiloxane-polycarbonate copolymer were measured, and the results are shown in Table 1 below.

[198]

[199] Comparative Example 7

[200] A polysiloxane-polycarbonate copolymer was prepared by the same method as described in Comparative Example 4, except that the polysiloxane-polycarbonate copolymer was prepared by using hydroxy-terminated siloxane BY16-752 (molecular weight: 3,000, Dow Corning). The physical properties of the prepared polysiloxane-polycarbonate copolymer were measured, and the results are shown in Table 1 below.

[201]

[202] Table 1

[Table 1]

Physical properties		Examples				
		1	2	3	4	5
Type of silicon monomer		ester	urethane	phosphate	Linear-PDMS	ester
Siloxane amount (wt%)		4.5	4.5	4.5	4.5	4.5
Molecular weight of silicon monomer (M_n)		4,000	4,000	4,000	3,000	4,000
Molecular weight of oligomer (M_v)		3,000~6,000	3,000~6,000	3,000~6,000	3,000~6,000	8,000~12,000
Addition time of silicon monomer		1st polarization step	1st polarization step	1st polarization step	1st polarization step	2nd polymerization step
Si-PC molecular weight (M_v)		21,200	21,000	20,900	21,300	19,800
Impact strength (kg cm/cm)	Room temp.	82	78	81	80	75
	-50℃	62	60	61	61	58
Reaction ratio of silicon monomer (%)		99 or more	99 or more	99 or more	99 or more	99 or more
Ductility ratio under impact loading at -50℃ (%)		100	100	100	90	100

[203] [Table 1] (Continued)

Physical properties		Comparative Examples						
		1	2	3	4	5	6	7
Type of silicon monomer		-	-	-	ester	urethane	phosphate	Linear-PDMS
Siloxane amount (wt%)		0	0	0	4.5	4.5	4.5	4.5
Molecular weight of silicon monomer (M_n)		-	-	-	4,000	4,000	4,000	3,000
Molecular weight of oligomer (M_v)		-	-	-	1,000~2,000	1,000~2,000	1,000~2,000	1,000~2,000
Addition time of silicon monomer		-	-	-	oligomerization	oligomerization	oligomerization	oligomerization
Si-PC molecular weight (M_v)1)		21,000	31,200	70,800	21,100	21,400	21,200	21,800
Impact strength (kg cm/cm)	Room temp.	80	82	92	81	80	82	79
	-50℃	10	20	35	35	32	26	21
Reaction ratio of silicon monomer (%)		-	-	-	80	75	78	79
Ductility ratio under impact loading at -50℃ (%)		0	0	0	50	45	42	30

[204] 1)For Comparative Examples 1 to 3, a molecular weight (M_v) of linear polycarbonate

[205]

[206] As shown in Table 1 above, the polysiloxane-polycarbonate copolymer prepared according to the Examples showed superior low-temperature impact strength, silicon monomer reaction ratio and ductility ratio, as compared with the polysiloxane-polycarbonate copolymer (or linear polycarbonate) prepared according to the Comparative Examples.

[207] The method for measuring the above properties used in the Examples and the Comparative Examples were as follows.

[208] (a) H-NMR (nuclear magnetic resonance spectroscopy): This analysis was conducted by using Avance DRX 300 (Bruker).

[209] (b) Viscosity average molecular weight (M_v): The viscosity of methylene chloride solution was measured by using an Ubbelohde Viscometer at 20°C, and the limiting viscosity [η] therefrom was calculated according to the following equation.

[210] $[\eta]=1.23\chi 10^{-5} M\nu^{0.83}$

[211] (c) Impact strength: Impact strength was measured by using an impact test machine (RESIL IMPACTOR, CEAST Co., Ltd.) at room temperature and -50°C.

[212] (d) Ductility ratio measured under impact loading at -50°C: The ductility ratio was calculated by dividing the ductility of specimen by the ductility of all specimens, and then multiplying it by 100.

[213]

[214] [Explanation of Symbols]

[215] TEA: triethylamine

[216] PTBP: p-ieri-butylphenol

[217] Si-monomer: silicon monomer

[218] PTC cat.: phase transfer catalyst.

[219] Catalyst 1: first polymerization catalyst

[220] DMW: demineralized water

[221] MC: methylene chloride

[222] Catalyst 2: second polymerization catalyst

[223] BPA-Na: bisphenol A-Na

[224] CDC: phosgene (carbonyl dichloride)

Claims

[Claim 1] A method for preparing a polysiloxane-polycarbonate copolymer, which comprises:

a) a step of preparing an oligomeric polycarbonate having a viscosity average molecular weight of 3,000 to 20,000;

b) a step of admixing a hydroxy-terminated siloxane to the prepared oligomeric polycarbonate; and

c) a step of reacting the oligomeric polycarbonate and the hydroxy-terminated siloxane under an interfacial reaction condition to polymerize.

[Claim 2] The method for preparing the polysiloxane-polycarbonate copolymer according to claim 1, wherein the hydroxy-terminated siloxane added in the step b) has a number average molecular weight (M_n) of 2,500 to 15,000.

[Claim 3] The method for preparing the polysiloxane-polycarbonate copolymer according to claim 1, wherein the oligomeric polycarbonate and the hydroxy-terminated siloxane are mixed in a weight ratio of 80 : 20 to 99 : 1 in the step b).

[Claim 4] The method for preparing the polysiloxane-polycarbonate copolymer according to claim 1, wherein the oligomeric polycarbonate and the hydroxy-terminated siloxane are mixed in a weight ratio of 85 : 15 to 97 : 3 in the step b).

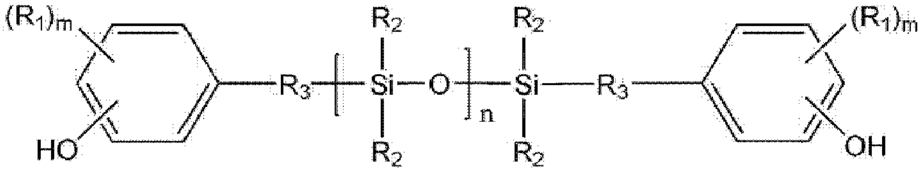
[Claim 5] The method for preparing the polysiloxane-polycarbonate copolymer according to claim 1, wherein the step a) is conducted within a pH range of 6 to 8; and the step b) and step c) are conducted within a pH range of 9 to 14.

[Claim 6] The method for preparing the polysiloxane-polycarbonate copolymer according to claim 1, wherein the polymerization of the step c) is conducted through first and second steps of polymerization.

[Claim 7] The method for preparing the polysiloxane-polycarbonate copolymer according to claim 1, wherein the polysiloxane-polycarbonate copolymer has a viscosity average molecular weight of 15,000 to 30,000.

[Claim 8] The method for preparing the polysiloxane-polycarbonate copolymer according to claim 1, wherein the polysiloxane-polycarbonate copolymer comprises, as repeating units, a hydroxy-terminated siloxane of the following chemical formula 1a or chemical formula 1; and a polycarbonate block of the following chemical formula 4:

[Chemical formula la]



in chemical formula la,

R_1 independently represents hydrogen atom, halogen atom, hydroxy group, or alkyl group, alkoxy group or aryl group having 1 to 20 carbon atoms;

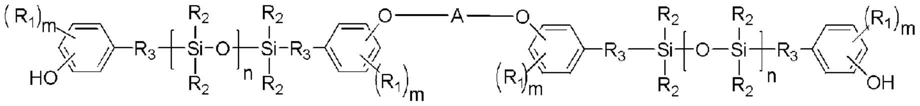
R_2 independently represents hydrocarbon group having 1 to 13 carbon atoms or hydroxy group;

R_3 independently represents alkylene group having 2 to 8 carbon atoms;

m independently represents an integer of 0 to 4; and

n represents an integer of 30 to 200;

[Chemical formula 1]



in chemical formula 1,

Ri independently represents hydrogen atom, halogen atom, hydroxy group, or alkyl group, alkoxy group or aryl group having 1 to 20 carbon atoms;

R_2 independently represents hydrocarbon group having 1 to 13 carbon atoms or hydroxy group;

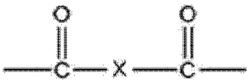
R_3 independently represents alkylene group having 2 to 8 carbon atoms;

m independently represents an integer of 0 to 4;

n independently represents an integer of 15 to 100; and

A represents a structure of the following chemical formula 2 or 3;

[Chemical formula 2]

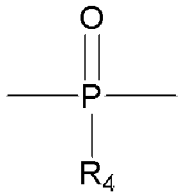


$$-\overset{\displaystyle O}{\overset{\|}{C}}-X-\overset{\displaystyle O}{\overset{\|}{C}}-$$

in chemical formula 2,

X is Y or NH-Y-NH, wherein Y represents linear or branched aliphatic group having 1 to 20 carbon atoms, cycloalkylene group, or mono- or polycyclic arylene group having 6 to 30 carbon atoms and being unsubstituted or substituted with halogen atom, alkyl group, alkoxy group, aryl group or carboxyl group;

[Chemical formula 3]

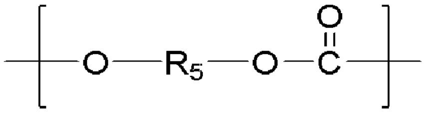


$$-\overset{\overset{O}{\|}}{\underset{\underset{R_4}{|}}{P}}-$$

in chemical formula 3,

R_4 represents an aromatic hydrocarbon group or aromatic/aliphatic mixed-type hydrocarbon group having 6 to 30 carbon atoms, or an aliphatic hydrocarbon group having 1 to 20 carbon atoms;

[Chemical formula 4]



$$\left[O-R_5-O-\overset{\overset{O}{\|}}{C} \right]$$

in chemical formula 4,

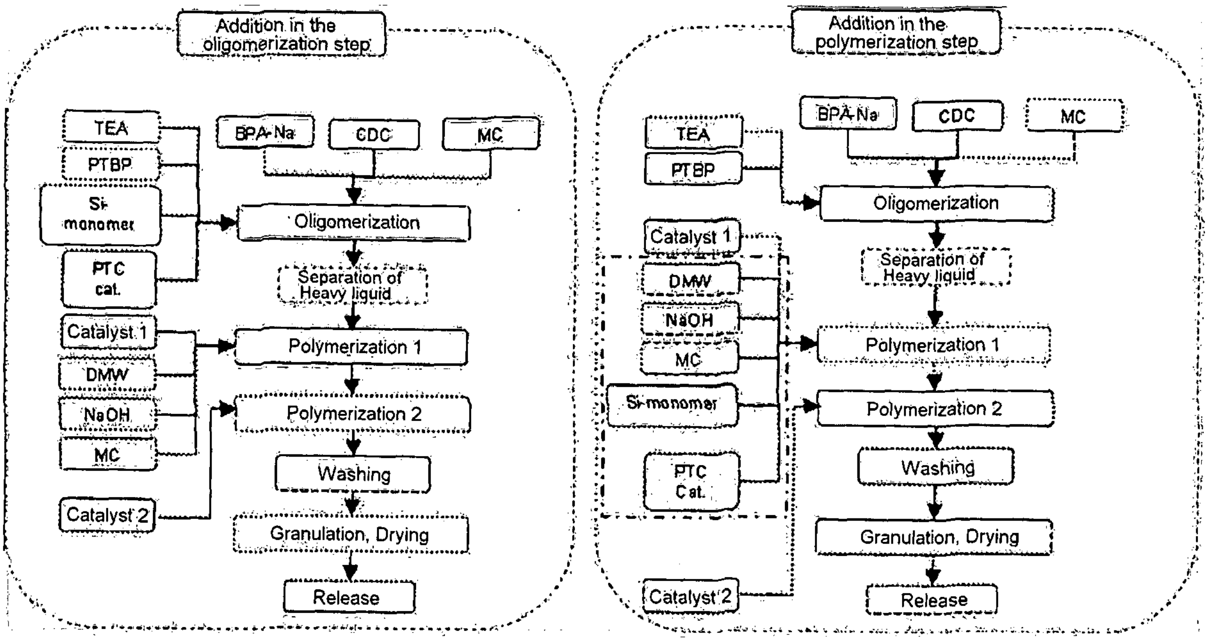
R_5 represents aromatic hydrocarbon group having 6 to 30 carbon atoms that is unsubstituted or substituted with alkyl group, cycloalkyl group, alkenyl group, alkoxy group, halogen atom, or nitro.

[Claim 9] A polysiloxane-polycarbonate copolymer prepared according to any of claims 1 to 8.

[Claim 10] A thermoplastic resin composition comprising the polysiloxane-polycarbonate copolymer according to claim 9 and an additive.

[Claim 11] A molded article prepared from the thermoplastic resin composition according to claim 10.

[Fig. 1]


Addition in the oligomerization step
TEA
PTBP
Si-monomer
PTC cat.
BPA-Na
CDC
MC
Oligomerization
Separation of Heavy liquid
Catalyst 1
DMW
NaOH
MC
Polymerization 1
Polymerization 2
Washing
Catalyst 2
Granulation, Drying
Release
Addition in the polymerization step
TEA
PTBP
BPA-Na
CDC
MC
Oligomerization
Catalyst 1
Separation of Heavy liquid
DMW
NaOH
MC
Polymerization 1
Si-monomer
Polymerization 2
PTC Cat.
Washing
Granulation, Drying
Catalyst 2
Release

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2012/011232

A. CLASSIFICATION OF SUBJECT MATTER

C08G 77/448(2006.01)i, C08G 64/18(2006.01)1, C08L 83/10(2006.01)1

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08G 77/448; C07F 7/08; C08G 77/04; C08G 65/48; C08G 64/24; C08L 83/10; C08G 77/445; C08G 64/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: polysiloxane-polycarbonate copolymer, viscosity molecular weight, hydroxy-terminated siloxane, oligomeric polycarbonate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2011-122767 A2 (SAMYANG CORPORATION) 06 October 2011 See paragraphs [19M57] , [71]-[75] , [83] -[88] ; claims 1-10	1-9 10, 11
Y	US 2008-0242804 Al (DHARA, D. et al.) 02 October 2008 See paragraphs [0043] , [0054] ; claims 1, 18-25	10, 11
A	KR 10-2011-0021630 A (SAMYANG CORPORATION) 04 March 2011 See paragraphs [0007]-[0028] ; claims 1-10	1-11
A	US 2009-0326183 Al (SCHULTZ, L. G. et al.) 31 December 2009 See paragraphs [0061H0063] , [0081] ; claim 1	1-11
A	US 5451632 A (OKUMURA, R. et al.) 19 September 1995 See column 7, lines 1-21 ; claims 1, 11; example 1A	1-11

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 27 March 2013 (27.03.2013)	Date of mailing of the international search report **29 March 2013 (29.03.2013)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-70 1, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer LEE, Dong Wook Telephone No. 82-42-481-8163

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

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