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(54) THERMOPLASTIC POLYMER COMPOSITIONS HAVING LOW FRICTION RESISTANCE

THERMOPLASTISCHE POLYMERZUSAMMENSETZUNGEN MIT GERINGEM REIBUNGSWIDERSTAND

COMPOSITIONS DE POLYMÈRES THERMOPLASTIQUES AYANT UNE FAIBLE RÉSISTANCE À LA FRICTION

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Description

[0001] This invention relates to thermoplastic polymer compositions containing a copolymer of a polysiloxane and an olefin polymer as a friction reducing additive in the thermoplastic polymer composition. The invention also relates to a process for the production of a thermoplastic polymer composition by melt kneading a polysiloxane with an olefin polymer and blending the thermoplastic polymer with the copolymer of polysiloxane and olefin polymer resulting from melt kneading. In one aspect of the invention the thermoplastic polymer is a polyacetal and the invention forms polyacetal compositions of low friction coefficient, but the invention also includes thermoplastic polymer compositions based on other thermoplastic polymers such as polyolefins.

[0002] Silanes and siloxanes are compounds containing silicon.

[0003] A silane is a compound derived from SiH4 . A silane often contains at least one Si-C bond. A silane usually contains only one Si atom.

[0004] A siloxane is a compound which contains at least one Si-0 bond.

[0005] A polysiloxane contains several Si-O-Si- bonds forming a polymeric chain, where the repeating unit is -(Si-O)-. An organopolysiloxane is sometimes called a silicone. An organopolysiloxane contains repeating -(Si-O)- units where at least one Si atom bears at least one organic group. "Organic" means containing at least one carbon atom. An organic group is a chemical group comprising at least one carbon atom.

[0006] A polysiloxane comprises terminal groups and pendant groups. A terminal group is a chemical group located on a Si atom which is at an end of the polymer chain. A pendant group is a group located on a Si atom which Si atom is not at the end of the polymeric chain.

[0007] A polymer is a compound containing repeating units which units typically form at least one polymeric chain. A polymer can be a homopolymer or a copolymer. A homopolymer is a polymer which is formed from only one type of monomer. A copolymer is a polymer formed from at least two monomers. A polymer is called an organic polymer when the repeating units contain carbon atoms.

[0008] Some polymers are thermoset: once cooled and hardened, these polymers retain their shapes and cannot return to their original form. Other polymers are thermoplastics: they can soften upon heating and return to their original form.

[0009] A functional group is a chemical group having a function, for example a reactive group.

[0010] A capping or end-capping reaction is a reaction where a functional group is changed or removed. A capping reaction can be conducted at the end of a polymerization reaction, to neutralize at least partly the remaining functional, reactive groups that can be present on the surface of the polymer. For example some or all of remaining functional, reactive groups such as, for example silanol or alkenyl groups, present at the surface of a macromolecule can be removed in a capping reaction. Another functional group can be introduced by a capping reaction.

[0011] A macromolecule is a molecule of important size. A polymer is a macromolecule.

[0012] An olefin polymer, also called a polyolefin is a polymer produced from an olefin (usually an alkene) as monomer. Some examples of thermoplastic olefin polymers are: polyethylene (PE) and polypropylene (PP). The olefin polymer can be a homopolymer or a copolymer.

[0013] Polyacetals are thermoplastic polymers obtained from the polymerization of formaldehyde or cyclic oligomers of formaldehyde. We use the term 'polyacetal' to include polyoxymethylene (also known as POM) and copolymers comprising mainly oxymethylene units. Polyacetals are characterized by a high crystallinity resulting in high tensile strength, stiffness, low coefficient of friction, excellent dimensional stability and mechanical properties such as stiffness, hardness and creep resistance and a high thermo-oxidative stability. They are mainly used to produce parts requiring high fatigue resistance combined with high mechanical and chemical resistance, for example sliding components and gears for office appliances, plastic gears used in precision devices, household electrical appliances or automobiles, bearings, and conveyor belts. Polyoxymethylene shows limited vibration and noise damping in specialty parts requiring fast sliding properties such as office appliances gears, conveyor belts, bearings or medical tubing connectors.

[0014] US Patent 4874807 describes that adding a silicone oil having a specified viscosity to a polyoxymethylene composition improves frictional and abrasive resistance characteristics and reduce frictional noise when sliding. However the silicone oil, which is a low viscosity liquid and incompatible with the polyoxymethylene phase, tends to separate and to bleed out over time and the improvements may disappear over time.

[0015] US Patent 6602953 describes a polyoxymethylene resin composition, which comprises a polyoxymethylene resin, 0.05 to 10 parts by weight of a silicone grafted polyolefinic resin and a silicone polymer. The ratio of silicone-grafted polyolefinic to the silicone polymer in the composition is 99/1 to 70/30. According to this patent, the presence of silicone grafted polyolefin improves the compatibility of the silicone polymer present in the composition with the polyoxymethylene resin while maintaining the mechanical properties of the polyoxymethylene and without deteriorating the frictional and abrasive resistance.

[0016] JP2009270025 describes a polyolefin-polyorganosiloxane copolymer obtained by melt-kneading and reacting polyolefin-type compound (100) having reactive functional groups and silicone-type compound (50-300) having reactive functional groups. The reaction rate is said to be 70% or more. JPH04146949 describes ethylene-ethyl acrylate copolymer modified with organopolysiloxane obtained by thermally mixing organopolysiloxane with ethylene-ethyl acrylate copolymer in the presence of peroxide.

[0017] JP200203461 1 describes resin composition comprising a polyoxymethylene resin and a polyolefin resin grafted with a silicone gum.

[0018] US6602953 describes polyoxymethylene resin compositions comprising a polyoxymethylene resin and a silicone compound-grafted polyolefinic resin.

[0019] We have found that the presence of free silicone polymer in such compositions even with a silicone grafted polyolefin is detrimental to the mechanical properties to some extent; the frictional and abrasive resistance will often be affected when the composition comes into contact with organic solvents. The free siloxane polymer will probably be washed away leaving unstructured surface.

[0020] It should be noted that associated methods are also described herein to aid in the understanding of the invention, but these do not form part of the claimed invention. Examples or embodiments described herein which do not fall under the definition of the claims do not form part of the present invention.

[0021] A polymer composition according to the invention consists of a thermoplastic polymer (A) selected from a polyacetal and a polyolefin, and a copolymer (B) of a polysiloxane (B1) and an olefin polymer (B2), and optionally, if the thermoplastic polymer (A) is a polyacetal, contains a stabilizer, characterised in that the copolymer (B) is a branched block copolymer and all the polysiloxane (B1) is reacted with the olefin polymer (B2) to produce a branched block copolymer (B) which is free of any siloxane homopolymer. Typically the copolymer (B) is present as an additive in the thermoplastic polymer (A). The copolymer (B) can for example be present in less than 10% by weight of the total composition, preferably less than 5, 4, 3, 2, 1 % by weight.

[0022] A process according to the invention for the production of a thermoplastic polymer (A) composition of reduced coefficient of friction comprises the steps of:

(i) melt kneading a polysiloxane (B1) containing ethylenically unsaturated groups with an olefin polymer (B2) under process conditions at which all the polysiloxane (B1) is reacted with the olefin polymer to produce a branched block copolymer (B) which is free of any siloxane homopolymer; and

(ii) blending the thermoplastic polymer (A) with the branched block copolymer (B) produced in step (i).

[0023] We have found that the branched block copolymer (B) shows improved compatibility with polyolefins or polyacetals. The use of such a branched block copolymer (B) as a solid lubricant additive in polyacetal or polyolefin compositions provides improved slidability (low coefficient of friction and low wear rate) without deteriorating the mechanical properties of the thermoplastic polymer composition. We have found that blending the branched block copolymer (B) into a polyacetal composition yields a material having a lower and constant coefficient of friction and improved wear resistance compared to a similar composition in which some of the polysiloxane is present as siloxane homopolymer.

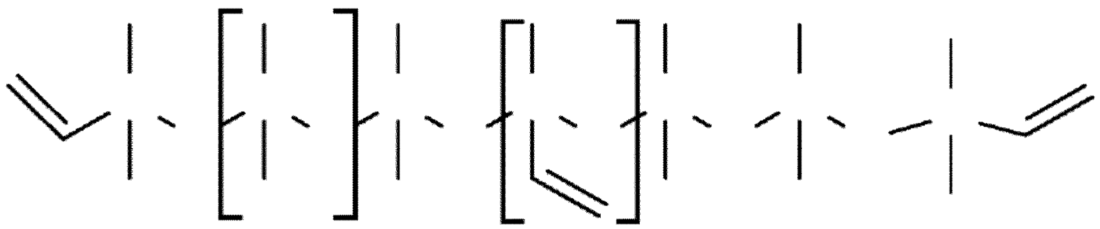
[0024] Preferably the branched block copolymer (B) is in pelletized or powdery form.

[0025] The ethylenically unsaturated groups in polysiloxane (B1) which are reacted with an olefin polymer to produce branched block copolymer (B) can for example be selected from vinyl, allyl, styryl, acrylic and methacrylic groups, or any other group containing a double bond or triple bond capable of reacting radically with a polyolefin chain during a melt kneading process.

[0026] The silicon-bonded groups in polysiloxane (B1) other than the ethylenically unsaturated groups are typically methyl groups but can be any other hydrocarbyl groups or any other groups which do not interfere with the silicone polyolefin radical reaction. Examples of other hydrocarbyl groups include phenyl groups and alkyl groups having 2 to 12 carbon atoms such as ethyl groups. Examples of other groups which do not interfere with the silicone polyolefin radical reaction include hydrogen, ether, ester, hydroxyl, and mercapto groups, and substituted alkyl groups such as hydroxyalkyl and mercaptoalkyl groups.

[0027] The level of ethylenically unsaturated groups in the polysiloxane (B1) is generally in the range from 0.05 to 2 mole % of all groups bonded to silicon, for example from 0.1 % to 1 %.

[0028] The ethylenically unsaturated groups can be present in end-capping groups on terminal silicon atoms of the polysiloxane (B1), and/or can be present in diorganosiloxane groups forming part of the polysiloxane chain (pendant groups). Preferably, the polysiloxane (B1) comprises both end-capping and pendant ethylenically unsaturated groups. For example vinyl groups can be present as terminal vinyldimethylsiloxy groups and/or as methylvinylsiloxy units in the polysiloxane chain. The polysiloxane (B1) may contain on average more than 2 ethylenically unsaturated groups per molecule. In one embodiment the polysiloxane (B1) contains at least 3 ethylenically unsaturated, for example vinyl groups per molecule. For example it can contain at least one terminal vinyldimethylsiloxy group and also methyl vinyl siloxy units randomly distributed in the polymer backbone. Such a polysiloxane can be represented by the formula



[0029] The polysiloxane (B1) can be 100% endcapped with units containing ethylenically unsaturated groups such as dimethylvinylsiloxy (-Si$(CH_3)_2CH=CH_2$) groups, but it can also contain terminal siloxane units having no ethylenically unsaturated groups. For example the polysiloxane (B1) can have mixed end functionality such as 70% dimethylvinylsiloxy terminal groups and 30% dimethylhydroxysiloxy (-Si$(CH_3)_2OH$) terminal groups.

[0030] The polysiloxane (B1) can for example be of a degree of polymerization in the range from 100 to 7000, corresponding to a molecular weight of about 7500 to 500000 g/mole.

[0031] The olefin polymer (B2) which is reacted with the polysiloxane (B1) is an addition polymer in which at least 50 molar % of the repeating units are units of an olefinic hydrocarbon such as ethylene, propylene, 1 -butene or styrene. The olefin polymer (B2) can be a homopolymer such as polyethylene, polypropylene or polystyrene, or can be a copolymer such as a copolymer of an olefin with an ethylenically unsaturated ester, for example a copolymer of ethylene with an acrylate or methacrylate ester or an ethylene vinyl acetate copolymer. The olefin polymer (B2) is conveniently an ethylene polymer or copolymer, and we have found that polyethylene and copolymers of ethylene with an acrylate or methacrylate ester are effective in reacting with the polysiloxane (B1) containing ethylenically unsaturated groups to produce branched block copolymers which improve the sliding properties and friction resistance of polyacetals. Examples of suitable copolymers include copolymers of at least 50% by weight ethylene with up to 50% of an acrylate or methacrylate ester such as methyl methacrylate, methyl acrylate or ethyl methacrylate, such as a copolymer of 95-60% by weight ethylene with 5-40% methyl methacrylate, alternatively a copolymer of 90-70% by weight ethylene with 10-30% methyl methacrylate.

[0032] The olefin polymer (B2) is preferably substantially free of reactive, functional groups.

[0033] The branched block copolymer (B) is produced by melt kneading the polysiloxane (B1) containing ethylenically unsaturated groups with the olefin polymer (B2), that is by mixing the polysiloxane (B1) and the olefin polymer (B2) under conditions where they are both in liquid form. Preferably, such conditions include heating. The polysiloxane (B1) and the olefin polymer (B2) are mixed under process conditions at which all the polysiloxane (B1) is reacted with the olefin polymer to produce a branched block copolymer (B) which is free of any siloxane homopolymer.

[0034] The polysiloxane (B1) and the olefin polymer (B2) are reactively mixed at a ratio usually in the range 10 to 90 parts by weight of the polysiloxane (B1) to 90 to 10 parts by weight of the olefin polymer (B2), for example 20 to 80 parts by weight of the polysiloxane (B1) to 80 to 20 parts by weight of the olefin polymer (B2).

[0035] The polysiloxane (B1) and the olefin polymer (B2) can be mixed effectively in a continuous mixer such as an extruder, which can be a uniaxial extruder, a biaxial extruder, or a multiaxial extruder. A twin screw extruder, particularly one having a length/diameter (LJD) ratio over 40, is generally suitable. The olefin polymer (B2) can for example be introduced into the main feed of a co-rotative twin screw extruder operating at a temperature high enough to melt the olefin polymer. The polysiloxane (B1) can be added into the already melted olefin polymer phase using for example a gear pump. To maintain the quality of working surroundings and avoid side reactions, inert gas flushing or deaeration using a single stage venting or multi-stage venting can be used.

[0036] Alternative plastic mixing equipment can be used, for example a batch internal mixer such as a Z-blades mixer or a Banbury mixer.

[0037] The temperature of mixing the polysiloxane (B1) and the olefin polymer (B2) is generally in the range 150 °C to 240°C. The residence time of the liquid phase reagents in an extruder can for example be 30 to 240 seconds, optionally 50 to 150 seconds. Within these ranges, the temperature and mixing time required to produce a branched block copolymer (B) which is free of any siloxane homopolymer can be determined; this will depend on the vinyl content of the polysiloxane, the shear rate of the mixing apparatus used and the feed rate through the mixing apparatus. The process conditions (temperature, and screw speed and feed rate when mixing in an extruder) should be adjusted to produce a branched block copolymer product having a zero shear viscosity from 50.000 Pas to 800000 Pas, more preferably from 100000 Pas to 500000 Pas at 190°C, measured according to the creep test method described by Jorg Lauger and Monika Bernzen in "Annual Transactions of Nordic Society of Rheology volume 8, 2000, page 161 ".

[0038] The branched block copolymer product (B) may be soluble or partially soluble in xylene at reflux temperature. If the branched block copolymer product is completely insoluble in xylene at reflux temperature, it is considered to be free of any siloxane homopolymer. It has been observed that nevertheless its performances for lowering the friction coefficient are not affected. The formation of a branched block copolymer (B) which is free of any siloxane homopolymer can be tested by extracting the product with xylene under reflux, and analysing the fraction which remains soluble after cooling the xylene solution at room temperature. In a preferred test procedure, the amount of xylene extract is mixed with an equal volume of toluene and allowed to cool to ambient temperature (about 255°C). Any unreacted olefin polymer (B2) and some polysiloxane polyolefin copolymer which is rich in polyolefin precipitate out of the xylene/toluene mixture leaving soluble polysiloxane polyolefin copolymer species, and any unreacted polysiloxane (B1), in solution.

[0039] The fraction of the branched block copolymer product (B) which is extracted by xylene under reflux and remains soluble in toluene/xylene after cooling is then analysed to determine (i) the molecular weight, (ii) the solubility in toluene/xylene as indicated by the Mark-Houwink-Sakurada parameters and (iii) the molecular structure by1 H NMR analysis.

[0040] Molecular weight analysis is carried out by gel permeation chromatography (GPC) calibrated by narrow and broad polystyrene standards. Molecular weight data obtained is compared to the polysiloxane (B1) from which the branched block copolymer product (B) was prepared. The polydispersity of a branched block copolymer product free of siloxane homopolymer is substantially greater than the polydispersity of the polysiloxane (B1), but shows a monomodal distribution.

[0041] The Mark-Houwink parameters (a, K) also can be obtained from gel permeation chromatography measurements. The Kuhn-Mark-Houwink-Sakurada equation gives a relation between intrinsic viscosity η and molecular weight M: $\eta = KM^a$, where K and a are constants. In gel permeation chromatography, the intrinsic viscosity of a polymer is directly related to the elution volume of the polymer. Therefore, by running several monodisperse samples of polymer in a gel permeation chromatograph (GPC), the values of K and a can be determined graphically using a line of best fit. Mark-Houwink parameters a and K lower than that of the polysiloxane indicate a lower solubility of the xylene extracted branched block copolymer product (B) than the polysiloxane due to olefin polymer units copolymerised with the polysiloxane.

[0042] In ^{1}H NMR analysis, the presence of olefin polymer units in addition to polysiloxane units in the xylene soluble extract of the branched block copolymer product (B) which has been diluted with toluene, cooled and filtered indicates that the polysiloxane (B1) has been copolymerised with olefin polymer (B2) since free olefin polymer such as polyethylene methyl methacrylate) is neither soluble in xylene nor in xylene/toluene mixture For example, when the olefin polymer (B2) is an ethylene methyl methacrylate copolymer, a signal of methacrylate groups can be measured by ^{1}H NMR analysis in the soluble fraction.

[0043] The thermoplastic polymer (A) can for example be a polyacetal or a polyolefin. The process of the invention is particularly suitable for producing a polyacetal composition of reduced coefficient of friction. The polyacetal can for example be a polyoxymethylene homopolymer such as that sold by DuPont under the trade mark 'Delrin' or a polyoxymethylene copolymer such as that sold by Ticona under the trade mark 'Hostaform C 9021 '. Polyoxymethylene homopolymers are obtained from the polymerization of formaldehyde or cyclic oligomers of formaldehyde and quenched with ether or ester groups at both terminal ends of the polymer chain. Polyoxymethylene copolymers are obtained from the polymerization of cyclic oligomers of formaldehyde such as trioxane with a comonomer such as dioxolane or ethylene oxide. The polyacetal can be a block copolymers of hydrogenated polybutadiene and an oxymethylene copolymer.

[0044] The melt flow index (MFI) of polyoxymethylene resin for use in the present invention as thermoplastic polymer (A) is preferably in the range 1 .0-100 g/10 min., for example 2.0- 80 g/10 min. (as measured on the basis of ASTM-D1238-57T).

[0045] A polyacetal composition according to the present invention can for example comprise 90 to 99.5% by weight of a polyacetal and 0.5 to 10% of the branched block copolymer (B) of polysiloxane (B1) and olefin polymer (B2).

[0046] The polyacetal composition can contain stabilisers, as are commonly used in polyacetal compositions, for example, a heat stabilizer and/or a weather (light) resistant stabilizer. Use of an antioxidant or a formaldehyde- or formic acid-trapping agent or simultaneous use thereof is effective as a heat stabilizer.

[0047] The antioxidant can be a hindered phenol-based antioxidant, for example, n-octadecyl-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)-propionate, n-octadecyl-3-(3'-methyl-5'-t-butyl-4'-hydroxyphenyl)-propionate, n-tetradecyl-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)-propionate, 1 ,6-hexanediol-bis-(3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate), 1 ,4-butanediol-bis-(3-(3,5-di-t-butyl-4-hydroxyphenyl)-propionate), triethyleneglycol-bis-(3-(3-t- butyl-5-methyl-4-hydroxyphenyl)-propionate), tetrakis-(methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)-propionatemethane, 3,9-bis(2-(3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy)-1 ,1 -dimethylethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane, N,N'- bis-3-(3',5'-di-t-butyl-4-hydroxyphenol)propionylhexamethylenediamine, N,N'-tetramethylenebis-3-(3'-methyl-5'-t-butyl-4-hydroxyphenol)propionyldi amine, N,N'-bis-(3-(3,5-di-t-butyl-4-hydroxyphenol)propionyl)hydrazine, N-salicyloyl-N'-salicylidenehydrazine, 3-(N-salicyloyl)amino-1 ,2,4-triazole, or N,N'-bis(2-(3-(3,5-di-butyl-4- hydroxyphenyl)propionyloxy)ethyl)oxyamide.

[0048] Formaldehyde or formic acid-trapping agents include, for example, (a) formaldehyde reactive nitrogen-containing compounds, (b) formaldehyde reactive nitrogen- containing polymers, and (c) hydroxides, inorganic acid salts, carboxylates, or alkoxides of alkali metals or alkaline earth metals.

[0049] The thermoplastic polymer (A) can alternatively be a polyolefin, for example polyethylene or polypropylene. The melt flow index of the polyolefin (A) can for example be in the range 1 .0-100 g/10 min. A polyolefin composition according to the present invention can for example comprise 90 to 99.5% by weight polyolefin and 0.5 to 10% of the branched block copolymer (B).

[0050] The thermoplastic polymer (A) and the branched block copolymer (B) can in general be mixed using any mixing method known for thermoplastic materials. They are preferably melt mixed at a temperature at which the thermoplastic polymer (A) and the branched block copolymer (B) are both in liquid form. The thermoplastic polymer (A) and the branched block copolymer (B) can be mixed in any of the apparatus described above for melt kneading the polysiloxane (B1) with the olefin polymer (B2), for example an extruder or for example a batch internal mixer such as a Z-blades mixer or a Banbury mixer. The thermoplastic polymer (A) and the branched block copolymer (B) can alternatively simply be mixed on an injection press.

[0051] The branched block copolymer (B) can thus be used as a solid lubricant additive in polyolefins or polyoxymethylene resin compositions providing improved slidability (low coefficient of friction and low wear rate) without deteriorating the mechanical properties of the matrix composition. The compositions comprising the thermoplastic polymer (A) and the branched block copolymer (B) can be shaped using any of the moulding processes used for thermoplastic materials, for example injection moulding, extrusion or blow moulding.

[0052] Compositions comprising polyacetal as thermoplastic polymer (A) with the branched block copolymer (B) can, for example, be used to produce sliding components and gears for office appliances, plastic gears used in precision devices, household electrical appliances and automobiles, or to produce bearings or conveyor belts or medical tubing connectors.

[0053] Compositions comprising a polyolefin such as polyethylene or polypropylene as thermoplastic polymer (A) with the branched block copolymer (B) can, for example, be used to produce extruded film having improved slip properties. The branched block copolymer (B) has improved compatibility with the polyolefin compared to a pure silicone additive.

[0054] The invention also provides the use of a solid copolymer (B) in a polymer composition of the invention, as additive in the thermoplastic polymer (A) selected from a polyacetal and a polyolefin, wherein the copolymer (B) is a branched block copolymer of a polysiloxane (B1) and an olefin polymer (B2), and all the polysiloxane (B1) is reacted with the olefin polymer (B2) to produce a branched block copolymer (B) which is free of any siloxane homopolymer. Preferably, the solid copolymer (B) improves the slidability and/or reduces the coefficient of friction and/or improves the wear resistance of the thermoplastic polymer (A).

[0055] The invention is illustrated by the following Examples, in which parts and percentages are by weight.

[0056] Weight percentages are based on the weight of the total composition unless indicated differently.

[0057] The Examples will be described with reference to Figure 1 of the accompanying drawings, which comprises refractive index chromatograms of the branched block copolymer products of Examples 1 and 9. Examples 1 to 11

[0058] 60 parts silicone gum (B1 a) was melt blended with 40 parts olefin polymer (B2a) in a 'Prism TSE 24 TC twin screw extruder. The silicone gum (B1 a) from Dow Corning is a vinyl dimethylsiloxy capped dimethylsiloxy, methylvinylsiloxy copolymer of an average molecular weight of 330000 gr/mole and a total vinyl content of 0.03 mole % of vinyl units (-CH=CH2) and a Williams plasticity of 60 mils (as measured by ASTM D926-98). The olefin polymer (B2a) is an ethylene methyl methacrylate copolymer (EMMA) from Sumitomo (Acryft WD 301 -F) containing 9.8 % of methyl methacrylate units and has a melt flow index of 6.5.

[0059] The silicone gum (B1 a) and olefin polymer (B2a) were melt blended at different temperatures, screw speeds and feed rates as shown in Table 1 below. The temperature was varied from 160 °C to 220°C, the screw rotational speed was varied from 150 to 350 rpm and the feed rate varied from 3 to 4 Kg/hour. The extruded strands were pelletized and dried at 65°C overnight. 4 samples were collected from each Example for analysis. The zero shear viscosity $\eta 0$ was determined by dynamic mechanical analysis (DMA) and value the creep test method described in Annual Transactions of Nordic Society of Rheology volume 8, 2000, page 161 . The complex viscosity and the storage modulus G' were measured at 1905 C and 0.0251 Hz. The results are shown in Table 1 .

Table 1

Example	Temp °C	Screw Speed (RPM)	OutPut (Kg/h)	η^* - 190°C (0.0251 Hz)	G' - 190°C (0.0251 Hz)	$\eta 0$ - 190°C
1	160	150	3	10960	1125	53 230
2	160	350	3	19020	2310	123 000
3	190	250	3.5	21285	2672	106 400
4	160	150	4	19048	2318	131 000

(continued)

Example	Temp °C	Screw Speed (RPM)	OutPut (Kg/h)	η^* - 190°C (0.0251 Hz)	G' - 190°C (0.0251 Hz)	$\eta 0$ - 190°C
5	160	350	4	19884	2433	223 000
6	190	250	3.5	23209	2958	-
7	220	150	3	48708	6964	681 000
8	220	350	3	64070	9253	850 000
9	220	150	4	46585	6537	582 700
10	220	350	4	60657	8679	-
11	190	250	3.5	25084	3264	-

[0060] Table 1 shows that the complex viscosity η^*, storage modulus G' and the zero shear viscosity $\eta\theta$ of the branched block copolymers (B) produced change as a result of changing the process conditions between the Examples.

[0061] Samples of the branched block copolymers produced in Examples 1 and 9 were extracted with xylene for further analysis. About 0.15g of each branched block copolymer was accurately weighted and placed into a glass flask. 10 mL of p-xylene was added using a micro dosing pipette. The sample was left to solubilise under xylene reflux (oil bath temperature 180°C) during 10 hours of continuous magnetic stirrer agitation. Then 5 mL of the solutions were mixed with 5 mL of toluene into 10 mL glass bottles. Each solution was cooled whilst gently shaking for 24 hours and then filtered through 0.2 μηι PTFE filters into 1 .5 mL glass auto sampler vials. All samples showed resistance while passing though the filter, due to the olefin polymer and olefin-rich branched block copolymer that has re- precipitated at room temperature. Polymer extracted with xylene and remaining dissolved after being diluted with toluene, cooled and filtered is deemed 'Silicone material' and comprises polysiloxane and/or siloxane-rich branched block copolymer. The proportion of branched block copolymer product remaining dissolved after being diluted with toluene, cooled and filtered is shown in Table 2 below.

[0062] Molecular weight information on the samples of Examples 1 and 9 is obtained by gel permeation chromatography (GPC) analysis of the polymer fraction which remains soluble in xylene/toluene after cooling and filtration. The analyses were carried out with a 'Viscotek GPC Max' using a triple detection capability Viscotek TDA305 unit composed of a differential refractometer, an online differential pressure viscometer and low angle light scattering (LALS: 7° and 90° angles of detection). Mobile phase: Toluene HPLC grade, Columns: 2 x PL Gel Mixed C from Varian - (7.5* 300 mm, 5 μηι particle size) + PL Gel Guard column, Flow: 1 mL/min; Injection volume: 100 μί; Run time: 37 min; Column temperature: 40° C, Detector temperature: 40° C; Software: Omnisec 4.6.1 (Viscotek), The detectors were calibrated by injection of a narrow Mw range polystyrene standard (Mw 68,100 g/mol) of known concentration. Correct run parameters are checked by using a narrow and broad Mw range polystyrene standards (respectively PS71 K and PS235K). Molecular weights data were also measured for the starting silicone polymer (B1 a). The results are shown in Table 2, which lists number average molecular weight Mn, weight average molecular weight Mw, polydispersity MWD = Mw/Mn, and Marl-Houwink constants M-H a and M-H logK.

Table 2

Example	Mn	MW	MWD	M-H a	M-H Log K	% of the Silicone in the Xylene Soluble Fraction %
9	191,000	433,800	2.27	0.68	-3.8	19.319.3
1	257,600	541,700	2.10	0.69	-3.9	227.87.8
Pure Silicone	377,900	645,700	1.71	0.73	-4.0	100

[0063] As can be seen from Table 2, the polydispersity MWD of the products of Examples 1 and 9 is much larger than that of the polysiloxane B1 a used as the starting material and the molecular weights (Mn, MW) are lower that of polysiloxane B1 a. The Mark-Houwink parameters a, log K of the products of Examples 1 and 9 are lower than that of polysiloxane B1 a, indicating a lower solubility of these branched block copolymer products in xylene/toluene compared to the pure silicone polymer B1 a. The low solubility of this fraction of the products of Examples 1 and 9 is believed to be due to the presence of ethylene methyl methacrylate copolymer units in the extracted branched block copolymer.

[0064] The refractive index chromatograms of the branched block copolymer products of Examples 1 and 9 and of polysiloxane B1 a are shown overlaid in Figure 1 . As can be seen from Figure 1 the refractive index chromatograms show a monomodal distribution excluding the possibility of having two populations.

[0065] The soluble fractions from samples of Examples 1 and 9, obtained after xylene extraction, dilution with toluene, cooling and filtering were analysed by1 H NMR. The samples were heated for 15 minutes at 40°C and then diluted in CDCl3 and analysed using NMR BRUKER AVANCE I (400 MHz), 5 mm probe. The1 H NMR spectrum shows presence of strong signal at 3.654 ppm attributed to the methyl group of the methyl methacrylate units. The ratio of this signal to the signal of methyl groups of the silicone gives the relative concentration of ethylene methyl methacrylate copolymer (EMMA) in the samples analysed. Table 3 shows the chemical shifts, integration and calculation of relative concentration of EMMA in the analysed xylene soluble fractions. The soluble fraction contains respectively 4.73 % and 9.72% of EMMA for samples of Examples 1 and 9. The presence of EMMA polymer units in the xylene soluble fraction indicates a presence of silicone/EMMA copolymer since EMMA polymer on its own is not soluble in xylene at room temperature. It also explains the lower solubility in toluene as compared to pure silicone. Therefore, the samples from Examples 1 and 9 which remain dissolved after being xylene extracted, diluted with toluene, cooled and filtered comprise a silicone-EMMA copolymer that contains a small fraction of ethylene methyl methacrylate copolymer branches. It is believed the extracted fraction is not a silicone homopolymer since the Mark-Houwink parameters are lower than that of pure silicone.

Table 3

	Chemical. Shift (ppm)	Example 1	Example 9
		Relative Integral	Relative Integral
$Si(CH_3)_2$	0.078	566.252	597.093
CH2-CH- $CO(OCH_3)$	3.654	1.186	2.71
EMMA %		4.73	9.72

[0066] Delrin® 150 NC010 high viscosity polyoxymethylene (POM) homopolymer commercially available from Dupont was mixed with the pelletised branched block copolymers produced in each of Examples 1 and 9 in a 'Prism TSE 24 TC twin screw extruder, at the concentration specified in Table 4. The samples were injected pressed at 230°C using DEMAG press injector to make test pieces suitable for friction coefficient determination. Two reference POM compositions were also tested: (1) pure POM and (2) POM containing polysiloxane B1 a silicone gum at the same level of silicone active.

[0067] Friction measurements were carried out using a low load tribometer with POM ball against the sample, with a normal load of 12.5N corresponding to 70MPa of contact load, speed of 8 mm/s over 10 mm of sliding distance at 25°C. Friction coefficients were collected after 50, 100, 200, 400 and 700 cycles. Table 4 gives the performances of each specimen.

Table 4

		50 cycles		100 cycles		200 cycles		400 cycles		700 cycles	
	Level in POM composition	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2
Pure POM	0	0.249	0.352	0.445	0.458	0.457	0.476	0.458	0.485	0.479	0.46
Silicone B1a	2	0.047	0.034	0.046	0.034	0.043	0.035	0.042	0.038	0.042	0.045
Example 9	3.3%	0.028	0.034	0.028	0.034	0.028	0.033	0.029	0.035	0.03	0.036
Example 1	3.3%	0.037	0.029	0.035	0.028	0.033	0.028	0.037	0.029	0.044	0.031

[0068] It can be seen from Table 4 that in general the silicone gum or the silicone polyolefin branched block copolymer (B) at a level of 2% silicone decreases the friction coefficient of the POM by a factor of 10. The silicone-EMMA copolymer products of Examples 1 and 9 show 15% lower friction resistance than the silicone gum based POM composition.

Claims

1. A polymer composition consisting of a thermoplastic polymer (A) selected from a polyacetal and a polyolefin, and a copolymer (B) of a polysiloxane (B1) and an olefin polymer (B2), and optionally, if the thermoplastic polymer (A) is a polyacetal, may contain a stabilizer, ***characterised in that*** the copolymer (B) is a branched block copolymer and all the polysiloxane (B1) is reacted with the olefin polymer (B2) to produce a branched block copolymer (B) which is free of any siloxane homopolymer.

2. A polymer composition according to Claim 1 **characterised in that** the olefin polymer (B2) is a copolymer of at least 50% by weight ethylene with up to 50% of an acrylate or methacrylate ester.

3. A polymer composition according to Claim 1 or 2 wherein the thermoplastic polymer (A) is polyoxymethylene.

4. A polymer composition according to Claim 2 or Claim 3 **characterised in that** the olefin polymer (B2) is a copolymer of 95-60% by weight ethylene with 5-40% methyl methacrylate or polyethylene.

5. A polymer composition according to any of Claims 1 to 4 **characterised in that** the branched block copolymer (B) has a zero shear viscosity of 50,000 to 8,000,000 Pa.s at 190°C.

6. A polymer composition according to any of Claims 1 to 5 **characterised in that** the branched block copolymer (B) is a copolymer of 20-80% by weight polysiloxane (B1) and 80-20% olefin polymer (B2).

7. A process for the production of a polymer composition, in accordance with claim 1, of reduced coefficient of friction, said process comprising the steps of

   (i) melt kneading a polysiloxane (B1) containing ethylenically unsaturated groups with an olefin polymer (B2) under process conditions at which all the polysiloxane (B1) is reacted with the olefin polymer thereby producing a branched block copolymer (B) which is free of any siloxane homopolymer; and
   (ii) blending a thermoplastic polymer (A) selected from a polyacetal and a polyolefin with the branched block copolymer (B) produced in step (i).

8. A process according to Claim 7 **characterised in that** the polysiloxane (B1) containing ethylenically unsaturated groups and the olefin polymer (B2) are melt kneaded in an extruder at a temperature in the range 150 °C to 240°C.

9. A process according to Claim 8 **characterised in that** the extruder is a biaxial or multiaxial extruder.

10. A process according to any of Claims 7 to 9 **characterised in that** the polysiloxane (B1) contains at least 3 vinyl groups per molecule.

11. A process according to any of Claims 7 to 10 wherein the thermoplastic polymer (A) and the branched block copolymer (B) are blended in an extruder or by mixing in an injection press.

12. A process according to any of Claims 7 to 11 wherein the thermoplastic polymer (A) is polyoxymethylene or an oxymethylene copolymer.

13. A process according to any of Claims 7 to 11 wherein the thermoplastic polymer (A) is a polyolefin.

14. Use of a solid copolymer (B) as additive in a polymer composition according to claim 1 with the thermoplastic polymer (A) selected from a polyacetal and a polyolefin, wherein the copolymer (B) is a branched block copolymer of a polysiloxane (B1) and an olefin polymer (B2), and all the polysiloxane (B1) is reacted with the olefin polymer (B2) to produce a branched block copolymer (B) which is free of any siloxane homopolymer.

15. Use according to claim 14, wherein the solid copolymer (B) improves the slidability and/or reduces the coefficient

of friction and/or improves the wear resistance of the thermoplastic polymer (A).

Patentansprüche

1. Polymerzusammensetzung, die aus einem thermoplastischen Polymer (A), das aus einem Polyacetal und einem Polyolefin ausgewählt ist, und einem Copolymer (B) aus einem Polysiloxan (B 1) und einem Olefinpolymer (B2) besteht und wahlweise, wenn das thermoplastische Polymer (A) ein Polyacetal ist, einen Stabilisator enthalten kann, **dadurch gekennzeichnet, dass** das Copolymer (B) ein verzweigtes Blockcopolymer ist und das gesamte Polysiloxan (B 1) mit dem Olefinpolymer (B2) umgesetzt wird, um ein verzweigtes Blockcopolymer (B) herzustellen, das frei von jeglichem Siloxanhomopolymer ist.

2. Polymerzusammensetzung nach Anspruch 1, **dadurch gekennzeichnet, dass** das Olefinpolymer (B2) ein Copolymer von mindestens 50 Gew.-% Ethylen mit bis zu 50 % eines Acrylat- oder Methacrylatesters ist.

3. Polymerzusammensetzung nach Anspruch 1 oder 2, wobei das thermoplastische Polymer (A) Polyoxymethylen ist.

4. Polymerzusammensetzung nach Anspruch 2 oder Anspruch 3, **dadurch gekennzeichnet, dass** das Olefinpolymer (B2) ein Copolymer von 95-60 Gew.-% Ethylen mit 5-40 % Methylmethacrylat oder Polyethylen ist.

5. Polymerzusammensetzung nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, dass** das verzweigte Blockcopolymer (B) eine Nullscherviskosität von 50 000 bis 8 000 000 Pa.s bei 190 °C aufweist.

6. Polymerzusammensetzung nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, dass** das verzweigte Blockcopolymer (B) ein Copolymer aus 20-80 Gew.-% Polysiloxan (B1) und 80-20 % Olefinpolymer (B2) ist.

7. Verfahren zur Herstellung einer Polymerzusammensetzung nach Anspruch 1 mit verringertem Reibungskoeffizienten, wobei das Verfahren die folgenden Schritte umfasst:

   (i) Schmelzkneten eines Polysiloxans (B1), das ethylenisch ungesättigte Gruppen enthält, mit einem Olefinpolymer (B2) unter Verfahrensbedingungen, bei denen das gesamte Polysiloxan (B1) mit dem Olefinpolymer umgesetzt wird, wodurch ein verzweigtes Blockcopolymer (B) hergestellt wird, das frei von jeglichem Siloxanhomopolymer ist; und
   (ii) Mischen eines thermoplastischen Polymers (A), ausgewählt aus einem Polyacetal und einem Polyolefin, mit dem in Schritt (i) hergestellten verzweigten Blockcopolymer (B).

8. Verfahren nach Anspruch 7, **dadurch gekennzeichnet, dass** das ethylenisch ungesättigte Gruppen enthaltende Polysiloxan (B1) und das Olefinpolymer (B2) in einem Extruder bei einer Temperatur im Bereich von 150 °C bis 240 °C schmelzgeknetet werden.

9. Verfahren nach Anspruch 8, **dadurch gekennzeichnet, dass** der Extruder ein biaxialer oder multiaxialer Extruder ist.

10. Verfahren nach einem der Ansprüche 7 bis 9, **dadurch gekennzeichnet, dass** das Polysiloxan (B1) mindestens 3 Vinylgruppen pro Molekül enthält.

11. Verfahren nach einem der Ansprüche 7 bis 10, wobei das thermoplastische Polymer (A) und das verzweigte Blockcopolymer (B) in einem Extruder oder durch Mischen in einer Spritzpresse vermischt werden.

12. Verfahren nach einem der Ansprüche 7 bis 11, wobei das thermoplastische Polymer (A) Polyoxymethylen oder ein Oxymethylen-Copolymer ist.

13. Verfahren nach einem der Ansprüche 7 bis 11, wobei das thermoplastische Polymer (A) ein Polyolefin ist.

14. Verwendung eines festen Copolymers (B) als Additiv in einer Polymerzusammensetzung nach Anspruch 1 mit dem thermoplastischen Polymer (A), ausgewählt aus einem Polyacetal und einem Polyolefin, wobei das Copolymer (B) ein verzweigtes Blockcopolymer aus einem Polysiloxan (B1) und einem Olefinpolymer (B2) ist und das gesamte Polysiloxan (B1) mit dem Olefinpolymer (B2) umgesetzt wird, um ein verzweigtes Blockcopolymer (B) herzustellen, das frei von jeglichem Siloxanhomopolymer ist.

15. Verwendung nach Anspruch 14, wobei das feste Copolymer (B) die Gleitfähigkeit verbessert und/oder den Reibungskoeffizienten verringert und/oder die Verschleißfestigkeit des thermoplastischen Polymers (A) verbessert.

Revendications

1. Composition polymère constituée par un polymère thermoplastique (A), choisi parmi un polyacétal et une polyoléfine, et un copolymère (B) d'un polysiloxane (B1) et d'un polymère d'oléfine (B2), et facultativement, si le polymère thermoplastique (A) est un polyacétal, pouvant contenir un agent stabilisant, **caractérisée en ce que** le copolymère (B) est un copolymère séquencé ramifié et l'intégralité du polysiloxane (B1) réagit avec le polymère d'oléfine (B2) pour produire un copolymère séquencé ramifié (B) exempt de tout homopolymère de siloxane.

2. Composition polymère selon la revendication 1, **caractérisée en ce que** le polymère d'oléfine (B2) est un copolymère d'au moins 50 % en poids d'éthylène avec jusqu'à 50 % d'un ester d'acrylate ou de méthacrylate.

3. Composition polymère selon la revendication 1 ou 2, dans laquelle le polymère thermoplastique (A) est le polyoxyméthylène.

4. Composition polymère selon la revendication 2 ou la revendication 3, **caractérisée en ce que** le polymère d'oléfine (B2) est un copolymère de 95 à 60 % en poids d'éthylène avec 5 à 40 % de méthacrylate de méthyle ou de polyéthylène.

5. Composition polymère selon l'une quelconque des revendications 1 à 4, **caractérisée en ce que** le copolymère séquencé ramifié (B) a une viscosité à cisaillement nul de 50 000 à 8 000 000 Pa.s à 190 °C.

6. Composition polymère selon l'une quelconque des revendications 1 à 5 **caractérisée en ce que** le copolymère séquencé ramifié (B) est un copolymère de 20 à 80 % en poids de polysiloxane (B1) et de 80 à 20 % de polymère d'oléfine (B2).

7. Processus de production d'une composition polymère, selon la revendication 1, à coefficient de friction réduit, ledit processus comprenant les étapes consistant à :

   (i) malaxer à l'état fondu un polysiloxane (B1) contenant des groupes éthyléniquement insaturés avec un polymère d'oléfine (B2) dans des conditions de processus où l'intégralité du polysiloxane (B1) réagit avec le polymère d'oléfine, produisant ainsi un copolymère séquencé ramifié (B) exempt de tout homopolymère de siloxane ; et
   (ii) mélanger un polymère thermoplastique (A) choisi parmi un polyacétal et une polyoléfine avec le copolymère séquencé ramifié (B) produit à l'étape (i).

8. Processus selon la revendication 7, **caractérisé en ce que** le polysiloxane (B1) contenant des groupes éthyléniquement insaturés et le polymère d'oléfine (B2) sont malaxés à l'état fondu dans une extrudeuse à une température comprise entre 150 °C et 240 °C.

9. Processus selon la revendication 8, **caractérisé en ce que** l'extrudeuse est une extrudeuse biaxiale ou multiaxiale.

10. Processus selon l'une quelconque des revendications 7 à 9 **caractérisé en ce que** le polysiloxane (B1) contient au moins 3 groupes vinyles par molécule.

11. Processus selon l'une quelconque des revendications 7 à 10, dans lequel le polymère thermoplastique (A) et le copolymère séquencé ramifié (B) sont mélangés dans une extrudeuse ou par mixage dans une presse à injection.

12. Processus selon l'une quelconque des revendications 7 à 11, dans lequel le polymère thermoplastique (A) est le polyoxyméthylène ou un copolymère d'oxyméthylène.

13. Processus selon l'une quelconque des revendications 7 à 11, dans lequel le polymère thermoplastique (A) est une polyoléfine.

14. Utilisation d'un copolymère solide (B) comme additif dans une composition polymère selon la revendication 1 avec

le polymère thermoplastique (A) choisi parmi un polyacétal et une polyoléfine, dans lequel le copolymère (B) est un copolymère séquencé ramifié d'un polysiloxane (B1) et d'un polymère d'oléfine (B2), et l'intégralité du polysiloxane (B1) réagit avec le polymère d'oléfine (B2) pour produire un copolymère séquencé ramifié (B) exempt de tout homopolymère de siloxane.

15. Utilisation selon la revendication 14, dans laquelle le copolymère solide (B) améliore la capacité de glissement et/ou réduit le coefficient de friction et/ou améliore la résistance à l'usure du polymère thermoplastique (A).

REFERENCES CITED IN THE DESCRIPTION

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